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Lattice Dynamics Studies of Negative Thermal Expansion Due to Two Low-temperature Lattice Instabilities.

SAHAN UDDIKA HANDUNKANDA

University of Connecticut - Storrs, sahan.handunkanda@uconn.edu

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Here I present a complete study of lattice dynamics of negative thermal expansion (NTE) material Scandium trifluoride (ScF₃) and discovery of NTE in mercurous iodide (Hg₂I₂). An inelastic x-ray scattering (IXS) study of ScF₃ reveals copious evidence of an incipient soft-mode instability indicating that the T=0 state of ScF₃ is very close to a structural quantum phase transition (SQPT). Is the anomalously strong and thermally persistent NTE behavior of ScF₃ a consequence of the SQPT? In order to address that, we have explored the coefficient of thermal expansion (CTE) and soft mode behavior of a second stoichiometric compound, situated near a SQPT. A detailed side-by-side comparison of the metal trifluorides and mercurous halides suggest strong similarities and a generic connection between the fluctuating ground state of incipient ferroelastic materials and SNTE. We find experimental evidences
for two-dimensional nanoscale correlations exist at momentum-space regions associated with possibly rigid rotations of the perovskite octahedra of ScF$_3$.

The discussion is extended by addressing the extent to which rigid octahedral motion describes the dynamical fluctuations behind NTE by generalizing a simple model supporting a single floppy mode that is often used to heuristically describe instances of NTE. Temperature-dependent infrared reflection measurement on single crystal ScF$_3$ is performed to understand the zone center lattice dynamics of ScF$_3$. In addition, I also carried out an instrumentation development project in the laboratory at the Department of Physics which will be briefly discussed in the last chapter.
Lattice Dynamics Studies of Negative Thermal Expansion Due to Two Low-temperature Lattice Instabilities

Sahan Handunkanda

M.S. Physics, University of Connecticut, Storrs, CT, 2014
B.S. Physics, University of Colombo, Sri Lanka, 2009

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Presented by
Sahan Handunkanda, M.S. Physics, B.S. Physics

Major Advisor
Jason Hancock

Associate Advisor
Barrett Wells

Associate Advisor
Douglas Hamilton

University of Connecticut
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1.1 Thermal expansion

Materials tendency to decrease or increase their volume when heated is known as thermal expansion. The vast majority of materials increase in dimension when they are heated corresponding to positive thermal expansion (PTE). While thermal expansion is common among all three phases of substances, in solids it may be isotropic or anisotropic. Substances expand in same amounts along any direction known as isotropic expansion, which is different from anisotropic case where materials expand in different amounts along different crystallographic orientations.

Thermal expansion in solids is a direct consequence of the anharmonic nature of interatomic forces between atoms (anharmonic potential) (Figure 1.1.1a). The mean separation between atoms correspond to the minimum potential is identified as the equilibrium distance between them. As the temperature is increased the potential energy of the system increases and the asymmetry of potential suggests an increase in mean separation, hence thermal expansion. On the other hand if the atoms behave in harmonic manner, then the mean
separation between atoms would not change even the vibrational amplitude increases with increasing temperature, hence no thermal expansion (Figure 1.1.1b).

Thermal expansion is typically quantified by using coefficient of thermal expansion (CTE), which simply is the relative change in material dimension within a given change in temperature at constant pressure. In order to measure the relative change along a certain directions in a solid object, the linear CTE, \( \alpha_L = (1/L)(\partial L/(\partial T))_P \), is defined and this is frequently used to quantify anisotropic thermal expansion. The magnitude of the thermal expansion is mostly expressed in terms of volumetric CTE, \( \alpha_V = (1/V)(\partial V/(\partial T))_P \) where \( V \) is volume, \( T \) is temperature and \( P \) is pressure. The CTEs is expressed in unit K\(^{-1}\) and for solids in general the CTEs are of the order of 10\(^{-6}\) and the unit ppm/K is used instead.

### 1.2 Lattice Dynamics

Lattice dynamics is the study of vibrations of the atoms in a crystal. It is an important phenomenon to understand and governs the key properties of materials such as thermodynamics, phase transition, thermal conductivity, thermal expansion, and sound wave propagation. More importantly it interacts with electromagnetic radiation. In lattice dynamics study the atomic motions are described by traveling waves. Each wave is characterized by wavelength \( \lambda \), angular frequency \( \omega \), amplitude and direction of travel. For the convenience
Figure 1.1.1: (a) The anharmonic potential is shown. The potential is asymmetric, so that increases in temperature (i.e. the amplitude of oscillation of atoms) leads to an increase in the mean interatomic separation, and hence to thermal expansion. (b) The harmonic potential is symmetric and as the temperature is increased the mean separation remains the same hence no thermal expansion.

wavelength is being replaced with wave vector \( k = \frac{2\pi}{\lambda} \).

Simplest form of lattice dynamics theory uses harmonic approximation. Considering the potential given in Figure 1.1.1a the Taylor series expansion around equilibrium distance between atoms, \( r_0 \) can be written as

\[
V(r) = V_0 + \frac{1}{2} \frac{\partial^2 V}{\partial r^2} (r - r_0)^2 + \frac{1}{3!} \frac{\partial^3 V}{\partial r^3} (r - r_0)^3 + \frac{1}{4!} \frac{\partial^4 V}{\partial r^4} (r - r_0)^4 + \ldots \quad \text{(1.2.1)}
\]

In harmonic approximation only the quadratic terms is retained. In most cases, the approximation is very effective and if not, we can start with it and then modify the model by adding higher order terms for better results of inter-
atomic forces, wave vectors and frequencies. Nevertheless, properties such as thermal conductivity, thermal expansion, and phase transition cannot be explained by the harmonic model.

Consider a crystal with one atom per unit cell, as an example, a 1D chain of atom, each of mass $m$. The atoms are connected by elastic springs, so the force between the atoms are directly proportional to relative displacement from the equilibrium position. Let us assume that the separation between consecutive atoms is $a$, so the position of the $n$th atom in 1D chain is $na$ (Figure 1.2.1). We define the displacement of $n$th atom to be $U_n$ and write equation of motion of an atom

$$F_n = C((U_{n+1} - U_n) - (U_n - U_{n-1})) = m\frac{d^2U_n}{dt^2} \quad (1.2.2)$$

where $C$ is the force constant.

For any coupled system, a **normal mode** is defined to be a collective oscillation where all particles move at the same frequency. Let us now attempt a solution
\[ U_n = U_0 e^{i(\omega t - kna)} \]  

(1.2.3)

where \( U_0 \) is the amplitude of oscillation and \( k \) is the wave vector.

Plugging the solution to Equation 1.2.2 we get

\[- m\omega^2 U_0 e^{i(\omega t - kna)} = C U_0 e^{i\omega t} \left[ e^{-ika(n+1)} + e^{-ika(n-1)} - 2 e^{-ikan} \right] \]  

(1.2.4)

\[ m\omega^2 = 2C[1 - \cos(ka)] = 4C \sin^2(ka/2) \]  

(1.2.5)

and we obtain the result

\[ \omega = 2 \sqrt{\frac{C}{m}} \left| \sin \left( \frac{ka}{2} \right) \right|. \]  

(1.2.6)

The relationship, \( \omega(k) \) is known as the dispersion relationship of the corresponding atomic structure. Figure 1.2.1 shows the dispersion relation and it is periodic in \( k \rightarrow k + 2\pi/a \). Following this we use the term \( k\)-space which is also known as reciprocal space. The periodic unit in reciprocal space is known as Brillouin Zone(BZ) and Figure 1.2.1 shows only the ”First Brillouin Zone” which has the boundaries at \( k= \pm \pi/a \).
One important consequence of dispersion relationship in 1D chain is that it allows us to calculate group velocity, $V_g = d\omega/dk$ and phase velocity, $V_p = \omega/k$. With the particular dispersion relation given in Equation 1.2.6 the group velocity

$$V_g = 2(Ca^2/m)^{1/2} \cos(ka/2).$$  \hspace{1cm} (1.2.7)

In long wavelength limit, where $\cos ka \sim 1-(ka/2)^2$, the dispersion relation becomes

$$\omega^2 = (C/m)(k^2a^2)$$  \hspace{1cm} (1.2.8)

and we obtain a result that the velocity in long wave length limit is independent
of frequency. Recalling that the sound wave is a vibration that has long wave
lengths, we obtain the result

\[ V_{\text{sound}} = a \sqrt{\frac{C}{m}}. \]  (1.2.9)

We discussed a classical system which has normal mode of frequency \( \omega \). The
corresponding quantum mechanical system will have eigenstates with energy

\[ E_n = \hbar \omega (n + \frac{1}{2}) \]  (1.2.10)

which the energy of a lattice vibrations is quantized and quantum of energy
is called \textit{Phonon}. This is analogues to quantized energy called photons of the
electromagnetic wave.

We now extend the discussion to analyze linear chain with two atomic species
(Figure 1.2.3). Writing down equations of motions

\[ \text{Figure 1.2.3: A linear chain of two atomic species} \]
\(- C_1(V_n - U_n) + C_2(V_{n-1} - U_n)) = m_1 \frac{d^2 U_n}{dt^2} \quad (1.2.11)\)

\(- C_2(U_n - V_n) + C_2(U_{n+1} - V_n) = m_2 \frac{d^2 V_n}{dt^2} \quad (1.2.12)\)

and writing down wave-like ansatz as before

\[ U_n = U_0 e^{i(\omega t - kna)} \quad (1.2.13) \]

\[ V_n = V_0 e^{i(\omega t - kna)} \quad (1.2.14) \]

leads to

\((m\omega^2 - C_1 - C_2)U_0 + (C_1 + C_2e^{-ika})U_0 = 0 \quad (1.2.15)\)

\((C_1 + C_2e^{ika})U_0 + (m\omega^2 - C_1 - C_2)U_0 = 0 \quad (1.2.16)\)

where for simplicity here we used \(m_1 = m_2\).

The solutions to this are obtained by finding the zeros of secular determinant

\[
\begin{vmatrix}
(m\omega^2 - C_1 - C_2) & (C_1 + C_2e^{-ika}) \\
(C_1 + C_2e^{ika}) & (m\omega^2 - C_1 - C_2)
\end{vmatrix} = 0
\]
which is

\[ \omega^2 = \frac{C_1 + C_2}{m} \pm \frac{1}{m} \sqrt{C_1^2 + C_2^2 + 2C_1C_2 \cos(ka)}. \]  

(1.2.17)

Figure 1.2.4: Dispersion relation of the 1D chain of two different atoms.

This method can be generalized for more complex three-dimensional materials and most of the advanced condensed matter textbooks explain this approach thoroughly. To complete the normal mode solution in three dimensional, the vibrational amplitude should be incorporated which can be used to calculate the total energy of the crystal as well.

1.3 Negative thermal expansion

It is not uncommon that some materials show the opposite behavior of PTE,
which they shrink upon heating give rise to negative thermal expansion (NTE). This is relatively new field of study, yet we have seen phenomenal development in recent years as many materials are discovered displaying this unusual behavior. The most popular example for NTE phenomenon is the liquid water-ice expansion below 4°C and above ice-water phase boundary.

Even though not all of the different mechanisms responsible for NTE are fully understood, generally the origin of NTE is viewed in two different ways. NTE could either arise from non-vibrational effect associated with electronic and magnetic instabilities or emerge from vibrational effect associated with intrinsic geometrical instabilities.

1.3.1 Negative thermal expansion from phase competition

The non-vibrational effects account for NTE are mostly related with phase transitions and one of the very well known example for this type of materials family is ferroelectrics. Interestingly, some ferroelectrics exhibit NTE or anomalous thermal expansion properties below the curie temperatures and their NTE originates from ferroelectric order which occurs due to the strong hybridization between cations and anions. Some of the notable examples in this category are PbTiO$_3$[2, 25, 26, 27], PbTiO$_3$ based compounds [28, 1], BaTiO$_3$[29], BiFeO$_3$[25], Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$[30], Ca$_3$Mn$_2$O$_7$[31], Ca$_3$Ti$_2$O$_7$[31] and Sn$_2$P$_2$S$_6$[32]. The NTE associated with the spontaneous polarization originating from Pb/Bi-O hybridization is reported for PbTiO$_3$-based compounds [28] and they have at-
tracted attention due to the precise capability of controlling NTE, not just in a single way but by using various methods such as the chemical modification, size effect, and physically by applying pressure. A couple of examples of ferroelectric NTE are shown in Figure 1.3.1.

![Figure 1.3.1: NTE in ferroelectrics. (a) Unit cell volume of 0.5PbTiO$_3$-0.5(Bi$_{1-x}$La$_x$)FeO$_3$ ($x = 0.0, 0.1,$ and $0.2$) as function of temperature. FE and PE mean ferroelectric and paraelectric, respectively. Taken from [1]. (b) Thermal expansion coefficient of volume in PbTiO$_3$. Taken from [2].](image)

The change of electron configuration can also cause NTE and abnormal thermal expansion properties to some materials. The volume increment upon cooling due to a valance transition has been reported for rare earth fulleride Sm$_{2.75}$C$_{60}$ [4]. NTE in BiNiO$_3$ [3] is attributed to atomic radius contraction caused by intermetallic charge transfer from Ni to Bi. Others display NTE due to intersite charge transfer, as reported in perovskites oxides such as SrCu$_3$Fe$_4$O$_{12}$[33] and LaCu$_3$Fe$_4$O$_{12}$[34]. Even semiconductors (e.g. Si, Ge, and GaAs [35, 36]), superconductors (e.g. MgB$_2$, Ba(Fe$_{0.926}$Co$_{0.074}$)$_2$As$_2$ [37, 38]) and Mott insulators (e.g. Ca$_2$RuO$_4$ based compounds [39, 40]) exhibit NTE or anomalous thermal
expansion properties as a result of change in electron configuration. There exist a number of ways to tune NTE due to phase competition, including controlling free electron concentration of semiconductors, modulating the metal insulator transition of Mott insulator, and introducing quenched disorder. An attribute of this approach is the potentially large CTE, although a drawback in most cases is persistence over only a narrow temperature range.

Figure 1.3.2: NTE due to valance transitions. (a) Temperature dependence of the unit cell volume of BiNiO$_3$. Low pressure-temperature and high pressure-temperature data are drawn as open and closed circles, and crosses show the weighted average volume in the transition region. From [3]. (b) The dilatometric linear thermal expansion of Bi$_{0.95}$La$_{0.05}$NiO$_3$ on heating and cooling showing a 20 K hysteresis. From [3]. (c) Temperature evolution of structure parameter unit cell volume of Sm$_{2.75}$C$_{60}$. From [4]

A change in volume in response to staggered or uniform spontaneous magneti-
zation is known as magnetovolume effect has been identified as the cause for anomalous thermal expansion of magnetic materials. The underlying nature of NTE or anomalous thermal expansion in magnetic materials is the coupling between magnetic order and the lattice. The first discovery of low thermal expansion material of this type happened to be in 1897 by Guillaume and it was the famous industrial alloy InVar (Fe$_{64}$Ni$_{36}$) [41]. Since then there are many known magnetic materials which exhibit NTE include alloys (GdAgMg [6]), iron based alloys (Nd$_2$Fe$_{17}$N$_x$[42], Gd$_2$Fe$_{17}$[43]), oxides ( (La$_{0.8}$Ba$_{0.2}$)MnO$_3$ [44]), sulphides(CdCr$_2$S$_4$ [45]), fluorides (perovskite MnF$_3$ [5] ) and nitrides (antiperovskite manganese alloy based nitrides [46]). These materials display a variety of unusual mechanical properties such as large, tunable CTE over a considerable temperature span. An excellent review of NTE in functional materials can be found in literature [47]

1.3.2 Negative thermal expansion from framework dynamics

Besides NTE from phase competition, there also exists a growing class of materials with strong, isotropic, robust and thermally persistent NTE that originates from vibrational mechanism, or in other words intrinsic structural degrees of freedom. NTE of this type has recently been described as structural negative thermal expansion (SNTE) [48].

SNTE is a fascinating and growing field of condensed matter physics due to the rarity of the phenomenon, stunning display of unconventional lattice
dynamics, and strong potential for structural applications where dimensional stability is required. This type of NTE phenomenon refers to the unusual tendency for materials to shrink when heated as a property of bond network topology and the associated fluctuations \cite{49, 50, 51} which is distinct from NTE arising from electronic or magnetic degrees of freedom described in section 1.3.1.

SNTE is most often discussed in connection with transverse fluctuations of a linkage between volume defining vertices, which may accompany the librational (rocking) vibrations in rigid bonds or hindered rotational motion of rigid polyhedral subunits. The most studied example that shows this type of behavior is ZrW$_2$O$_8$ (ZWO) \cite{7, 52, 53, 54, 55, 56}. This cubic material has a large unit cell, containing 44 atoms in the form of corner linked ZrO$_6$ octahedra and
WO₄ tetrahedra. The NTE behavior is strong (Figure 2.3.9) in ZWO ($\alpha_V = -27.3 \times 10^{-6}$/K up to 400K) compared to most of NTE materials of this class and reported over wide range of temperature range (0.3-1050 K). The ZrO₆ octahedra and WO₄ tetrahedra connect via the corner O atom, but one of the O in WO₄ is not connected to another unit and the origin of the NTE comes from transverse vibration of Zr - O - W bond [57]. At the same time, the NTE in ZWO survives even after a phase transition occurs at 430 K, but the volumetric thermal expansion coefficient decreases to $-18 \times 10^{-6}$/K. Well-known categories of materials in which the NTE behavior has been attributed to vibrational mechanisms include metal cyanides [58], various zeolite frameworks [59], $A_2M_3O_{12}$ series [60, 61], ZWO family[7, 62], ZrV₂O₇ family[63, 64], Prussian blue analogues[65], MOF-5 materials [66, 67] and metal fluorides [68].
1.4 Theoretical consideration of negative thermal expansion

1.4.1 Grneisen theory and thermal expansion

As introduced by German Physicist Eduard Grneisen [69, 70], Grneisen theory assumes that the phonon frequencies of a crystal are modified as the volume changes. The changing frequencies would allow calculating thermodynamic functions with in harmonic approximation. This approach is known as quasi-harmonic approximation. See reference [71] for more details.

Within Grneisen theory, for a crystal with many normal modes, the mode Grneisen parameter is defined, which explains the effect that changing the volume of a crystal lattice has on its vibrational properties, and as a consequence, the effect that changing temperature has on the size or dynamics of the lattice. Since thermal expansion is a result of the anharmonic nature of bonds, quantification of the anharmonicity in a solid can be achieved with mode Grneisen parameter, $\gamma(q)_i$. The mode-dependent Grneisen parameter for a phonon mode $i$ at a reciprocal lattice point $q$ can be defined as

$$\gamma(q)_i = -\frac{\partial \log \omega(q)_i}{\partial \log V}$$

(1.4.1)

where $V$ is the unit cell volume, and $\omega(q)_i$ is the frequency of the $i$th mode of vibration, which itself is a function of a wave vector $q$ in the BZ.

Equation 1.4.1 implies that for a NTE material, $\gamma(q)_i$ is negative, for modes
soften with increasing temperature and positive, for modes stiffen with increasing temperature. The overall expansion behavior of a material depends on the combined contributions from all modes, therefore materials with negative mode Gruneisen parameters are not necessarily NTE materials. Often thermal expansion is quantified by mean Gruneisen parameter, obtained by integrating Equation 1.4.1 over all modes:

\[ \bar{\gamma} = -\frac{\alpha_v B V}{C_v} \]  

(1.4.2)

where \( B \) is bulk modulus and \( C_v \) is constant volume heat capacity. As \( B, C_v, \) and \( V \) are positive for materials in thermodynamic equilibrium, NTE materials necessarily possess a negative mean Gruneisen parameter.

### 1.4.2 Rigid unit mode picture

Studies have shown that the lattice vibrations responsible for NTE in ZWO are in the energy scale of around 2 meV [55, 50, 72, 73]. The bond stretching and bond bending modes are mostly frozen at this energy scale and vibrations which respect and maintain internal polyhedral distances and bond angles have special significance. The \( \text{WO}_4 \) tetrahedral stretching and bending modes are not thermally excited at the low temperatures where NTE begins, [56] suggesting a hierarchy of energy scales: stiff bond stretching, intermediate bond bending, and a set of low-energy external modes of rigid polyhedra.
units called rigid unit modes (RUMs). The latter set may be supported at low-energy only in certain regions of reciprocal space which are particular to the system under consideration.

The RUM model was first used to explain the displacive phase transitions in silicates [74, 75]. It was developed to describe the behavior of materials with crystal structures that can be described as frameworks of linked polyhedra (examples are ScF$_6$ octahedra in ScF$_3$ and WO$_4$ tetrahedra in ZWO). Vallade and coworkers [76] have shown that the softening of an optical mode nearby an acoustic phonon causes the phase transition of the material quartz and the whole phonon branch has a low frequency at each $k$ values, hence must be associated with RUMs not only at one $k$ value, but along the whole branch. The idea of RUMs acting as soft modes for displacive phase transition was later developed for silicates using a split atom method.

The RUM model has given a number of other new insights and most importantly it has also been used to explain the origin of negative thermal expansion in framework structures. Phonons described by RUM model are associated with collective motion of polyhedra and those collective motions cause atomic displacement without distorting the polyhedra. Therefore these modes are often identified as NTE modes in SNTE materials. Usually the polyhedra vibrational energies are very high when they are distorted compared with the energy when they are not distorted. As a result, we generally expect RUM modes to have low energies. For ZWO the manifold of momenta supporting
RUMs is very complex, as identified through classical calculations [54] using split atom approach. Simplest case of RUMs associated NTE is described in cubic lattice systems ScF$_3$ and ReO$_3$ and more importantly their RUMs correspond to simple momentum space manifolds. ScF$_3$ has only four atoms per unit cell and forms with corner linked octahedra of ScF$_6$. High symmetry points of Brillouin zone (BZ), corresponds to in phase rotation of each stack of octahedra ($M$ point) and out of phase rotation of each stack of octahedra ($R$ point) defines the boundaries of RUM in ScF$_3$ material. Please see Figure 5.1.1 for a better view on this.

Welches and coworkers have developed a simple qualitative picture explaining NTE [77] in ReO$_3$ like structures. It is related with geometrical frame work and is associated with the rotation of stiff structural units or bond bending of the shared corner atom of the polyhedra units by preserving the rigid unit structure (RUM). For simplicity the rotation of a 2D perovskite (2D frame work of linked squares) is considered and the important point is that the area or lattice constant is reduced by the rotation as a straightforward geometrical effect(Figure 1.4.1).

Considering the potential energy of rotation due to thermal fluctuations, $\frac{1}{2} I \omega^2 \langle \theta^2 \rangle_T = \frac{1}{2} k_B T^2$ where $I$ is the moment of inertia of the units, $\omega^2$ is average or Einstein frequency for the rotations, $\langle \theta^2 \rangle_T$ is the equilibrium fluctuating value of $\theta^2$ at temperature $T$, $k_B$ is Boltzmanns constant. Considering the lattice area reduction, from $A_0$ to $A_0 \cos^2 \theta$ the lattice constant obeys the relation $a = a_0(1 - \eta_a \theta^2)$ and the expression $\frac{\Delta a}{a} = -\frac{\eta_a k_B T}{I \omega^2}$ is obtained, which then reduces to CTE
\( \alpha_L = -\frac{\eta_L k_B}{I_\alpha^2} \). Here \( \eta_L \) is identified as geometrical constant which is equal to unity in this case. Chapter 5 discusses a model that we developed to approximate the staggered rotation in 2D square lattice and proves that the above constant equals to 1/2 in a 2D lattice with few squares, where harmonic wave limit is applied and 2/3 in a lattice with large number of square units, where circle wave limit is applied.

As shown the geometrical effect on the CTE leads to a negative CTE. At the same time since the frequency of modes appears at the bottom of the CTE it resembles that the softer modes contribute more to the CTE. A particularly soft dynamic distortion of this structure preserves bond lengths and internal polyhedral bond angles while decreasing the volume of the time-averaged structure as the vibrational amplitude is increased through thermal activation.

This classical picture has been widely discussed in general reviews of the NTE.
phenomenon[78, 79, 80, 81].

1.4.3 Tension effect and NTE

SNTE is commonly described using a mechanism called tension effect which is thoroughly discussed in the review [8]. The simplest form of the tension effect considers a linear molecule which consists of three atoms. As the center atom of the linkage move transversely, the corner atoms move towards each other, assuming the bonds are rigid. Applying this into three dimensional (3D) structure immediately implies that the structure decreases it’s dimensions, hence NTE. As the corner atoms of the linkage move further away from each other the amplitude of the transverse fluctuation of the center atom decreases and results in increasing volume. This results in increasing stretch or the tensions of the bonds, suggesting negative Grneisen parameter. Thermal ellipsoids displayed by 3D systems such as ScF$_3$ and ReO$_3$ are consistent with the tension effect and the mechanism is most useful in interpreting the NTE of CN$^{-}$ framework structures such as AgCN, AuCN, CuCN and Ni(CN)$_2$. RUM model is a special case discussed under tension effect.

1.4.4 Thermodynamics of NTE materials

A study [82] has shown that for materials with positive compressibility and NTE, the first law of thermodynamics reads as $dQ = dU - PdV$. The author has mathematically proved, that the first law of thermodynamics ($dQ = dU + PdV$) holds true only if either both the compressibility and thermal expansion are
Figure 1.4.2: Representation of the tension effect. A linear linkage of three atoms is shown in left. This can distort such a way that the central atom displaces transverse direction or the two end atoms displace in opposite ways. In both cases the bonds stay in rigid and the two end atoms move inwards in the vertical direction. Taken from [8]

negative or both of them are positive. A different [83] study has proposed the isentropic (constant entropy) volume expansivity, $\alpha_V = (1/V)(\partial V/\partial T)_S$ for materials with NTE instead of standard definition of isobaric (constant pressure) CTE, $\alpha_V = (1/V)(\partial V/\partial T)_P$.

There are plenty of materials found to be possessing NTE property and thousands of literature have been published directly or indirectly related with NTE phenomenon, but only a handful numbers of thermodynamic analysis on NTE materials are found in literature. So readers who are interested would find it is worth working in this field.

1.5 Perovskites
Perovskite oxides, a class of solid materials with chemical formula ABO$_3$, contains examples of perhaps every possible type of material behavior. Underpinning the competing interactions behind this diversity are fascinating cascades of structural transitions associated with tilts of the BO$_6$ octahedra, which are strongly influenced by the A-site ions through geometric tolerances[84, 85]. A-site-free perovskites based on oxygen are rare, as the B ion must take on the extremal +6 valence state, and the only known instance is ReO$_3$. A moderately-sized NTE effect occurs at low temperature in this material[86] and can be understood in terms of a model of rigid unit modes (RUMs) described in section 1.4.2. Though that is the case with oxides, A site free perovskite fluorides or in other words MF$_3$-type structures are not rare because of the common trivalent(+3) state found in most of the metals in the periodic table, especially among transition metals and lanthenides.

1.6 Trifluorides and their structures

Figure 1.6.1 shows a global structural phase diagram of MF$_3$ perovskites, where M is a +3 metal ion. For large ($r_5 > 0.85A$) ionic radius $r_5$ (Shannon), fluorine ions can pack around the M ion with high F coordination up to n=8 or 9 in common large-gap optical materials of orthorhombic and tysonite type structures which are commonly formed with rare earth metal ions.

Order-disorder type second order phase transitions has been reported for LaF$_3$ - NdF$_3$[87] (refer Figure 1.6.1), from low temperature trigonal($P\bar{3}c1$) to high
Figure 1.6.1: Global structural phase diagram of MF$_3$ type perovskites.

temperature hexagonal ($P6_3/mmc$) phases which both are two modifications of tysonite type structure[88]. SmF$_3$ - GdF$_3$ crystallize from melt to tysonite type structure and upon cooling they transform into orthorhombic($Pnma$) $\beta$-YF$_3$ [89] type structure. Structural phase transitions occurred in TbF$_3$, DyF$_3$ and HoF$_3$ are accounted for some sort of impurity[90, 91, 92] in the system and no transition has been reported for pure systems. ErF$_3$ - YbF$_3$, LuF$_3$ and YF$_3$ yield a new high temperature form of $\alpha$-YF$_3$ type[92].

Below $r_s < 0.8\text{Å}$, perovskites form with simple-cubic symmetry($Pm3\bar{m}$) at high temperatures. At low $r_s$, and among the 3d metal trifluorides, a structural cubic-to-rhombohedral($R\bar{3}c$) phase boundary is apparent, with the exception
of MnF$_3$. ScF$_3$ is the only trifluoride with cubic symmetry at room temperature and can be considered to be the standout among all and will be discussed thoroughly throughout the thesis.

1.7 Scandium trifluoride(ScF$_3$)

1.7.1 Negative thermal expansion in ScF$_3$

Recently, nonmagnetic ionic insulator ScF$_3$ has drawn particularly intense attention in the chemistry community[9] as the first instance of a perovskite-structured material with strong, isotropic, and thermally persistent NTE, a distinction which no longer appears to be an isolated case[93]. ScF$_3$ displays strong NTE (-42 ppm/K < $\alpha_V < 0$) over a temperature window of 1000 K, but is also unusual in its lack of any type of phase transition whatsoever within the solid state.

Cubic ScF$_3$ has 4 atoms per unit cell and consists of corner-inked octahedra which fill space in three dimensions with unit cells $a = b = c$. The high symmetry points in the first Brillouin zone (BZ) in reciprocal space are labeled zone center $\Gamma$(0, 0, 0), zone face center $X$ ($2\pi/a(1/2, 0, 0)$), zone edge center $M(2\pi/a(1/2, 1/2, 0))$, and zone corner $R(2\pi/a(1/2, 1/2, 1/2))$. Sc has the longest Shannon effective ionic radius of all 3d transition metal trifluorides, and the lattice dimension parameter $a = 4.02$ Å at room temperature is very close to twice the sum of these radii for Sc (0.745) and F (1.19 Å), suggesting chemical
bonding is ionic.

1.7.2 Pressure induced phase transition in ScF₃

Cubic ScF₃ further stands out among substances in that it has the most stable structural phase of any known solid trifluoride, retaining cubic symmetry from its high melting point >1800 K to <0.5 K[9, 94]. A finite-temperature cubic to rhombohedral (c-r) transition can be induced however through application of slight pressure [95, 96] (<0.2 GPa ~ 2000 atm), chemical substitution of Ti[20], Al[19], or Y[97] for Sc, and even by the weak stresses induced by polymeric impregnation of powder samples[21], suggesting that the quantum nature of the cubic phase at low temperature is delicate and susceptible to even mild perturbations.

X-ray diffraction [95, 9] and Raman spectroscopy[95] results have revealed that at room temperature ScF₃ undergoes a pressure induced phase transition from c-r between 0.5 and 0.8 GPa and rhombohedral to orthorhombic structure above 3.0 GPa. As suggested by the authors[95] the first transition point which is quite low as hydrostatic pressure is the result of disturbance of the balance between short-range dipole-dipole(of fluorine ions) and long-range Coulomb interactions which is related to rotation of the ScF₆ octahedra around a threefold axis. The rotation of octahedra corresponds to \( R = \pi / a (1, 1, 1) \) point in cubic phase BZ and the c-r phase transition occurs due to condensation of this mode (Figure 1.7.1).
Observed pressure dependence of the transition temperature is \( dT_c/dp \sim 525 \) K/GPa \([9, 95, 96]\). The c-r phase transition in \( \text{ScF}_3 \) is never realized down to 0.4 K \([94]\) in atmospheric pressure and using inelastic x-ray scattering (Chapter:2) results, we estimate that pressures as small as 740 bar = 0.074 GPa would be sufficient to drive the transition upward to 0 K. The sensitivity of the phase boundary suggests that the nature of the cubic phase is delicate at low temperature and susceptible to even mild perturbations \([21, 20, 20, 19]\). Section 2.3.10 further discusses this.

If suitable substrates of \( \text{ScF}_3 \) are developed, new functionalities may be reached in film synthesis, as cooling from the growth temperature would effectively stretch epitaxial films. Significant efforts in the physics groups of Profs. Barrett Wells in Physics Department have already produced thin films of NTE \( \text{ScF}_3 \) \([98]\). Thin films of \( \text{ScF}_3 \) are grown using pulsed laser deposition, and while large fraction of a film is having very good epitaxy and small mosaic, remaining regions are polycrystalline. Unique features of this material such as large band gap, non-oxide nature, poor adhesion under pressure and high saturated vapor pressure remain as significant challenges to overcome.

1.7.3 Electronic structure of \( \text{ScF}_3 \)

In formation of \(\text{ScF}_3\), from a scandium atom and a fluorine atom, the scandium atom loses its three valence electrons (and turn to \( \text{Sc}^{3+} \)) to three fluorine atoms (and form \( \text{F}^- \)), which each of the fluorine has just enough space to accept it. We
must realize that unlike other 3d type transition metal trifluorides Sc$^{+3}$ in ScF$_3$ has $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^0$ configuration and hence no free $d$ electrons. One consequence is that ScF$_3$ has no local moment magnetism and no free electrons, implying that the available degree of freedom are purely lattice origin.

The band structure of ScF$_3$ clearly shows a band gap of at least 8 eV which is an indication of strongly bound valence electrons and empty conduction band, permitting classification as an ionic insulator. It should be noted that ReO$_3$ (introduced in 1.5), a material isostructural to ScF$_3$, happens to be a good
metal. The vastly different electronic structures of otherwise similar materials might be interesting to further investigate.

Since both materials are SNTE materials, it is meaningful to compare the electronic structures of each with its own distorted structure. Using first principle calculations, a comparative study [99] has been carried out and the electronic band structure of distorted ReO$_3$ (O atoms are displaced perpendicular to Re-O-Re bond) has shown a small destabilization of the flat conduction band compared with conduction band of non-distorted structure. The atomic displacement was attributed to formation of antibonding orbitals and the authors conclude that this results in destabilizing the distortion of ReO$_3$ structure. On the other hand the electronic band structure of distorted ScF$_3$ structure hardly changes from its non distorted counterpart. Therefore it is concluded that the ScF$_3$ favors the distortion more than that of ReO$_3$ and as a result the CTE of ScF$_3$ ($\alpha_V = -42\times 10^{-6}/K$ in 60 K to 110 K temperature window and $\sim -25\times 10^{-6}/K$ at 300 K) is larger than ReO$_3$ ($\alpha_V = -7.68\times 10^{-6}/K$ in 5 K to 300 K temperature range).

1.8 Motivation

A central question in the study of SNTE is whether basic structural mechanics principles and intuition can be applied to guide discovery of new materials that display this anomalous effect. For example, metallic ReO$_3$ and insulating ScF$_3$ with open perovskite structure display SNTE over a wide range of tem-
peratures, but why do other open perovskites most commonly exhibit positive thermal expansion (PTE)? or can composite materials be formed with thermal expansion over a wide temperature window, or do stresses inevitably shift the structural phase to one with PTE? Why is SNTE so rare, inevitably yielding to PTE in response to disorder and application of pressure?

In pursuit of conceptual control of the phenomenon, innovative approaches have been offered which link thermally activated transverse vibration of structural units to a tendency to draw in lattice dimensions. Rigid unit approaches view polyhedral molecular units (i.e., metal-anion tetrahedra and octahedra) rather than ions as the fundamental building blocks of a material and attempt to link the states built from rotational zero modes of the free molecules to the low-energy modes of the crystal. In this view, intramolecular degrees of freedom are effectively integrated out, and the nature of their coordinated motion as a function of lattice topology and connectivity is the central feature of SNTE. New discoveries of robust SNTE have reinvigorated the field and raised the question of whether strict molecular rigidity is an appropriate starting point or if, instead, it is more appropriate to consider only the rigidity of the stiffest bonds in a view of the materials as a framework of struts.
Chapter 2

Lattice dynamics study of ScF$_3$ using inelastic x-ray scattering

2.1 Introduction to Inelastic X-ray Scattering

Inelastic x-ray scattering (IXS) is an experimental technique which is used to investigate distinct forms of material dynamics. In simple words, a collection of a photon is sent in and the energy and the momentum of the scattered photons are analyzed which carry information of disparate excitations of the material. These excitations basically are differentiated by their energies and a schematic is provided in Figure 2.1.1.

![Excitations schematic](image)

Figure 2.1.1: Excitations that may probe using IXS, From [10]
We can identify several distinct methods used in order to probe those excitations and since there are no sharp boundaries among excitations energies, some of them may be probed using more than one technique. Table 2.1.1 lists some of the techniques that fall under the broad interpretation of the IXS.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Incident photon energy</th>
<th>Energy transfer</th>
<th>Information of the material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compton</td>
<td>100 keV</td>
<td>keV</td>
<td>Electron momentum density</td>
</tr>
<tr>
<td>Magnetic Compton</td>
<td>100 keV</td>
<td>eV</td>
<td>Density of unpaired spin</td>
</tr>
<tr>
<td>RIXS(Rasonance)</td>
<td>4-20 keV</td>
<td>0.1 - 50 eV</td>
<td>Electron structure and excitations</td>
</tr>
<tr>
<td>SIXS(Soft x-ray)</td>
<td>0.1-2 keV</td>
<td>0.01 - 5 eV</td>
<td>Electronic and magnetic structure and excitations</td>
</tr>
<tr>
<td>NIS(Nuclear IXS)</td>
<td>10-30 keV</td>
<td>1 - 100 meV</td>
<td>Element specific phonon and Density of state (DOS)</td>
</tr>
<tr>
<td>X-ray Ramam</td>
<td>10 keV</td>
<td>50 - 1000 meV</td>
<td>Edge structure, Bonding, Valence</td>
</tr>
<tr>
<td>NRIXS</td>
<td>10 keV</td>
<td>0.01 - 10 eV</td>
<td>Electronic structure and excitation</td>
</tr>
<tr>
<td>IXS</td>
<td>10-25 keV</td>
<td>1 - 100 meV</td>
<td>Atomic dynamics and phonon dispersion</td>
</tr>
</tbody>
</table>

Table 2.1.1: List of techniques broadly grouped under the heading of Inelastic X-Ray Scattering. From[10]

### 2.1.1 IXS advantages over other spectroscopic techniques

One of the significant advantages of IXS is the access to small samples. The
synchrotron radiation of high flux and brilliance is capable of focusing the beam to $\sim 100$ microns diameter easily. Even $\sim 10$ microns in diameter can be achieved with some losses. The facts that incoming x-ray photon energy of $\sim 20$ keV is significantly higher than the measured energy transfer of $\sim 1-200$ meV and the energy and momentum of photon is directly proportional to each other lead to other compelling advantageous of using IXS such as decoupling of the energy and momentum transfer, achieving high momentum resolution and independence of energy resolution from energy transfer. The Thompson cross section for x-rays is smaller than the absorption scattering cross section at least by one order of magnitude. This could prevent multiple scattering from the sample and incoherent scattering at higher energies by only penetrating into the top 0.01 or 0.1 mm of the sample. Therefore most materials have very short attenuation length for x-rays which eventually results in lower background signal as well. But in case of neutron, the scattering cross section dominates hence multiple scattering can be a problem. On the other hand higher absorption cross section in x-rays could easily leads to radiation damage of the material. Nevertheless, it is worthwhile to mention that neutron holds the edge when higher energy resolution is needed but some of the samples can’t be measured using neutron scattering or diffraction experiments as they highly absorb neutrons. Some of the common examples are Cadmium, Samarium and Europium.

Next section in current chapter is dedicated to elaborate general scattering
theory using both classical and quantum mechanical perspectives. It will be followed by a discussion on probing phonons from a theoretical point of view. In last section, I will discuss the IXS experimentation to investigate the lattice dynamics, especially, phonons in crystalline material ScF$_3$.

2.2 Scattering theory

Consider scattering of an x-ray beam from two atoms in an arbitrary lattice planes of a sample which are separated by distance $r$. Unlike in x-ray diffraction the lattice planes can be nonparallel. Let's assume the incoming x-ray wave vectors are parallel and are denoted by $\vec{k}_i$. The scattered wave vectors (parallel) are $\vec{k}_f$. See Figure 2.2.1 for clear view.

![Figure 2.2.1: X-ray scattering from an arbitrary atoms](image)

In order to determine whether the interference is constructive or destructive, we need to figure out the phase difference between two waves. Phase difference can be obtained by considering the path length difference and can be written
as

\[ \Delta l = l_2 - l_1. \] (2.2.1)

From triangle ABC,

\[ l_1 = |\vec{r}| \sin(\beta) = |\vec{r}| \sin(90 - \alpha) = |\vec{r}| \cos(\alpha) \] (2.2.2)

and using vectors we may write

\[ \vec{k}_i \cdot \vec{r} = |\vec{k}_i||\vec{r}| \cos(\alpha). \] (2.2.3)

Since

\[ |k_i| = \frac{2\pi}{\lambda} \] (2.2.4)

\[ \vec{k}_i \cdot \vec{r} = \frac{2\pi}{\lambda} |\vec{r}| \cos(\alpha) \] (2.2.5)

\[ l_1 = \frac{\lambda}{2\pi} \vec{k}_i \cdot \vec{r}. \] (2.2.6)
Likewise from triangle ACD,

\[ l_2 = \frac{\lambda}{2\pi} \mathbf{k}_f \cdot \mathbf{r}. \]  

(2.2.7)

Therefore the path length difference can be written as

\[ \Delta l = \frac{\lambda}{2\pi} (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} \]  

(2.2.8)

and the phase difference is given by

\[ \Delta l = \frac{2\pi}{\lambda} (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r} \]  

(2.2.9)

here \( \mathbf{Q} \) is defined as scattering vector where,

\[ \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i \]  

(2.2.10)

The scattering wave vector, \( \mathbf{Q} \) and the spatial arrangement of the atoms in the sample are key factors when determining the signal at the detector. The spatial positioning of atom is important since it determines the tendency of sample to scatter the incoming wave. We can introduce the density of scattering atoms in the sample to be \( \rho(\mathbf{r}) \) and assume the scattering density depends on the
spatial arrangement of atoms.

Figure 2.2.2: Radiation from source (S) to detector (D) via the sample

Using plane wave approximation and incorporating all above variables, an expression for the amplitude of the signal at the detector (scattering wave amplitude), $f_D$ from a wave emitted by point at tip of the $\vec{r}$ can be written as,

$$f_D \propto \rho(\vec{r}) e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{r}}$$  \hspace{1cm} (2.2.11)$$

$$f_D \propto \rho(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}}$$  \hspace{1cm} (2.2.12)$$

This is specifically derived for one particular point in the sample. Therefore to calculate the total amplitude at detector we need to integrate over the sample volume.
\[ f_D \propto \int_V \rho(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} d\vec{r} \quad (2.2.13) \]

where \( V \) is the total volume of the sample.

Fourier transformation of scattering density leads to the expression

\[ \rho(\vec{Q}) = \int \rho(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} d\vec{r} \quad (2.2.14) \]

which is similar to the amplitude of the signal at the detector.

To describe the scattering density within one unit cell let us assume the atoms in the unit cell don’t interact with each other and have their own local scattering density \( \rho_j(\vec{r'}) \) where

\[ \vec{r}' = \vec{r} - \vec{r}_j \quad (2.2.15) \]

Figure 2.2.3: Reflection geometry where the blue solid circle represents the \( j^{th} \) atom where \( \vec{r}_j \) and \( \vec{r} \) initiate at the unit cell origin
The total scattering density

\[ \rho(\vec{r'}) = \sum_j \rho_j(\vec{r'} - \vec{r}_j) \quad (2.2.16) \]

Now rewriting the total scattering, plugging \( \rho_j(\vec{r'}) \) and multiplying by 1 = \( e^{i\vec{Q}.\vec{r}_j}e^{-i\vec{Q}.\vec{r}_j} \)

\[ \rho(\vec{Q}) = \sum_j e^{i\vec{Q}.\vec{r}_j} \int \rho(\vec{r'}) e^{i\vec{Q}.\vec{r'}} d\vec{r'} \quad (2.2.17) \]

Here the integral term is known as atomic form factor \( f_j(\vec{Q}) \) which is a property of atoms themselves and the summation term \( \sum_j e^{i\vec{Q}.\vec{r}_j} \) depends on where the atoms are located in the lattice. Finally the intensity of scattered beam is given by

\[ S(\vec{Q}) = \langle |\rho(\vec{Q})|^2 \rangle = \sum_{jk} f_j(\vec{Q}) f_k(\vec{Q}) \langle e^{i\vec{Q}.(\vec{r}_j - \vec{r}_k)} \rangle \quad (2.2.18) \]

which is termed as static structure factor.

2.2.1 Dynamic structure factor \( S(\vec{Q}, \omega) \)

In previous section I have formulated a mathematical expression described scattering from arbitrary atoms instantaneously at a given time. But we can extend our analysis further to consider scattering from sample atoms at different
times. This of course, results in a phase shift in the scattering wave.

Redefining the scattering density in momentum space and introducing phase shift \( e^{-i\omega t} \),

\[
\rho(\vec{Q}, t) = \sum_j f_j(\vec{Q}) e^{i(\vec{Q} \cdot \vec{r}_j(t) - \omega t)}
\]  \hspace{1cm} (2.2.19)

Averaging all time to get the total scattering

\[
\rho(\vec{Q}, \omega) = \int \rho(\vec{Q}, t) e^{-i\omega t} dt
\]  \hspace{1cm} (2.2.20)

Writing the intensity of the scattering

\[
S(\vec{Q}, \omega) = \int \rho(\vec{Q}, t') e^{-i\omega t'} dt' \times \int \rho(-\vec{Q}, t) e^{-i\omega t} dt
\]  \hspace{1cm} (2.2.21)

Shifting \( t \) by \( t + t' \)

\[
S(\vec{Q}, \omega) = \int \int \rho(\vec{Q}, t') \rho(-\vec{Q}, t + t') e^{-i\omega t} dt dt'
\]  \hspace{1cm} (2.2.22)

Performing an average over all time origins

\[
S(\vec{Q}, \omega) = \int \langle \rho(\vec{Q}, 0) \rho(-\vec{Q}, t) \rangle e^{-i\omega t} dt
\]  \hspace{1cm} (2.2.23)
Substituting back from Equation 2.2.19

\[
S(\mathbf{Q}, \omega) = \sum_{jk} f_j(\mathbf{Q}) f_k(\mathbf{Q}) \int \langle e^{i\mathbf{Q}.\mathbf{r}_j(0)} e^{-i\mathbf{Q}.\mathbf{r}_k(t)} \rangle e^{-i\omega t} dt
\] (2.2.24)

This is a critical equation in IXS which carries both spatial and time evolution information about excitations of the system and known as dynamical structure factor. More importantly for us the signal or the spectra collected in IXS experiment is directly proportional to dynamic structure factor \(S(\mathbf{Q}, \omega)\) of the material.

2.2.2 Quantum mechanical perspective

Let me start by considering the electron-photon interaction Hamiltonian. Conventionally it can be separated into two terms \(H_0\) and \(H_i\), where non interacting term reads

\[
H_0 = \sum_j \frac{1}{2m} \mathbf{p}_j^2 + \sum_{jj'} V(r_{jj'})
\] (2.2.25)

and electron - photon interaction term is given by

\[
H_i = \sum_j \frac{e^2}{2mc^2} \mathbf{A}^2(\mathbf{r}_j) - \frac{e}{mc} \mathbf{A}(\mathbf{r}_j).\mathbf{p}_j
\] (2.2.26)

While \(\mathbf{A}\) and \(V\) denotes the electromagnetic field vector and scalar potentials,
the electron momentum and position are denoted by $\vec{p}$ and $\vec{r}$. In Hamiltonian, $H_i$ the first terms with $A^2$ term dominates in nonresonant scattering processes while the second term leads in resonant scattering (case where the incoming energy is tuned into absorption edge of the atom). The nonresonant scattering cross section depends on dynamic structure factor and has the form of Equation 2.24. Since we only deal with nonresonant scattering, from here onwards I would only take $H_i^{(1)} = \sum_j \frac{e^2}{2mc^2} A^2(\vec{r}_j)$ term into consideration.

Introducing the photon creation ($a^\dagger_{k\alpha}$) and annihilation ($a_{k\alpha}$) operators the vector potential can be written as

$$\vec{A}(\vec{r}) = L^{-3/2} \sum_{k,\alpha} \left( \frac{\hbar}{\omega_k} \right)^{1/2} c(\epsilon_{\alpha}a^\dagger_{k\alpha} e^{i\vec{k}.\vec{r}} + \epsilon_{\alpha}a_{k\alpha} e^{-i\vec{k}.\vec{r}})$$

(2.2.27)

where $\omega_k$, $\alpha$ and $k$ denote the angular frequency, polarization and wave vector of photon respectively. $L^3$ is normalization box volume.

Let us now consider photon in three dimensional box of side $L$. The photon states are quantized and only allowed $k$ values given by $2\pi/L(n_x, n_y, n_z)$ where $n_x, n_y$ and $n_z$ are integers.

Any possible final-state wave-vector $k$ corresponds to a point in wave vector space with coordinates $(k_x, k_y, k_z)$. Then we can define the density of $k$ states (number of $k$ points per unit volume) to be $L^3/(2\pi)^3$. In three dimensional system the $k$ space volume between $k'$ and $k' + dk'$ is $4\pi^2 k'^2 dk'$. Therefore the number of $k$ states in the region between $k'$ and $k' + dk'$ is

42
\[(\frac{L}{2\pi})^3 4\pi k'^2 dk'\]  \hspace{1cm} (2.2.28)

Hence the number of points for \( k \)-vectors going into an element of solid angle \( d\Omega \) (Solid angle of sphere is \( 4\pi \)) for polarization state \( \alpha \) with energies between \( E' \) and \( E' + E' \) is

\[(\frac{L}{2\pi})^3 k'^2 dk' d\Omega\]  \hspace{1cm} (2.2.29)

Defining the density of state per unit energy \( g(E') \), where \( E' = \hbar c k' \) is the energy corresponding to wave vector \( k' \) the total number of states between photon energies \( E' \) and \( E' + dE' \) could be written as

\[g(E')dE' = (\frac{L}{2\pi})^3 k'^2 dk' d\Omega\]  \hspace{1cm} (2.2.30)

\[g(E') = (\frac{L}{2\pi})^3 (\frac{k'^2}{\hbar c}) d\Omega\]  \hspace{1cm} (2.2.31)

Normalization corresponds to one particle per box volume \( L^3 \), so the number of particles crossing per unit area per unit time is given by the incident photon velocity divided by the \( L^3 \) which is defined as the incident flux
Incident flux = \( \frac{c}{L^3} \) \tag{2.2.32} 

Consider scattering process from photon initial state \((k\alpha)\) to final state \((k'\alpha')\) and sample intial state \(\lambda\) to sample final state \(\lambda'\). Using the Fermi golden rule the rate of transition of scattered flux into solid angle \(d\Omega\) can be written as

\[
\text{Scattered flux} = \frac{2\pi}{\hbar} |\langle k'\alpha'\lambda' | H_{i}^{(1)} | k\alpha\lambda \rangle|^2 \frac{L^3 k'^2}{8\pi^3 \hbar c} d\Omega \] \tag{2.2.33}

Then the differential cross section to solid angle \(d\Omega\) can be defined as (The cross section will be elaborated in section 2.2.3)

\[
\frac{d\sigma}{d\Omega} = \frac{\text{Scattered flux}}{\text{Incident flux}} = \frac{|\langle k'\alpha'\lambda' | H_{i}^{(1)} | k\alpha\lambda \rangle|^2}{4\pi^2 \frac{L^6 k'^2}{\hbar^2 c^2}} \tag{2.2.34}
\]

Substituting for \(|H_{i}^{(1)}|\),

\[
\langle k'\alpha'\lambda' | H_{i}^{(1)} | k\alpha\lambda \rangle = \frac{1}{L^3 \frac{\hbar c}{mc^2}} \frac{\hbar c}{(\omega_k \omega_{k'})^{1/2}} (e^* a e) \langle \lambda' | \sum_{j} e^{-i(k-k')\cdot r_j} | \lambda \rangle \] \tag{2.2.35}

Using \(\omega = ck\) and considering the energy conservation condition for the scattering process, we obtain the partial differential cross section
\[
\frac{d^2 \sigma}{d\Omega dE} = \left( \frac{\epsilon^2}{mc^2} \right) \frac{2k'}{k} |\epsilon_1 \ast \epsilon_2|^2 \langle \lambda | \sum_j e^{-i(\vec{k} - \vec{k}') \cdot \vec{r}_j} |\lambda' \rangle \langle \lambda' | \sum_{j'} e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_{j'}} |\lambda \rangle \delta(E_{\lambda} - E_{\lambda'} + \hbar \omega)
\]

(2.2.36)

Here wave vector \( \vec{q} = \vec{k} - \vec{k}' \) and taking sum over all possible final state \( \lambda' \)

\[
\frac{d^2 \sigma}{d\Omega dE} = \frac{k'}{k} |\epsilon_1 \ast \epsilon_2|^2 S(\vec{Q}, \omega)
\]

(2.2.37)

where

\[
S(\vec{Q}, \omega) = \sum_{\lambda \lambda'} \sum_{jj'} p_\lambda \langle \lambda | \sum_j e^{-i\vec{Q} \cdot \vec{r}_j} |\lambda' \rangle \langle \lambda' | \sum_{j'} e^{i\vec{Q} \cdot \vec{r}_{j'}} |\lambda \rangle \delta(E_{\lambda} - E_{\lambda'} + \hbar \omega)
\]

(2.2.38)

and \( p_\lambda \) is the probability of initial state \( \lambda \).

Time dependency To introduce the time dependency, let us write down the delta function in its integral representation

\[
\delta(E_{\lambda} - E_{\lambda'} + \hbar \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(E_{\lambda'} - E_{\lambda})\eta / \hbar} e^{-i\omega t} dt
\]

(2.2.39)

Writing down the wave function in Schrodinger representation

\[
|\psi(t)\rangle = U(t)|\psi(0)\rangle
\]

(2.2.40)
where

\[ U(t) = e^{-iHt/\hbar} \quad (2.2.41) \]

and the matrix element of the operator can be written as

\[ \langle \psi(0) | A | \psi(0) \rangle. \quad (2.2.42) \]

In this representation, operators are constants and all the time dependence is carried by the states. Now defining the operator in Heisenberg picture, in which the operators carry the time dependency,

\[ A(t) = U(t)\dagger AU(t) \quad (2.2.43) \]

it is obvious that \( A(0) = A \).

Let us go back to our derivation. Introducing two operators \( A, A' \) and considering Equation 2.2.39 we can write,
\[
\sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | A'| \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | A'| \lambda \rangle e^{i(E_{\lambda'} - E_\lambda) t / \hbar} e^{-i\omega t} dt \quad (2.2.44)
\]

Applying the operations \( e^{-iE_\lambda t / \hbar} \langle \lambda | \lambda \rangle \) to previous equation

\[
\sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | A'| \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | A'| \lambda \rangle e^{i(E_{\lambda'} - E_\lambda) t / \hbar} e^{-i\omega t} dt
\]

(2.2.45)

Using the completeness property over sum over \( \lambda' \) we can write

\[
\sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | A'| \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \lambda | A_0(t) | \lambda \rangle \quad (2.2.46)
\]

Using Equation 2.2.46 we can write Equation 2.2.38 as

\[
S(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \rho(\vec{Q}, 0) \rho^+(\vec{Q}, t) \rangle \quad (2.2.47)
\]

Taking the sum over all electrons \( j \), the density fluctuation operator is defined by

\[
\rho(\vec{Q}) = \sum_j e^{-i\vec{Q} \cdot \vec{r}_j} \quad (2.2.48)
\]
which is the Fourier transformation of electron density operator

\[
\rho(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j).
\]  
(2.2.49)

It is worthwhile to note that we can obtain an expression for static structure factor \(S(\vec{Q})\) simply by integrating the dynamic structure factor (Equation 2.2.47) over transfer energy \(\omega\)

\[
S(\vec{Q}) = \hbar \int_{-\infty}^{\infty} S(\vec{Q}, \omega) d\omega
\]  
(2.2.50)

### 2.2.3 Scattering cross section

The cross section is a quantification of an effective area in which the scattering event occurs and denoted by \(\sigma\). In scattering experiments, one is often interested in knowing how likely a given event occurs. However, the scattering rate depends strongly on experimental variables such as the density of the target material, the intensity of the beam, or the area of overlap between the beam and the target material. To control for these differences, one can factor out these variables, resulting in an area-like quantity known as the cross section.

The cross section is a scalar that only quantifies the intrinsic rate of an event. In contrast, the "differential cross section" \(d\sigma/d\Omega\) is a function that quantifies the intrinsic rate at which the scattered projectiles can be detected at a given
angle (where $\Omega$ represents solid angle). The total cross section $\sigma$ would simply be the integral of $d\sigma$.

The cross-section for non-resonant scattering from a material is usually divided into the product of a term relating to the probe-sample interaction and the dynamic structure factor, $S(Q, \omega)$, which is more directly related to atomic motions in the sample. Scattering rate of photons from incident beam (from initial state) to scattered beam (to final state) scattered into solid angle $d\Omega$ within energy width $dE$ and momentum transfer $\vec{Q}$ is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_2}{k_1} k^2_r |\epsilon_1 * \epsilon_2|^2 S(Q, \omega)$$

(2.2.51)

where $k_1$ and $k_2$ are incident and scattered momentum states of the photons and $\epsilon_1, \epsilon_2$ are corresponding polarization states. Photon has usual energy momentum relationship of $E = h\omega_{ph} = hc|\vec{k}| = hc/\lambda$. Thompson scattering cross section or scattering by free electrons (($d\sigma/d\Omega)_{Th}$) is defined as $r^2_e |\epsilon_1 * \epsilon_2|^2$ where $r_e = e^2/m_e c^2$ is classical electron radius.

2.2.4 IXS for phonons

Inelastic neutron scattering (INS) has long been the method for studying the lattice dynamics of crystals. As introduced earlier in the chapter, IXS is a key technique, which could replace the INS since significant recent development of synchrotron-related instrumentation. Fundamentally they are different as IXS
probes electron cloud around the atom while INS probes the nuclear motion. Worthwhile comparison of two techniques was already made in section 2.1.1. In this section basic theory of the inelastic scattering technique will be illustrated.

Figure 2.2.4: Typical features appear on high energy resolution inelastic scattering spectrum

Roughly speaking, in an IXS experiment a high energy x-ray beam incidence into the sample and scattered beam is collected at the detector after reflecting back from a set of analyzers. The fact that energy of scattered beam is different from incidence beam makes this process inelastic unlike elastic scattering process x-ray diffraction. Therefore using IXS experiments both the change in momentum and change in energy of lattice vibrations can be measured.

Let us assume that the incoming photon wave vector is \( \vec{k}_i \) and has the energy of \( E_i \) while the wave vector and energy of an outgoing photon is \( \vec{k}_f \) and \( E_f \).
respectively.

\[ E_i = \hbar \omega_i, E_f = \hbar \omega_f \]  

(2.2.52)

The change in energy can be written as

\[ \Delta E = E_f - E_i = \hbar \omega_f - \hbar \omega_i \]  

(2.2.53)

Change in energy of photons can be related to two processes occur inside the crystal named phonon creation where \( E_f > E_i \) and phonon annihilation where \( E_f < E_i \). Therefore the difference in energies can be considered as phonon energy, \( \hbar \omega_{ph} \). Likewise, considering the momentum conservation within the system (Crystal and interactive photons), phonon-created has momentum \( \vec{k}_i \rightarrow \vec{k}_f \pm \vec{G} \) and phonon-annihilated has momentum of \( \vec{k}_f \rightarrow \vec{k}_i \pm \vec{G} \), where \( \vec{G} \) is reciprocal lattice vector of the crystal. Please refer the Figure 2.2.5.

Figure 2.2.5: Phonon creation is shown on left and phonon annihilate process on right

2.2.5 Scattering from phonons in theoretical perspective

In the derivation of section 2.2.2 we assumed that the x-ray energy transfer is
much greater than the lattice vibrational energies. If we consider low energy transfer in scattering events then we can no longer omit the lattice vibration and have to include those effects in electron density fluctuations. By assuming the atom vibrates along with the electron cloud attached to it, we may write

\[ \rho(\vec{Q}) = \sum_{j} e^{-i\vec{Q}.\vec{r}_j} = \sum_{m} e^{-i\vec{Q}.\vec{R}_m} \left[ \sum_{j(m)} e^{-i\vec{Q}.(\vec{r}_j - \vec{R}_m)} \right] \quad (2.2.54) \]

Summation of \( m \) is taken over all atoms in the crystal while second summation runs over all electron in \( m \)th atom. Here the second summation represents the Fourier transformation of the electron density of individual atom and is well-known atomic form factor (\( f(\vec{Q}) \) - recall Equation 2.2.17). Introducing time dependency into Equation 2.2.48

\[ \rho(\vec{Q}, t) = Z f(\vec{Q}) \sum_{m} e^{-i\vec{Q}.\vec{R}_m(t)} \quad (2.2.55) \]

Where \( Z \) is the atomic number, By introducing the atomic displacement \( \vec{u}_m(t) \) due to lattice vibrations from its equilibrium position we could write

\[ \rho(\vec{Q}, t) = Z f(\vec{Q}) \sum_{m} e^{-i\vec{Q}.(\vec{r}_m + \vec{u}_m(t))} \quad (2.2.56) \]

Substitute back to Equation 2.2.47 we get

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\[ S(\vec{Q}, \omega) = \frac{Z^2}{2\pi \hbar} f^2(\vec{Q}) \int_{-\infty}^{\infty} e^{-i\omega t} dt \sum_{m,m'} \langle e^{-i\vec{Q}\cdot\vec{R}_m(0)} e^{-i\vec{Q}\cdot\vec{R}_{m'}(t)} \rangle \]

\[ = \frac{Z^2}{2\pi \hbar} f^2(\vec{Q}) \sum_{m,m'} \langle e^{i\vec{Q}\cdot\vec{u}_m(0)} e^{i\vec{Q}\cdot\vec{u}_{m'}(t)} \rangle (2.2.57) \]

Now let us expand the phonon displacement \( u_m(t) \) in terms of the corresponding time dependent phonon creation and annihilation operators to obtain

\[ u_m(t) = \sum_{\vec{Q}_0, \epsilon} e(\vec{Q}_0, \epsilon) \left( \frac{\hbar}{2NM\alpha_{\vec{Q}_0, \epsilon}} \right)^{1/2} (\alpha_{\vec{Q}_0, \epsilon} e^{-i\omega_{\vec{Q}_0, \epsilon} t} + \alpha_{\vec{Q}_0, \epsilon}^* e^{i\omega_{\vec{Q}_0, \epsilon} t} ) (2.2.58) \]

where phonon creation operator is \( \alpha_{\vec{Q}_0, \epsilon}^+(t) = \alpha_{\vec{Q}_0, \epsilon} e^{i\omega_{\vec{Q}_0, \epsilon} t} \) and phonon annihilation operator is \( \alpha_{\vec{Q}_0, \epsilon}(t) = \alpha_{\vec{Q}_0, \epsilon} e^{-i\omega_{\vec{Q}_0, \epsilon} t} \). Here \( \vec{Q}_0 \) and \( \epsilon \) denotes the phonon wave vector and the polarization vector respectively. \( \omega_{\vec{Q}_0, \epsilon} \) is phonon angular frequency. \( e(\vec{Q}_0, \epsilon) \) is phonon eigen vector and \( N \) is total number of atoms in the crystal.

Manipulating the thermal average exponential using Baker-Hausdorff theorem we can obtain the expression. (Of course I do not work out the detailed derivation here and anyone who is interested can refer the article [100])

\[ \langle e^{-i\vec{Q}\cdot\vec{u}_m(0)} e^{i\vec{Q}\cdot\vec{u}_{m'}(t)} \rangle = e^{-\left(\frac{(\vec{Q}\cdot\vec{u}_m(0))^2}{2(\vec{Q}\cdot\vec{u}_{m'}(t))^2}\right)^{1/2} \left(\vec{Q}\cdot\vec{u}_m(0)\vec{Q}\cdot\vec{u}_{m'}(t)\right)^{1/2}} (2.2.59) \]

where we define Debye-Waller factor \( e^{-2W} \) as
Expanding right hand side of equation for small phonon displacement (This is the case in general) we can write

\[ e^{-2W} = e^{-((\vec{Q} \cdot \vec{u}_m)^2)} \]  \hspace{1cm} (2.2.60)

where \( x, y \) are Cartesian components. Higher order terms are neglected as they represent multi-phonon scattering. Finally we can write the equation 2.2.57

\[
S(\vec{Q}, \omega) = \frac{Z^2}{2\pi \hbar} f^2(\vec{Q}) \sum_{m, m'} e^{i(\vec{Q} \cdot (m-m'))} \left[ 1 + \sum_{x, y} \vec{Q}_x \vec{Q}_y \langle \vec{u}_{m,x}(0) \vec{u}_{m',y}(t) \rangle \right].
\]  \hspace{1cm} (2.2.62)

Use equation 2.2.58 to evaluate displacement-displacement correlation function

\[
\langle \vec{u}_{m,x}(0) \vec{u}_{m',y}(t) \rangle = \sum_{\vec{Q}_0, \epsilon} e_x(\vec{Q}_0, \epsilon) e_y(\vec{Q}_0, \epsilon) \left( \frac{\hbar}{2NM\omega_{\vec{Q}_0, \epsilon}} \right) \langle n_{\vec{Q}_0, \epsilon} \rangle e^{-i\omega_{\vec{Q}_0, \epsilon} t} e^{i\vec{Q} \cdot (m-m')} 
\]

\[ + \langle n_{\vec{Q}_0, \epsilon} + 1 \rangle e^{i\omega_{\vec{Q}_0, \epsilon} t} e^{-i\vec{Q} \cdot (m-m')} \]  \hspace{1cm} (2.2.63)

where BoseEinstein occupation factor for phonon \( (Q_0 \epsilon) \) defined as
\[ \langle n_{\vec{Q}_0,\epsilon}^\dagger \rangle = \frac{1}{e^{\beta \omega_{\vec{Q}_0,\epsilon}} - 1}. \]  

(2.2.64)

Using the definition of delta function,

\[ \sum_m e^{i \vec{K} \cdot \vec{m}} = \frac{L^3}{(2\pi)^3} \sum_G \delta(\vec{K} - \vec{G}). \]  

(2.2.65)

we obtain the final expression for scattering from lattice vibrations

\[ S(\vec{Q}, \omega) = \frac{Z}{\hbar} f^2(\vec{Q}) e^{-2W} \frac{L^3}{(2\pi)^3} \left[ \sum_G \delta(\vec{Q} - \vec{G}) \delta(\omega) + Z^2 f^2(\vec{Q}) e^{-2W} \frac{L^3}{(2\pi)^3} \right] \]

\[ \times \sum_{\vec{Q}_0,\epsilon} \frac{1}{2M \omega_{\vec{Q}_0,\epsilon}} |\vec{Q} \cdot \nabla^2(\vec{Q}_0\epsilon)|^2 \langle n_{\vec{Q}_0,\epsilon}^\dagger \rangle \delta(\omega + \omega_{\vec{Q}_0,\epsilon}) + \langle n_{\vec{Q}_0,\epsilon} + 1 \rangle \delta(\omega - \omega_{\vec{Q}_0,\epsilon}) \]

\[ \times \delta(\vec{Q} + \vec{Q}_0 - \vec{G}). \]  

(2.2.66)

Here the first term represents the elastic scattering. Second term represents one-phonon inelastic scattering with energy gain (phonon annihilation) and one-phonon inelastic scattering with energy loss (phonon creation) respectively. Multi-phonon scattering are represented by higher order terms. They are small in general unless the temperature is very high and omitted as stated in the middle of the derivation process.

2.3 Inelastic X-ray Scattering on ScF$_3$
2.3.1 The Experiment

In order to study the lattice dynamics of ScF$_3$, which has a simple cubic unit cell (Figure 2.3.1) of space group Pm$ar{3}$m the experiment was performed in the HERIX (High energy resolution inelastic x-ray scattering) beam line (Sector 30) at Advanced Photon Source (APS) at Argonne National Laboratory (ANL). We carried out inelastic x-ray scattering measurement with high energy-resolution x-ray at temperature range from 3.8 K to 300 K. The HERIX instrument (Figure 2.3.2) is capable of acquiring energy gain/loss spectra at 9 momentum transfer values simultaneously. The energy of the incident X-ray beam was 23,724 eV and the designed scattering angle range (032 degrees) permits simultaneous investigation of lattice dynamics along approximately one BZ edge per spectral collection time. The energy transfer was scanned by rotating the analyzer crystals, and with 1.5 meV energy resolution, over 4 ScF$_3$ BZ edges of kinematic (momentum) range, energy transfer spectral range of 200meV, complete mapping of the one and multi-phonon scattering processes for even the stiffest vibrations expected for ScF$_3$, (80meV) was achievable.

2.3.2 Single crystal ScF$_3$

Single crystal of ScF$_3$(Figure 2.3.3) was a part of international collaboration with Dr. Vladimir Voronov of the Kirenskii Institute of Siberia and was reported [95, 96] to be grown via flux-melt technique containing 40 % ScF$_3$ was placed into a platinum ampoule (with 0.2 mm walls) and sealed in nitrogen atmosphere.
Figure 2.3.1: Simple cubic structure of ScF$_3$ lattice where pink spheres are Sc atoms and orange spheres represent F atoms. From [11]

Figure 2.3.2: Schematic of IXS spectrometer layout (a) and photograph (b) of the 9 m arm of the spectrometer at sector 30 of APS. The schematic is not to scale. The main components, the direction of incident beam and scattered beam are shown. Sample is mounted on a four circle rotational mount and the detector array is kept as much as close to the sample. Analyzer array is mounted at far end of the arm which is capable of rotate about 32 degrees which is corresponding to maximum of 75 nm$^{-1}$ momentum transfer.

This ampoule was lowered down the vertical tube furnace (axial temperature gradient 12 K/mm) from 1400 K region at 20 mm/day speed during 14 days.
Figure 2.3.3: (a) Single crystal ScF$_3$ received from Vladimir Voronov. We named them for identification purpose in future usage. (b) Simple cubic structure formation of ScF$_3$ lattice drawn in to scale where purple spheres are Sc atoms and red spheres represent F atoms.

The high momentum resolution (0.02 Å$^{-1}$), nine-analyzer collection scheme, and microfocused x-ray beam permits measurements of the dynamical structure factor [101] within a transparent, isotropically pure, single-crystalline grain [95, 96] of mosaic width 0.002$^0$ (Figure 2.3.7(a)), as measured on the strong $(H,K,L) = (1,1,0)$ Bragg reflection indexed to the four-atom simple cubic cell (Lattice parameter $a = 4.016$ Å at temperature $T = 300$ K).

NTE in ScF$_3$ was discovered only recently, and all most all the subsequent reports on this effect have been reported in powder samples. We are only the second single crystal of ScF$_3$ investigators and first ever to carry IXS measurements on ScF$_3$. The IXS measurements were taken on crystal piece Gamma
(Figure 2.3.4(b)) and the crystal mount used at HERIX beam line is shown in Figure 2.3.4(a).

Figure 2.3.4: (a) Crystal mount used in sector 30 experiment. (b) Dimensions of the crystal Gamma. Crystal sits on wax in order to carry out X-ray diffraction measurement.

First of all we carried out x-ray diffraction measurement in x-ray laboratory at Institute of Material Sciences at University of Connecticut. X-ray diffraction data was taken in order to figure out crystal orientation. We located strong Bragg peaks at (110) and (010) and used them to define crystal orientation as shown in Figure 2.3.5. The 2θ angles were consistent (Figure 2.3.5) with previously reported powder x-ray diffraction data (Figure 2.3.6). It is always advantageous to have at least a rough idea on crystal orientation before we begin a synchrotron experimentation as it saves us the beam time.
Figure 2.3.5: Diffraction spots appeared on 2D area detector. Crystal plane is $z=0$ and sample Gamma is used. Lattice planes are shown in dotted lines.

Figure 2.3.6: X-ray diffraction data on powder ScF$_3$ sample.
2.3.3 Lattice parameter measurement

Measurement of lattice parameter is carried out and it is being reported as the first ever single crystal lattice parameter measurement of ScF$_3$. Lattice volume as a function of temperature determined from tracking the Bragg peak (3,0,0) in single-crystalline ScF$_3$ together with the lattice volume over a larger thermal window determined on powder samples [9] is shown in Figure 2.3.7(b). The percentage of lattice constant expansion ($\Delta a / a$) over 296 K (4 K - 300 K) is calculated to be 0.2979 % while the percentage volume expansion ($\Delta V / V$) is determined to be 0.9279 %.

![Figure 2.3.7](image)

Figure 2.3.7: (a) Mosaic width $\sim 0.002^\circ$, as measured on the strong (H,K,L) = (1,1,0) Bragg reflection indexed to the four-atom simple cubic cell (lattice parameter $a = 4.016$ A at temperature $T = 300$ K) (b) Lattice volume as a function of temperature determined from tracking the Bragg peak (3,0,0) in single-crystalline ScF$_3$. Inset: The lattice volume over a larger thermal window determined on powder samples[9].
2.3.4 Phonon dispersion relation

Dispersion through different cuts were investigated in reciprocal space at 300 K and 8 K and most interesting dispersion emerged along the $M - R$ branch. This is because the entire branch gets softer ($\sim 3.5$ meV at 300 K) with low dispersion.

As explained earlier (section 2.2.1), we have measured a fundamental property which contains information on the spatial and temporal fluctuation of the lattice degree of freedom in ScF$_3$. Figure 2.3.8 shows an overview of the lowest-energy mode dispersion in ScF$_3$ along high-symmetry directions determined by fitting the structure factor to a damped harmonic oscillator model (Please refer section 2.3.14 for detailed explanation) along the cut from the Brillouin zone (BZ) face.

Figure 2.3.8: Overview of the lattice mode dispersion at select momenta and energies. Strong branch softening along the $M - R$ cut is shown by arrows. The longitudinal (LA) and transverse (TA) acoustic branches are shown. Black solid lines are a guide to the eye. Red circles in the inset mark the momenta $R + \delta (2.39,1.43,0.45)$ and $M + \epsilon (2.39,1.43,0.02)$
center $X$ to the BZ edge center $M$, an optic mode crosses the acoustic branches and softens dramatically to a low energy of 3.5 meV at room temperature. Cooling the sample to 8 K results in a dramatic and uniform softening of this entire $M-R$ branch to $\sim 1$ meV, further suggesting an approach to a structural instability near zero temperature.

2.3.5 M-R branch and NTE

The mechanism of ScF$_3$ NTE behavior has been explained by the transverse fluctuations of octahedra around the axis F-Sc-F of ScF$_6$. Since these fluctuations which support RUM, correspond to momentum at $M$ and $R$ points in the reciprocal space which preserves the octrahedra integrity and do not involve bond bending and stretching mode in the crystal, it appeared to be the most interesting points to study. So we carried out the second phase of the IXS measurement specifically at $M$ and $R$ points for 15 different temperatures down to 3.8 K (Minimum we could achieve) and observed phenomenal physics. Other than the phonon softening that we mostly expected we were able to observe an elastic peak appearance as the temperature is lowered.

The low $M-R$ branch is a near-degenerate manifold of cooperative vibrational modes which are soft because they largely preserve the internal dimensions of the stiff metal-anion molecular subunits. In order to retain local constraints of bond distances and angles, staggered rotations induce a shrinking of the cell dimensions, establishing a long-range coupling between local transverse
Figure 2.3.9: (100) planar section of the octahedra, illustrating the displacement pattern of modes attributed to NTE. The area of the box in (b) is reduced by $\cos^2 \theta$ of the area in (a)

linkage fluctuations and lattice volume that has long been ascribed as the cause of structural NTE.

2.3.6 M-R branch and phase transition

$M - R$ is an important mode branch in perovskites because temperature-driven condensation of modes on this branch can describe many structural transitions which accompany ordering transitions of other types [84, 102, 103]. These soft modes circumscribe the BZ edges (Figure 2.3.10) within a very narrow window of energy set by the $M - R$ branch dispersion, with the $R$ point 200 $\mu$eV lower at all temperatures measured, consistent with an approach to the symmetry-lowered rhombohedral $R\bar{3}c$ structure, as observed in other 3d BF$_3$ systems.

The rhombohedral $R\bar{3}c$ structure is related to the high temperature cubic Pm$\bar{3}$m
structure via a staggered octahedral tilt around the ⟨111⟩ axis, corresponding to a frozen R$_4^+$ lattice distortion (Figure 2.3.11a). The staggered ⟨111⟩ octahedral rotation angle is therefore the order parameter of the rhombohedral phase. The free-energy curvature and origin of cubic-phase stabilization in trifluorides has been addressed in a body of theoretical and computational work aimed to generally understand perovskite structural phases. Density functional theory [104], molecular dynamics [105], and exact electrostatic energy considerations [106] of the insulating AlF$_3$ prototype trifluoride suggest that Madelung energy including static electric dipole-dipole and induced dipoleinduced dipole interactions compete to determine the stability of the cubic phase, and result in a low-temperature rhombohedral phase.

Figure 2.3.10: First Brillouin zone of simple cubic material ScF$_3$. High symmetry points are shown as well.
It has been pointed out [106] that these competing influences could cancel identically for larger metal radii, marginally stabilizing the cubic phase for all temperatures, and it appears this limit is realized for ScF$_3$. This suggestion is supported by related previous work using momentum-integrated time-of-flight neutron spectroscopy on bulk powder samples of ScF$_3$ that showed a temperature dependence of high-energy $< 10$ meV peaks in the neutron-weighted density of states and included calculations suggesting the curvature of the R$^+_4$ mode is quartic in the tilt angle [68]. In what follows we present a momentum, energy, and temperature-resolved investigation of the approach to the quantum phase transition between the simple cubic and rhombohedral phases and its effects on the lattice dynamics of perovskite ScF$_3$.

Figure 2.3.11: (a) The lowest vibrational modes at the $M$ point. ($M^+_3$ distortion)  
(b) The lowest vibrational modes at the $R$ point. The rhombohedral phase can be described as a static tilt according to the $R^+_4$ pattern.
2.3.7 Central peak of ScF$_3$

Background of central peak

An elastic peak was observed, accompanying with soft mode as SrTiO$_3$ approaches structural phase transition and this was first discovered by Norwegian physicist Tormod Riste in 1971[17]. Prior to this discovery he had worked on magnetic systems and observed elastic-like peaks and soft modes associated with spin diffusion on these systems. While he was continuously working on this, he was able to confirm the simultaneous existence of two modes such as quasi-elastic peak (central peak) and soft mode near the critical region of a phase transition in SrTiO$_3$[12]. At the same time, he observed the central peak dominates the scattering close to the transition temperature (Figure 2.3.12).

Gen Shirani was interested in this phenomenon and was able to carry an elegant experimental work at Brookhaven national lab using various samples. Most of his interpretations came with the help of high-resolution spectra of strain-free SrTiO$_3$ samples[12]. By observing these spectra, two clear energy scales associated with soft phonon energy and central peak linewidth were identified. In other words, in addition to the relative short relaxation time of the system characterizing the soft phonon, there exists a large relaxation time characterizing the narrow central peak. Apart from that he clearly observed the divergence of central peak as the transition temperature approaches and confirmed that the structural phase transition deviated from mean field
theory like behavior. Since then the central peak has been observed associated with phase transition in many other perovskite structures such as KMnF₃[12], LaAlO₃[107], RbCaF₃[108], PbTiO₃[109]. Central peak was also observed in materials with vastly different properties like insulating Pb₄Ge₃O₁₁, NaNO₃[110], KH₂PO₄[111], metallic ZrTe₃[112], Ferroelastic LaAlO₃[107], Ferroelectrics SrTiO₃[17], Lead Germanate[113], KH₂PO₄[111], Ferromagnetic material Rb₂CrCl₄[114], Antiferromagnetic materials Y MnO₂[115], CsCoBr₃[116], Superconductors BSCCO[117], YBa₂Cu₃O₆.₆[118], Nb₃Sn[119].

Figure 2.3.12: (a) Inelastic spectra of SrTiO₃ measured at several temperatures. Left side shows the soft mode behavior and right side shows divergence of central peak. From [12]. (b) Inelastic spectra of SrTiO₃ (left) and KMnF₃ (right) for approximately equal ΔT=T-Tₖ. From [12].

2.3.8 What causes central peak?

Though central peaks have been observed in nearly all systems exhibiting structural phase transitions, their origins are still under debate[120]. While one class
of theories has proposed that the central peak is the result of intrinsic nonlin-
ear mechanisms such as the presence of solitons[121], another class of theories
suggests that it is an extrinsic effect due to defects[120]. At the beginning,
there were theoretical grounds for believing in the existence of the central peak
in three dimensions as well as lower dimensional systems [121, 122]. Mecha-

nisms related to defects have been proposed and are based on the observations
that the central peak is sample dependent[123]. In a ferroelectric material, the
central peak can even be made to disappear by annealing the sample[124]. In
the defect mechanism, the central peak is associated with the local distortion
of the atoms about the defect[125, 119]. This displacement field gives rise to
diffuse scattering of x-rays or neutrons and is usually referred to as Huang
scattering. Even though the Huang scattering is usually observed near Bragg
peaks, enhanced scattering at $\omega_0 = 0$ may still appear in the presence of soft
modes at the soft mode q-vector. In this case, the soft mode should be coupled
with impurities and further evidence for this extrinsic effect came through an
experiment[13] on SrTiO$_3$(Figure 2.3.13). There the central peak intensity was
enhanced with an increase in defect concentration but the exact relationship
was found to be not proportional. Further, the exact dependency was difficult
to compare among different impurity systems as well[14]
Figure 2.3.13: Central peak due to defects and impurities. (a) Integrated central peak intensity of hydrogen reduced SrTiO$_3$ as a fuction of $T-T_c$ [13]. (b) The temperature dependence of the central peak height of the as-grown KH$_3$(SeO$_3$)$_2$ crystal (+) and the crystals used repeatedly (0, x)[14]

High momentum resolution x-ray data near phase transition temperature could be decomposed into a sharper peak and a broader peak which proposed two length scales associated with the dynamics of both soft mode and the central peak. Even though the origin of these peaks was debatable, the scattering intensities measured by probing the surface and the bulk of the same sample separately supported the fact that the sharp component is not an intrinsic property but related to the difference between the bulk and the outer surface of the sample.
Figure 2.3.14: Broad and narrow features within the central peak. Solid and dotted curves in (a) represent fitting models, Lorenzian squared and Lorenzian function respectively[15]. (b) X-ray scans of $\frac{1}{2}$ (1,1,5) R point along [0 1 1] direction with 100 keV photon energy beam hitting at the center of the crystal and (c) beam hitting the crystal corner of the crystal. )[16]

Other than the extrinsic effects such as impurities and defects the appearance of the central peak can be sorted out due to intrinsic behaviors such as fluctuations due to phonon density, solitons, nonlinear effects etc. Central peak originated from intrinsic mechanisms was reported in NaNO$_3$ due to the mobility of NO$_3^-$ ions as it approaches order-disorder phase transitions[110]. Theoretical work by Krumhansal and Schrieffer suggested that the domain walls or cluster boundaries between large ordered regions in the crystal may cause central peak as well[126, 127]. In LaAlO$_3$ the central peak mode(s) has been interpreted in terms of phonon density fluctuations and flipping of clusters of tilted octahedra.
between different orientations[128].

2.3.9 Central peak of ScF$_3$ and mode softening

Figure 2.3.15 shows the temperature-dependent IXS spectra for ScF$_3$ at $M(2.5,1.5,0)$ and $R(2.5,1.5,0.5)$ points, where the dynamical structure factor is particularly strong for the modes of Figures 2.3.11a and 2.3.11b. Clear soft mode behavior is observed concomitant with the emergence of a strong elastic peak, which onsets at $\sim 80$ K and strengthens dramatically as the temperature is lowered. The elastic peak emergence is also observed at momenta away from the high-symmetry M-R cut from data collected in an adjacent analyzer channel. Figure 2.3.16 shows IXS data at $M + \epsilon (2.39,1.43,0.02)$ and $R + \delta (2.39,1.43,0.45)$ momentum points, where the optical branch is much stiffer (56 meV) and displays a milder degree of softening, making the distinction between the elastic peak and soft mode phenomena more apparent in the raw data. In all cases, a transfer of spectral weight from the optical mode to the central peak feature is observed as the temperature is lowered.

All data were fit using a resolution-convoluted model for the dynamical structure factor, which includes a damped harmonic oscillator and a detailed balance condition to describe the lattice mode, and a resolution-limited elastic central peak, consistent with previous analyses of this phenomena in SrTiO$_3$ and other materials [12] (see section 2.3.14). This analysis allows us to extract the soft mode frequency and strength $A_0$ of the central peak. Figure 2.3.17 shows that
the temperature dependence of the lowest soft mode frequency behaves approximately as $\omega^2 \propto (T - T_c)$ as expected from classical mean-field theories.
of structural phase transitions [120]. This simple extrapolation of the R point soft mode frequency suggests that the phase transition occurs at $T_c \sim -39$ K, so it does not occur for any finite temperature, consistent with observations [9, 20, 19, 97]

![Figure 2.3.17: Resolution convoluted fitting of the IXS data in figure 2.3.16 results in squared mode energies](image)

Central peaks and mode softenings observed in the context of the 110 K cubic-to-tetragonal transition of incipient ferroelectric SrTiO$_3$ [12, 17, 129, 130] , are commonly associated with an approach to a structural phase transition. There, the elastic central peak has maximum strength at $T_c$ but begins to appear up to 25 K higher [12, 130]. In the present case, we observe(Figure 2.3.19) no maximum in elastic scattering at any finite temperature and the intensity continues to strengthen at the lowest temperatures measured (3.8 K). In ScF$_3$, the effect of the central peak begins above 80 K, suggesting that precursor
Figure 2.3.18: Resolution convoluted fitting of the IXS data in figure 2.3.16 results in elastic peak intensity. Elastic peak begins to appear near 80 K, which is 120 K above the extrapolated transition temperature.

Figure 2.3.19: Central peak intensity observed in SrTiO$_3$ [17]. Elastic peak begins to appear 25 K above the transition and the intensity reaches its maximum at the transition temperature.

effects occur as high as 120 K above our extrapolated transition temperature.

The thermally robust central peak in ScF$_3$ occurs in our strain-free, (naturally) isotopically pure, color center-free single crystals with a narrow (0.002) mosaic.

Interestingly, the elastic peak begins to strengthen at the same temperature scale
at which the thermal expansion saturates, which is discussed further below.

Based on the appearance of the central pin through a broad manifold of momenta throughout the Brillouin zone, we have observed localized excitations in the fluctuation spectrum below 100 K. Below $T_c$ in the related material TiF$_3$[18], needlelike 111-oriented domains proliferate throughout the material, and we speculate that the localization of excited states may be a precursor effect related to the formation of the domain structure in the ordered state.

### 2.3.10 Quantum phase transition in ScF$_3$ and phase transitions in other transition metal trifluorides

Figure 2.3.21 shows a structural phase diagram of MF$_3$ perovskites limited to cubic or rhombohedral phases, where M is a trivalent metal ion $^1$. The 3d metal trifluorides display a reversible structural cubic-to rhombohedral (c-r) phase boundary. This sequence of 3d transition metal trifluoride compounds is rhombohedral at room temperature, with the exception of $M = Sc$, which appears at the zero-temperature terminated c-r phase boundary. Indeed, no rhombohedral phase transition has been observed for ScF$_3$ down to 0.4 K [94], suggesting that near this composition, the structural phase can be driven by a parameter other than temperature (varying of the cation radius), implying that the ground state of this ionic insulator is very near a quantum phase transition (QPT). Remarkably, this happens to occur at a point where the Metal ion has

---

MnF$_3$ forms a triclinic structure [131] which is a result of unusually strong magnetic and Jahn-Teller effects [5]. It is not included in the phase diagram.
stoichiometric occupation with a full electronic shell, permitting a clean study of fluctuating quantum matter from structural degrees of freedom without also having to consider additional electronic and magnetic degrees of freedom. The phase boundary is most likely continuous, considering the observation that the c-r transition in TiF$_3$ appears to be second order[132]. Cubic ScF$_3$ further stands out among substances in that it has the most stable structural phase of any known solid trifluoride[23].

Figure 2.3.20: Cubic and rhombahedral unit cells associated with two phases of transition metal trifluorides other than ScF$_3$ are shown. As shown the rhombahedral phase is associated with rotated ScF$_6$ sub units. Gray circles represent scandium atoms and light blue circles represent fluorine atoms.

The c-r structural transition can be stabilized at finite temperature through substitution of other metals (Al, Ti, Y) for Sc, or in pure ScF$_3$ through application of very low hydrostatic pressures [95, 95] (>$0.2$ GPa) at cryogenic temperatures. Remarkably, using the observed pressure dependence of the transition temperature $dT_c/dp \sim 525$ K/GPa [9, 95, 96], and the putative transition tem-
perature $T_c \sim 39$ K, one can estimate that pressures as small as 740 bar = 0.074 GPa would be sufficient to drive the transition upward to 0 K, permitting a clean manner in which to observe a structural quantum phase transition. The sensitivity of the phase boundary to these external changes suggests that the nature of the cubic phase is delicate at low temperature and susceptible to even mild perturbations. Chemical substitutions of Sc by Ti [20], Al [19], and Y [97] have been reported and $T_c$ is presented in Figure 2.3.21. The phase boundary in $\text{Sc}_{1-x}\text{Ti}_x\text{F}_3$ appears to linearly interpolate between the end members $\text{ScF}_3$ and $\text{TiF}_3$ with no maxima or minima at intermediate compositions, consistent with a picture where the substitution of wellmatched ionic radii ($r_{\text{Ti}} = 0.670$ Å; $r_{\text{Sc}} = 0.745$ Å) uniformly affects the potential landscape and gradually changes the phase stability.

### 2.3.11 $\text{ScF}_3$ systems and disorder

On the other hand, substitution of ions with radii much smaller ($r_{\text{Al}} = 0.535$ Å) or much larger ($r_{\text{Y}} = 0.90$ Å) than Sc stabilizes the rhombohedral phase, suggesting the role of disorder is strong for these substitutions. We quantify the disorder in these solid solutions by using the variance of the B-site ion distribution $\sigma_B^2 = \langle r_B^2 \rangle - \langle r_B \rangle^2$ as determined from the nominal chemical formula in these solid solutions, and plot the disorder phase diagram in Figure 2.3.22. The trend in $T_c(\sigma_B^2)$ is an example of the general case, wherein electronic (superconducting, magnetic) and structural (ferroelectric, ferroelastic) transitions
Figure 2.3.21: Structural phase diagram showing the c-r phase boundary vs the B-site mean radius in 3d transition metal trifluorides and in the solid solutions Sc$_{1-x}$Al$_x$F$_3$ and Sc$_{1-x}$Y$_x$F$_3$. Data taken from Refs [18, 19, 20, 21, 22].

have opposite sensitivities to disorder, as determined through studies of the A-site variance effect on phase stability [133, 134]. The latter case, relevant here, occurs because local strain associated with substitution has the effect of disrupting long-range propagation of strain, enhancing the stability of the lowered-symmetry phase. Generalizing these trends to B-site disorder near the composition ScF$_3$, we separately fit the transition temperatures $T_c(x) = T_c^0 - p_1 \sigma_B^2$ to the doped compositions of Al and Y substitution and find that extrapolating transition temperatures of the doped compositions to the ideal case $\sigma_B^2 = 0$
gives roughly similar $T^0_c = 75$ K (Al) and 104 K (Y), which is near the temperature scale where we observe a strong elastic peak emergence (Figure 2.3.19) and the thermal expansion coefficient departs from linear dependence on temperature (Figure 2.3.7). Empirically, $T_c > 0.4$ K is observed for pure ScF$_3$, suggesting a strong deviation from previous studies [133, 134] and qualitatively different physics in the pure limit.
Figure 2.3.22: Disorder phase diagram for ScF₃. Compositional disorder is quantified via the B-site variance $\sigma_B^2 = \langle r_B - \langle r_B \rangle \rangle^2$, which has the effect of increasing the stability of the lowersymmetry, rhombohedral structural phase. Red and orange symbols show the effect of Y and Al substitution, respectively. Dotted lines indicate a linear fit to the $T_c(\sigma_B^2)$, not including the pure sample ScF₃. The vertical axis intercept reveals a temperature scale $\sim 80$-100 K, where central peak elastic scattering and thermal expansion saturation are also observed in pure ScF₃.

### 2.3.12 Transverse motion of F atoms

The ScF₆ octahedra in pure ScF₃ move collectively in a state of strong orientational fluctuation [106, 135], the strength of which can be estimated from
powder refinement of the anisotropic thermal parameter $U_{33}$, associated with transverse F motion. The orientational fluctuations are significant [9], approaching $2\sqrt{U_{33}}/a \sim 9.2$ full width at half maximum (FWHM) at room temperature, significantly larger than the isostructural oxide ReO$_3$ [133].

![Transverse vibrations of Fluorine atom](image)

Figure 2.3.23: Transverse vibrations of Fluorine atom

In this regime, the influence of long-ranged strain draws in the lattice, leading to a robust and sizable NTE effect. At elevated temperatures, long-range strain fields imposed by local constraints propagate over much shorter distances, and the fluctuation spectrum lacks a central peak and appears more conventional. The long-range strain effects we have observed are likely present in the physics of structural transitions in perovskite and other structural classes, but are particularly enhanced in ScF$_3$ at low temperature.

2.3.13 Elastic parameters of ScF$_3$

The combined energy (1.5 meV) and momentum (0.2 nm$^{-1}$) resolution allowed us to observe the phonon branches extending over the entire lattice spectral bandwidth of 85 meV. We have made special efforts and acquired IXS spectra relevant to the acoustic modes along [110] and [100]. The acoustic mode ener-
gies were plotted against several reduced momenta near (300) and (220) in the brillouin zone as shown in Figure 2.3.24.

Figure 2.3.24: Acoustic phonon energies along different directions in reciprocal space. The slope simply gives the acoustic velocities of corresponding modes along different directions for ScF$_3$. LA and TA stands for longitudinal acoustics and transverse acoustics respectively

\begin{align*}
    v_p[100] &= (c_{11}/\rho)^{1/2} \\
    v_s[100] &= (c_{44}/\rho)^{1/2} \\
    v_p[110] &= (c_{11} + c_{12} + 2c_{44}/2\rho)^{1/2} \\
    v_s[110] &= (c_{11} - c_{12}/2\rho)^{1/2}
\end{align*}

83
Where $\rho$ is the density of the sample. $v_p$ and $v_s$ are longitudinal and transverse acoustic wave velocities respectively which are defined along both the principle axis [100] and [110]. Data were fit to determine the transverse and longitudinal sound speeds separately as summarized in Figure 2.3.24. The value obtained for $v_s[100]$ is 2871.7 ms$^{-1}$. $v_p[100]$ and $v_p[110]$ are 7809.3 ms$^{-1}$ and 7118.1 ms$^{-1}$ respectively. Given the density of ScF$_3$ is 2.53 g/cm$^3$ and using Equations 2.3.2 - 2.3.5 the elastic parameters $C_{11}$, $C_{12}$, and $C_{44}$ are determined. Using elastic parameters the bulk modulus (B) and the shear modulus (G) of the crystal were calculated. The corresponding relationships for cubic symmetry are elaborated in section 7.2.1 in Chapter 7. Our values from IXS measurements are summarized in Table 2.3.2 and compared with previously estimated values based on calculations[96, 94] for ScF$_3$ and previously estimated values based on measurements for ZrW$_2$O$_8$ [136] and for ReO$_3$[137]. Figure 2.3.25 and 2.3.26 show some of the elastic properties derived from the measured elastic constants.

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>A (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScF$_3$ (ours)</td>
<td>161.4</td>
<td>63.13</td>
<td>21.8</td>
<td>95.88</td>
<td>32.73</td>
<td>0.44</td>
</tr>
<tr>
<td>ScF$_3$ [96]</td>
<td>172.7</td>
<td>18.9</td>
<td>18.6</td>
<td>70.2</td>
<td>41.92</td>
<td>0.24</td>
</tr>
<tr>
<td>ScF$_3$[94]</td>
<td>230</td>
<td>17.3</td>
<td>18.0</td>
<td>88.2</td>
<td>53.34</td>
<td>0.17</td>
</tr>
<tr>
<td>ZWO [136]</td>
<td>128.4</td>
<td>47.5</td>
<td>27.4</td>
<td>74.5</td>
<td>433.9</td>
<td>0.68</td>
</tr>
<tr>
<td>ReO$_3$[137]</td>
<td>717</td>
<td>71.1</td>
<td>103</td>
<td>286</td>
<td>190.98</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 2.3.2: Summary of elastic properties of similar type of materials. Bulk modulus (B), Shear modulus (G) and Zener anisotropy (A) are shown as well.

Experimentally determined coefficients $C_{11}$ and $C_{44}$ are very much agree with
calculated values but $C_{12}$ is off by 45 GPa. It is clear from the equation 2.3.3 that $C_{12}$ is related to transverse acoustic phonon along [110] direction. Therefore the difference is obviously related to corresponding phonon energies measured using IXS. One could argue that transverse acoustic phonons along [110] should be stiffer than along [100] which results in decrease in $C_{12}$. On the other hand the zener anisotropy value estimated from our measurements is close to 1 compared with the theoretical zener anisotropy value. As a result, we argue that our measurements interpret the isotropic nature of the single crystal ScF$_3$ more accurately than calculations.

Figure 2.3.25: Poisson ratio obtained from elastic parameters
Figure 2.3.26: Youngs modulus obtained using elastic parameters

2.3.14 Modeling IXS data using Damped Harmonic Oscillator (DHO)

The cross section of photon scattering to some solid angle dΩ with momentum transfer Q and into some energy width dE is

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k_2}{k_1} r_c^2 |\epsilon_1 \ast \epsilon_2|^2 S(Q, \omega)
\] (2.3.5)

Where \( k_1 \) and \( k_2 \) are incident and scattered momentum states of the photons and \( \epsilon_1, \epsilon_2 \) are corresponding polarization states.\[10\]

The most relevant analysis of this type has been done by Shapiro and co authors in 1972, when they analyzed neutron scattering data of SrTiO₃. The scattering can also be related to linear response of the dynamic susceptibility \( \chi(Q, \omega) \) as discussed there[12] and has the form of,
\[ S(Q, \omega) = \frac{1}{\pi} \frac{1}{1 - \exp^{-\beta\omega}} \text{Im}[\chi(Q, \omega)] \] (2.3.6)

The damped harmonic oscillator (DHO) response used to describe phonons in solid is,

\[ \chi(Q, \omega)^{-1} = \omega_\infty(Q)^2 - \omega^2 - i\omega\Gamma(\omega) \] (2.3.7)

most importantly with a frequency dependent damping constant

\[ \Gamma(\omega) = \Gamma_0 + \frac{\delta^2}{\gamma - i\omega} \] (2.3.8)

Here the additional frequency dependent damping represents another decay channel with relaxation time of \( 1/\gamma \) and coupling strength of \( \delta \). Combining Equations 2.3.6, 2.3.7 and 2.3.8 Shapiro separated the dynamic structure factor into two components, central peak and soft phonon mode.

Since the energy resolution is limited in IXS measurements, we avoided using the same DHO function. Instead we chose a DHO with a constant damping constant(\( \Gamma_0 \)) and a resolution limited Lorentzian(L) as our model to fit the experimental data. The model was convoluted with the resolution function and then was evaluated at each data point. The width (\( \omega_L \)) of the resolution limited Lorentzian and the center frequency (\( \omega_0 \)) were fixed to 0.1 and 0 respectively, while the amplitude (\( A_0 \)) was kept as a free parameter. All fit parameters of DHO were set free except the sample temperature, which (T) was fixed to the
measured value.

Fit parameters used can be identified as, $A$ - the amplitude of the DHO, $\omega_\infty$ - the center frequency of the DHO, $A_0$ - the amplitude of the Lorentzian and $\Gamma_0$ - the full width half max of the DHO.

The Lorentzian is defined as:

$$L(\omega, \omega_L, \omega_0, A_0) = \frac{A_0 \omega_L}{2\pi} \frac{1}{(\omega - \omega_0)^2 + (\omega_L/2)^2}$$  \hspace{1cm} (2.3.9)$$

The DHO is given by:

$$DHO(\omega, \omega_\infty, T, \Gamma_0, A) = \frac{A}{(1 - \exp^{-\omega/T})\pi} \frac{\omega \Gamma_0}{(\omega_\infty^2 - \omega^2)^2 + (\omega \Gamma_0)^2}$$  \hspace{1cm} (2.3.10)$$

The resolution function at each temperature was experimentally determined by
Figure 2.3.28: Schematic of the dynamical structure factor used to fit the data measuring the elastic scattering of a plexiglass and an example of the resolution function is shown in Figure 2.3.27.

To explain the quality of the individual fits at R point and at M point, some of the raw data and corresponding fits are presented.
Figure 2.3.29: Sample of fit quality at momentum points R (left column) and M (right column). The red points and blue lines resemble data and the fit respectively.
Figure 2.3.30: Sample of fit quality at momentum points \(R + \delta\) (left column) and \(M + \epsilon\) (right column).
Chapter 3
Comparative study of two incipient ferroelastics,
ScF$_3$ and Hg$_2$I$_2$

3.1 Introduction

As introduced in Chapter 1, ScF$_3$ is a prominent SNTE system forming in the so called “open” perovskite structure. Recent work [28] has described the configurational potential for $R$ point distortions as having a nearly quartic form at small displacement, presenting an interesting limit of lattice dynamics.

Inelastic investigations discussed in Chapter 2 on single crystals show a soft-mode instability and other phenomena that indicate a structural transition with extrapolated critical temperature $T_c < 0$, meaning that while similar compounds like TiF$_3$ realize a cubic-to-rhombohedral structural phase transition, this transition is never realized in ScF$_3$, except under an extremely small $< 1$ kbar hydrostatic pressure at cryogenic temperatures. These special circumstances are contextualized in Figure 3.2.1a, which shows the global structural phase diagram of 3$d$ transition metal trifluorides BF$_3$ as a function of the B$^{+3}$ ionic radius, $r_B$. The occurrence of the endpoint of a structural phase boundary so near the ground state of a stoichiometric compound is extremely rare, as
is the pronounced SNTE property of \( \text{ScF}_3 \). The confluence of these unusual circumstances raises the question of whether certain types of NTE can arise as unusual behavior above structural quantum phase transitions (SQPTs) due in this case to strong geometrical fluctuations of the incipient ferroelastic state (IFE) occurring either through quantum effects, or classical energy landscape flattening. To directly address this issue, we have explored the thermal expansion behavior and lattice fluctuation spectra in optical/detector quality single crystals of a second stoichiometric IFE in mercurous iodide, \( \text{Hg}_2\text{I}_2 \), known colloquially as protiodide [138].

We note that incipient lattice instabilities have recently attracted renewed interest [139] in light of their use to develop a 50% increase [140] in superconducting transition temperature of Nb-doped \( \text{SrTiO}_3 \) in an exceptional limit of the strong coupling theory [141], while the recent observation of electronic coupling to a substrate phonon in FeSe films raises questions regarding the possible role of substrate lattice fluctuations in stabilizing film superconductivity [142]. The common appearance of incipient soft modes also in SNTE materials potentially opens promising areas for future work combining SNTE and superconductivity to realize new emergent phases enabled by extremal strain conditions. Previous evidence from our study of \( \text{ScF}_3 \)[23] and other systems [134] has determined that quenched disorder can have dramatic effects on structural instabilities, and we have restricted our attention to pure stoichiometric systems, in contrast to a recent study of a SQPT achieved through chemical substitution, showing
prominent elastic and thermodynamic anomalies near the SQPT in LaCu$_{6x}$Au$_x$ [143]. We note that in contrast, both ScF$_3$ and Hg$_2$I$_2$ lie very close to the critical endpoint of a structural phase boundary without the additional effects of quenched disorder.

3.2 Low-T structure and scattering evidence for the IFE behavior of Hg$_2$I$_2$ and ScF$_3$

Figure 3.2.1b summarizes the known structural phase diagram of the mercurous halides Hg$_2$X$_2$ (X=Cl,Br,I) as a function of the X ionic radius [144], $r_X$.

The high symmetry structure in this case is body-centered tetragonal (BCT; Figure 3.2.1e) and can be described as a dense packing of X-Hg-Hg-X linear molecules oriented along the tetragonal c axis[145]. The basic structural unit that defines the high-temperature unit cell is an elongated square dipyramid (ESD) formed as a cage with parts of 10 X$^-$ ions surrounding a Hg dimer oriented along c, shown in Figure 3.2.1b inset and Figure 3.3.1b.

Single crystals of Hg$_2$I$_2$ and Hg$_2$Br$_2$ were prepared from purified materials using physical vapor deposition as previously reported [144]. Diffraction and inelastic X-ray scattering (IXS) data were collected using the HERIX spectrometer in sector 30 of the Advanced Photon Source, Argonne National Laboratory. Figure 3.2.2 shows the lattice parameters of IFEs ScF$_3$[9] and Hg$_2$I$_2$ along with data from their nearest realized structural transitions in TiF$_3$ [20] and Hg$_2$Br$_2$, respectively, for comparison. In the case of TiF$_3$ (Figure 3.2.2a),
Figure 3.2.1: Structural phase diagrams of (a) 3$d$ transition metal trifluorides and (b) mercurous halides. Insets show the basic volume-defining polyhedral units: (a) the BF$_6$ octahedron and (b) the elongated square dipyramid (ESD). Development of the structure for (c) the trifluorides and (d) the mercurous halides with the ionic radii indicated as spheres. The basic polyhedral structural unit is superposed in each case. (e) Comparison of the observed bond distances (symbols) and expectations based on hard sphere packing (dashed lines).
Figure 3.2.2: Temperature-dependent lattice parameters of (a,c) ScF$_3$, TiF$_3$, and (b,d,f) Hg$_2$I$_2$, and Hg$_2$Br$_2$. (e) shows a schematic free energy landscape of realized and incipient ferroelastics. Arrows show the fluctuation domain in each case.
Figure 3.2.3: Rocking curves measured at (330) bragg peak for optical and
detector quality Hg\(_2\)Br\(_2\) and Hg\(_2\)I\(_2\) crystals cleaved along \(\langle 110 \rangle\) planes grown
by physical vapor deposition method by Brimrose Technology Cooperation.

the cubic-torhombohedral transition has profound effects on the lattice dimen-
sions, showing a signature step of first order transition and subsequent con-
tinuous order parameter development, shrinking \(\sim 3\%\) between the structural
transition temperature \(T_c\) and base temperature [19]. The hexagonal c axis
on the other hand displays SNTE similar in magnitude to the negative CTE
observed in ScF\(_3\) in the same temperature range. The lattice expansion of the
realized transition in Hg\(_2\)Br\(_2\) bears remarkable resemblance, with a significant
reduction in tetragonal c axis lattice parameter below the transition, changing
4.5\% between 150K and base temperature. The transition appears to be nearly
continuous, consistent with prior work [146].

The c axis of Hg\(_2\)I\(_2\) however shows a clearly negative CTE below 100K shown in
Figure 3.2.2d, reaching a significant low-temperature value of -5ppm/K. While
negative values of the c-axis compressibility have been noted in mercurous
halides [147], SNTE in Hg\(_2\)I\(_2\) has not been reported to our knowledge. The
similarities to the fluorides are striking - both realized transitions TiF$_3$ and Hg$_2$Br$_2$ show strong positive CTE below their respective transitions while the IFE systems tuned near their SQPTs show strengthening NTE at the lowest temperatures. The magnitude of the negative CTE in the iodide case (-5ppm/K) is about one third of the maximum magnitude in the trifluoride case (-14ppm/K) and the range of thermal persistence is also reduced about 10-fold. These reductions can be partially explained by the large mass difference between the two materials classes and the correspondingly different energy scale of thermal fluctuations required to induce bond-stretch fluctuations, whose presence may mute the long-range effects coupling bond-bend modes to lattice dimensions. We remark that at the outset the geometrical similarities in the structure of these two classes and explore more detailed analysis of the influences driving these incipient structural transitions in each case below.

3.3 Discussion and SNTE material design principles

The halide ESD is not regular, but rather compressed, defined by X-X bond lengths of three varieties: the long X-X bonds (green) lying in the basal plane, the short X-X bonds (blue) oriented along the tetragonal c axis, and apical X-X bonds (red). Figure 3.2.1d shows reported literature values of the lengths of the three types of X-X bond distance [145, 148, 149, 138, 150, 151]. The basal planar (green) X-X bonds cluster well$^2$ with a clear trend far in excess of the diagonal.

---

The clustering for the X-X (a) bonds is due to the simple relation to structure - this bond distance is simply the a lattice parameter and can be determined from a single reflection and Braggs
dashed line that indicates simplest expectation based on sphere packing. The apical (red) bonds trend with ionic radius and stay near the X ionic diameter, indicating the apical half octahedron is somewhat flattened relative to a regular ESD, but roughly satisfies the simple packing conditions. On the contrary, the coriented (blue) X-X bond is near the ionic diameter only for X=Cl (calomel) and deviates significantly for X=Br and even more so for the IFE X=I, implying these short bonds along c are in a state of compression due to forces provided by the rest of the framework. The natural source of this compression is a net tension in the X-Hg-Hg-X linear molecule along the c axis through the ESD center.

Starting from the BCT phase, the relevant distortion to the low-temperature orthorhombic phase is a staggered shift of the Hg-Hg dimer from the ESD central axis in the 110 direction of the basal plane (Figure 3.2.1f). The structural transition then corresponds to condensation of the transverse acoustic wave at the X point of the BCT Brillouin zone (shown in Figure 3.3.2b inset) [146, 153]. For these realized improper [146, 154] ferroelastic materials, Tc > 0 and the T = 0 energy landscape consists of four minima corresponding to the possible saturated shifts of the Hg dimers (Figure 3.2.1b). For larger ionic radius, these minima flatten and coalesce to the central axis for X=I and no symme-
Figure 3.3.1: Structure of 3$d$ transition metal trifluorides in the (a) high-temperature cubic phase and (b) the low-temperature rhombohedral phase. Structure of the mercurous halides in (c) the high-temperature body-centered tetragonal and (d) low-temperature orthorhombic phases. Inelastic X-rays scattering measurement of (e) ScF$_3$ at the simple-cubic $R$ point, corresponding to the soft mode of the rhombohedral transition and (f) Hg$_2$I$_2$ at the BCT $X$ point, corresponding to the soft mode of the orthorhombic transition. Insets show the Brillouin zone in each case. Soft mode frequency squared resultant from fitting to a damped-harmonic oscillator model for (g) ScF$_3$ at $R$ point and (h) Hg$_2$I$_2$ at $X$ point. Dashed lines indicate the extrapolation to negative absolute temperature and indicate the proximity to an incipient ferroelastic transition.
try breaking is observed. The flattening of the energetic landscape however induces strong temperature-dependent fluctuations of the staggered shift, as is observed experimentally from X-ray diffraction data as large transverse dimensions of the Hg thermal ellipsoids, approaching $2\sqrt{U_{11}} = 0.38$ Å at $T = 150$ K for Hg$_2$I$_2$ [151]. We propose that the origin of the coalescing minima can be viewed as an effect of two competing forces: the compressive stress on the c-oriented XX bonds and the tensile stress on the X-Hg-Hg-X linear molecule by its environment. For X=I, these forces have a near-canceling effect which stabilizes the high-symmetry BCT structure and stabilizes transverse dimer fluctuations inside the ESD.

In the language of structural mechanics, the development of a state of self stress (SSS) in the ESD polyhedral unit [155] increases its tensile integrity (aka tensegrity [156]). As is known in structural mechanics of frameworks, the development of a SSS is accompanied by reduction of the zero mode count [155, 157, 158], and the transition may be regarded as a reduction of this off-axis degree of freedom.

The critically-tensioned linear molecule inside the ESD unit exhibits large transverse fluctuations of the Hg dimer and leads to the observed negative thermal expansion along this axis (Figure 3.2.1d). This size-induced stiffening is also apparent in the lowering of the melting temperature and triple points as the X ion grows, since the entropy of the BCT phase is reduced by the stiffening of the ESD. To elucidate the connection between the unusual lattice parameter
behavior in scandium trifluoride and protiodide, we consider evolution of the basic trifluoride octahedral subunit with $r_B$, used as a baseline for comparison of relative size effects. Figure 3.3.1c shows that to a good approximation, the unit cell dimension F-B-F ionic distance (a lattice parameter) trends with $r_F + r_B$ while the nearest F-F distance grows to values significantly in excess of the $2r_F$. We note further that for $r_B > 0.75$ Å in the rare-earth class and beyond, trifluorides take on other crystal structures with B site coordination larger than n=6 in the orthorhombic tysonite (n=8), and hexagonal (n=9) [159] structures. Together, these observations suggest an effective reduction of the overall stiffness of the BF$_6$ octahedron for large B ions through reduced interaction of the anions situated at the octahedral vertices. In this case, a large number of SSSs are removed as the octahedral unit loses tensegrity with increasing $r_B$. Notably, fluctuations of the F position transverse to the B-F-B bond are very large in ScF$_3$, approaching $2\sqrt{U_{33}} = 0.24$ Å [135, 160, 161] at $T = 150$ K, consistent with this picture. In contrast to the mechanism in the mercurous iodide, we expect that the onset of pliancy of octahedral molecules stabilizes the cubic phase, as many states are available with the average cubic structure. This situation is also manifest in the high melting point of ScF$_3$, where the high entropy of transverse bond fluctuation competes with the fluid phase up to 1800 K.

Figure 3.2.1a,b show inelastic X-ray scattering spectra at the momentum points corresponding to the soft mode instabilities in IFEs ScF$_3$ and Hg$_2$I$_2$. The trifluoride low-temperature phase can be described as a staggered tilt of octahedra
Figure 3.3.2: Structure of 3d transition metal trifluorides in the (a) high-temperature cubic phase and (b) the low-temperature rhombohedral phase. Structure of the mercurous halides in (c) the high-temperature body-centered tetragonal and (d) low-temperature orthorhombic phases. Inelastic X-rays scattering measurement of (e) ScF$_3$ at the simple-cubic $R$ point, corresponding to the soft mode of the rhombohedral transition and (f) Hg$_2$I$_2$ at the BCT $X$ point, corresponding to the soft mode of the orthorhombic transition. Insets show the Brillouin zone in each case. Soft mode frequency squared resultant from fitting to a damped-harmonic oscillator model for (g) ScF$_3$ at $R$ point and (h) Hg$_2$I$_2$ at $X$ point. Dashed lines indicate the extrapolation to negative absolute temperature and indicate the proximity to an incipient ferroelastic transition.
around the 111 axis (Figure 3.2.1f). This fluctuation has the \((\pi, \pi, \pi)\) spatial texture of the \(R\) point in the simple cubic Brillouin zone, shown in Figure 4a. Also shown is a surface plot of the dynamical structure factor \(S(R, \omega)\) obtained using IXS [23]. At high temperature, a Stokes and anti-Stokes mode at low frequency of 3.4 meV softens considerably, approaching an extrapolated transition temperature \(T_c \approx -39\) K, as shown in Figure 3.2.1c. This singular point in the response function is suggestive of a flattening of the free energy landscape in an approach to an unrealized structural phase transition and strongly supports our identification of \(\text{ScF}_3\) as an IFE. Similarly, Figure 3.2.1b,d show the evolution of \(S(X, \omega)\) with temperature and an avoided condensation of a soft mode at the \(X\) point of the body-centered tetragonal Brillouin zone in \(\text{Hg}_2\text{I}_2\). \(S(X, \omega)\) again shows Stokes/anti-Stokes mode pairs that imply a putative transition at \(T_c \approx -23\) K. This is fully consistent with previous studies on single crystals using energy-integrated diffuse X-ray scattering showing \(T_c \approx -20\) K [162].

The transition metal trifluoride and mercurous halide materials bear strong similarities besides the unusual strengthening of the SNTE effect at low temperature. In both cases, molecular units form a high-symmetry structure whose bonds are on average straight and are situated so as to define the linear dimensions of the crystal, \(a\) in \(\text{ScF}_3\) and \(c\) in \(\text{Hg}_2\text{I}_2\). On approach to zero temperature, high energy bond stretch excitations become frozen out quickly as soft residual angular fluctuations are reduced more gradually, leading to a net increase of the
average linear dimension upon cooling. The incipient nature of the transition is vital to this condition to avoid a staggered strain symmetry breaking which disrupts the coupling of angle to dimension. In this sense, the SNTE in ScF$_3$ and Hg$_2$I$_2$ can be viewed as resultant from competition with an incipient improper ferroelastic phase. We generalize this understanding in a proposal that candidate SNTE materials may be identified in systems which have (i) bond-bend instability at zero temperature coupled to the lattice dimensions, (ii) low quenched disorder and stoichiometric composition, with the most pronounced effects occurring at temperatures below bond-stretch fluctuations.
4.1 Introduction to diffuse scattering

X-ray radiation scattered by a perfect crystal would lead discrete Bragg peaks in reciprocal space. The scattering arises from a crystal lattice which deviates from the perfectness is known as diffuse scattering. This could be attributed to various reasons such as impurities, stresses, vacancies, dislocations, grain boundaries and most importantly thermal vibrations of the atoms in the crystal. The diffuse scattering caused by atomic thermal vibrations is known as thermal diffuse scattering (TDS) and TDS measurement carries valuable information on the lattice dynamics of crystalline materials. Even though TDS probes lattice dynamics like IXS technique, TDS is differentiated from IXS as it is momentum resolved but energy-integrated measurement technique unlike IXS. In other words, TDS spectrum or image simply carries the reciprocal space information of the sample at an instant time. Nevertheless TDS is probably most useful as a complementary technique to IXS since it can be utilized to investigate large area of momentum space in relatively less time.

First discovery of TDS happened in 1920 by observing unexpected reflections
in Laue diffraction. Since then plenty of experiments and explanations were proposed on this technique and first ever experimentation of applying TDS to probe lattice dynamics was carried out by Olmer [163] in 1948. Following this, the early measurements on TDS were limited by low accuracy and low efficiency of the experimentation data acquisition as well as computational power at that time. During this time the emergence of neutron scattering surpassed the TDS experimentation until recent advances in X-ray sources and related instrumentation. Third generation synchrotron radiation with high brightness x-ray sources and two dimensional x-ray detectors can now be used to obtain highly precise and efficient TDS measurements within quick time and with abundance of information. Modern computers further support in handling and modeling sophisticated data in order to interpret the results more accurately.

4.2 Diffuse Scattering study of single-crystalline compound ScF$_3$

4.2.1 Experiment

Beside the strong NTE of ScF$_3$ another important property of this material is the apparent absence of cubic to rhombohedral phase transition which is found in every other trifluorides which adapt the cubic high temperature phase (All of them are rhombohedral in room temperature except MnF$_3$ is monoclinic). Calculations have shown that the restorative potential for certain octrahedral tilt
motion at the $R$ point in the BZ has a near vanishing quadratic component\cite{68}. This fact challenges the very notion of the phonon at low temperatures in this material and important influences on quantum phenomena are expected. The study (Chapter 2) of ScF$_3$ at HERIX beamline at APS has shown fascinating lattice effects which are not observed in most of the AB$_3$ type materials. The most phenomenal observation is that in the approach to zero temperature, the $M - R$ phonon branch softens dramatically and it appears that the low-energy state of ScF$_3$ is nearly critical in the sense that the branch energy is very near zero and the charge susceptibility at the $R$ point is very high. This suggests that the material could respond strongly to long-range strain forces, which would modify the critical dynamics of the lattice. In order to better understand the extent to which long range interaction plays a role in the critical dynamics of this nearly critical system we carried out a diffuse x-ray scattering experiment as a function of temperature and the momentum especially near the $R$ point and studied the energy integrated scattering with improved momentum resolution. This measurement was also carried out at APS at ANL.

4.2.2 Negative thermal expansion of ScF$_3$ and diffuse scattering

Work aimed to develop a mechanistic understanding of the NTE effect in ScF$_3$ and similar behavior in the more complex open-framework NTE compound ZrW$_2$O$_8$ has compared complementary experiments to simulations with an outstanding debate as to the role of molecular rigidity in the NTE mechanism.
One may naturally expect such an approach to apply when considering the hierarchy of energy scales within the lattice degrees of freedom. For transition metal perovskites, these break down as bond-stretching motion at high (50-100 meV) energy, bond-bending motion at medium (20-50 meV) energy, and a lower (1-3 meV) set of external modes described as coordinated motion of units which respect the internal dimensions of molecular sub-units such as the ScF$_6$ octahedra\cite{164, 165, 166}.

This tiered energy structure suggests that some normal modes are frozen out at temperatures where the phonon(boson) population is much lower than one. For example, the lowest zone-center optical mode in ScF$_3$ observed at 24 meV\cite{161} has a boson population $n \sim 0.62$ at 300 K, suggesting that these uniform intramolecular distortions are frozen out even at room temperature while the much softer (3.6 meV \cite{23}) intermolecular degrees of freedom on the zone boundary dominate with a population number $\sim 6.7$. Bose-Einstein distribution relation given in Equation 4.2.1 was used to calculate approximate boson population or the average number of phonon.

The average phonon number depends on temperature $T$, the energy of the phonon $E$ and Boltzmann constant $k_B$. Each phonon carry energy, $E = \hbar \omega$, where $\hbar$ is plank constant and $\omega$ is phonon frequency.

$$\langle n \rangle = \frac{1}{e^{(E/k_B T)} - 1} \quad (4.2.1)$$
Therefore a view of lattice dynamics which shifts focus from the atom to molecular sub-units as the basic building blocks may be appropriate to describe certain phenomena like NTE. Building on this idea, some researchers find an adequate description of NTE in terms of rigid molecular units which draw in the lattice when thermally activated, with still finer points of debate on which senses of motion are appropriate for which particular system [56, 57, 167], or across which momentum manifolds rigid external modes exist [54]. Others have suggested that molecular rigidity is neither necessary nor favorable as an NTE mechanism [167, 46, 160, 168]. Quite separately from any consideration of NTE, detailed specific interest in the perovskite space group landscape has suggested that the octahedral internal degrees of freedom can remain fixed in coordinated tilt patterns [169].

4.2.3 Results and discussion

![Thermal diffuse scattering images of (a) (100) (b) (110) (c) (111) planes taken for ScF₃.](image)

Figure 4.2.1: Thermal diffuse scattering images of (a) (100) (b) (110) (c) (111) planes taken for ScF₃.

If applicable, the open perovskite $Pm\bar{3}m$ structure of ScF₃ is capable of support-
ing rigid molecular modes along one-dimensional manifolds along the simple cubic Brillouin zone (BZ) edges. Inelastic x-ray scattering work (2) analyzing the temporal correlations of single-crystal ScF$_3$ has shown the presence of a soft mode manifold circumscribing the BZ edges[23]. Here we extend this study using high energy resolution diffuse x-ray scattering and find that these soft modes imply 2D spatial correlations associated with NTE.

Figure ?? shows a momentum surface of the elastic X-ray intensity in single-crystal ScF$_3$ taken at $T=300$ K with a high-resolution incident beam and an image plate at sector 30-ID-C of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). Momentum space is indexed to the simple cubic four-atom unit cell using Miller indices $HKL$ and the surface sampled is an Ewald sphere (ES) shown approximately in Figure 4.2.2. The ES samples approximately the $HK0$ plane near the origin, but finite curvature extends the sampled volume along the $L$ direction. Cuts in the $H$ (horizontal) direction are taken at equivalent half-integer values of $K$, but correspond to different $L$ positions along the scattering rods, as described in Figure ???. Lorentzian fits to these transverse cuts produce widths corresponding to about 1/0.18∼5.5 unit cells, independently of where the cut is made along the $M−R$ branch. We conclude that scattering rods are present along the BZ edges, reflecting short-range 2D nanoscale correlations of order 6 unit cells. The weak dispersion of optic modes reported previously[23] along this cut further suggests a decoupling of planar correlations corresponding to 2D coordinated rotations. In terms of
microscopic interactions, the lack of dispersion along the $M$-$R$ branch can be interpreted as a very low steric barrier - the energy cost to twist the Sc-F-Sc bond is very low. This produces an effective decoupling of the phase of coordinated octahedral motion in one plane with another.

Figure 4.2.2: Inset: Experimental geometry for the diffuse scattering experiments in single-crystal ScF3. Main panel shows a $H = 0.5$ cross section of the Ewald sphere. Blue and orange arcs indicate the extrema of the crystal rocking angle ($1^\circ$).
Figure 4.2.3: (a) Diffuse scattering intensity collected using the experimental geometry in Figure 4.2.2. Mid-zone intensity at $M$ points are indicated by dashed circles and are found in almost every BZ. Dashed lines indicate cuts through the intensity patterns shown in (b). Each cut in (a) is taken at an equivalent $K$ value but corresponds to a different $L$ value. The negligible change in widths is strong evidence of 2D spatial correlations.
Chapter 5

Two dimensional constrained lattice model to study ScF$_3$ lattice

5.1 Introduction

In this chapter we address the extent to which rigid octahedral motion describes the dynamical fluctuations behind NTE by generalizing a simple model supporting a single floppy mode that is often used to heuristically describe instances of NTE. We also discuss the tendencies of this model toward dynamic inhomogeneities and its application to thermal diffuse scattering data presented in Chapter 4.

Figure 5.1.1b shows the simple cubic BZ of ScF$_3$ with break outs indicating the nature of the correlated motion comprising $M$-$R$ zone boundary modes. The experimentally-observed (Chapter 4) decoupling of coordinated rotations within planar manifolds suggests there is prominent importance of the lattice dynamics of a 2D section, shown in Figure 5.1.2a,b. A model consisting of stiff diamonds connected by hinged joints shown in Figure 5.1.2a,b appears in numerous contexts in the literature describing the NTE phenomenon as a physical model wherein one may understand that collective motion of a rigid
network can generically provide a NTE influence\cite{80, 79, 81}. The diamonds could represent metal-anion octahedra in the structural NTE perovskites \( \text{ScF}_3 \) or \( \text{ReO}_3 \), but the idea has been used to describe more complex structures\cite{79, 170, 171, 80, 81}. Here, we momentarily enforce the rigidity of the molecular units in an analysis of this two-dimensional constrained lattice model (2D CLM) to study the rigid limit expectations before comparing to experiment in order to provide insights into the limitations and strengths of rigid models in the NTE problem.

![Figure 5.1.1](image)

Figure 5.1.1: (a) A \( 5 \times 5 \times 5 \) crystallite of \( \text{ScF}_3 \) in the average structure (125 octahedra). (b) The hollow cube shows the simple cubic BZ with shaded regions indicating the positions of observed scattering rods from the data in Figure 4.2.3. Breakouts show possible real-space staggered rotation patterns which preserve internal octahedral dimensions at the indicated high-symmetry momentum-space points. Red and blue shading in the diamonds indicate equal but opposite magnitudes of rotation.

### 5.2 Two-dimensional constrained lattice model

The 2D CLM consists of corner-linked diamonds with coordinate origin at its
center of mass (COM). The $N_\diamond = N_x N_y$ diamonds are attached by hinged joints, so that their motional degrees of freedom are constrained. The CLM is isostatic, or marginally constrained, in the sense that even in the thermodynamic limit, there is exactly one internal degree of freedom: a staggered rotation of each diamond by an angle $\theta$. Increasing $\theta$ from zero contracts the lattice from initial area $A_0$ to an area $A_0 \cos^2 \theta$, and thermal activation of this collective mode is often attributed as the origin of NTE [80, 172, 170, 171]. Efforts to expand this model to field theories which respect the high-energy constraints of bond-stretch and bond-bend degrees of freedom include mimicking polyhedral pliancy through a split-atom approach [164], by lowering the degree of constraint [51, 165], or permitting some diamonds to be replaced by springs [166], and unusual properties such as NTE are found in each case. When there is no staggered
rotation, $\theta = 0$, and a diamond center can be located at position $\mathbf{r}(\theta = 0) = (n_x, n_y)a_0$. When $\theta \neq 0$, the distance between neighboring diamond centers is reduced by a multiplicative factor $\cos \theta$ and each position vector is scaled similarly $\mathbf{\tilde{r}}(\theta) = (n_x, n_y)a_0 \cos \theta$ with velocity $\mathbf{\dot{\tilde{r}}}(\theta) = -(n_x, n_y)a_0 \dot{\theta} \sin \theta$. The velocity vectors of each diamond always point directly toward or away from the COM. The total translational kinetic energy summed over all diamonds in the crystal is:

$$K_{\text{trans}}^\diamond = \frac{1}{2} I_c \dot{\theta}^2 \sin^2 \theta \quad (5.2.1)$$

where $I_c = \sum_{n_x, n_y} m_\diamond ((n_xa_0)^2 + (n_ya_0)^2)$ is the moment of inertia of a similar crystal where diamonds are replaced by points, each of mass $m_\diamond$.

Including the rotational kinetic energy of each diamond and summing, the total kinetic energy of the 2D CLM is

$$K = \frac{1}{2} N_\diamond I_c \dot{\theta}^2 + \frac{1}{2} I_c \dot{\theta}^2 \sin^2 \theta = \frac{1}{2} N_\diamond I_c \dot{\theta}^2 (1 + k^2 \sin^2 \theta) \quad (5.2.2)$$

where $k = \sqrt{\frac{k}{N_\diamond I_c}} = \sqrt{\gamma N_\diamond}$ and $\gamma$ depends on the aspect ratio of the crystal and mass distribution for the diamonds ($\approx 1.79$ for a square crystallite of ScF$_3$). Finally, we introduce the lowest Fourier component of an intermolecular bond-bending potential at the hinges $\kappa(1 - \cos \theta)$ to stiffen the structure from collapse. Microscopically, this influence arises from a competition between mutual repulsion of like charges including dipolar contributions and anion
polarizability and is considered low for trifluorides with a large B-site atomic radius such as Sc [106]. The total energy, expanded for a small angle to the harmonic case, is then

\[ E = \frac{1}{2} N_\diamond I_c (1 + k^2 \sin^2 \theta) \dot{\theta}^2 + \frac{1}{2} N_b \kappa \dot{\theta}^2 \] (5.2.3)

where \( N_b \approx 2N_\diamond \) is the total number of intermolecular linkages. One may view Equation 5.2.3 as a generalization of a harmonic oscillator (\( k \rightarrow 0 \)) describing a residual degree of freedom resultant from integrating out high-energy bond-stretch and bond-bend degrees of freedom.

Significantly, the total effective inertia of the FM has a rotational part (the first term) which scales with system size in an intensive way (\( \propto N_c \)), while the translational kinetic energy scales extensively (\( I_c \propto N_\diamond^2 \)). As the thermodynamic limit is approached, molecular units at the boundary of a free crystallite must traverse macroscopic distances within a single FM cycle while experiencing enormous force gradients, pointing to a necessary breakdown of rigidity and falsifies the rigid approach on physical grounds. A homogeneous FM in an infinite system therefore has an infinite kinetic energy density, and the effect favors inhomogeneous spatial textures through intramolecular deformations at a penalty of elastic potential energy. In what follows we entertain the possibility that the nanoscale correlations we observe are a signature of such a breakdown, as an alternative approach to a conventional phonon population
of optical modes.

In the limit of small-angle and large system size \(k\), one can integrate Equation 5.2.3 to find

\[
\frac{(t - t_0)^2}{(k\theta_0/\omega_p)^2} + \frac{\theta^2}{\theta_0^2} = 1.
\]

where \(\theta_0\) is the amplitude and \(\omega_p = \sqrt{N_b \kappa N_c I_c} = \sqrt{g/R}\) is the angular frequency of small oscillations in the limit \(k=0\). Several aspects of the thermodynamic FM are distinct from the harmonic case: (i) The period \(\tau = \frac{4k\theta_0}{\omega_p} = 4\theta_0 \sqrt{\frac{\kappa}{N_b N_c I_c}}\) diverges and is proportional to the amplitude of oscillation, (ii) the time-averaged classical probability distribution \(P(\theta)\) dwells much longer near the extrema than the harmonic case, and (iii) the system spends a vanishingly small time in the average structure \(\theta = 0\) (Figure 5.2.1b). The latter two points are apparent in recent molecular dynamics simulations of ScF\(_3\) that reach similar surprising conclusions of nearly vanishing probability for straight Sc-F-Sc bonds at elevated temperatures [173]. A physical expression of this peculiar distribution in the present model can be seen in the time-averaged area, related to the moments of this distribution, \(\langle A \rangle_t = A_0 \langle \cos^2 \theta(t) \rangle_t = A_0 (1 - \eta \theta_0^2)\), where \(\eta = 1/2\) for the sinusoidal \(k = 0\) case and \(\eta = 2/3\) for the thermodynamic limit \(k \to \infty\)

\(^{4}\), showing that the strain dynamics of the 2D CLM enhances NTE over its harmonic counterparts. The lessons from these results on the CLM is that the

The area of the 2D lattice at time \(t\) is given by \(A(t) = N_x N_y \cos^2 \theta(t) \sim N_x N_y (1 - \theta(t)^2)\). Time
collective motion of the dilating FM is slow and anharmonic, dwelling near extrema as a feature of its dynamics.

Figure 5.2.1: (a)(d) show classical solutions for \( \theta(t) \) which follow from Equation 5.2.3. These are plotted for different values of \( k_0 \), which uniquely quantifies the anharmonic behavior. The time axes in (a) and (c) are scaled by the FM period

We note that the dispersion away from the zone boundaries is very steep, approaching the longitudinal acoustic velocity, suggesting the dominant importance of the BZ edge modes to NTE. We are therefore positioned to compare the experimental \( a(T) \) for ScF\(_3\) with that of an uncorrelated stack of \( N_\circ = N_e^2 \)

averaging \( \theta(t)^2 \) over a period \( \tau \) for both the harmonic and circle wave limits:

\[
\langle \theta^2 \rangle_{\text{harm}} = \frac{1}{\tau} \int_0^\tau \left( \theta_0 \cos\left( \frac{2\pi t}{\tau} \right) \right)^2 dt = \frac{1}{2} \theta_0^2
\]

\[
\langle \theta^2 \rangle_{\text{circ}} = \frac{1}{\tau} \int_0^\tau \left( \theta_0 \sqrt{1 - \left( \frac{t}{\tau} \right)^2} \right)^2 dt = \frac{2}{3} \theta_0^2
\]

The circle wave limit spends significantly more time near the extrema than the harmonic case, resulting in a larger time averaged value for \( \langle \theta^2 \rangle \). Hence, the NTE effect due to FM oscillations is amplified for larger systems exhibiting stronger anharmonicity.
thermally averaged 2D CLMs of area $A(T) = A_0 \langle \cos^2 \theta \rangle_T \approx A_0 (1 - \langle \theta^2 \rangle_T)$. The lattice parameter of the stack is then $a(T) = a_0 \langle \cos^2 \theta \rangle_T^{1/3} \approx a_0 (1 - \langle \theta^2 \rangle_T / 3)$, where we sum over the BZ edges to obtain

$$\langle \theta^2 \rangle_T = \frac{1}{Z} \int_{-\infty}^{\infty} d\theta dL \theta^2 e^{-\beta H} = \frac{2k_B T}{N_b \kappa} \frac{1}{1 + \frac{K_0(\delta)}{K_1(\delta)}}$$

(5.2.5)

$\beta = 1/k_B T$, $Z$ is the classical partition function, $\delta = \frac{N_b \nu_x}{4k^2 k_B T} = \frac{I_0 \omega_p^2}{4k_B T \gamma}$, and $K_n(\delta)$ is the order $n$ modified Bessel function of the second kind.

### 5.3 Application of model to experimental results

We determined $a(T)$ and the transverse anion thermal parameter $U_{33}(T) = (a_0/2)^2 \langle \theta^2 \rangle_T$ using model and the plots (Figures 5.3.1a and 5.3.1b) are shown along with existing experimental data [23, 160] using the observed $N_x = 5.5$ for different values of $\omega_p$. The inertial parameters for ScF$_3$ and $a_0 = 4.0285$ Å is used. Best agreement is met when $\hbar \omega_p \approx 1.6$ meV, which is similar in magnitude to the observed branch energy at low temperature (1.2-1.4 meV) and somewhat lower than the observed values at ambient temperature (3.4-3.6 meV). We remark that existing computational work gives mode energies ranging from 3 to 6.5 meV [161, 68, 160], and that inclusion of other low-energy modes off of the high-symmetry cut is expected to raise this effective energy scale somewhat.

Remarkably, this analysis has the implication of an intricate link between the following experimental quantities: (i) the length scale $\approx 6$ unit cells we observe
in diffuse x-ray scattering, (ii) the energy scale $\simeq 1$ meV for the $M - R$ branch reported using IXS, and (iii) the degree of dimensional fluctuation measured through the coefficient of thermal expansion measured using x-ray diffractometry. Recent purely theoretical analyses of square and kagome lattices crossing the isostatic limit using different approaches have also pointed to emergent nanometer length scales [174, 175, 117]. In contrast, the present results use a simple approach motivated by experimental observations to relate disparate experimental observables in a real material system.

Recent classical molecular dynamics simulations and general arguments have suggested the strict rigidity of molecular units is not possible or necessary for NTE [167, 135, 160, 168], fully consistent with the finite correlation length implied by our experiments and divergent kinetic energy density in the thermodynamic limit of the CLM. Here we propose a mechanism of strain relief and kinetic energy lowering consistent with experiments, the quantized nature of the vibrational spectrum, and the hierarchy of stiffness present in the bond patterns. The pileup of translational kinetic energy at the boundary of a dilating region implied by molecular rigidity could be alleviated by introducing bond-bend intramolecular polyhedral deformations. Within a FM cycle, the separation between the edges of two adjacent, dilating nanoregions is minimized if the phases of oscillation $\phi_1$ and $\phi_2$ differ by $\phi_1 - \phi_2 = \pm \pi/2$. These two choices keep the edges in contact without parting the junction and lower the translational kinetic energy significantly. We can demonstrate this savings
by considering the kinetic energy of a homogeneous excitation of a 2D CLM in a long, narrow solid shown in Figure 5.3.1, $N_x \times N_y$, with $N_x \gg N_y$ is given in Equation 5.2.2 with moment of inertia $I_c^{(1)} = 2m_o a^2 N_x^3 N_y/3$. An inhomogeneous excitation with a domain wall at the origin separating a region of FM phase 0 (maximum volume) for $x > 0$ and FM phase $\pi/2$ (minimum volume)
for $x < 0$ has an effective crystal moment of inertia which is 4 times lower
\[ I_c^{(2)} = m_x a^2 N_x^2 N_y / 6 = \frac{1}{4} I_c^{(1)}. \]
A similar calculation for two semiplanes in contact gives
\[ I_c^{(2)} = \frac{1}{2} I_c^{(1)}, \]
in any case lowering the energy. The interface between these regions must feature excited optical modes with an elastic energy penalty made possible by the enormous lowering of translational kinetic energy.

The molecular velocity field in this scenario may be described as monopole-antimonopole pairs. The topological defects proposed here are resultant from the alleviation of strain at the interface and are protected at a ≃ 20 meV scale. While details of a possible superstructure await further experiments and modeling, we identify a large kinetic energy lowering occurs through the formation of a $\pi/2$ phase slip defect, which may pose intrinsic challenges to theories which embark with a classical approach. For a large single 2D planar section, the $\pm \pi/2$ phase slip could occur in multiple ways, potentially benefitting the stability of the proposed excitations. A three-dimensional extension of such defect field is beyond the scope of the present work, but may give rise to nontrivial topological textures in the phase field of the FM, raising the interest in lattice systems with unconventional dynamics. Future time-resolved and coherent x-ray scattering experiments are likely to address the phase relationship intrinsic to the nanoscale correlations in NTE materials.
Chapter 6

Infrared study of ScF$_3$

6.1 Introduction

Even though it is arguable that the molecular rigidity decides the NTE on framework structures [68, 160, 168, 167], studies have shown that coordinated tilt pattern of octahedra [169] is common among ReO$_3$ type structures of space group $Pm\bar{3}m$. These coordinated motions are identified as low energy modes hence known as soft modes and correspond to Brillouin zone (BZ) edge of simple cubic BZ. Further experimental evidences supported by theoretical modeling [48] has proposed that these soft modes can possibly relate with two-dimensional nanoscale correlations exist at momentum-space region.

It is clear that the dynamics of the ScF$_3$ structure and its properties are mostly discussed in connection with the degrees of freedom associated with off center of the BZ. Here we make an attempt to investigate zone center optical phonons in order to find if any correlation exists between zone center and off-zone center phonon modes and to study the temperature dependence optical properties by using infrared (IR) reflectance and time domain terahertz (TD-THz) transmission spectroscopy.
6.2 Measurements

IR measurements were carried out using single crystal ScF$_3$. Sample was polished and half of the polished surface was coated with gold using standard metal evaporator in the laboratory at the Department of Physics at University of Connecticut. The amount of gold was chosen such that the thickness of gold layer was higher than that of the skin depth for far-IR radiation which is about 50 nm.

Far-IR reflections were measured using Bruker 66v Fourier Transform Infrared Spectrometer (FTIR) in the laboratory. Sample was kept under vacuum in an optical continuous flow cryostat runs with liquid helium and sample temperature was measured using Cernox sensor mounted near the sample. Temperature was recorded in the range of 30 - 300 K. The spectra was collected with a bolometric detection covering the range of frequencies 100 - 1000 cm$^{-1}$ using a multilayer beam splitter (T222) and a glow-bar as the source of radiation.

To investigate optical properties at further low frequencies, we performed TD-THz spectroscopy. Laser pulses (Pulse width = 70 fs) produced by KMLabs Griffin -10 Ti:Sapphire pulsed laser system were directed to broad area inter-digital photoconductive THz antenna from BATOP optoelectronics in order to generate THz radiation in the range of 10 - 80 cm$^{-1}$. THz detection was achieved with electro-optic sampling method by using ⟨100⟩- oriented ZnTe crystal. The spectrometer was purged with dry nitrogen air. Single crystal ScF$_3$
sample with dimensions of 4.7 mm×4.24 mm×3.59 mm was taped onto the sample holder at the edges. The sample chamber which consists of two kapton windows was kept under high vacuum and was attached to vibration-free, cryogen-free optical cryocooler. Measurements were taken down to 30 K.

### 6.3 Lorentzian model fitting

The most common way to fit dielectric dispersion in ordinary crystals is the three-parameter model, where the dielectric function is modeled by the sum of independent damped harmonic oscillators (Lorentzians),

\[
\tilde{\epsilon}_r(\omega) = \epsilon_\infty + \sum_n \frac{\omega_{pn}^2}{\omega_{T0n}^2 - \omega^2 + i\omega\gamma_{T0n}}
\]  

(6.3.1)

where \(\epsilon_\infty\) is the high-frequency (electronic) dielectric constant, \(\omega_{pn}\) is the plasma frequency of the n-th transverse vibrational mode of frequency \(\omega_{T0n}\) and \(\gamma_n\) is its damping constant or line width.

Consider an atom and assume that the nucleus mass is massive compared with electrons. We can treat the electrons in the atom are connected with springs to the nucleus. So the motion of an electron is described by a damped harmonic oscillator and we can write

\[
m \frac{d^2r(t)}{dt^2} + m\gamma \frac{dr(t)}{dt} + m\omega_0^2 r(t) = -eE(t)
\]  

(6.3.2)

where the second term represents the damping with damping constant \(\gamma\) and
the third term represents the Hooke’s law restoring force with characteristics frequency $\omega_0$. Last term is the force on the electron due to local electric field $E$. The interaction of the electron with magnetic field has been neglected here. Assuming the solution $r(t) = r_0 e^{i\omega t}$ the local electric field varies as $E(t) = E_0 e^{i\omega t}$. By applying this to the above equation we could obtain the local polarization or induced dipole moment

$$p = e r_0 = \frac{e^2 E_0}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma},$$  \hspace{1cm} (6.3.3)$$

The total polarization, $P = \langle N \rangle p$, where $N$ is number of atoms per unit volume. Further $P = \epsilon_0 \chi E$, where electric susceptibility $\chi = \tilde{\epsilon}_r - 1$. Here $\epsilon_r$ is relative dielectric permitivity which is in general a complex number and frequency dependent. By taking all this in to account we can write down

$$\tilde{\epsilon}_r(\omega) = 1 + \frac{Ne^2}{me \omega_0} \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma},$$  \hspace{1cm} (6.3.4)$$

By introducing oscillator strength $\omega_p = (Ne^2/m\epsilon_0)^{1/2}$ and considering total of $n$ electrons per atom

$$\tilde{\epsilon}_r(\omega) = \epsilon_{\infty} + \sum_{i=1}^{n} \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\gamma_i},$$  \hspace{1cm} (6.3.5)$$

6.4 Factorized model fitting
However four parameter factorized form of dielectric function has long been discussed\cite{176, 177, 178}, especially to model ionic crystals\cite{179, 176, 180} with large LO-TO splitting. It is advantageous to use the model since it allows different damping constants hence different relaxation time for the LO and TO phonon modes as stated below.

\[
\tilde{\epsilon}_r(\omega) = \epsilon_\infty \prod_n \frac{\omega_{LOn}^2 - \omega^2 + i\omega \gamma_{LOn}}{\omega_{TOn}^2 - \omega^2 + i\omega \gamma_{TOn}} \tag{6.4.1}
\]

where \(\omega_{TOn}\) is n-th transverse vibrational mode and \(\omega_{LOn}\) is n-th longitudinal vibrational mode. \(\gamma_{LOn}\) and \(\gamma_{TOn}\) are corresponding damping coefficients.

The complex permittivity in a material is directly proportional to the susceptibility which is a measure of the polarizability of the materials for an external electric field. In general permittivity depends on frequency of applied electric field (Equation 6.3.5) and the atomic structure or in other words how strongly the electrons bound into the atom. Therefore optical properties such as optical conductivity, refractive index, absorption coefficient are directly related to materials complex permittivity. When electromagnetic waves interact with matter they undergo various phenomena such as transmittance, absorption, reflections etc. and such phenomena are governed by so called optical properties of materials. Therefore experimentalists use different experimental techniques to measure the above mentioned phenomena and are successfully able to understand the fundamentals of material behaviors by studying their optical
properties. How EM radiation interact with different media of different refractive indexes is governed by famous Fresnel’s equations. I do not derive the whole set of equations here. In general they have the form

\[
\begin{align*}
r_s &= \frac{n_i \cos \theta_i - n_t \sqrt{1 - \left(\frac{n_i}{n_t} \sin \theta_i\right)^2}}{n_i \cos \theta_i + n_t \sqrt{1 - \left(\frac{n_i}{n_t} \sin \theta_i\right)^2}} \quad (6.4.2) \\
r_p &= \frac{n_i \sqrt{1 - \left(\frac{n_i}{n_t} \sin \theta_i\right)^2} - n_t \cos \theta_i}{n_i \sqrt{1 - \left(\frac{n_i}{n_t} \sin \theta_i\right)^2} + n_t \cos \theta_i} \quad (6.4.3)
\end{align*}
\]

The above equations exhibit the relationship between the refractive indices and reflection coefficients of \(s\) and \(p\) polarization of light. There \(\theta_i\) is incident angle and \(n_i\) and \(n_t\) are refractive indices of two media for incident and transmitted EM waves.

The total reflection is given by

\[r = \frac{r_p + r_s}{2}. \quad (6.4.4)\]

Ratio of reflected power to incident power is identified as reflectance, \(R\) and can be expressed in terms of reflection coefficient as

\[R = |r|^2. \quad (6.4.5)\]
For almost normal incidence of light $\theta_i = 0$ and both polarizations have the same contributions to the reflectance. I should also emphasize that in general refractive index of a material is complex and frequency dependent hence it is more accurate to denote it as $\tilde{n}(\omega)$. When an EM wave incident normal to the interface between air and a medium of refractive index $\tilde{n}(\omega))$ the reflectance can further be simplified to

$$R = \left| \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1} \right|^2. \quad (6.4.6)$$

Materials refractive index $\tilde{n}(\omega) = \sqrt{\tilde{\epsilon}_{r}(\omega)\tilde{\mu}_{r}(\omega)}$. For non magnetic material $\tilde{\mu}_{r}(\omega)=0$. Therefore the reflectance can be represented in terms of frequency dependent permittivity, $\tilde{\epsilon}_{r}(\omega)$ such that

$$R = \left| \frac{\sqrt{\tilde{\epsilon}_{r}(\omega)} - 1}{\sqrt{\tilde{\epsilon}_{r}(\omega)} + 1} \right|^2. \quad (6.4.7)$$

The relationship between the measured reflectance, $R$ and the models discussed earlier infers from equations 6.3.5, 6.4.1 and 6.4.7.

We analyzed our data shown in Figure 6.6.1 using both Lorentzian oscillator model and factorized form model mentioned earlier. The Chi squared valued from best fit was obtained and factorized formula better fits with data with lower Chi squared. The best fit parameters obtained at 300 K are tabulated in Table 6.6.3 for comparison. Figure 6.4.2 compares the TO frequencies obtained
Figure 6.4.1: A sample spectra taken for ScF$_3$. The frequency-dependent optical behavior of ScF$_3$ is divided in regions: T for transmission (or “transparency”), A for absorption and R for reflection.

from both models. We see a strong absorption feature in the broad reststrahlen band in our data. Therefore we added one additional oscillator (total of three oscillators in both models) in the fitting process. The implication of this is discussed later in this chapter. Fit to 300 K data estimated the $\epsilon_\infty$ to be 1.92 and it was used for low temperature fittings as a fixed parameter.

6.5 Zone center modes

The cubic structure of perovskite ScF$_3$ belongs to $Pm\bar{3}m$ space group. The Sc atoms and F atoms occupy the Wyckoff positions 1a(0,0,0) and 3d(1/2,0,0) corresponding with the point group $O_h$. Four atoms per unit cell suggests 12 branches in which 3 of them are acoustics. The irreducible representation of normal mode vibrations at the BZ center of the point group has the form
Figure 6.4.2: Compare the parameters obtained from factorized form model and Lorentzian model. Black markers are obtained from Lorentzian model and colored plots are from factorized form model.

\[ \Gamma_0 = T_{2u} + 3T_{1u} \] [95]. Out of them \( T_{2u} + 2T_{1u} \) are optical modes and \( 2T_{1u} \) are identified as IR active modes. None of the modes are Raman active while \( T_{2u} \) mode is neither Raman nor IR active and is known as “silent mode”. None of the mode is Raman active while \( T_{2u} \) mode is neither Raman nor IR active which is known as silent mode. For non polar crystals the IR active modes are triply degenerate with two transverse optical (TO) modes and one longitudinal optical (LO) mode in each branch. But in case of polar crystals like ScF₃ the TO and LO modes are split at ZC due to the well-known phenomenon which the displacement of charges in long wave length LO modes create dipole moments. The electric field induced by dipole moment has additional contribution to the restoring force hence the LO mode has higher energy than TO mode. This is known as LO-TO splitting.
ScF$_3$ has no Raman-active modes under ambient pressures owing to its cubic symmetry. However at 0.6 GPa, the staggered octahedra tilt around $\langle 111 \rangle$ and the structure corresponds to rhombohedral phase which results in Raman active modes. More interestingly the rhombohedral structure undergoes second structural transition at about 3 GPa.

### 6.6 Infrared measurement results

Reflectivity data along with the best fits of equation 6.4.1 are plotted in Figure 6.6.1 in the temperature range 30-300 K for ScF$_3$. Reflectivity clearly indicates
two reststrahlen bands as predicted by group theory of the crystal symmetry. Increase in reflectivity on cooling due to reduced scattering (reduced damping constant) at low temperatures are clearly visible.

Previous [161] IR absorption spectra on ScF$_3$ powder sample has shown two absorption bands at 220 cm$^{-1}$ and 520 cm$^{-1}$ which correspond to Sc-F-Sc bending and Sc-F stretching respectively. Simulations performed beyond quasi harmonic approximation has successfully reproduced experimental values such as lattice parameter, energy gap and lattice dynamics in ScF$_3$. Bond stretching modes get softer as the temperature is increased and bond bending modes get stiffer as temperature goes up but both modes are shifted about 6 cm$^{-1}$ within 300 K temperature window.

Figure 6.6.1: Measured reflectance of ScF$_3$ sample at different temperatures.
Our results are agreed well with most of the calculations and comparison is tabulated in Table 6.6.4. As seen in Figure 6.6.2(c) the low energy TO mode of Sc-F-Sc bond bending mode stiffen about 3 cm$^{-1}$ as the temperature increases within 270 K temperature window. From here onwards, this mode is called as TO1. The highest energy TO mode(TO2) or stretching mode soften by 5 cm$^{-1}$(Figure 6.6.2(a)). The values obtained from Kramers-Kronig consistent analysis are somewhat difference than the values published from powder transmission measurements [161] which may result from the single crystalline nature. The low and high energy LO phonons (LO1 and LO2) exhibit similar behavior as the TO phonons. Figure 6.6.2(b) and Figure 6.6.2(d) plots temperature dependence of LO mode frequencies.

Further, temperature dependence $\epsilon(\omega)$ was obtained and the infrared absorption, $\text{Im}(\epsilon(\omega))$ and infrared loss function, $\text{Im}(-1/\epsilon(\omega))$ are plotted in Fig. 3. The peak values corresponds to TO and LO phonons respectively.

Around 600 cm$^{-1}$, a dip can be seen in the reststrahlen band, indicating additional absorption in ScF$_3$. This has been previously observed in many fluoride

<table>
<thead>
<tr>
<th>Model</th>
<th>$\omega_{TO1}$</th>
<th>$\omega_{LO1}$</th>
<th>$\gamma_{TO2}$</th>
<th>$\gamma_{LO2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factorized formula</td>
<td>214</td>
<td>277</td>
<td>9.05</td>
<td>8.61</td>
</tr>
<tr>
<td></td>
<td>493</td>
<td>675</td>
<td>16.07</td>
<td>19.95</td>
</tr>
<tr>
<td></td>
<td>592</td>
<td>587</td>
<td>47.64</td>
<td>45.31</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>214</td>
<td></td>
<td>8.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>493</td>
<td>-</td>
<td>16.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>-</td>
<td>49.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.6.3: Compare the fit models at 300 K. Units are given in cm$^{-1}$
systems such as RbCaF$_3$, CsCaF$_3$, KZnF$_3$ [182], CaF$_2$, SrF$_2$, BaF$_2$ [?], LiF [183, ?] and NaF [?]. In case of LiF Willett-Gies and co authors have assigned the feature to two phonon absorption process following Eldridge [?] and in other cases it was assigned to multiphonon absorption. Best fits in most cases were obtained by fitting data with factorized formula. The temperature dependence of ScF$_3$ multiphonon absorption is larger than the single phonon absorption and softens about 11 cm$^{-1}$ within 270 K temperature interval.

In general the poles of $\epsilon(\omega)$ in Eqn. 2 are identified as TO phonon energies and zeros of $\epsilon(\omega)$ represent energies of LO phonons. But according to Berreman and Unterwald [176] if they are much closer to one another they only produce weak absorption in dispersion curve and can be depicted to two or more phonons. Therefore the weak absorption feature appeared around 600 cm$^{-1}$ (Figure 6.6.3(b)) which corresponds to the third pole of $\epsilon(\omega)$ in Equation 6.4.1 is assigned to a multiphonon process. The zero counterpart is found in loss function as shown in Figure 6.6.3(a).

### 6.6.1 Discussion

<table>
<thead>
<tr>
<th>Source</th>
<th>$\omega_{TO1}$</th>
<th>$\omega_{LO1}$</th>
<th>$\omega_{TO2}$</th>
<th>$\omega_{LO2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ours</td>
<td>$\sim 214$</td>
<td>$\sim 277$</td>
<td>$\sim 493$</td>
<td>$\sim 675$</td>
</tr>
<tr>
<td>Calculations[161]</td>
<td>$\sim 215$</td>
<td>$\sim 275$</td>
<td>$\sim 485$</td>
<td>$\sim 695$</td>
</tr>
<tr>
<td>Calculations[68]</td>
<td>$\sim 190$</td>
<td>$\sim 359$</td>
<td>$\sim 496$</td>
<td>$\sim 665$</td>
</tr>
<tr>
<td>Calculations[99]</td>
<td>$\sim 200$</td>
<td>$-$</td>
<td>$\sim 450$</td>
<td>$-$</td>
</tr>
<tr>
<td>Calculations[181]</td>
<td>$\sim 211$</td>
<td>$\sim 154$</td>
<td>$\sim 477$</td>
<td>$\sim 590$</td>
</tr>
</tbody>
</table>

Table 6.6.4: Comparison of our experimental results with previous calculations at 300 K. Units of energies are cm$^{-1}$. 
Figure 6.6.2: (a),(c) TO phonon energies & (b),(d) LO phonon energies obtained for ScF$_3$ by fitting the reflection with factorized formula at different temperatures. Corresponding linewidths obtained are shown in insets.

The large ionicity in ScF3 could be the reason for broad bands of LO-TO splitting. Highest LO mode energy for ScF$_3$ is 675 cm$^{-1}$ and for LiF, LO energy was found to be 669 cm$^{-1}$[183]. Since ScF$_3$ ionicity is comparable to that of LiF one could expect this.

Highest TO and LO modes are associated with bond stretching modes. Softening of the modes as temperature is increased can be attributed to weaken
lattice constant due to elongation of bonds. Combined analysis\cite{160} of the pair distribution function (PDF) of synchrotron X-ray total scattering, extended X-ray absorption fine structure (EXAFS), and neutron powder diffraction (NPD)
has shown that the Sc-F nearest-neighbor distance strongly expands with increasing temperature. Apart from that relaxation of anharmonic two phonon process could lower its self energy too. On the contrary, purely opposite behavior of the low TO and LO modes could be arising from ferroelastic mode (CITE) for ScF$_3$ crystal. This is similar to ferroelectric modes which are commonly observed in oxide perovskites at zone center [184, 185, 186] and at zone boundaries [187, 188].

![Graph of the real part of the dielectric function for ScF$_3$ with temperature.](image)

**Figure 6.6.4**: Variation of the real part of the dielectric function for ScF$_3$ with temperature.

As stated by Lowndes [180] the factorized formula follows the constraint $\sum_k \gamma_{k,TO} = \sum_k \gamma_{k,LO}$ to ensure that the $\text{Im}\ \epsilon(\omega)$ remains positive for a passive medium. The $\gamma$ values we obtained from fitting our data at 300 K is only 1.5\% (Table II.) different from each other hence very well satisfied the condition mentioned.

According to Figures 6.6.2a and 6.6.2b the low energy TO and LO phonons
stiffen as the material shrinks with temperature. Therefore Gruneisen parameter should be positive. But in Figures 6.6.2c and 6.6.2d, TO and LO mode energies soften as the material shrinks hence Gruneisen parameter should be negative. But the predicted results do not match with previous calculations [68]. This confirms the anharmonic nature of lattice dynamics of ScF$_3$ as predicted earlier[68, 161].

LyddaneSachsTeller relation:

Suppose a light damped system so that we can set $\gamma = 0$. Then Eqn. 5.4 reduces to

$$\tilde{\epsilon}_r(\omega) = \epsilon_\infty + \frac{\omega_p^2}{\omega_0^2 - \omega^2}$$  \hspace{1cm} (6.6.1)

Then at certain frequencies $\epsilon_r$ can fall to zero. We label this frequency $\omega=\omega'$. Hence we may write

$$0 = \epsilon_\infty + \frac{\omega_p^2}{\omega_0^2 - \omega'^2}$$  \hspace{1cm} (6.6.2)

Let us define the static dielectric constant of zero frequency permittivity, $\epsilon_r(0)$

$$\tilde{\epsilon}_r(0) = \epsilon_\infty + \frac{\omega_p^2}{\omega_0^2}$$  \hspace{1cm} (6.6.3)

By simplifying Equation 6.6.2 and Eqn. Equation 6.6.3 we derive the relationship
\[ \omega_r^2 = \omega_{TO}^2 \frac{\epsilon_r(0)}{\epsilon_\infty} \]  

(6.6.4)

To understand the physical meaning of the frequency \( \omega^2 \) at \( \epsilon_r(\omega)=0 \) consider the guess law. In a medium with no free charges the guess law reads

\[ \nabla \cdot D = \nabla \cdot (\epsilon_r \epsilon_0 E) \]  

(6.6.5)

Generalized form of electric field propagates through a medium is given by

\[ E(r, t) = E_0 e^{i(k \cdot r - \omega t)} \]  

(6.6.6)

When we apply the EM wave form into Equation 6.6.5 we assume that \( \epsilon_r \neq 0 \). Therefore we conclude that \( k \cdot E = 0 \) and hence determine that the wave vector is perpendicular to that of electric field. But if \( \epsilon_r=0 \), we can conclude that \( k \cdot E \neq 0 \). These types of waves are known as longitudinal waves. So we can write down Equation 6.6.4 as

\[ \omega_{LO}^2 = \omega_{TO}^2 \frac{\epsilon_r(0)}{\epsilon_\infty} \]  

(6.6.7)

This relation is known as Lyddane-Sachs-Teller(LST) relation, which is commonly presented in the form.

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It is also known [177, 189] for high symmetric crystals and for N number of optical modes the LST relation becomes

\[
\frac{\epsilon_r(0)}{\epsilon_\infty} = \frac{\omega^2_{LO}}{\omega^2_{TO}}
\]  

(6.6.8)

Obtaining \( \epsilon_r(0) \) for ScF\(_3\):

The simple relation given in Equation 6.6.9 is used to derive \( \epsilon_r(0) \) for ScF\(_3\). It is also important to realize that the terms zero frequency relative permittivity, static relative permittivity or static dielectric constant are used to identify the same quantity, \( \epsilon_r(0) \). The capacitance of a capacitor is directly proportional to the static dielectric constant of the dielectric. The static dielectric constants for ScF\(_3\) is almost temperature independent and are tabulated in Table 6.6.5. We use \( \epsilon_\infty = 1.92 \) which is obtained from fitting the data to factorized form model.

<table>
<thead>
<tr>
<th>Temp(K)</th>
<th>( \epsilon_r(0) )</th>
<th>Temp(K)</th>
<th>( \epsilon_r(0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.04</td>
<td>200</td>
<td>6.03</td>
</tr>
<tr>
<td>50</td>
<td>6.04</td>
<td>250</td>
<td>6.02</td>
</tr>
<tr>
<td>70</td>
<td>6.05</td>
<td>300</td>
<td>6.01</td>
</tr>
<tr>
<td>100</td>
<td>6.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.6.5: Static dielectric constant for ScF\(_3\) obtained from LST relation

One of the main objective of our measurement is to figure out if any correlation exists between the lowest energy mode in zone boundary \( M – R \) branch and
zone center optical phonons. At 300 K the two phonon absorption is observed at 592 cm\(^{-1}\) and within 270 K temperature window the corresponding energy decreases about 11 cm\(^{-1}\) as the temperature increases.

<table>
<thead>
<tr>
<th>Assigned phonon pair</th>
<th>Combined energy from calc.</th>
<th>Our expt. results</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO((X)) + TA((X))</td>
<td>(\sim 547.4) [161]</td>
<td>(\sim 592)</td>
</tr>
<tr>
<td>TO(M) + TA(M)</td>
<td>(\sim 597.5) [161]</td>
<td>(\sim 592)</td>
</tr>
<tr>
<td>TO((X)) + LA((X))</td>
<td>(\sim 639.8) [161]</td>
<td>(\sim 592)</td>
</tr>
<tr>
<td>TO((X)) \textit{bend} + LA((X))</td>
<td>(\sim 632.6) [161]</td>
<td>(\sim 592)</td>
</tr>
</tbody>
</table>

Table 6.6.6: Two phonon absorption possibilities, if only high symmetric points are considered

Szigeti[190] and Lax and Burstein [191] have shown that the sum and difference processes of lattice vibrations could arise from the second order dipole moment and third order anharmonic interactions by studying the effect of these interactions on IR and Raman spectra. If that is the case the multiphonon absorption feature can be assigned into two-phonon absorption which then can be viewed in two different ways. It could be either a summation process such as two phonon creation or difference process such as creation and annihilation of an existing phonon.

The phonon creation and annihilation is possible but it would require a combination of LO2 mode with other lower mode. The possibility of LO2 mode involvement in the two phonon absorption is omitted since it is not possible to create longitudinal modes with almost normal incident reflection. Apart from that the fact that the two-phonon absorption feature in IR data doesn’t smear
out as the temperature is lowered suggests that it only involves two-phonon emission (sum) mode, rather than emission and absorption (difference) mode.

Figure 6.6.5: Most probable combination of two phonons are shown. They could be arising from sharp DOS which is shown in extended blue area in combined plots of phonon dispersion and corresponding DOS. Directions along \( \Gamma - M - R \) and along \( \Gamma - X - M \) are considered. A mode lies at momentum point \(-\mathbf{q}\) with in red (at momentum point \(\mathbf{q}\) in green) areas of dispersion plot corresponding to higher energy DOS peak and a mode lies at momentum point \(\mathbf{q}\) with in red (at momentum point \(-\mathbf{q}\) in green) areas in the lower energy DOS peak excite and correspond to two phonon absorption. Dispersion plots are taken from [24].

One set of possibility of two phonon creation is a combination of TO1 mode at momentum \(\mathbf{q}\) with different low energy mode at momentum \(-\mathbf{q}\). From the measurement we found that the TO1 mode stiffen with temperature by 3 cm\(^{-1}\). In order to satisfy energy conservation the second phonon involve in the process should soften by about 14 cm\(^{-1}\) (\(-11(\text{two phonon}) = +3 (\text{TO1 mode}) - 14\)). According to the literature [24, 68] none of the branches soften this much.
within 300 K range as temperature is increased. Therefore we could omit the possibility of TO1 mode involvement in two phonon absorption.

The other possibility of two phonon feature is TO2 phonon is excited at momentum \( q \) while another low energy phonon is excited at momentum \(-q\). The DOS around TO2 mode (hardest TO mode) is very narrow and hence almost dispersionless through out the first BZ. Therefore the second phonon can arise from any where in the BZ such that the momentum is conserved. In order to satisfy the energy conservation the other phonon mode should have energy around 100 cm\(^{-1}\). Calculation and experimentation results\([68, 161, 24]\) show five noticeable peaks in ScF\(_3\) phonon density of state (DOS). They are related to five optical phonon branches (degenerated TO, splitted TO - LO pair). The lowest peak of density of states obtained by Li et al.\([68]\) centers at 13 meV (104 cm\(^{-1}\)) which very much satisfy the energy requirement of the second phonon. Therefore we conclude that TO2 mode and any mode corresponds to reciprocal space points in the whole \( X - M, \Gamma - M \) and \( \Gamma - R \) branches can combine in order to give two phonon absorption in ScF\(_3\). If we only consider the high symmetry points then the possibilities gets narrow down to a few as shown in Table 6.6.6.
Chapter 7

Resonant Ultrasound Spectroscopy

7.1 Introduction

Resonant Ultrasound Spectroscopy (RUS) is an ultrasonic used measurement technique which was fully developed in late 80s. Ultrasonic measurements provide valuable information on elasticity related properties of solids such as elastic constants, shear modulus, young’s modulus, bulk modulus and poisson ratio etc. RUS has distinctive advantages over all the other methods which could be used to carry out these types of measurements. More importantly RUS requires very less amount of materials in order to achieve accurate results and one good spectrum may be more than enough to fully characterize the elastic properties of a given sample. Another great aspect is RUS measurements are fast, nondestructive and result in very less time consuming experiment. The most challenging part of RUS experiment is data interpretation, which usually involves solving few algorithms to back calculate elastic properties using measured normal mode frequencies and material geometry. Advances of computer programming and new technology has eased those challenges quite extensively.
7.2 Elastic properties and constitute equations

Before we discuss the experimental techniques further, we have to understand the types of materials properties which we could probe using RUS like technique. In general, simple equations can be used to generalize physical effects caused by external forces applied into a solid. In addition to those basic formulas, there are other equations which are constructed accounting for materials properties. These equations are called constitute equations. The constitute equations comprise of set of relationships between strain and stress. The unknown parameters from the resulting equations are related with elastic properties of given material and can be determined experimentally.

For an elastic material the generalized Hook’s law can be stated as

\[
\sigma_{ij} = c_{ijkl} e_{kl}, \text{ where } i,j,k,l = 1,2,3 \quad (7.2.1)
\]

This assumes a linear relationship between stress tensor components (\(\sigma_{ij}\)) vs strain tensor components (\(e_{kl}\)). Such relations, are referred to as a set of constitutive equations and they serve to describe the material properties of the medium and can be applied to materials deformation when subject to external forces. There are total of 81, \(c_{ijkl}\) constants and it is identified as ”elastic stiffness” tensor. If we write the reverse formula of the form,
\[ e_{ij} = s_{ijkl} \sigma_{kl}, \text{where} \; i,j,k,l = 1,2,3 \] (7.2.2)

We identify the \( s_{ijkl} \) as "elastic compliance" tensor of the material. The symmetry of stress and strain tensor would imply,

\[ c_{ijkl} = c_{jikl} = c_{ijlk} = c_{jilk} \] (7.2.3)

\[ s_{ijkl} = s_{jikl} = s_{ijlk} = s_{jilk} \] (7.2.4)

As a consequence, only 36 constants are independent of each other. and the generalized Hook’s law in terms of 36 independent stiffness constants can be written in matrix form as

\[
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix}
= \begin{pmatrix}
c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\
c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\
c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\
c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66}
\end{pmatrix}
\begin{pmatrix}
e_1 \\
e_2 \\
e_3 \\
e_4 \\
e_5 \\
e_6
\end{pmatrix}
\] (7.2.5)

In terms of elastic compliance tensor this reads,
\[
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix} =
\begin{pmatrix}
\sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz} \\
\sigma_{xx} & \sigma_{yy} & \sigma_{zz} \\
\sigma_{xx} & \sigma_{yy} & \sigma_{zz} \\
\sigma_{xx} & \sigma_{yy} & \sigma_{zz} \\
\end{pmatrix}
\]

Figure 7.2.1 provides better understanding of the notation used in equations 4.5 and 4.6. Notations used in equations are related to the given notations in the Figure 7.2.2 such that \( \sigma_1 = \sigma_{xx}, \sigma_2 = \sigma_{yy}, \sigma_3 = \sigma_{zz}, \sigma_4 = \sigma_{xy}, \sigma_5 = \sigma_{xz} = \sigma_{zx}, \sigma_6 = \sigma_{yx} = \sigma_{yx} \). Here \( \sigma_{xx}, \sigma_{yy} \) and \( \sigma_{zz} \) denote compression components while \( \sigma_{xy}, \sigma_{xz} \) and \( \sigma_{yz} \) denote shear components. In simple terms, Shear force is a force acting tangentially over the surface of a body. For example, friction between the tires of a vehicle and road is a shear force. On the other hand, a compression or compressive force is a force acting axially on the body.
Finally, the condition that the strain energy be a function only of the state of the material leads to $c_{ijkl} = c_{klij}$, which reduces the number of independent elastic constants to 21. Any further reductions depend on the symmetry of the crystal under consideration. Only the lowest-symmetry crystal, triclinic with a one-fold axis of rotation, has 21 elastic constants.

7.2.1 Symmetries in cubic systems and other important properties

If we recall the matrices defined in equation 4.5 and 4.6 we can identify three different types of constants in them. Some of the elements are related with compression while some of them define only shear components. The remaining
set of elements represent coupling between compression and shear. Figure 7.2.2 provides clear view on the point illustrated above.

Cubic crystal system is the simplest and most symmetric out of all seven crystal systems, which exhibits four threefold rotational axes oriented at 109.5 degrees (the tetrahedral angle) with respect to each other (It is identical with respect to x, y and z axis). The symmetry arrangement of the cubic crystal results in non zero but symmetric compression components, non zero diagonal shear components, zero off diagonal shear components and zero shear/compression coupling components (Please compare Figure 7.2.1 and equation 4.7). Therefore the cubic lattice elasticity matrix has the form of

$$
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix} =
\begin{pmatrix}
\begin{array}{ccc|ccc}
\end{array}
\end{pmatrix}
\begin{pmatrix}
\epsilon_1 \\
\epsilon_2 \\
\epsilon_3 \\
\epsilon_4 \\
\epsilon_5 \\
\epsilon_6
\end{pmatrix}
$$

Figure 7.2.2: Information hidden in elastic stiffness tensor elements are shown in matrix form for clear view
Elastic constants \((c_{ij})\) play an important role in solids since it is directly related to inter-atomic bond rigidity hence the interatomic potentials. Furthermore elastic properties such as Bulk modulus \((B)\), Poisson ratio \((\nu)\), Zener anisotropy \((A)\), Shear modulus \((G)\) etc. can be easily determined by using elastic constants. Bulk modulus is simply the ratio of pressure applied from all directions into the solid to the fractional change in the volume of the solid \(\Delta P/\Delta V/V\)). In simple words it implies the pressure (usually measured in GPa) which needs to be applied in order to reduce the volume of the materials by 100% or its the measure of the ability of a substance to withstand changes in volume when under compression on all sides. The reciprocal of bulk modulus is known as ”compressibility” and is not only a property of solids but also liquids and gases. In cubic structures bulk modulus is related to elastic constants such that \(B = (C_{11} + 2C_{12})/3\).

Crystals anisotropy can be determined using Zener anisotropy constant which is a dimensionless constant. For cubic crystal it is related to elastic constants.
by $A = 2C_{44}/(C_{11} - C_{12})$. Poisson’s ratio is the ratio of transverse contraction strain to longitudinal extension strain in the direction of stretching force ($\nu = -e_{\text{transverse}}/e_{\text{longitudinal}}$). Tensile deformation is considered positive and compressive deformation is considered negative. The definition of Poisson’s ratio contains a minus sign so that normal materials have a positive ratio. For isotropic crystals the Poisson’s ratio can be determined by using the equation $A = (3B - 2G)/(6B + 2G)$ where $G$ denotes the shear modulus of the crystal. In practical perspectives Poisson’s ratio compares the strength or resistance of the material against deformation in lateral and longitudinal axes of different materials. As an example Copper($\nu = 0.35$) [192] resists lateral deformation more effectively than natural rubber($\nu = 0.4999$) [192].

### 7.3 Resonant ultrasound spectroscopy fundamentals

Couple of most conventional methods used to measure elastic properties of solids are pulse-echo techniques and continuous-wave method. It is important to understand that the key feature to both of these methods is plane wave propagation. Time of flight of plane wave propagated through the sample held in between two piezoelectric transducers along with the sample thickness and correction to transducer effects are used to measure the ultrasonic sound velocity.
RUS offers an approach which differs fundamentally from the more conventional methods just described. RUS does not rely on the plane-wave approximation; indeed there are no plane waves. Instead, RUS is based on the measurement of the vibrational eigenmodes of samples of well defined shapes, usually parallelepipeds or spheres. A typical experimental arrangement is illustrated in Figure 7.4.1. A parallelepiped shaped sample is held by two piezoelectric transducers. One of the transducer excites the samples with range of frequencies corresponding to a large number of vibrational eigenmodes of the sample. The opposite transducer receives the resonant response of the sample. Once the transducer frequency matches with an eigenfrequency of the sample a large response(signal) can be observed. The eigenfrequencies depend on the elastic constants, the sample shape, the orientation of the crystallographic axis with respect to the sample, and the material density. By measuring a large number of resonant frequencies on one sample it is possible to obtain information
about all of these quantities. (The square of the frequencies depends on the product of the elastic constants and the linear dimensions of the sample; thus, elastic constants and linear dimensions cannot be determined independently.) Usually the sample shape, crystallographic orientation, and density are known and one can determine the complete elastic constant matrix from such a spectrum. There is no need to prepare a different sample with different crystalline orientations. It is apparent that RUS overcomes many of the deficiencies of more conventional methods used to measure elastic constants.

It is even possible to use samples of dimensions 1 mm. Since there is no plane wave approximation there are no diffraction effects to worry about. A very low contact force is being used between the transducer and the sample with the availability of sensitive electronics. The absence of a bond is very useful for temperature dependent measurements because differential thermal contraction often leads to bonds breaking, or at best strains being applied to the sample under investigation. Further it is far more important near phase transitions. One good spectrum is more than enough to determine all the elastic constants hence no need to prepare material in different crystalline direction. This would help in measuring even low symmetry samples.

### 7.4 ScF$_3$ sample and RUS setup used

In order to study elastic properties of ScF$_3$ by determining its elastic moduli, an RUS experiment was performed in Los Alamos National Laboratory under the
supervision of Albert Migliori and Boris Maiorov. Albert Migliori is a leading expert in the use of RUS as a solid state tool and is responsible for developing the previous versions of similar measurement techniques into so called “RUS” technique by expanding the limits in terms of loading and low level electronics.

As is mentioned above parallelepiped shape is very common and more importantly very easy to work with, in RUS measurement. We discussed about this with our collaborator who prepares samples and were very lucky to receive a parallelepiped crystal with dimensions 4.7 mm × 3.59 mm × 4.24 mm (Figure 7.4.1). Since it could be little tedious to work with small sample sizes, we believed our crystal would be an ideal one for RUS measurements in terms of both size and the shape. The RUS spectra were collected between 300 kHz and 800 kHz using parallelepiped shaped single crystal ScF₃ of mass 0.1791 g and
density 2.503 g/cm$^3$. Helium flow cryostat was used and minimum of 7 K was achieved.

**7.5 RUS measurement on ScF$_3$**

Typical examples of RUS signal are shown in Figure 7.5.1 and Figure 7.5.2. The amplitude of the resonance signal as measured by one transducer against the driving frequency of the other transducer is recorded and when the sample or the object in between two transducers is resonating with the driving frequency a peak or a pulse appears as shown. The corresponding frequency is identified as the "resonance frequency". Figures 7.5.1 and 7.5.2 shows measurements taken on ScF$_3$ at two different temperatures and it is clearly visible that the resonance frequency is shifted towards higher values as the temperature is lowered.

The variation of two resonance frequencies around 360 kHz and 775 kHz were measured as the temperatures is lowered down to 7 K. Both resonances responded in a similar manner as shown in Figures 7.5.3 and 7.5.4. Towards the lower end of temperatures a sharp increase in frequency could be observed. The red line indicates how the line width (Gamma) of the resonance signal varies against the temperature.

The line width of the resonance signal is proportional to the dissipation of ultrasonic energy caused by dynamic fluctuations such as vibrations in the system. Below $\sim$ 40 K drastic increase in resonance line width and sharp
Figure 7.5.1: Typical example of RUS signal. Two sharp peaks indicate resonance vibrations of ScF$_3$ lattice around 500 kHz

Figure 7.5.2: Resonance vibrations around 600 kHz
increases in resonance frequency are observed, revealing that some source of energy dissipation is activated in the system at \( \sim 40 \) K. This was neither a straight forward nor an expected result for this material therefore could be very challenging to interpret. Apart from the above observations if we closely observe the line width variation in both spectra, a clear indication of discontinuity can be observed in the temperature window of 75 - 100 K. It is intriguing that we have already discussed the same temperature range in the context of central peak appearance, the thermal expansion saturation and extrapolated temperatures for disordered ScF\(_3\) systems in section 2.3.7, 2.3.3 and 2.3.11 respectively.

In an attempt to understand our results it is worthwhile to compare them with previous results obtained using similar techniques and systems. Almost identical behavior of resonance line width was previously observed in SrTiO\(_3\)\[193]\ and it is clearly visible below \( \sim 105 \) K, the temperature at which it breaks its cubic symmetry to tetragonal, a well known ferroelastic transition. The variation of the line width was explained with connection to mobile twin wall formation and common among most of the ferroelastic materials. In fact for SrTiO\(_3\) highly mobile ferroelastic twin walls in tetragonal phase was proposed by Kityk et al. \[194]\ even before. Apart from notable increase in dissipation in energy Scott et al. have observed \[193]\ an abrupt fall in resonance frequencies below 105 K transition. Both of these features were attributed to the increase in number density of domain walls and their mobility(damping).
Variation in resonance frequencies with respect to temperature in SrTiO$_3$, is not only different but also opposite of what we saw in ScF$_3$.

Elastic relaxation associated with structural phase transition of LaAlO$_3$ has been discussed in earlier study[128]. The authors have observed that the RUS resonances harden and underdamp when temperature is lowered and was attributed to the freezing of domain boundaries at low temperatures. In general underdamping suggests higher Q-factor. Therefore either the line width($\Gamma/\Delta f$) should increase with same(or less) rate of change as the frequency($f$) or line width should decrease as the temperature is lowered. More interestingly, none of them is true for our system ScF$_3$.

![Figure 7.5.3: Temperature dependence resonance(around 775 kHz) for crystal ScF$_3$. Red line indicates the energy dissipation or the width of the resonance peak as a function of temperature](image-url)
Figure 7.5.4: Temperature dependence resonance (around 380 kHz) for crystal ScF$_3$. Red line indicates the energy dissipation or the width of the resonance peak as a function of temperature.

Soft modes (acoustic or optic) coupled with acoustic phonon modes is common among perovskites associated phase transition and almost all of them are known to be displacive phase transitions. Appearance of elastic or quasi-elastic peak near the phase transition temperature was first observed in 1971 by Riste (Please refer chapter 1 for more details) by performing a neutron scattering experiment which is known as the central peak and was thoroughly discussed in Chapter 2. In general the relaxation time for the central peak mode indicates 110 MHz. As an example for LaAlO$_3$ central peak has the time scale of 20 ns[128]. One of the theory proposes that central peak could emerge from a combination of phonon density fluctuations and flipping of clusters of
tilted octahedra between different \langle111\rangle, \langle011\rangle and \langle001\rangle axes [128]. Further studies have shown that in the corresponding temperature interval the twin wall widths become wider [195] and a variety of other anomalies appear in the evolution of strain parameters and optic phonon frequencies [196].

\(\text{ZrW}_2\text{O}_8\) [136] elastic constants \(C_{11}, C_{12} \text{ and } C_{44}\) gets harden as the temperature decreases. This infers that the material gets stiffer as the temperature is lowered which is consistent with the results obtained for similar type material ScF\(_3\). In contrast ScF\(_3\) predicts more sensitive elasticity behavior, in the context of approaching to quantum phase transition.

We have not yet carried out the full analysis of refining temperature dependent elastic constants \(C_{ij}'s\) of ScF\(_3\). It will be carried out as next phase of the same project and demands advanced computer simulations. Once it will be taken care of I would expect that the role of elasticity on the instability of incipient ferroelastic modes of ScF\(_3\) as it approaches to quantum phase transition would unravel.
8.1 Introduction

materials and their significant properties are well understood by studying their electron system and their basic structure. By far physics has mostly contributed to unravel mysteries behind new phenomenon of these materials. Even though the invention of the transistor happens in 1947 [197], the first ever semiconductor effect was observed by Michael Faraday in 1833 [198] and since then material science has come a long way and it still is uncovering new material types. Some of them have the potential to be the future of humankind perhaps in near future or 100s of years from now. In order to understand materials behavior we need to understand the fundamentals through their electron arrangement or the structure. As an example almost all the properties of semiconductors are well understood and very well explained in terms of theory (simple one-electron theories such as the local-density approximation (LDA) of density-functional theory or Hartree-Fock theory) and they have been developed up to an optimum level that they could be useful in terms of experiment. We know semiconductors are relatively simple electron systems since
the valence states involve incompletely filled s or p electron shells. There are other classes of materials which have partially filled d or f electron shells, hence high electron density and the effects of coulomb repulsion are important. We identify these types of systems as strongly correlated electron systems. Examples of this category includes high-temperature superconductors, topological Kondo insulators and Mott insulators. A wide range of condensed matter researchers are interested in strongly correlated systems since they display of very interesting properties. Out of various sorts of experimental techniques, one of the most used and succeeded techniques to investigate them is to study the optical properties at different frequencies as temperature is varied. Examples of such properties are optical conductivity $\sigma(\omega)$, refractive index $n(\omega)$, dielectric constant $n(\omega)$ etc. Optical properties are very important to study fundamental materials properties such as energy band structure, impurity levels, excitons, localized defects, lattice vibrations, and certain magnetic excitations. As an example the frequency-dependent complex dielectric function $\epsilon(\omega)$ or the complex conductivity $\sigma(\omega)$ is directly related to the energy band structure of solids. For semiconductors, the core dielectric constant $\epsilon_0$ is typically a large number and the contribution due to the free carriers is small at infrared and visible frequencies. For metals, the free carrier absorption is dominant over the entire optical frequency range. Another example is that the impurity spectra are studied most directly by infrared absorption and transmission measurements. Even the optical lattice modes at $q = 0$ are sensitively probed
by infrared spectroscopy, which we have applied to study ScF$_3$ and already discussed in Chapter 6.

### 8.2 Fourier Transformed Infrared Spectrometer

We designed and developed an instrumentation in order to carry out optical measurements, which would cover broad frequency range ($1 \text{ cm}^{-1} < \omega < 10000 \text{ cm}^{-1}$) and wide temperature ($4 \text{ K} < T < 400 \text{ K}$) range. Development of the instrumentation was carried out in the laboratory at the Department of Physics, University of Connecticut. A Bruker 70v Fourier Transformed Infrared (FTIR) spectrometer and a combination of photovoltaic and bolometer detectors cover frequencies of $150 \text{ cm}^{-1} < \omega < 10000 \text{ cm}^{-1}$. In order to focus the beam from FTIR to the sample and then to the detector we designed an optical layout consists of off-axis aspherical mirrors. More importantly we invented a method to construct low-cost aspherical mirrors which were then installed in the mirror layout.
As we know, typical spherical mirror gives a well-defined focus only if the source, mirror and image are collinear. Thus if we need source and the image to be non collinear so that it subtends an angle from the mirror, then spherical mirror could not be a good choice as it distorts the image somewhat at the focus (Figure 8.2.1). What best suits for this matter is ellipsoidal mirrors. While precise construction of an ellipsoidal surface is possible for specialized purposes, the parameter space for ellipsoidal mirrors is sufficiently large in a way that mass production is impractical and approximations to the ellipsoidal shape will be constructed instead.

8.2.1 Mirror design

Text book optical systems typically consist of spherical mirror which gives a well defined focus only if the source, mirror and image are colinear. In practice the source and the image subtend a finite angle $\alpha$ as viewed from the mirror,
distorting the fidelity of the mirror as an image component. Here we show how to construct aspheric mirrors from low-cost prescription lenses. Aspheric corrections to the mirror shape can accommodate off-axis optical arrangements. Optical design can be limited by available components. We consider the general problem of focusing a source at a distance $s$ to an image at a distance $t$ with incident angle $\alpha$. The ideal mirror shape which accomplishes this goal is a part of a prolate ellipsoid. Prolate ellipsoid of revolution is

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} = 1 \quad (8.2.1)$$

with $a > b = c$.

If a source of light is placed at $(d, 0, 0)$ then the emitted light will traverse the same distance from the source to any point on the mirror, to the other focus independently of which surface point it reflects. The prolate ellipsoid is special, because a spherical wave emitted at one focus, reflected from any point on the interior surface is sent to the other focus where it arrives with a phase independent of where the wave front was reflected. Constructive interference between all pathway guarantees a crisp tight focus in this ideal case. Any segment of the full prolate ellipsoid would then constitute an ideal optical element for our purpose.

Figure 8.2.3 shows the prolate ellipsoid with two planes of interests. Due to the cylindrical symmetry first consider the plane $y = 0$. The intersection of
Figure 8.2.2: Prolate ellipsoid with two planes of interests. Two planes are orthogonal to each other. Unit vector represents the center of the to be constructed mirror. Two orthogonal ROCs are given by the projections of the planes on the ellipsoids

$y = 0$ plane with the given ellipsiod makes an ellipse in $y = 0$ plane as shown in Figure 8.2.2. The corresponding ellipse has foci at $(-d, 0, 0)$ and $(d, 0, 0)$. Consider the point $(x_0, 0, z_0)$ at the perimeter of the ellipse in $y = 0$ plane. Defining the parameters as shown in Figure 8.2.2, we find the ROCs using known $s, t, \alpha$. Writing the ellipse coordinates as a parametric function in 2D space and using standard formula for ROC, the radius of curvature at point $(x_0, 0, z_0)$ in xz plane can be written as

$$R_{xz} = \frac{2st}{(s + t) \cos \left( \frac{\alpha}{2} \right)}$$  \hspace{1cm} (8.2.2)
Figure 8.2.3: Prolate ellipsoid with foci at \((-d, 0, 0)\) and \((d, 0, 0)\). \((x_0, 0, z_0)\) denotes the center position of the to be constructed mirror with specifications \(s\), \(t\) and \(\alpha\). They denote the object distance, image distance and the angle in between respectively.

In order to solve for the ROC, orthogonal to \(R_{xz}\) we now consider the more difficult case in which the ROC lies in a plane perpendicular to the \(y = 0\) plane. To achieve this, lets do a simple coordinate transformation such that the \(z\) axis of the new coordinate system \((z')\) is in parallel with the normal vector as shown in Figure 8.2.3. Lets the plane of interest be \(y'z'\) and the ROC at point \((x_0, 0, z_0)\) in \(y'z'\) plane can be found as (Please see Appendix ?? for detailed calculations.)

\[
R_{y'z'} = \frac{2st\cos(\alpha/2)}{(s + t)} \quad (8.2.3)
\]

Likewise the two orthogonal ROCs are found at a point in an ellipsoidal surface and should correspond to an arbitrary toroidal surface. Therefore we have
developed a method to construct low-cost aspherical surface from toroidal shape approximated to ellipsoidal shape (Figure 8.2.4). For a given value of s, t and $\alpha$ radius of curvatures are calculated numerically. It is then converted in to the unit of “Diopters” so that the mirror grinding person would recognize it and be able to make the mirrors with correct specifications. As I have mentioned earlier the precise construction of an ellipsoidal surface is impractical due the need in high technology hence high cost. The method we developed can be used to overcome this.

Figure 8.2.4: Exact surface in which the mirror is grinded is the ellipsoidal shape shown in green. But in our design process we used toroidal surface shown in red as an approximations to the ellipsoidal shape. The point of interest in which the two orthogonal ROC were calculated is $(x_0, 0, z_0)$. Orange bordering around the point of interest approximately represents the mirror surface obtained.

Optical lay out combined with optical cryocooler was designed in order to
perform IR reflectively and transmission spectroscopy. Selected parameters for mirrors in optical lay out are given in Table 8.1. The corresponding mirror layout is shown in Figure 8.2.5.

Figure 8.2.5: Optical layout combined with cryocooler. Specifications of each mirrors are given in Table 6.1. Gray colored mirrors are plane mirrors and the whole layout can be rotated around them. A sharp aperture is placed at the focus of $M_0$ mirror. This defines the object to $M_1$ mirror which forms an image at the sample space. Light reflects from and transmits through the sample are collected by $M_{2r}$ and $M_{2t}$ mirrors and refocused into detectors (Red colored) by $M_{3r}$ and $M_{3t}$ mirrors.

8.2.2 Vibration-free, cryogen-free optical cryocooler
<table>
<thead>
<tr>
<th>Mirror name</th>
<th>Incident angle (α)</th>
<th>Object distance, in inches(s)</th>
<th>Image distance in inches(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₀</td>
<td>25°</td>
<td>∞</td>
<td>9</td>
</tr>
<tr>
<td>M₁</td>
<td>30°</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>M₂₀</td>
<td>30°</td>
<td>9</td>
<td>∞</td>
</tr>
<tr>
<td>M₂ₜ</td>
<td>30°</td>
<td>9</td>
<td>∞</td>
</tr>
<tr>
<td>M₃₀</td>
<td>40°</td>
<td>∞</td>
<td>6</td>
</tr>
<tr>
<td>M₃ₜ</td>
<td>40°</td>
<td>∞</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 8.2.7: Specifications of mirrors used in mirror layout shown in Figure 8.2.5. Here ∞ means the beam is parallel. The mirror notation is used for identification purpose.

One of the main instrumentational project in the laboratory is combining optical layout with vibration-free, cryogen-free optical cryocooler for low temperature optical measurements. In order to achieve this, one of the chamber of cryostat had to be modified, so that it can be used for low temperature optical measurements. To accomplish this, several parts were custom made with the help of machine shop engineer in Physics. These parts, combining with spherical square from Kimball Physics, feed through rod from MDC vacuum and translational stage from Newport were assembled together. One of the main consideration, to reduce the temperature difference between the cold finger of the cryostat (at the center) and the sample holder is, how to minimize the heat gain by the sample holder in form of radiation from outside. This was achieved by a custom made radiation shield, consists of three pieces made of Aluminum.

### 8.3 Time-Domain Terahertz(TD- THz) spectrometer

We built a TD- THz spectrometer as our next phase of instrumentation. THz will
Figure 8.2.6: Custom made components for optical cryocooler.

cover the frequency range of $1 \text{ cm}^{-1} < \omega < 1150 \text{ cm}^{-1}$ and this spectrometer consists of several apparatus (Figure 8.3.2) such as KMLabs Griffin -10 Ti:Sapphire pulsed laser, photoconductive THz emitter, high precision linear stage delay line. The laser has the ability to produce femtosecond pulses (transform limited of 10 fs) at 95 MHz repetition rate. Incoming laser pulses were compressed and split into two beams, high intense (greater than 200 mW but less than 600 mW) laser beam (pump beam) burst in to photoconductive THz emitter in order to
generate THz and the less intense probe laser beam was used for detection of THz.

8.3.1 Introductory to TD-THz spectrometer

Terahertz spectroscopy is a technique which is utilized to measure physical phenomena within the time scale of sub picoseconds. While THz systems are used in both spectroscopic and imaging applications the generation and detection of THz radiation is performed using pump-probe approach. The first THz generation was achieved in late 70s by studying the response of photoconductors to laser pulses. In the late 80s, the first practical pulsed THz system was invented and photoconductive antennas was used to generate and detect THz radiation. The other well-known method to generate THz radiation is the non-linear optical phenomenon known as second harmonic generation. Subfemtosecond laser pulses burst in to non-linear electro-optic crystals are capable of generating THz radiation of high frequency which is not possible with photoconductive antenna arrays.
Laser pulses are used to generate and detect THz and this is usually done by splitting the laser pulses into two beams which are identified as pump beam and probe beam. Typical laser pulse duration would be 10 to 120 fs and in most cases the pump beam is higher in energy than the probe beam and is capable of generating electromagnetic transient through career excitation of a photoconductive antenna or electro-optic crystal. The electromagnetic transient which is in the range of few ps corresponds to THz wave. In order to detect THz wave, one of the beam is delayed, in most cases by using mechanical delay line. The THz E-field would be measured as a function of time difference between the pump and the probe beam. The THz detection is carried out either by using the inverse process of the generation achieved by photoconductive antenna or by using electro-optic effect with the aid of electro-optic crystals. Compare with other spectroscopic techniques THz has its own differences. When we utilize FTIR or Raman spectroscopy, the signal is directly proportional
to the intensity or in other words we measure the number of photons which we detect at each frequency, \( |E(\omega)|^2 \). In contrast, with THz spectroscopy we obtain the time dependent electric field \( E(t) \) which measures not only the photon energy but also when the photon arrives to the detector. As a result the measured signal contains the information about both the amplitude and phase of the THz wave. This allows to calculate both real and imaginary part of dielectric constants of a material in a straight forward way compared with FTIR, in which we have to use Kramers-Kronig (KK) transformation to obtain corresponding quantities. As an example if we measure the THz transmission of a sample, then the ratio of Fourier transformation of sample signal (time domain THz signal) to Fourier transformation of reference signal gives the complex transmission of the sample with respect to the reference. Since the complex transmission is related to complex refractive index (not in a trivial way but can be solved analytically) an iterative method of calculation can be used to solve for refractive index hence dielectric function. But in case of IR spectroscopy, we calculate the power ratio of raw signal of sample to reference signal as the reflectance and hence obtain only the real part of refractive index. In order to find imaginary part we have to use KK transformation.

Another distinct advantageous of THz spectroscopy is that its capability of probing soft phonons. FTIR can also be utilized for low frequency (above 60 \( \mu \)m wavelength or less than 5 THz) measurements but the detection has to be carried out using Bolometers which require liquid Helium to operate with,
therefore the data collection is much harder and expensive. In addition the FTIR signal has low signal to noise ratio compared with THz signal in the same frequency range.

It is also worthwhile to mention that THz signal can be used as fingerprints to identify many molecules, especially most of the organic polymers have unique absorption features at THz frequency. Apart from that THz can see through most of the non metallic materials which are opaque to optics. Even thin (~ nm or 10 µm) metallic samples are probed with THz in order to determine their carrier concentration, due to the absorption arises from free carriers.

8.3.2 Our TD-THz spectrometer

The femtosecond laser pulse is separated into the probe and pump beams. The energy of the pump beam is about 700 mw and the energy of the probe beam is about 100 mW. The laser beam is split using a polarized beam splitter. laser pulse is linearly polarized and the beam splitter decomposes the polarization of the beam in two perpendicular components. One of the components will be the pump beam while the other perpendicular component will be the probe beam. A half wave plate is used before the beam splitter such that by changing the polarization angle the amount of energy for each component is controlled thus, the energy ratio between pump and probe pulses can be adjusted. A mechanical delay line is introduced in pump beam path and the maximum translation is 150 mm which corresponds to ~ 1 ns. The THz radiation is
generated by biased photonconductive antenna (or arrays of antennas) excited by pump laser beam. Main feature of an antenna is the gaped metal electrodes which are deposited on a semiconductor substrate. The pump beam excites the gap which leads to the generation of photocarriers. The free carriers are then accelerated by an external bias voltage and the accelerated electrons produce THz radiation.

![Diagram of THz spectrometer](image)

Figure 8.3.2: Current THz spectrometer.

Generated THz pulse focuses into sample and refocuses into a detection crystal ZnTe (using set of off-axis parabolic mirrors of focal lengths of 4 inches), where it meets with the probe beam. The THz spot and the probe laser spot should overlap on the detection crystal in order to achieve maximum efficiency. So the output signal is typically proportional to the convolution of the probe beam and the THz pulse. The output signal is detected using lock-in detection as one has to detect very small changes in polarization in the probe beam or very low signal compared with the noise (very low signal to noise ratio (SNR)).
order to recover signals at low signal-to-noise ratios requires a strong, clean reference signal with the same frequency as the received signal. To achieve this, the waveform which carries the bias voltage to THz emitter is used as the reference signal to lock-in amplifier. The frequency lies in the range of kilohertz.

![Figure 8.3.3: Comparison between electro-optic detection and antenna detection setups](image)

It is always important to optimize the system in order to achieve high SNR. This involves optimizing both signal generation and detection. One of the key aspect is the sampling rate at which the signal collect. The sampling rate should be at least twice of the THz bandwidth(BW). This is determined by Nyquist Shannon sampling theorem. Our system with BATOP photoconductive antenna emitter is capable of producing 3 THz of maximum BW and hence the sampling rate should be greater than at least 6 THz. In other words the sampling interval should be less than \( \sim 160 \text{ fs} \) which converts to \( \sim 0.02 \text{ mm} \) of delay in between each data point in the scan. If this is not achieved aliasing could occur and as a result high frequency component would be harder to recovered.

We should keep in mind that the optics alignment (and laser focusing), es-
pecially with four off-axis parabolic mirrors is key when the high frequency component of the THz signal is detected. If PCA array is used for detection (Please refer Figure 8.3.3 to understand the differences of the set ups from EO detection), the accurate alignment becomes more critical. In order to achieve this we need to match the laser beams at both the emitter and detector ends. This can be done by removing the antennas from the setup and guiding the emitter beam through THz optics(parabolic mirrors) to the last mirror before the detector position. Then we need to repeat it for the detector laser beam till it reaches the last mirror before the emitter position. Both beams should be coincident on both end mirrors. We use iris diaphragms or an IR viewer to confirm it. After this step we know that both beams are completely collinear through our setup. Then we integrate our antennas into the setup. When we put back the antennas we have to make sure that the position of the antenna with respect to the optical beam is correct such away that a good illumination is assured. Additionally we have to put the antenna at the correct distance from the first parabolic mirror.

The virtual source point should be in the focal distance of the parabolic mirror. The virtual source point for the BATOP antenna is roughly 18.7 mm behind the antenna chip(Figure8.3.4 ). Then we perform a THz scan and find the delay line position corresponds to the signal peak. After that we move the delay line to the maximum signal position and optimize the THz signal. Now we believe that the antennas should be illuminated fine and we concentrate on
the alignment of the THz part. We tilt the mirrors until we get the maximum signal strength and the maximum THz bandwidth also should be achieved at the same delay position. We confirm the position of the delay line from time to time, as the THz beam path length can be changed a bit in the process of adjusting the parabolic mirrors.

![Figure 8.3.4: The virtual source point for the BATOP antenna is roughly \( L - d = 18.7 \) mm behind the antenna chip](image)

The SNR can always be increased by averaging. If the number of collections(sampling) at a given delay (at a single data point) can be increased, higher SNR can be achieved but with longer total scan time duration. So it is always pivotal to decide the optimum numbers of sampling to average when data is collected.

Frequency resolution is very important when spectra are collected. If we
want to study features which our instrument is not capable of resolving, that is pointless. So the resolution that the spectrometer can deliver is always critical. Frequency resolution depends on scan range of a particular scan. As an example if we require to observe a narrow absorption peak of 1 GHz, then we need to achieve minimum of 1 GHz resolution which corresponds to 1 ns of delay. That is the maximum delay we could achieve with our system therefore the maximum resolution as well. On the other hand if we want to study features of 100 GHz wide, then the related delay is only 10 ps or about couple of millimeters.

THz radiation is very sensitive to atmosphere. Water and CO₂ molecules in atmosphere result in strong wiggles in time domain signal which is then interpreted as sharp absorption features in frequency domain. The frequencies of such features correspond to different vibrational modes of the molecules. This can be overcome by purging instrument with dry Nitrogen air.

It is also important to realize that 0.3 THz wave has wavelength of 1 mm. The theoretical limit of focus or diffraction limited spot diameter at sample at this wavelength is about 2 mm (using ~ Fλ/D, where the focal length of parabolic mirror, F is 4 inches and the diameter of parabolic mirror, D is 2 inches.) If we are to use samples with similar dimensions we approach the diffraction limit hence we always have to incorporate a low frequency cutoff to spectroscopy. In order to make sure that long wave lengths (which are longer than the sample) do not pass around the sample we setup an aperture smaller than the sample
and make sure it is very close to the sample surface hence very much near the focus of the beam. In this case the lower cut off is determined by the aperture diameter. Another approach is to apply silver glue around the sample.

Photoconductive antenna

We use couple of photoconductive antennas. One of them is large area photoconductive antenna known as Tera-SED from Laser Quantum and the other is broad area interdigital photoconductive THz antenna with micro lens array and hyperhemispherical silicon lens from BATOP optoelectronics [199].

The laser beam must be collimated at the position of the antenna. The optimum laser beam diameter must be found. The minimum optical power per illuminated pixel on the antenna is about 1 mW. The hexagonal pitch is 30 um. The illuminated diameter for 100 pixels is therefore about 300 um for 1 mW/pixel. I propose to use a laser beam diameter of about 200 um at first. Since we do not have a powerful fs laser, we cannot make experiments to find the optimized power density on such an array antenna. The minimum laser beam diameter is given by the maximum power of 10 mW per pixel. For 10 pixel (100 mW) the minimum illuminated diameter would be about 100 um. You may need a telescope to adjust the collimated laser beam on the antenna to the mentioned diameter of 200 um.
8.3.3 THz signal

Figure 8.3.5: Time Domain THz signal

Figure 8.3.6: Frequency Domain THz signal
Equation of an ellipsoid is given by,

\[ \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \]  \hspace{1cm} \text{(A.3.1)}

Consider the plane \( y = 0 \), cuts the given ellipsoid. The equation of the new ellipse on \( y = 0 \) plane is given by,

\[ \frac{x^2}{a^2} + \frac{z^2}{b^2} = 1 \]  \hspace{1cm} \text{(A.3.2)}
Where $d$ is the distance from the center to either focus. $a$ and $b$ are transverse
diameter(along x-semi major axis) and conjugate diameter(along z- semi minor
axis) respectively.

Consider a point of the ellipse $(x_0,0,z_0)$ and then let us define the distance from
$(+d,0,0)$ to $(x_0,0,z_0) = t$, distance from $(-d,0,0)$ to $(x_0,0,z_0) = s$ and angle made
by $(+d,0,0),(x_0,0,z_0),(-d,0,0) = \alpha$

Finding unknown using known $s, t, \alpha$

\[
a = \frac{s + t}{2} \quad \text{(A.3.3)}
\]
\[
b = \sqrt{a^2 - d^2} \quad \text{(A.3.4)}
\]
\[
d = \sqrt{s^2 + t^2 - 2st \cos \alpha} \quad \text{(A.3.5)}
\]
\[
x_0 = \frac{t^2 + (2d)^2 - s^2}{4d} - d \quad \text{(A.3.6)}
\]
\[
z_0 = \frac{ts \sin \alpha}{2d} \quad \text{(A.3.7)}
\]

We can write the ellipse as a parametric function in 2D space by defining

\[x = a \cos \vartheta, \quad z = b \sin \vartheta\]

The radius of curvature at a certain point(determined by the parameter) is
\[
\frac{(dx)^2 + (dz)^2}{((\frac{d}{d\theta})^2 + (\frac{dz}{d\theta})^2)^{3/2}}
\]

By considering \((0,0,0)\) and \((x_0,0,z_0)\) points the angle \(\theta = \tan^{-1}(z_0/x_0)\)

Finally the radius of curvature at point \((x_0,0,z_0)\) in \(xz\) plane can be given as

\[
R_{xz} = \frac{st(s+t)^2(1 + \cos \alpha)}{(s^2 + t^2 + 2st \cos \alpha)^{3/2}} \sqrt{1 + \cos \alpha}
\]

Radius of curvature, perpendicular to the above ROC

Let us do it stepwise,

Step i. The normal vector at point \((x_0,0,z_0)\) can be found by representing the equation of the ellipsoid as a function

\[
F(x, y, z) = \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} - 1
\]

The normal vector at any point on the ellipsoid can be found by \(\nabla F\)

\[
\nabla F = \frac{2x \hat{i} + 2y \hat{j} + 2z \hat{k}}{\sqrt{(\frac{2x}{a^2})^2 + (\frac{2y}{b^2})^2 + (\frac{2z}{b^2})^2}}
\]
The normal vector at point \((x_0, 0, z_0)\)

\[
\nabla F = \frac{2x_0 \hat{i} + 2z_0 \hat{k}}{\sqrt{\left(\frac{2x_0}{a^2}\right)^2 + \left(\frac{2z_0}{b^2}\right)^2}} \tag{A.3.12}
\]

Step ii. finding the equation of the normal vector in xz plane

The equation of the normal vector in 2D, which goes through \((x_0, 0, z_0)\) can be written as,

\[
(z - z_0) = m(x - x_0) \tag{A.3.13}
\]

Where \(m\) is the gradient and can be found using normal vector

\[
m = \frac{z_0a^2}{x_0b^2} \tag{A.3.14}
\]

The equation of the line becomes

\[
z = \left(\frac{z_0a^2}{x_0b^2}\right)x + z_0\left(1 - \frac{a^2}{b^2}\right) \tag{A.3.15}
\]

This line cuts \(z = 0\) (xaxis) at point \(x = \frac{-1 + \frac{a^2}{b^2}}{\frac{z_0a^2}{x_0b^2}}\) lets take this length as \(0L\),

where \(0L = \frac{-1 + \frac{a^2}{b^2}}{\frac{z_0a^2}{x_0b^2}}\)

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Step iii. Coordinate transformation (fig 1)

Let us rotate the coordinate system by an angle $\alpha$ around y axis clockwise

![Coordinate transformation diagram](image)

Figure A.3.8: two coordinate systems

Step iv. coordinate are related with each other by,

\[
x = x' \cos \alpha - z' \sin \alpha, \quad y = y', \quad z = x' \sin \alpha + z' \cos \alpha
\]  
(A.3.16)

Therefore the equation of the ellipse in new coordinate representation

\[
\frac{(x' \cos \alpha - z' \sin \alpha)^2}{a^2} + \frac{(y')^2}{b^2} + \frac{(x' \sin \alpha + z' \cos \alpha)^2}{a^2} = 1
\]  
(A.3.17)

If you look at the fig 2, the new coordinate system’s ellipsoid cuts the plane $x' = 0L \cos \alpha$ (which goes along the normal vector to the original coordinate
system’s ellipsoid at point \((x_0, 0, z_0)\)
\[
\left( \frac{z'}{\sqrt{\frac{x_0^2b_4}{z_0^2a_4^4} + 1}} + \frac{b_0^2x_0^2z_0(b_2^2 - a_2^2)}{\sqrt{\frac{x_0^2b_4}{z_0^2a_4^4} + 1}} \right)^2 + \frac{b_6^2x_0^2z_0^2(z' - b_2^2 + a_2^2)}{a_0^6} + y'^2 = 1
\]

(A.3.19)

If you rearrange the term to look like an ellipse, it can be written as

\[
\frac{(z' - z_c)^2}{a'^2} + \frac{y'^2}{b'^2} = 1
\]  

(A.3.20)

Here \(a', b', z_c\) can be represented in known terms \(s, t, \alpha\) and the radius of curvature at the same point in \(y'z'\) plane can be found by writing \(y' = b' \sin \beta\) and \(z' = a' \cos \beta - z_c\)

\[
R_{\beta'z'} = \frac{(\frac{dy'}{d\beta})^2 + (\frac{dz'}{d\beta})^2}{|\frac{dy'}{d\beta} \frac{dz'}{d\beta^2} - \frac{dz'}{d\beta} \frac{dy'}{d\beta^2}|}^{3/2}
\]  

(A.3.21)

By solving the parametric equation and substituting the known terms for \(a', b'\) we could get the radius of curvature in \(z'y'\) plane.
$$R_{y'z'} = \frac{2st \cos(\alpha/2)}{(s + t)}$$  \hspace{1cm} (A.3.22)


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