Atomic Dynamics and Anomalous Thermodynamic Behavior of Novel Compounds

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We discuss recent advances in modeling of anomalous thermodynamic properties using the techniques of lattice dynamics and scattering experiments. Our work on negative thermal expansion (NTE) in several 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. Our studies on vibrational and thermodynamical properties of lithium-based superionic conductors enable to understand the role of phonon instabilities and their correlation to structural distortions, leading to phase transitions in these compounds.

Keywords: Phonons, Inelastic neutron scattering, Ab-initio, Phase transition

Introduction

Many macroscopic physical properties like phase transition, thermal expansion, specific heat and many others depend on the microscopic motion of various atoms inside a solid. Such collective and coherent motion of atoms forms travelling waves known as lattice vibrations. These vibrations are quantized in energy; the quantized vibrations are termed as “Phonons”. In insulators, where there are no free electrons, phonons play a vital role in determining the elastic, dielectric, optical and thermodynamical properties. 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.

Unlike Raman scattering and infrared absorption, which essentially probe only the long wavelength phonons, inelastic neutron and X-ray scattering can directly probe the phonons of all wavelengths in the entire Brillouin zone. 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 classical and 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 [1-13] variety of oxide materials to understand the role of phonons in their functional properties like negative thermal expansion, superionic conduction, multiferroicity etc. The motivation for studying the various compounds and significant results from some of our work are discussed below.

Negative Thermal Expansion Behaviour

During the last two decades anomalous or negative thermal expansion (NTE) has been reported in many frame-work solids. We have been investigating [2-5] these compounds to understand the underlying mechanism. Here we summarize the results obtained from our studies [3] on M2O (M=Ag, Cu and Au) compounds.

The compounds M2O crystallize in a simple cubic lattice. The M atoms are linearly coordinated by two oxygen atoms, while oxygen is tetrahedrally coordinated by M atoms. Ag2O shows a large isotropic negative thermal expansion (NTE) over its entire temperature range of stability, i.e. up to ~ 500 K, while Cu2O only shows a small NTE below room temperature. We have performed inelastic neutron scattering measurements of the phonon energy spectrum of Cu2O (Fig. 1 (a)) and Ag2O, and ab-initio density functional theory (DFT) calculations of all the three metal oxides (i.e. M2O with M = Au, Ag and Cu). The Grüneisen parameters are calculated from the volume dependence of phonon energies (\(\Gamma = -\frac{\partial \ln E}{\partial \ln V}\)) in the entire Brillouin zone, which are then used for computing the thermal expansion behavior (Fig. 1(b)). The calculated thermal expansions of Ag2O and Cu2O are negative, in agreement with available experimental data, while it is found to be positive for Au2O.

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The nature of the low energy phonon modes contributing to the NTE can be visualized through animations [3] of lattice vibrations. The eigenvectors of a selection of them have been plotted on Fig. 2. The $\Gamma$ (0,0,0), X (½, 0, 0), M (½, ½, 0) and R (½, ½, ½) refer to specific points in the Brillouin zone corresponding to different wavelengths. The lowest-energy long-wavelength ($\Gamma$-point) optic phonon corresponds to the rotation of $M_2O$ tetrahedral. The lowest energy X-point phonon involves bending of M-O-M chains. In this phonon the various M atoms forming an $M_2O$ tetrahedron have different displacements indicating significant distortion of the tetrahedron. This phonon seems to contribute maximum to NTE in Ag$_2$O. The M-point phonon involves rotation, translation as well as distortion of the $M_2O$ tetrahedra, while for R-point phonon the amplitude of all the atoms is similar and it indicates translational motion of $M_2O$ as a rigid unit.

The compounds Ag$_2$O and Au$_2$O have nearly identical lattice parameters (Ag$_2$O = 4.81 Å and Au$_2$O = 4.80 Å) and similar Ag/Au-O bond lengths. We show that the nature of chemical bonding and open space in the unit cell are directly related to the magnitude of thermal expansion coefficient. In order to understand the nature of the M-O bonding we have calculated the electronic charge density for the three compounds. We find that the bonding character of the Ag-O bond is more ionic than that of the Cu-O bond. We find that the Au-O bond is highly directional with the charge density elongated towards the O atom i.e. indicating a covalent nature. However, the covalent and directional Au-O bond rigidifies the Au$_2$O tetrahedra, making them less susceptible to distortion, bending or rotation than their Ag$_2$O counterpart. This reveals the microscopic origin of the large NTE in Ag$_2$O.

Now if we compare the Cu$_2$O and Ag$_2$O cases, for which the nature of bonding is very similar, we find that both the compounds exhibit negative thermal expansion at low
temperatures. However there is a large difference in the magnitude of the thermal expansion coefficient. The Cu–O (1.87 Å) bond length is much smaller than the Ag–O (2.08 Å) bond. The Cu,O tetrahedral units are therefore much more compact than Ag,O, rendering distortion less favorable in Cu,O as compared to Ag,O. The difference in the open space in the unit cell between the two compounds leads to differences in the magnitude of the distortions and hence difference in the NTE coefficient.

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 [6, 7] based on computational methods now plays a vital role in characterizing and predicting the structures and properties of complex materials on the atomic scale.

Lithium oxide is a superionic material that exhibits high ionic conductivity above 1200 K. In this case, Li ions are the diffusing species, while oxygen ions constitute the rigid framework. At ambient conditions Li,O occurs in the anti- fluorite structure. Oxygen ions are arranged in a face-centered-cubic sublattice with lithium ions occupying the tetrahedral sites. We have calculated the phonon spectrum using ab-initio density-functional theory and the generalized gradient approximation. The calculated phonon dispersion relation [6] at relaxed lattice parameter a = 4.57 Å (at 0 K) is in good agreement (Fig. 3) with reported experimental data. The compound exhibits superionic transition in the vicinity of 1200 K. Hence we have performed phonon calculations at various unit cell parameters corresponding to high temperatures. As expected, the phonon frequencies are generally found to soften with increase of volume. The softening is found to be small for all the phonon modes except for the lowest transverse acoustic (TA) branch along the [110] direction at Brillouin zone boundary. The eigenvector of the TA phonon has been plotted (Fig. 4(a)) corresponding to the unit cell parameter of a= 4.88 Å. We find that the lithium atoms in alternate layers move opposite to each other along [001] while oxygens are at rest. Hence increasing the temperature could lead to migration of lithium ions from one site to another vacant site along [001] direction, which can easily be visualized from Fig. 4 (a). The change in the TA phonon frequency (Fig. 4(b)) with increasing lattice parameter shows that the lowest TA phonon along [110] at zone boundary softens sharply at volume corresponding to the superionic regime. At the superionic transition, some of the lithium atoms might just have sufficient energy to move from their ideal positions and start diffusing. It is possible that the softening of these phonons might be the precursor to the process of diffusion.

Phase Transitions in Multiferroic Perovskites
The interest in perovskite-like oxides continues for decades because of many attractive phenomena observed in these compounds. Among them are structural phase transitions, ferroelectricity high-Tc superconductivity, colossal magnetoresistance, charge and orbital ordering, complex magnetic properties, etc. Phonons play a vital role to understand the underlying physics [8-13]. For example, manganites, RMnO3 (R = Dy-Lu, In, Y, and Sc), have been a subject of interest for...
decades. These materials belong to a distinguished class of multiferroics, since they exhibit ferroelectricity and magnetism simultaneously.

Yttrium manganese oxide (YMnO$_3$) keeps attracting a keen interest as it is known to exhibit ferroelectricity and antiferromagnetism simultaneously. At ambient conditions the compound has a hexagonal structure with the space group P6$_3$cm. Above 1258 ±14 K, a ferroelectric to paraelectric phase transition occurs, and the system crystallizes in a different hexagonal space group P6$_3$/mmc. We have carried out inelastic neutron scattering measurements on YMnO$_3$. Measurements are accompanied by ab-initio calculations of phonon spectra for the sake of interpretation and analysis of the measured phonon spectra. The experimental structure and the measured neutron inelastic spectrum are found (Fig. 5) to be better described by the ab-initio calculations when the magnetic structure is included, reflecting that the lattice couples to the magnetic structure.

Phonon dispersion relations in the entire Brillouin zone have been calculated [9] in both the high- and low-temperature hexagonal phases of YMnO$_3$. The phonon modes in the low-temperature phase are found to be stable in the entire Brillouin zone. However, in the high-temperature phase phonon instability is clearly noticed at the high-symmetry wave-vector K (1/3, 1/3, 0). The unstable mode is highly anharmonic in nature, and it becomes stable at high temperatures due to anharmonicity. It has been proposed that the condensation of the unstable phonon mode at K point drives the transition to the low-temperature structure of YMnO$_3$. It is found that this K-point mode is not a polar mode. However, ferroelectricity in YMnO$_3$ arises from the coupling of the unstable K-point mode with a stable mode at the Γ-point. The latter mode is polar in nature and, therefore, contributes to the ferroelectricity in the low-temperature phase. The eigenvectors of these modes have been extracted from our ab-initio DFT calculations. The atomic-displacement pattern of these modes is shown in Fig 6. At the K-point, the mode consists of an unequal displacement of two Y atoms in opposite direction, along with an out-of-phase rotation of MnO$_5$ bipyramid units around the c-axis. The unequal amplitude of the vibrations of the O atoms induces a distortion of the MnO$_5$ units. The displacement pattern of the stable mode at the Γ-point consists of vibration of O atoms belonging to the plane formed by the Mn atoms of the MnO$_5$ units.
Conclusions

The work described here uses the techniques of lattice dynamics calculations and inelastic neutron scattering measurements to understand the thermodynamic properties of various compounds. The role of atomic vibrations in various thermodynamical properties like thermal expansion, specific heat, temperature- and pressure- driven phase transitions and ionic conduction in various compounds is explained.

References