

Anomalous Thermal Expansion in Framework Compounds

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We have carried out lattice dynamics calculation of the phonon spectra to understand the anomalous thermal-expansion behavior in ZrV_2O_7 , ZrP_2O_7 and $\text{Sc}_2(\text{MoO}_4)_3$. Our calculations show that thermal-expansion behavior of these compounds is mainly governed by the nature of vibration of low-energy translational and rotational modes up to about 10 meV. The calculations are able to explain the large difference in thermal-expansion behavior of these compounds.

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I. INTRODUCTION

Negative thermal expansion (NTE) materials are potentially important in various fields like ceramic, optical, and electronic industries. The wide range of applications and anomalous behavior of frame work compounds has lead to considerable interest to study the vibrational properties of these compounds. The compounds ZrV_2O_7 and ZrP_2O_7 have two different crystal structures [1, 2] in the low- and high-temperature regimes. The low temperature phase of these compounds has positive thermal expansion. In the high-temperature phase, ZrV_2O_7 shows negative thermal expansion [1], while for ZrP_2O_7 , thermal expansion is positive [2, 3]. The high-temperature phase of both the compounds has cubic structure (space group $pa\bar{3}$). There is a considerable difference in the bond length of P-O (1.48 Å) and V-O (1.68 Å). $\text{Sc}_2(\text{MoO}_4)_3$ shows [4] NTE above 178 K in its orthorhombic (Pbcn) phase, while below 178 K, it occurs in a monoclinic ($P2_1/c$) phase with positive volume thermal expansion coefficient (α_V). The basic structure of these compounds consists of corner-sharing $\text{ZrO}_6/\text{ScO}_6$ octahedral and $\text{VO}_4/\text{PO}_4/\text{MoO}_4$ tetrahedral units.

It is well known that thermal expansion in insulators arises from anharmonic nature of phonon vibrations. Earlier we reported [5–7] inelastic neutron scattering experiments and lattice dynamical calculations for several frame work solids to understand their negative thermal expansion behavior. Here, we report our studies for ZrV_2O_7 , ZrP_2O_7 , and $\text{Sc}_2(\text{MoO}_4)_3$ to understand the large difference in thermal expansion behavior in these compounds. The high-temperature phase of these compounds has nearly about 40 atoms per primitive cell. We have quantitatively reproduced the thermal-expansion behavior in the high-temperature phase of these compounds through a calculation of mode Grneisen parameters. We have not attempted the calculations in the low-temperature phase of these compounds, which have a large number of 1080 atoms per primitive cell in ZrV_2O_7 and ZrP_2O_7 , and 136 atoms in $\text{Sc}_2(\text{MoO}_4)_3$.

II. THEORY

The general form of potential for our calculations is given by the following expression:

$$V(r) = \left\{ \frac{e^2}{4\pi\epsilon_0} \right\} \left\{ \frac{Z(k)Z(k')}{r} \right\} + a \exp \left\{ \frac{-br}{R(k) + R(k')} \right\} - \frac{C}{r^6} - D \exp [-n(r - r_0)^2/2r].$$

The interatomic potential basically consists of Coulomb term, Born Mayer short range interaction term and van der Wall attraction term. The covalent nature of the P-O/V-O/Mo-O bonds is described by the fourth term. The polarizability of the oxygen atoms is introduced in the framework of the shell model [8]. The parameters of the potential used in the calculations are chosen such that they satisfy the static and dynamic equilibrium conditions of crystal lattice. The calculated structure is in agreement with the available experimental structural data at ambient pressure. The crystal structures at $T = 0$ is obtained by minimization of free energy with respect to atomic coordinates and lattice parameters at various pressures. The equilibrium crystal structures obtained at various pressures have been further used for the calculation of phonon frequencies in the entire Brillouin zone. The detailed procedure for the lattice dynamical calculations and thermal expansion coefficient is given in our previous publications [9–13].

The calculation of thermal expansion involves [12, 13] the identification of anharmonic phonons and calculation of their Grüneisen parameter. We are using quasiharmonic approximation for the calculations of volume dependence of phonon frequencies. Quasiharmonic approximation includes only the implicit anharmonic effect due to the change in unit cell volume. The explicit anharmonicity becomes significant only at very high T , and it comes due to very large thermal amplitude. The phonon frequencies as a function of wave vectors in the entire Brillouin zone and its volume dependence are calculated. In quasiharmonic approximation, volume thermal expansion coefficient is given as

$$\alpha_V(T) = \frac{1}{BV} \sum_i \Gamma_i C_{V_i}(T).$$

Where V is the volume of the unit cell, B is the bulk modulus, $\Gamma_i = -\frac{\partial(\ln \omega_i)}{\partial(\ln V)}$ is the Grüneisen parameter due to i^{th} phonon mode and $C_{V_i}(T)$ is the specific heat due to i^{th} phonon mode at temperature T . Since $C_{V_i}(T)$ is positive for all modes at all temperatures, the nature of thermal expansion coefficient being positive or negative is only governed by the Grüneisen parameters. We calculated Γ_i by calculating phonon frequency (ω) at different pressures and calculated bulk modulus B by using relation $B = -VdP/dV$.

III. RESULTS AND DISCUSSION

III-1. Phonon Spectrum

The calculated phonon density of state and partial density of state for ZrP_2O_7 and ZrV_2O_7 are shown in Fig. 1. In case of ZrP_2O_7 , the experimental measurement [14] of

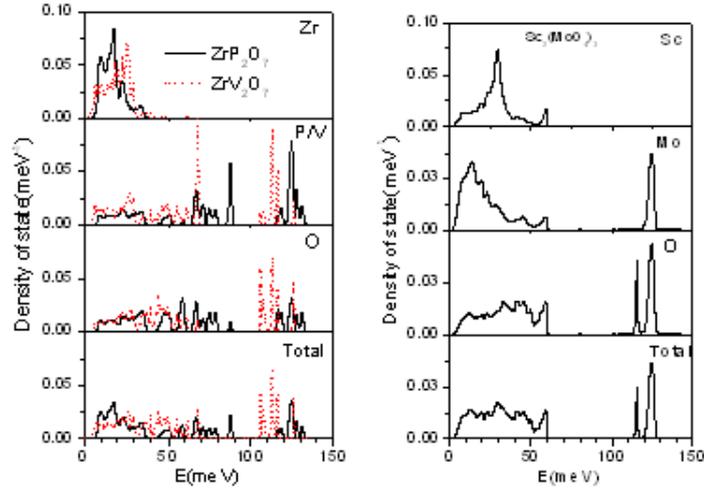


FIG. 1: Calculated partial density of state of various atoms in ZrV_2O_7 and ZrP_2O_7 and in the orthorhombic phase of $\text{Sc}_2(\text{MoO}_4)_3$.

the zone centre phonons is available only in the high-T phase. The phonon spectra in the high-temperature as well as low-temperature phase are expected to span the same energy range due to the similarity of their structures. The calculated range of phonon frequencies in Fig. 1 matches that reported from the Raman measurements [14] in the low-temperature phase. The calculated phonon spectrum shows that the overall range of phonon frequencies in ZrP_2O_7 is up to 135 meV in comparison of 125 meV in ZrV_2O_7 [9]. The Zr vibrations in both the compounds (Fig. 1) extend up to 35 meV. However, the peaks in the partial density of states of Zr in ZrP_2O_7 shift towards lower energies. The vibrations due to P/V and O atoms contribute to the entire energy range. The shorter P-O (1.48 Å) bond length in comparison with V-O (1.68 Å) results in shifting of stretching modes to higher energies. This in turn shifts the band gap in the phonon spectra of ZrV_2O_7 from 70–105 meV to 90–110 meV in ZrP_2O_7 .

The contribution of various atoms in the phonon $\text{Sc}_2(\text{MoO}_4)_3$ is illustrated by the partial density of states shown in Fig. 1(b). The Sc atoms contribute in energy range of 0–60 meV, while the Mo and oxygen atoms contribute in the entire energy range upto 135 meV. Above 110 meV, the contributions are mainly due to Mo-O stretching modes.

III-2. Calculation of thermal expansion

The calculated pressure dependence of phonon frequencies has been used for the calculation of the Grüneisen parameter $\Gamma(E)$, averaged for all phonons of energy E in the Brillouin zone. In ZrP_2O_7 , the modes of energy between 2.5 to 10 meV have slight negative Grüneisen parameters, while modes above 10 meV have positive $\Gamma(E)$ values up to about 4. This is quite different from ZrV_2O_7 , where low-energy modes of about 2 meV have large negative $\Gamma(E)$ values (Fig. 3) and high-energy modes above 10 meV have slight positive values. The $\Gamma(E)$ values for $\text{Sc}_2(\text{MoO}_4)_3$ lie in between ZrP_2O_7 and ZrV_2O_7 .

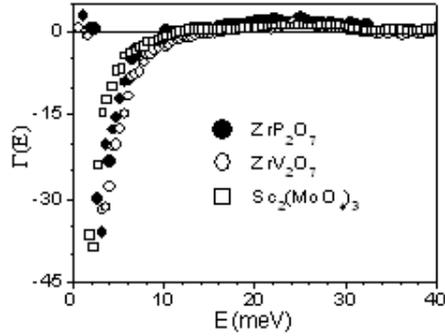


FIG. 2: Calculated Grüneisen parameter $\Gamma(E)$ averaged over phonons of energy E in ZrP_2O_7 , ZrV_2O_7 , and $\text{Sc}_2(\text{MoO}_4)_3$.

The calculated $\Gamma(E)$ and specific heat contribution have been used to derive the temperature dependence of the volume thermal expansion coefficient. Our calculation in ZrP_2O_7 shows (Fig. 2) that only phonon modes of energy from 2.5 to 10 meV give a small negative contribution to the thermal expansion coefficient (α_V). The large positive contribution from high energy modes above 10 meV results in a total positive thermal expansion coefficient. In case of ZrV_2O_7 , the negative contribution (about 95%) to α_V is from low energy modes below 9 meV. It is because of the large negative value $\Gamma(E)$ of

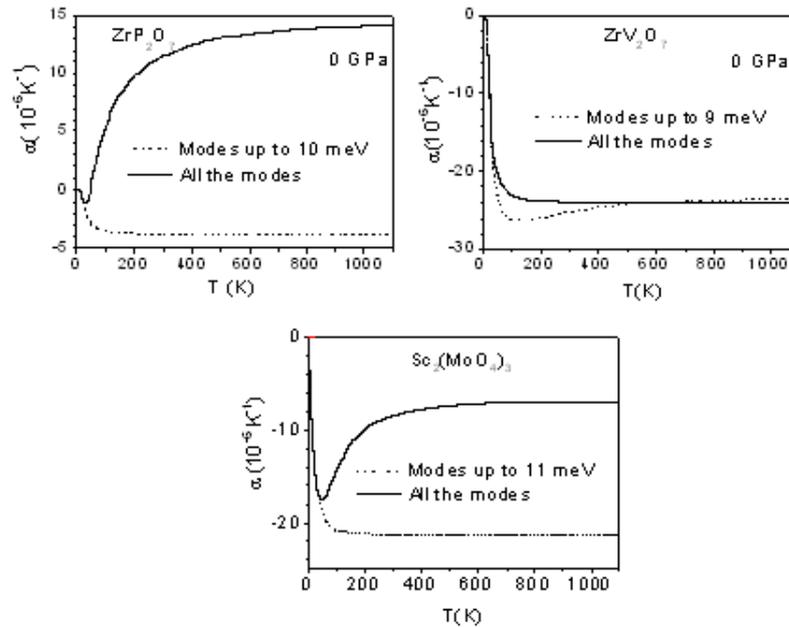


FIG. 3: Calculated volume thermal expansion coefficient in ZrP_2O_7 , ZrV_2O_7 , and $\text{Sc}_2(\text{MoO}_4)_3$.

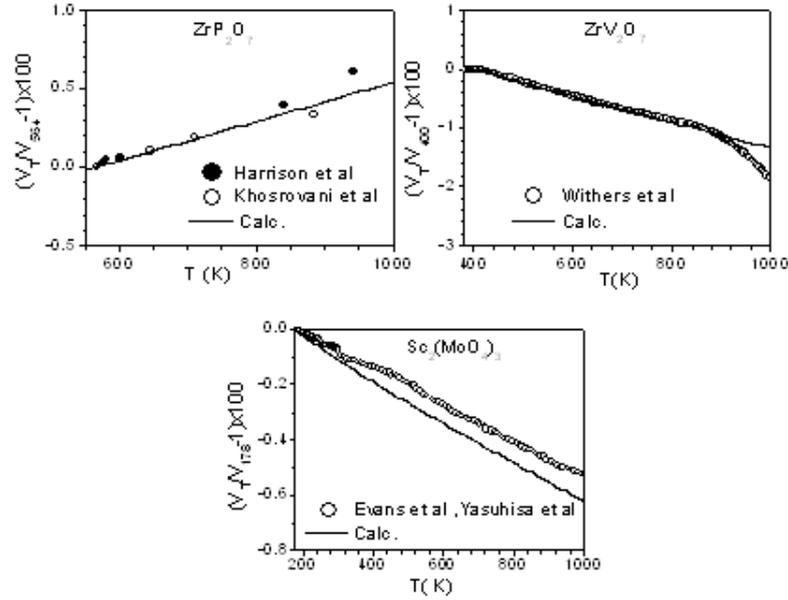


FIG. 4: Comparison between the calculated and experimental thermal-expansion [1–4, 15] behavior of ZrP_2O_7 , ZrV_2O_7 , and $\text{Sc}_2(\text{MoO}_4)_3$.

several phonons below 9 meV that α_V has a large negative value. For $\text{Sc}_2(\text{MoO}_4)_3$, the low-energy modes below 11 meV result in large negative ($-21 \times 10^{-6} \text{ K}^{-1}$) contribution (Fig. 3) to α_V . However the large positive contribution from high energy modes results in relatively small negative α_V in comparison to ZrV_2O_7 .

The comparison between the calculated and experimental data [1–4] of volume thermal expansion for the high-temperature phase of ZrP_2O_7 , ZrV_2O_7 , and $\text{Sc}_2(\text{MoO}_4)_3$ is shown in Fig. 4. The contribution of various phonons to the thermal expansion has been calculated for ZrV_2O_7 as a function of phonon energy. The maximum negative contribution to α_V at 500 K is from the modes of energy from 4 to 7 meV. However, in case of ZrP_2O_7 , we find that at 600 K, the maximum positive contribution is from modes of energy from 12 to 25 meV. For $\text{Sc}_2(\text{MoO}_4)_3$, the maximum negative contribution to thermal expansion coefficient at 500 K is from the modes of energy from 1.5 to 4.5 meV.

The nature of the phonons may also be visualized from the calculated partial contributions of the phonons of different energies to the mean square vibrational amplitude (Fig. 5) of the various atoms. The modes up to 3 meV involve equal displacement of all the atoms, which correspond to the acoustic modes. For ZrP_2O_7 , in the energy range of 3 to 25 meV, all the oxygen and zirconium atoms have almost the same amplitude of vibration, while phosphorus has a very small amplitude. All the atoms of ZrO_6 have same amplitude, indicating that only translation motion of ZrO_6 is involved. The P atoms have much smaller amplitude in comparison to that of O atoms. This indicates simultaneous translation and

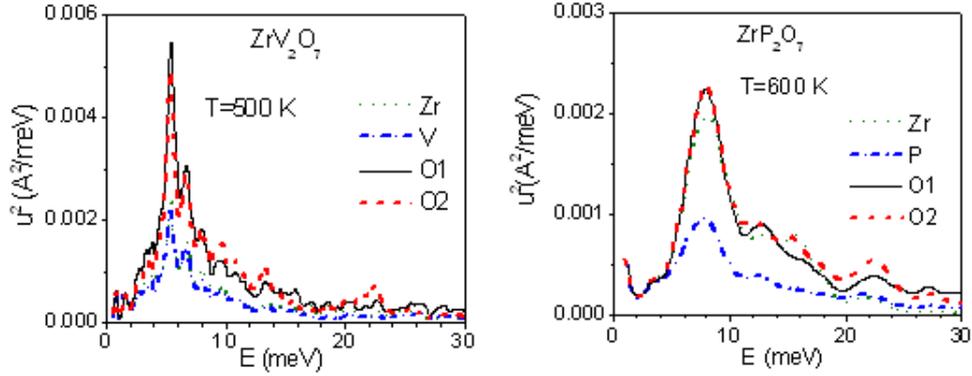


FIG. 5: Calculated contribution to the mean squared amplitude of various atoms arising from phonons of energy E in ZrV_2O_7 and ZrP_2O_7 . The atoms for ZrV_2O_7 and ZrP_2O_7 are labeled as indicated in Ref. [1] and [3], respectively.

rotation of PO_4 tetrahedral units.

This is quite different from cubic ZrV_2O_7 , where in the energy range of 2 to 15 meV, the O1 and O2 atoms connected to ZrO_6 and VO_4 have larger amplitudes in comparison to those of Zr and V. Further, the various oxygen atoms constituting the tetrahedra have nearly same values of vibrational amplitudes, which indicate the translation and rotation of the ZrO_6 octahedral and VO_4 tetrahedral units.

We note that when we replace P by V, the unit cell volume (570 \AA^3) of ZrP_2O_7 is much reduced in comparison to that of ZrV_2O_7 (685 \AA^3). The smaller unit cell volume in ZrP_2O_7 seems to restrict the rotational motion of the ZrO_6 octahedron. The simultaneous rotation of both the ZrO_6 and VO_4 may be responsible for the negative thermal-expansion behavior in ZrV_2O_7 . Overall, the magnitude of the negative Grüneisen parameters of the low-energy modes is much less in ZrP_2O_7 . By including the contribution of the high-energy modes, we obtain a positive thermal expansion in ZrP_2O_7 unlike that in ZrV_2O_7 .

The phonon modes responsible for NTE in $\text{Sc}_2(\text{MoO}_4)_3$ involve significant internal distortions of ScO_6 octahedral and MoO_4 tetrahedral units.

IV. CONCLUSIONS

The calculated values of thermal expansion coefficient in the high-temperature phase of $\text{Sc}_2(\text{MoO}_4)_3$ and ZrP_2O_7 are in good agreement with the reported experimental data. The major contribution to thermal expansion comes from low-energy phonon modes, including the transverse acoustic mode. The change in bond length from V-O to P-O shifts the energy range of the phonon spectrum to higher energy in ZrP_2O_7 in comparison to ZrV_2O_7 . Our calculations show that the low-energy phonon modes in ZrV_2O_7 involve both the rotational and translational motion of ZrO_6 octahedron, while in case of ZrP_2O_7 , these modes have

only translation motion at ambient pressure. The rotational vibrations of ZrO_6 polyhedra shift to high energies in ZrP_2O_7 compared to that in ZrV_2O_7 . The smaller unit cell volume in ZrP_2O_7 seems to restrict the rotational motion of ZrO_6 octahedron. The simultaneous rotation of both the ZrO_6 and VO_4 may be responsible for the negative thermal-expansion behavior in ZrV_2O_7 . In $\text{Sc}_2(\text{MoO}_4)_3$, both the ScO_6 octahedra and MoO_4 tetrahedra have the liberation motion. Our calculation shows that NTE in material occurs because of coupled liberation motion of polyhedral units.

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