Dynamics of Novel Compounds

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We discuss lattice dynamical and inelastic neutron scattering studies on a variety of functional material to understand their anomalous thermodynamic properties. Our studies on negative thermal expansion (NTE) in variety of compounds provided understanding of the underlying mechanism. Specific anharmonic phonons have been identified that are responsible for NTE in terms of translation, rotation and distortion of atomic polyhedral units. Extensive studies on multiferroic and perovskite materials enable to identify the spin phonon coupling, structural distortions and their correlation to phonon instabilities, leading to phase transitions in these compounds. The studies on vibrational and thermodynamical properties of lithium-based superionic conductors provide a correlation between lithium diffusion and dynamical instability.

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Introduction
The thermodynamical properties of materials like phase transition, thermal expansion, specific heat and many others are governed by the atomic dynamics in a solid. In crystalline solids, these motions are collective and coherent and forms travelling waves known as lattice vibrations. These vibrations are quantized in energy; the quantized vibrations are termed as “Phonons. To have a microscopic level understanding of solids, it is important to probe its structure and dynamics. Structure can be determined by various diffraction techniques while dynamics can be studied by inelastic scattering of light, X-rays or neutrons, etc. Light scattering techniques can probe only long wavelength phonons hence give limited information, however inelastic neutron and X-ray scattering can probe the phonons of all wavelengths; hence provide the complete dynamical spectrum of the system. Experimental studies at high pressures and temperatures are often limited and accurate models for theoretical studies of various materials are of utmost importance. For this purpose, theoretical studies based on lattice dynamical methods are necessary for exploring the entire spectrum of thermal vibrations in crystals. The experimental data is used to validate the theoretical models. Once a model is validated successfully, this may further be used to predict the thermodynamic properties at various thermodynamical conditions. We have used the state of the art density functional theory methods to compute the total energy and forces, and hence the phonons in entire Brillouin zone for various compounds. To validate the theoretical results, the inelastic neutron scattering experiments have been performed. We have studied [1-21] variety of technologically important materials to understand the role of phonons in their functional properties like negative thermal expansion, super-ionic conduction, spin-phonon coupling and phase transitions in multiferroics etc. The motivation for studying the various compounds and significant results for some of our work is discussed below.

Negative Thermal Expansion Behaviour
The discovery of large negative thermal expansion (NTE) in ZrW₂O₈ over a very broad temperature range triggered a keen interest in the field [22-26]. The NTE behaviour was observed in several metal-oxide frameworks [25, 27, 28]. The observation of even larger NTE behavior in Zn(CN)₂ led to further impetus and discovery of NTE in a large number of
cyanide compounds[1, 29-34], e.g., Cd(CN)₂, Ag₃Co(CN)₆, KMn[Ag(CN)₂]₃, and MCN (M=Ag,Au,Cu). Usually materials contract in all directions under hydrostatic pressure; however, there exists a small number of materials known to expand along specific directions [23, 34-38]. This unusual pressure behavior, known as negative linear compressibility (NLC), is remarkably rare but has potential applications in high-pressure environments, such as optical telecommunication lines, shock absorbers, and highly sensitive pressure detectors. Both NLC and NTE are practically relevant to pressure sensitive switches and temperature detectors for seismic, sonar and aircraft applications. ZnAu₂(CN)₄ is known to exhibit NTE and exceptionally large NLC simultaneously [23, 32]. The temperature dependence of the unit cell parameters of ZnAu₂(CN)₄ (space group P6₃/m) indicates [23, 32] that the thermal expansion is anisotropic and negative along the hexagonal c-axes (α_c ~ 36.9×10⁻⁶ K⁻¹, α_a ~ -57.6×10⁻⁶ K⁻¹). The NLC along the c-axes at ambient pressure is reported to be ~42TPa⁻¹, which is much larger than any other compound showing NLC behavior [23]. The compound has a large positive linear compressibility (PLC) in a-b plane which compensates the NLC along the c-axes. The honeycomb structure of ZnAu₂(CN)₄ consists of polyhedral units and is believed to be responsible for its anomalous features. The compound also exhibits pressure driven structural phase transition at ~1.8GPa [23].

The measured inelastic neutron spectra [39] at various temperatures ranging from 150 K to 400 K as shown in Fig 1. The spectra show sharp peaks at about 4, 7, 12, 22, 25, 42, 50 and 70 meV. Modes between 20-30 meV are subject to a significant change in energy as a function of temperature, indicating the anharmonic nature of these modes. The measured spectra at 150 K and 225 K are shown only up to 55 meV due to the effect of the Bose-Einstein population factor affecting higher energy phonons when cooling down. The energy of the C-N stretching mode is about 280 meV, which is not captured in the present measurements, using a cold neutron spectrometer. Since thermal expansion and other thermodynamical properties are driven by low energy modes, the measured spectral range is quite appropriate.

![Fig. 1: The temperature-dependent inelastic neutron scattering spectra of the ambient pressure phase of ZnAu₂(CN)₄ along with the calculated neutron-weighted phonon spectrum.](image)

The thermal expansion behaviour of a compound arises from anharmonic atomic vibrations. It is expected that some of the phonons contribute to NTE while others contribute to normal (positive) expansion of the material. The anomalous behaviour can be understood [39] by calculating the mode Grüneisen parameters and elastic compliance of the material [40]. We have calculated the anisotropic pressure dependence of phonon frequencies, and used it to derive the Grüneisen parameters, Γₐ and Γ_c, due to change in lattice parameters ‘a’ and ‘c’ respectively, as shown in Fig 2. The Grüneisen parameters show large negative values below 20 meV. The calculated linear thermal expansion coefficients at 300 K are 44×10⁻⁶ K⁻¹ and -55×10⁻⁶ K⁻¹ along the a- and c-axes, respectively. The net volume thermal expansion coefficient is 33×10⁻⁶ K⁻¹. We have compared the experimentally measured [23, 32] fractional change in lattice parameters and volume with our calculated results as a function of
Fig. 3: (a) The calculated and measured [32] fractional change in lattice parameters and volume as a function of temperature, in the ambient pressure phase of ZnAu₂(CN)₄, and (b) the calculated contribution of various phonons of energy E to the linear thermal expansion along the a- and c-axes at 300 K.

Temperature (Fig 3(a)). We found that the calculated linear expansion along the a-axes is in a good agreement with the measurements; however, along the c-axes the calculations are slightly underestimated.

We have computed [39] the linear thermal expansion coefficient as a function of phonon energy at T=300 K (Fig 3(b)). It is interesting to see that modes which are contributing to the positive expansion in the a-b plane contribute to negative expansion along the c-axes. This unusual behaviour is attributed to large negative value of \( s_{13} \) (-0.057 GPa\(^{-1}\)) and hence related with NLC behaviour of the compound. It suggests that any change in c-axes would lead to change in the a-axes in opposite way. Hence as temperature increases the c-axes decreases and expands the a-axes. It is interesting to note that, although the anisotropic Grüneisen parameters are negative for compression along all the directions (Fig. 2), the combination of NLC and Grüneisen parameter leads to NTE (Fig. 3 (a)) only along the hexagonal-axis.

We find that the low energy modes dominated by dynamics of Au atoms play a major role in leading to anomalous behavior in thermal expansion. Analysis of the displacement pattern of these modes shows that all these modes involve perpendicular displacement of Au, C and N atoms to the -Zn-NC-Au-CN-Zn- linkage. The magnitude of this displacement is largest for Au in these modes. These kinds of anharmonic modes bend the -Zn-NC-Au-CN-Zn- linkage and contract the c-axes as well as expand the a-b plane.

Superionic Diffusion and Phonon Instability

The performance of energy storage devices depends crucially on the properties of their component materials. An excellent example of innovative materials science is the discovery of the rechargeable lithium battery. The materials research [5, 6, 18] based on computational methods now plays a vital role in characterizing and predicting the structures and properties of complex materials on the atomic scale. We have studied lithium based battery materials Li₂O, LiAlSiO₄ and LiMPO₄ (M=Fe, Mn). Here we present results obtained from our studies on LiAlSiO₄.

The compound β- eucryptite (LiAlSiO₄) is known to exhibit super-ionic conduction in the high temperature phase above 700 K. We have performed inelastic neutron scattering measurement and extensive molecular dynamics simulation studies to understand the mechanism of superionic conduction[18]. At high temperature, the anharmonic contributions are significantly large and broaden the phonon spectrum. The phonon spectra in energy range from 30 meV – 50 meV are highly contributed by Li dynamics. This region in the phonon spectra is highly broadened with increase in temperature, which can be seen from the experimental inelastic neutron scattering (Fig. 4) as well as calculated molecular dynamics phonon density of states. The mean square displacement (MSD) of various atoms has been calculated as a
function of temperature. At high temperatures, the calculated MSD (Fig 5a) of Al, Si and O atoms saturate with time. However, for Li atoms it is found to increase with time, which is a clear signature of Li atom diffusion inside the crystal. We have calculated (Fig. 5(b) the diffusion coefficient at various temperatures for Li atoms from the slope of the mean square displacement as a function of time using the Einstein relation[41].

In order to understand the microscopic mechanism of superionic conduction phenomenon in \( \beta \)-eucryptite, the trajectories of Li atoms are analyzed at various temperatures up to 1400 K. We found that few Li atoms have high mean square displacements and show jump like behavior along the z direction (along the hexagonal c-axis) as compared to that along the x- or y-axis (in the a-b plane). The diffusion process at 1400 K seems to be anisotropic. The analysis of pair correlation functions as a function of temperature indicates that the intrachannel correlated motion of lithium atoms along the hexagonal c-axis is the major process for Li conduction. This gives one dimensional superionic conduction along the hexagonal c-axis in \( \beta \)-eucryptite[18]. The work offers a fundamental microscopic framework with the perspective to improve the utilization of the studied material for practical applications.

**Phonons and Phase transitions in Multiferroics and Perovskites**

The interest in multiferroic materials continues for decades because of many attractive phenomena like structural phase transitions, magneto-electric coupling, magneto-elastic coupling charge and orbital ordering etc. We have studied [7-11] GaFeO\(_3\) and YMnO\(_3\), PrMnO\(_3\), CaMnO\(_3\) and NaNbO\(_3\) to understand spin phonon coupling and phase transitions. Here we present summary of results obtained from our studies on multiferroic compounds GaFeO\(_3\).

The compound GaFeO\(_3\) belongs to the class of multiferroics and shows a magneto-electric coupling at low temperature. The orthorhombic structure [10, 42] of GaFeO\(_3\) has eight formula units per unit-cell, with two different symmetry inequivalent sites of
iron and gallium atoms; Fe1, Fe2, and Ga1 and Ga2, respectively. The tetrahedral sites are occupied by Ga1, while Ga2, Fe1 and Fe2 occupy all the octahedral sites (Fig. 6(a)). The electric polarization is found [42] to be along the b axis at ambient conditions. Anti-site disorder on the Fe and Ga sites [42] leads to a ferrimagnetic structure below 225 K [42]. We have performed a detailed analysis of lattice dynamics and spin phonon coupling in GaFeO3. We have measured the phonon density of states over a wide temperature range 150-1198 K. We did not observe any anomalous change in spectra other than broadening of the spectra due to temperature. To investigate the material from microscopic scale we have computed the phonon spectrum from first principles density functional theory. The calculation is done in the ordered phase, by first considering the magnetic interactions and then neglecting them to better explore the possible interplay and effect of the spin degrees of freedom on the lattice dynamics.

In Fig. 6(b) we have compared the experimental and calculated phonon spectra[7]. The magnetic calculation shows a very good agreement with the experimental spectra. We notice some differences in the low energy part of the phonon spectra. The difference comes in fact from the value of the Fe magnetic moment in the two models. The main effect of the Fe spin degrees of freedom is to soften the calculated phonon energies around 30 meV, bringing them closer to the experimental values. This demonstrates the role of magnetic interactions in GaFeO3 and provides the signature of a spin-phonon coupling behavior in the compound.

The high pressure measurements [43], up to 70 GPa (increasing and decreasing cycles), revealed a very rich phase diagram of GaFeO3. In order to understand the mechanism of phase transitions we have performed the ab-initio total energy calculation of different high pressure phase in various magnetic configurations. We found that the Pbnnm phase is the most stable when adopting the G-type antiferromagnetic ordering, while the R3c phase stabilizes with the A-type antiferromagnetism. The calculated enthalpy difference in the various phases shows that the Pbnnm phase is stable above 30 GPa (Fig. 7(a)) when comparing to Pcn21n. The application of pressure leads to a change in the correlation between the electronic motions and affects the magnetic interaction. The pressure increase leads to a quenching of the Fe magnetic moment in the Pbnnm phase at 36 GPa, resulting in an increase of the total energy and a sudden drop of the volume. We also find that the Fe magnetic moment is quenched in the R3c phase, when the pressure is raised to 45 GPa. A comparison of the experimental and calculated equation of state from calculations is shown in Fig. 7(b).
Fig. 7 (a) The calculated enthalpy difference in the Pc21n and R3c phases with respect to the Pbnm phase of GaFeO₃ as a function of pressure. (b) The calculated equation of state of various phases of GaFeO₃ and a comparison with available experimental data [43]. V refers to the volume per formula unit at pressure P. V₀ refers to the volume per formula unit of Pc21n phase at ambient pressure.

Conclusions
We have studies a variety of functional materials using the techniques of lattice dynamics calculations and inelastic neutron scattering measurements to understand the thermodynamic properties of various compounds. We have successfully explained the role of phonons in various anomalous properties like thermal expansion, temperature- and pressure-driven phase transitions and super-ionic conductivity in various compounds.

References