MODELING OF ANOMALOUS THERMODYNAMIC PROPERTIES USING LATTICE DYNAMICS AND INELASTIC NEUTRON SCATTERING

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Abstract

This paper summarizes the recent developments of the modeling of anomalous thermodynamic properties. It has been shown that lattice dynamics calculations along with inelastic neutron scattering measurements can be employed to reveal phonon properties and to predict thermodynamic properties of various compounds including materials with negative thermal expansion. There is a large variation in the thermal expansion, specific heat and equation of state pertaining to the compounds described in this paper. The interatomic potentials as determined for various compounds have been able to successfully model the thermodynamic behaviour. The variations in phonon spectra manifest in the thermodynamic properties of various compounds at high pressure and temperature.

Introduction

The study of lattice vibrations is of considerable interest because several physical properties of crystals like specific heat, thermal expansion, thermal conductivity and phase transitions are related to the vibrations of atoms in solids [1-4]. We have developed models of interatomic potentials for several compounds of interest, which allow to calculate the structural and dynamical properties as a function of pressure and temperature. The data obtained from neutron scattering and optical experiments are used to test and validate models of interatomic potentials [1,2]. The models are then used for calculating various thermodynamic properties at high pressures and temperatures. We are able to provide the predictions of equation of state, specific heat and thermal expansion. A brief description of the scientific interest and results obtained for various compounds are given below.

Results and discussion

The compounds ZrW$_2$O$_8$, HfW$_2$O$_8$ and ZrMo$_2$O$_8$ are of considerable interest [5] 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. Our lattice dynamical calculations for ZrW$_2$O$_8$ and HfW$_2$O$_8$ [5-10] reproduced the observed anomalous thermal expansion in these compounds. The unusually dominant contributions of the transverse acoustic, librational and translational optic modes below 8 meV lead to a large NTE. High pressure inelastic neutron scattering experiments conducted [9-12] by us on polycrystalline samples of cubic ZrW$_2$O$_8$ and ZrMo$_2$O$_8$ confirm phonon softening (Fig. 1). The thermal expansion as derived from the phonon measurements is in good agreement with that obtained from diffraction data. This indicates that unusual phonon softening of low energy modes is able to account for the NTE in these compounds.

Zircon, ZrSiO$_4$ is an important host silicate mineral for radioactive elements uranium and thorium in the earth’s crust. Initially, phonon dispersion relation in this compound were measured [13] at Dhruva reactor at low energies upto 32 meV. For the reasons of high intensity and good resolution further measurements [14,15] upto 80 meV were extended at ISIS (UK) and LLB (France) (Fig.2). These extensive measurements upto 80 meV provide a rare example of such studies carried out on any material. The lattice dynamical model produces a very good description of the available data. The model is further used to calculate [15,16] the free energies as a function of pressure and

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Fig. 1 : The comparison between the calculated and experimental inelastic neutron scattering spectra for cubic ZrW$_2$O$_8$. The experimental data for cubic ZrW$_2$O$_8$ is at 160 K and at pressures of 0.0 and 1.7 kbar. The experimental spectra at P=0.3 kbar and 1.0 kbar fall in between those of P=0 and 1.7 kbar, and have not been shown here for the clarity (after ref. [11]).

Fig. 2 : The experimental phonon data (symbols) along [100] with the lattice dynamical calculations (lines) for zircon (after refs. [13-15]).
temperature in the zircon as well as the high-pressure scheelite phase, which reproduce the relative stability of the two phases across their observed phase transition pressure of about 10 GPa.

Neutron inelastic scattering experiments (Fig. 3) to determine the phonon density of states and lattice dynamical calculations of thermodynamic properties (Fig. 4) were successfully carried out [16-26] for compounds $MPO_4$ (M=Al, Ga, Fe), garnet minerals $M_3Al_2Si_3O_{12}$ (M=Fe, Mg, Ca and Mn), X-ray image storage materials MFX (M=Ba, Sr, Pb; X=Cl, Br, I), LiYF$_4$, LiYbF$_4$, and ZnCl$_2$. These studies have enabled a microscopic understanding of the variations in the phonon spectra in these compounds and their manifestations in various thermodynamic properties like the specific heat, thermal expansion and equation of state.

**Conclusion**

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. These studies have also been exploited to study the anomalous properties like large negative thermal expansion in various compounds.

**References**


**ABOUT THE AUTHOR**

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.