INELASTIC NEUTRON SCATTERING AND LATTICE DYNAMICS OF NOVEL COMPOUNDS

R. Mittal and S. L. Chaplot
Solid State Physics Division
Bhabha Atomic Research Centre

Abstract

Using a combination of lattice dynamical calculations and inelastic neutron scattering experiments, we have studied the phonon properties of a variety of solids. The materials studied find a wide range of applications, which include the negative thermal expansion materials and other technologically important samples, and also geophysically relevant minerals. Often we have made it possible to provide the predictions of the thermal expansion and the equation of state when experimental data are not yet available. It has been shown that a proper description of negative thermal expansion may require consideration of both the acoustic and optic phonon modes in the entire Brillouin zone.

Introduction

A crystal is described as a perfect periodic three-dimensional array of atoms. However, the atoms are not static at their lattice sites but vibrate about their mean positions with energies governed by the temperature of the solid. The collective motions of atoms in solids form traveling waves (called lattice vibrations), which are quantized in terms of “phonons”. The study of lattice vibrations is of considerable interest because several physical properties of crystals like their specific heat, thermal expansion, phase transitions are related to the vibrations of atoms in solids [1-3].

The experimental studies of lattice vibrations are carried out using techniques like Raman spectroscopy, infrared absorption (IR), inelastic neutron scattering, inelastic X-ray scattering, etc. Unlike Raman and infrared studies which probe only the long wavelength excitations in one-phonon scattering, inelastic neutron and X-ray scattering can directly probe the phonons in the entire Brillouin zone. While inelastic neutron scattering is widely used for such measurements, inelastic X-ray scattering has also been recently used at intense synchrotrons sources for the study of phonons in a few materials.

Experimental studies at high pressures and temperatures are often limited and accurate models for the compounds are of utmost importance. A major goal of research therefore has been theoretical predictions of the thermodynamic properties. The success of the models in predicting thermodynamic properties depends crucially on their ability to explain a variety of microscopic and macroscopic dynamical properties. These include an understanding of the crystal structure, elastic constants, equation of state, phonon frequencies, dispersion relations, density of states and thermodynamic quantities like the specific heat and thermal expansion. The experimental neutron and long wavelength optical data are used to test and validate models of interatomic potentials, which in turn have been used to predict thermodynamic properties at high pressures and temperatures.

We have developed models of interatomic potentials for several novel compounds which allow to calculate the structural and dynamical properties as a function of pressure and...
temperature. In order to validate the interatomic potentials, we have carried out inelastic neutron scattering experiments on polycrystalline and single crystal samples at different facilities namely, Dhruya reactor, Trombay (India), ILL (France), ISIS (UK) and ANL (USA).

Sections below give brief information about the experimental technique and the lattice dynamics calculations respectively, while the results and discussion, and conclusions are presented later.

**Experimental**

Inelastic-neutron-scattering (INS) experiments [3] may be performed using both single crystals and polycrystalline samples, which provide complementary information. The single crystals may be used to obtain the details of the phonon dispersion relation (PDR), namely the relation between the phonon energies and their wavevectors, for selected values of the wavevectors. On the other hand, the polycrystalline samples provide the phonon density of state (PDOS) integrated over all wave vectors in the Brillouin zone. The inelastic-neutron-scattering experiments require much larger-sized samples (single crystals of the order of 1 cm³ and powder samples of about 10 cm³ upwards) than those used in optical spectroscopies. Measurements of the phonon dispersion relations and density of states can in principle be carried out using both reactors as well as spallation sources. However, thermal neutrons (E ~ 25 meV) from a nuclear reactor are best suited for the measurements of the acoustic and low-frequency optic modes in a single crystal. On the other hand, the high energies of neutrons from a spallation source enable measurements over the entire spectral range and are best exploited for the measurements of the phonon density of states.

**Lattice Dynamical Calculations**

Lattice dynamical calculations [2] of the vibrational properties may be carried out using either a quantum-mechanical ab-initio approach or an atomistic approach involving semiempirical interatomic potentials. However, due to structural complexity of the compounds which we have studied, detailed calculations are carried out using semiempirical models. The interatomic potentials consist of Coulombic and short-ranged Born-Mayer type interactions. The parameters of the potentials have been evaluated using the structural and dynamical equilibrium conditions as well as other known experimental data. The optimized parameters are used for lattice dynamics studies of the system.

**Results and Discussion**

**Negative thermal expansion compounds: ZrW₂O₈, HfW₂O₈ and ZrMo₂O₈**

The compounds ZrW₂O₈, HfW₂O₈ and ZrMo₂O₈ are of considerable interest [4] due to their large isotropic negative thermal expansion (NTE) in their cubic phase over a wide range of temperatures up to 1443 K, 1050 K and 600 K, respectively. This remarkable feature makes these compounds potential constituents in composites to adjust thermal expansion to a desired value. Thermal expansion in insulating materials is related to the anharmonicity of lattice vibrations. We have carried out lattice dynamical calculations for these compounds using a transferable interatomic potential [4-8]. The phonon frequencies as a function of wave vectors in the entire Brillouin zone and its volume dependence in quasiharmonic approximation are calculated. The calculations predicted that large softening of the phonon spectrum involving librational and translational modes below 10 meV would be responsible for NTE in these compounds. In order to check our prediction we have carried out high-pressure inelastic neutron scattering experiments [8-10] at several pressures up to 2.5 kbar on polycrystalline samples of ZrW₂O₈ and ZrMo₂O₈ using IN6 spectrometer at ILL, France. In case of ZrW₂O₈ at 1.7 kbar, phonon softening of about 0.1-0.2 meV is observed (Fig. 1) for
phonons below 8 meV. Similar shift is observed for ZrMo$_2$O$_8$ at 2.5 kbar. The Grüneisen parameters of phonon modes have been determined as a function of their energy. The experiments validate our lattice dynamical calculations (Fig. 1). In order to check the quality of interatomic potential model the phonon density of states data has also been recently obtained up to 160 meV for HfW$_2$O$_8$ using time of flight technique at IPNS (USA) in collaborative experiments [7].

Silicate mineral zircon, ZrSiO$_4$

Zircon, ZrSiO$_4$ is an important host silicate mineral for radioactive elements uranium and thorium in the earth’s crust. Since it is a natural host for the radioactive elements in the crust, it is a potential candidate for nuclear waste storage. High pressure and temperature stability of zircon is therefore of considerable interest.
The phonon dispersion relation has been measured (Fig. 2) in zircon (ZrSiO₄) from neutron experiments at Dhruva reactor, Trombay, at low energies up to 32 meV [11]. The measurements at high energies require good resolution and high intensity of the neutron beam. We have further extended the measurements up to 70 meV (Fig. 2) using the time of flight technique [12] at ISIS, UK. These extensive phonon measurements up to 70 meV provide a rare example of such studies carried out using a pulse neutron sources on any material. Such extensive measurements have been performed on only a few mineral systems even using a continuous reactor source. A lattice dynamical model was used to plan the experiments and analyze the data, as well as to calculate the elastic constants, long-wavelength phonon frequencies and thermal expansion [13]. The calculations are in good agreement with the experimental data.

**Quartz structure compound FePO₄**

The quartz structure compound FePO₄ is of interest to understand the nature of bonding in tetrahedral coordinated phosphates. Detailed lattice dynamical studies [14] involving experimental inelastic neutron scattering measurements and theoretical shell model calculations of the vibrational and thermodynamic properties have been undertaken for FePO₄. The calculations are in good agreement with numerous experimental data including phonon density of states measurements (carried out in our collaboration) and thermal expansion for FePO₄. The calculated pressure variation of phonon frequencies shows that a zone boundary mode at (1/3,1/3,0) becomes soft at 4 GPa, which may be associated with the mechanical instability of the quartz structure of FePO₄ at high pressure.

**Mineral garnets**

Garnets are rock-forming minerals and are important constituents of the upper crust, upper mantle and the transition zone. Garnets are also hosts for aluminium in the upper mantle.

![Fig. 3 Comparison of the calculated (full line) (a) specific heat, (b) thermal expansion and (c) equation of state of the garnet mineral almandine Fe₃Al₂Si₃O₁₂ with available experimental data (symbols). The references for the experimental data are available in Ref. [16] (after Ref. [16]).](image)

The lattice dynamical calculations of various microscopic and macroscopic phonon properties of the aluminosilicate garnets almandine, pyrope, grossular and spessartine (given by M₃Al₂Si₃O₁₂, where M=Fe, Mg, Ca or Mn,
respectively) are carried out using a transferable interatomic potential [13, 15, 16]. These studies are fairly involved as these garnets have complex crystal structures (cubic, space group $Ia$3d) with 80 atoms/primitive cell. The calculated neutron-weighted density of states are in overall good agreement with measurements (carried out in our collaboration) for almandine and data available for other garnet minerals from the literature. Due to their structural similarities, the phonon spectra of these garnets are overall similar. Subtle differences are however observed in their phonon densities of states arising from the vibrational contributions from the Fe, Mg, Ca and Mn atoms, respectively in almandine, pyrope, grossular and spessartine. The calculations have enabled a microscopic interpretation of the available experimental data and the transferable potentials have been extremely useful in deriving the various thermodynamic properties (Fig. 3) at high pressure and temperatures.

**X-ray image storage materials MFX (M=Ba, Sr, Pb; X=Cl, Br, I), and intermetallics Zr$_2$M (M=Ni, Fe)**

Neutron inelastic scattering experiments to determine the phonon density of states, and lattice dynamical calculations of thermodynamic properties were successfully carried out [17,18] for X-ray image storage materials MFX (M=Ba, Sr, Pb; X=Cl, Br, I) using a transferable interatomic potential based on a shell model. The model is validated by the inelastic neutron scattering measurements of phonon density of states for BaFCl (Fig. 4) carried out using the triple axis spectrometer at Trombay. The model is then transferred to BaFBr, BaFI, SrFCl, SrFBr, PbFCl and PbFBr by changing only the potential parameter associated with the radii of Sr, Pb, Br and I atoms. The differences in the calculated phonon spectra in these compounds arise from both mass and potential variations, and are shown to manifest in the thermodynamic properties. We have made it possible to provide predictions on the thermal expansion and the equation of state in these compounds where experimental data are not yet available.

Intermetallic compounds Zr$_2$Ni and Zr$_2$Fe show superconductivity at 1-2 K. Lattice dynamical calculations and measurements of the phonon density of states were carried out [19-21] in these materials in order to understand the electron-phonon interaction.

**Conclusions**

A combination of lattice dynamics calculations and inelastic neutron scattering measurements have been successfully used to study the phonon properties and their manifestations in thermodynamic quantities like the specific heat, thermal expansion and equation of state. The experiments validate the models and the models in turn have been fruitfully used to calculate the phonon spectra and various thermodynamic properties at high pressures and temperatures. The calculations have been very useful in the planning, execution and analysis of the experiments and have enabled microscopic...
interpretations of the observed data. These studies have also been exploited to study the anomalous properties like large negative thermal expansion in various compounds.

References


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About the authors…

**Dr R. Mittal** joined the 34th batch of BARC Training School after completing M.Sc. (Physics) from H. N. B. Garhwal University. Subsequently he joined the Solid State Physics Division, BARC, in 1991. Since then, he is involved in inelastic neutron scattering experiments and lattice dynamics computations.

**Dr S. L. Chaplot** is from the 18th batch of BARC Training School. He works in the Solid State Physics Division in the areas of neutron scattering, lattice dynamics and computer simulations.