

Negative thermal expansion in framework compounds

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Abstract. We have studied negative thermal expansion (NTE) compounds with chemical compositions of NX_2O_8 and NX_2O_7 ($\text{N} = \text{Zr}, \text{Hf}$ and $\text{X} = \text{W}, \text{Mo}, \text{V}$) and M_2O ($\text{M} = \text{Cu}, \text{Ag}$) using the techniques of inelastic neutron scattering and lattice dynamics. There is a large variation in the negative thermal expansion coefficients of these compounds. The inelastic neutron scattering experiments have been carried out using polycrystalline and single crystal samples at ambient pressure as well as at high pressures. Experimental data are useful to confirm the predictions made from our lattice dynamical calculations as well as to check the quality of the interatomic potentials developed by us. We have been able to successfully model the NTE behaviour of these compounds. Our studies show that unusual phonon softening of low energy modes is able to account for NTE in these compounds.

Keywords. Inelastic neutron scattering; lattice dynamics; negative thermal expansion.

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1. Introduction

Large isotropic negative thermal expansion (NTE) from 0.3 to 1050 K was discovered in cubic ZrW_2O_8 [1]. Since then many experimental and theoretical simulation studies [1–10] have been carried out to determine phonon spectrum and its relevance to NTE in framework solids. Besides oxide-based framework materials, NTE behaviour has been observed in molecular framework materials [2] containing linear diatomic bridges such as the cyanide anion. These compounds may be used to form composites with tailored thermal expansion coefficients. Composites containing the NTE material ZrW_2O_8 have been examined for use in fiber-optic communication systems, low thermal expansion and high conductivity composite.

The compounds with chemical compositions of NW_2O_8 [1,5] and NV_2O_7 ($\text{N} = \text{Zr}, \text{Hf}$) [6,7] have been found to possess very large negative thermal expansion. The structure of these compounds is cubic, which consists of $\text{ZrO}_6(\text{HfO}_6)$ octahedra and $\text{WO}_4(\text{VO}_4)$ tetrahedra. All oxygen atoms in NV_2O_7 have two-fold coordination,

whereas in NW_2O_8 one of oxygen belonging to WO_4 tetrahedra is coordinated with only one W atom. In the case of NW_2O_8 (space group P2_13) compounds all the phases stable at zero pressure are found to have a negative thermal expansion, while in NV_2O_7 (space group $\text{Pa}\bar{3}$) compounds only the high-temperature phase exhibits strong NTE behaviour.

Recent diffraction measurements [8] show NTE below 300 K in Cu_2O and up to its decomposition temperature of about 500 K in Ag_2O . These compounds have cubic structure [8] (space group $\text{Pn}\bar{3}\text{m}$). The $M(\text{Cu,Ag})$ atoms are linearly coordinated by two oxygen atoms, while oxygen is tetrahedrally coordinated by four M atoms.

There has been considerable interest in the study of negative thermal expansion compounds. Recent papers have described work on the structure and thermodynamic properties of these compounds using a combination of diffraction and spectroscopic techniques [11–13]. Powder X-ray diffraction, powder neutron diffraction electron microscopy, EXAFS and differential scanning calorimetry have been used to study structural properties as a function of temperature for these compounds. In this paper we report the results obtained from our study [14–20] of negative thermal expansion (NTE) compounds with chemical compositions of NX_2O_8 and NX_2O_7 ($\text{N} = \text{Zr, Hf}$ and $\text{X} = \text{W, Mo, V}$) and M_2O ($\text{M} = \text{Cu, Ag}$) using the techniques of inelastic neutron scattering and lattice dynamical calculations. Section 2 gives details about the experiments and lattice dynamical calculations, followed by the results and discussion and conclusions in §§3 and 4 respectively.

2. Experimental and lattice dynamical calculations

Inelastic neutron scattering measurements of phonon density of states from the powder samples and the phonon dispersion relation from single crystals using the steady state and pulsed neutron sources have been used to validate the interatomic potentials for various NTE compounds. The measurements using the polycrystalline samples of ZrW_2O_8 [14] and ZrMo_2O_8 [19] are carried out at ILL (France), HfW_2O_8 [15] at ANL (USA) and Cu_2O [20] at Trombay (India). We have also measured the phonon dispersion relation [21] from a single crystal of ZrW_2O_8 using 1T1 spectrometer at LLB (France).

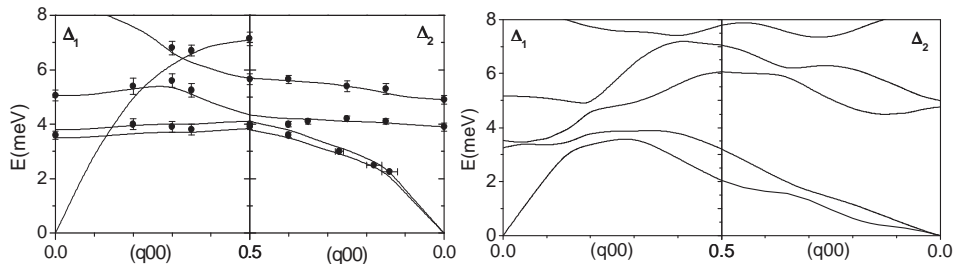


Figure 1. (Left) Low-energy phonon dispersion in ZrW_2O_8 as deduced from measurements [21] at $T = 11$ K. The lines are guide to the eye. (Right) Calculated phonon dispersion relation for ZrW_2O_8 .

A semiempirical interatomic potential consisting of Coulombic and short-ranged terms is used for the calculations. The polarizability of the atoms has been introduced in the framework of shell model [22,23]. The parameters of the potentials were determined from the static and dynamic equilibrium conditions of the crystal. The current version of the program DISPR [24] has been used for the lattice dynamical calculations. The procedure for the calculations of thermal expansion is given in our previous publications [25,26].

3. Results and discussion

3.1 Neutron inelastic scattering: Phonon dispersion relation and phonon density of states

ZrW₂O₈ has a cubic structure with space group P2₁3 and four formula units per primitive cell [1]. There are 132 distinct dispersion branches along [1 0 0] direction. The 132 phonon modes along [1 0 0] direction can be classified as $\Delta = 66\Delta_1 + 66\Delta_2$. The low energy phonon dispersion relation was measured on a single crystal of ZrW₂O₈ (8 mm × 4 mm × 2 mm) using the 1T1 spectrometer at LLB, Saclay. The comparison between the experimental and calculated phonon dispersion relation is shown in figure 1.

The experimental data of density of states $g^{(n)}(E)$ for ZrW₂O₈ at 160 K and different pressures are shown in figure 2. The spectra at high pressures show an unusually large softening. In conformity with the predictions (figure 1), the phonon modes of energy below about 5 meV soften by about 0.15 meV at 1.7 kbar with respect to ambient pressure. At energies above 5 meV, the shift of the spectrum is much less than that at lower energies. These observations (figure 2) are in very good agreement with our lattice dynamical calculations considering the inherent limitations in experiment (e.g. incoherent approximation) and theory. In ZrMo₂O₈

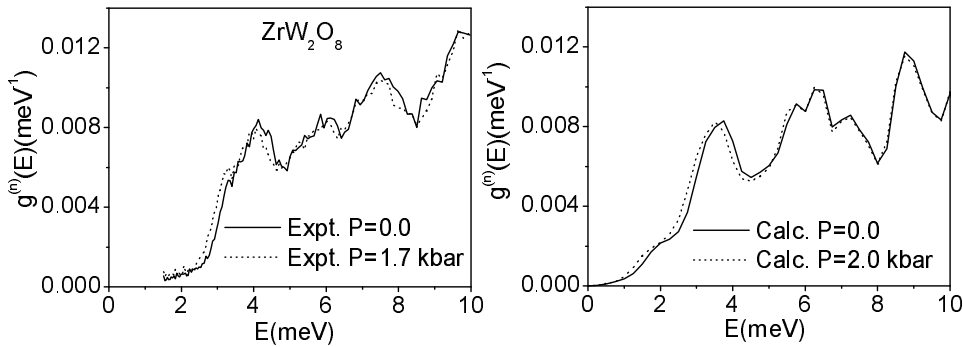


Figure 2. The comparison between the calculated and experimental inelastic neutron scattering spectra for cubic ZrW₂O₈ [14]. The experimental data for cubic ZrW₂O₈ is at 160 K and at pressures of 0.0 and 1.7 kbar. The experimental spectra at $P = 0.3$ kbar and 1.0 kbar fall in between those of $P = 0$ and 1.7 kbar, and have not been shown here for clarity.

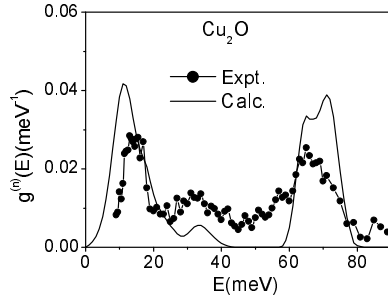


Figure 3. Comparison between the experimental and calculated phonon spectra [20] for Cu_2O .

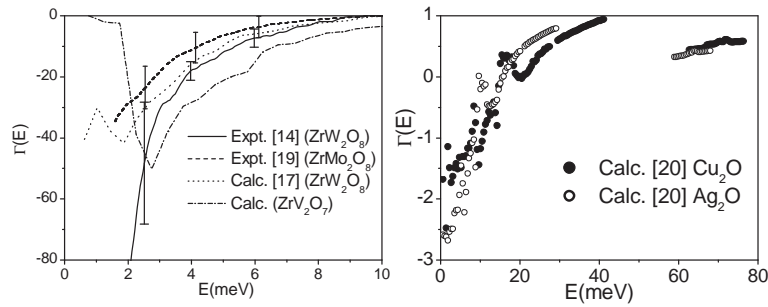


Figure 4. The Grüneisen parameter ($\Gamma(E)$) [14,17,19,20] averaged over phonons of energy E . The experimental [14,19] values are determined using the neutron data of phonon density of states as a function of pressure.

[15] at 2.5 kbar, phonon softening of about 0.1–0.3 meV is observed for phonons below 8 meV.

The experimental one-phonon spectrum for Cu_2O is obtained by subtracting the multiphonon contribution, which has been calculated using the Sjolander formalism [27]. Figure 3 shows the measured and calculated one-phonon density of states for Cu_2O . The calculated spectrum is in fair agreement with the measurements. The two peaks observed centred at about 13 and 70 meV in the experimental data are very well reproduced by the calculations.

3.2 Thermodynamic properties: Grüneisen parameter and thermal expansion

The pressure dependence of the phonon spectrum has been used for obtaining Grüneisen parameter (figure 4), which show that low energy phonon modes have very large negative values of Grüneisen parameters. These low energy phonon modes are the most relevant to NTE. Our calculations show that nearly 50% of the NTE in the cubic phase of ZrW_2O_8 and ZrV_2O_7 arises from just two lowest phonon branches and almost all the NTE is contributed from the modes below 10 meV. The experimental data of ZrW_2O_8 include a small sharp drop in volume at about 400 K associated with a disordering phase transition which also reduces the volume by about 0.4%. The calculated relative thermal expansion for both the cubic ZrW_2O_8

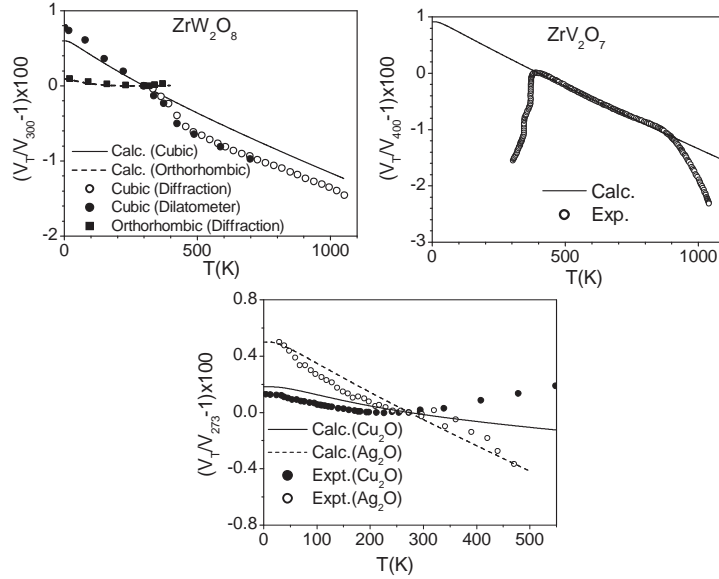


Figure 5. The experimental and calculated relative volume thermal expansion. V_T , V_{273} , V_{300} and V_{400} are the cell volumes at temperature T , 273 K, 300 K and 400 K respectively. There is a small sharp drop in volume for cubic ZrW_2O_8 at about 400 K associated with an order disorder phase transition [1]. Low temperature phase of ZrV_2O_7 has positive thermal expansion coefficient [6]. The structure is a $3 \times 3 \times 3$ superstructure of high temperature. The calculations have only been carried out in high temperature phase of ZrV_2O_7 . Experimental data: cubic ZrW_2O_8 [1], orthorhombic ZrW_2O_8 [11], cubic ZrV_2O_7 [6], Cu_2O [8], and Ag_2O [8]. Calculations: ZrW_2O_8 [17], orthorhombic ZrW_2O_8 [17], cubic ZrV_2O_7 , Cu_2O [20], and Ag_2O [20].

and HfW_2O_8 is shown in figure 5. Low temperature phase of ZrV_2O_7 has positive thermal expansion coefficient. The structure is a $3 \times 3 \times 3$ superstructure of high temperature phase. Our calculations are carried out in the ZrV_2O_7 phase with NTE behaviour. Above 900 K, the experimental data for ZrV_2O_7 show a sharp drop in the volume at about 900 K, which could not be reproduced by our model calculations (figure 5).

The thermal expansion of the orthorhombic phase is observed [11] to be anomalous; it is negative below 300 K and positive above 300 K. Above 400 K, the orthorhombic phase transforms to cubic phase. The calculation of thermal expansion in the orthorhombic phase of ZrW_2O_8 is compared with the experiments in figure 5 which shows a very good agreement. Compared to the cubic phase, the negative thermal expansion contributed by the phonons below 8 meV is much reduced, which allows the high energy modes to dominate at high temperatures and yield a net positive expansion above 270 K in calculations.

For M_2O ($\text{M} = \text{Cu}, \text{Ag}$) compounds the contribution from the two lowest energy modes is only about 10%, whereas these modes contribute about 50% to the NTE in ZrW_2O_8 or ZrV_2O_7 . It should be noted that for Cu_2O the magnitude of NTE is

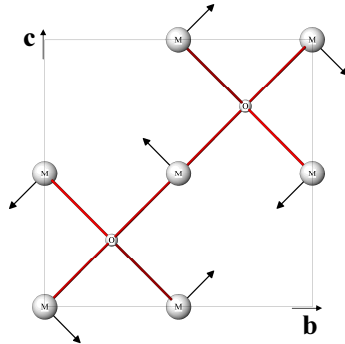


Figure 6. Polarization vector of the T_{2u} mode [20] involving rotation of M_4O ($M = Cu, Ag$) tetrahedra about the a -axis perpendicular to b - c plane.

small ($-8 \times 10^{-6} \text{ K}^{-1}$) in comparison to cubic ZrW_2O_8 ($-27 \times 10^{-6} \text{ K}^{-1}$). However, for Ag_2O , the negative thermal expansion coefficient $-20 \times 10^{-6} \text{ K}^{-1}$ is comparable with that of ZrW_2O_8 . Phonons below 15 meV are responsible for the NTE, and a positive contribution from phonons above 15 meV reduces the magnitude of the negative thermal expansion coefficient above 100 K. The comparison between the calculated and experimental data for the NTE is shown in figure 5.

In order to understand the nature of phonons responsible for NTE we have calculated the partial contributions of the phonons of different energies to the mean square vibrational amplitude of various atoms at 300 K. For ZrW_2O_8 , modes up to 1 meV are largely acoustic in nature, but one of the oxygen atoms has larger amplitude than other atoms. For modes between 1 and 4 meV, oxygen atoms constituting the WO_4 tetrahedra have significantly different values of their vibrational amplitudes, which indicate distortions of the tetrahedra. Above 4 meV the amplitude of all the atoms is relatively small. In the case of ZrV_2O_7 modes up to 2 meV involve equal displacement of all the atoms, which correspond to the acoustic modes. Above 2 meV, oxygen atoms constituting VO_4 and ZrO_6 have nearly same values of their vibrational amplitudes, indicating rotation of the ZrO_6 octahedral and VO_4 tetrahedral units.

For $Cu_2O(Ag_2O)$ modes up to 3(1.5) meV have similar amplitudes, which correspond to the acoustic modes. Cu atoms have larger amplitudes in comparison to oxygen atoms for energies 9–12(5.5–7.5) meV in $Cu_2O(Ag_2O)$. The mode at about 10.5(6.5) meV in $Cu_2O(Ag_2O)$ corresponds to the T_{2u} mode at zone centre. This mode is plotted (figure 6) using the calculated eigenvectors, which shows librational motion of M_4O tetrahedra arising from the transverse vibrations of M atoms. Such a librational mode could lead to negative expansion.

4. Conclusions

The experimental results show that our lattice dynamical models are realistic enough to serve as a basis for understanding the unusual phonon properties of the NTE compounds. The large softening of low energy phonon modes is able to explain the NTE behaviour of the compounds studied by us. The experiments

validate the prediction made by the lattice dynamical calculations. The calculated NTE coefficients agree very well with the reported experimental data.

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