

Negative thermal expansion in cubic ZrMo_2O_8 : Inelastic neutron scattering and lattice dynamical studies

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Disordered cubic $\text{ZrMo}_2\text{O}_8(Pa\bar{3}, Z=4)$ is known to display isotropic negative thermal expansion (NTE) below 600 K. We report high-pressure inelastic neutron scattering experiments up to 2.5 kbar in this material using the IN6 spectrometer at Institut Laue-Langevin. The observed phonon softening of about 0.1–0.3 meV for phonons below 8 meV is able to account for the NTE below 100 K. The phonon spectrum in the entire energy range up to 150 meV has been measured using the HRMECS spectrometer at Argonne National Laboratory. The ordered phase (space group $P2_13$) of cubic ZrMo_2O_8 has not yet been synthesized. However, we have calculated the phonon spectrum and thermal expansion in this phase for comparison with the known ordered phase of cubic ZrW_2O_8 .

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I. INTRODUCTION

Studies of oxide materials exhibiting negative thermal expansion (NTE) are of interest both from a fundamental scientific and their potential applications. Isotropic NTE is found^{1–5} in cubic AX_2O_8 ($A=\text{Zr}, \text{Hf}; X=\text{W}, \text{Mo}$) up to high temperatures. These compounds are of particular interest because of the large temperature range over which NTE occurs and its isotropic nature. The compounds can be used for the preparation of controlled thermal expansion composites where the NTE material to some extent compensates for the positive thermal expansion of the other component. For example, composites containing the NTE material ZrW_2O_8 have been examined for use in fiber optic communication systems.^{6(a)} The preparation and properties of $\text{Cu}/\text{ZrW}_2\text{O}_8$ ceramic composites have been investigated with a view to explore the feasibility of a low-thermal-expansion and high-conductivity composite.^{6(b)} Cubic ZrMo_2O_8 is currently being examined as a component of controlled thermal expansion ceramic-polymer composites.^{6(c)}

The AX_2O_8 compounds have framework structure consisting of corner-linked AO_6 octahedral and XO_4 tetrahedral units. The volume negative thermal expansion coefficient of ZrW_2O_8 and HfW_2O_8 (space group $P2_13, Z=4$) at room temperature is about $-29 \times 10^{-6} \text{ K}^{-1}$. They undergo an order-disorder phase transition^{1,2} at about 400 K. One of the terminal oxygens of WO_4 tetrahedra becomes disordered over two crystallographic sites and the space group changes from $P2_13$ (ordered phase) to $Pa\bar{3}$ (disordered phase). ZrMo_2O_8 and HfMo_2O_8 have been synthesized with the disordered phase only. The structure of the disordered phase of ZrMo_2O_8 indicating the two possible sites for O atom is shown in Fig. 1. The volume thermal expansion coefficient for disordered cubic ZrMo_2O_8 at 300 K is about $-15 \times 10^{-6} \text{ K}^{-1}$. ZrW_2O_8 and HfW_2O_8 show a cubic to orthorhombic (space group $P2_12_12_1$) phase transition⁷ at pressures

around 2.1 kbar and 6 kbar, respectively. For disordered ZrMo_2O_8 there is no phase transition³ below 6 kbar. ZrMo_2O_8 also crystallizes^{8,9} in orthorhombic, monoclinic, and trigonal structures which show anomalous thermal expansion behaviour.

In quasiharmonic approximation,¹⁰ the contribution from each phonon mode of energy E_i to the volume thermal expansion coefficient is given by $\alpha_V = (1/BV)\Gamma_i C_{Vi}(T)$ (where $\Gamma_i = -\partial \ln E_i / \partial \ln V$) is the mode Grüneisen parameter, C_{Vi} is the specific heat contribution of the phonon mode of energy E_i , B is the bulk modulus, and V is the unit cell volume). Since C_{Vi} is positive for all modes at all temperatures, NTE would result only from large negative values of the Grüneisen parameter for certain phonons. The Γ values for these phonons have to be large enough to compensate the normal positive values of all other phonons.

Previous analysis of the observed NTE, specific heat, and phonon density-of-states measurements^{11–13} in ZrW_2O_8 and HfW_2O_8 suggested that low-energy modes play an important role for the understanding of the NTE behavior. These measurements indicated fairly large negative values of the Grüneisen parameters. Grüneisen parameters of the zone-center optically active modes of energies above 5 meV have also been estimated¹⁴ in both the Zr and Hf compounds from high-pressure Raman scattering experiments. Combining lattice dynamical calculations with high-pressure inelastic neutron scattering experiments we could clearly show^{15–20} that the large softening of several low-energy phonons below 8 meV is mainly responsible for the negative thermal expansion in ZrW_2O_8 and HfW_2O_8 .

For a complete understanding of NTE in this class of compounds it is essential to confront the W with the Mo family, which as outlined above show appreciable differences in terms of NTE. While specific heat measurements²¹ are available for disordered ZrMo_2O_8 , experimental data of phonon modes by optical or inelastic neutron scattering mea-

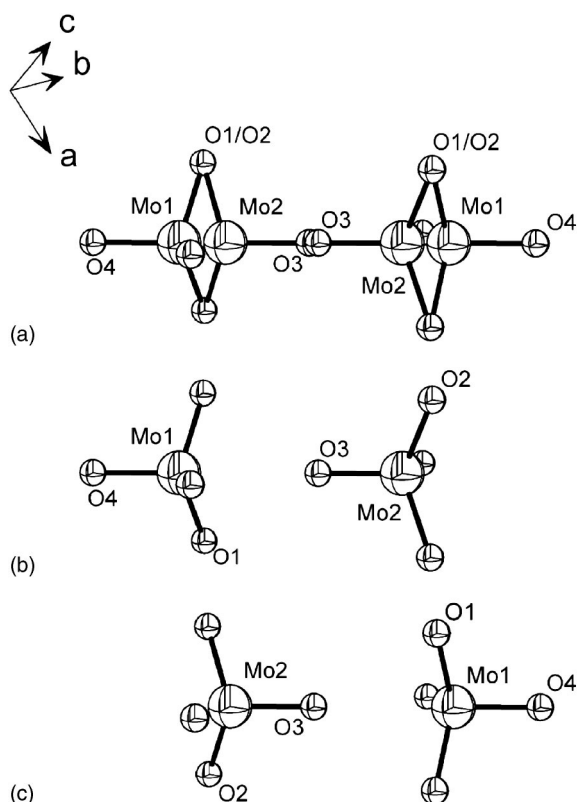


FIG. 1. The MoO_4 groups in cubic $ZrMo_2O_8$ are disorderly oriented along the $[111]$ axis leading to the average structure shown in panel (a). This can be viewed as a superposition of the two possible local structures shown in panels (b) and (c). The Mo-O3 and Mo-O4 bonds are along the $[111]$ axis.

measurements do not exist. The analysis of the NTE behavior requires the Grüneisen parameters averaged over the whole Brillouin zone, which may be directly obtained from the measurement of the pressure dependence of the phonon density of states by high-pressure inelastic neutron scattering. Here we report the experimental results of such measurements for the phonon spectra below 10 meV in disordered $ZrMo_2O_8$ and use them for calculating the NTE behavior. We also report the phonon spectra in the entire energy range up to 150 meV.

For disordered $ZrMo_2O_8$ (space group $Pa\bar{3}$) one of the terminal oxygen atoms of MoO_4 tetrahedra is disordered over two crystallographic sites. However, we have not included this disorder in the lattice dynamical calculations which are carried out using the ordered structure (space group $P2_13$). As the ordered phase of $ZrMo_2O_8$ has not yet been synthesized, the calculations have been compared with data for the known ordered phase of cubic ZrW_2O_8 .

II. EXPERIMENT

Cubic $ZrMo_2O_8$ was prepared by the carefully controlled thermal dehydration of $ZrMo_2O_7(OH)_2 \cdot 2H_2O$ as previously described.²² The high-pressure inelastic neutron scattering experiments at up to 10 meV were carried out on a polycrystalline sample using the IN6 spectrometer at the Institut Laue

Langevin (ILL). Pyrolytic graphite (002) is used as a monochromator. The second-order reflection from the monochromator is removed by a beryllium filter cooled to liquid nitrogen temperature. An incident energy of 3.12 meV with an elastic resolution of 80 μ eV was chosen and the measurements were performed in the energy gain mode. The angular range of the spectrometer is from 10° to 113° . About 10 g of sample was compressed using argon gas in a pressure cell available at ILL. The use of argon gas as a pressure transmitting medium allowed us to perform measurements at 160 K which is above its critical point. For $ZrMo_2O_8$ there is no phase transition³ up to 6 kbar. The present measurements on the cubic phase were performed at ambient pressure, 0.3, 1.0, and 2.5 kbar. The inelastic neutron scattering signal was corrected for the contributions from argon at the respective pressures, absorption from the sample, and for the empty cell.

The ambient pressure inelastic neutron scattering measurements for $ZrMo_2O_8$ in the full spectral range up to 150 meV were carried out using the HRMECS spectrometer at Argonne National Laboratory. The spectrometer is equipped with large detector bank which covers a wide range (-10° – 140°) of scattering angles. A polycrystalline sample of 25 g was placed inside a sealed aluminum container. An incident neutron beam of energy 200 meV was selected, permitting data to be collected over a wide range of momentum transfers (Q from 4 to 19 \AA^{-1}). This was needed to ensure a uniform sampling of wave vectors Q over the Brillouin zone, effectively fulfilling the incoherent approximation.²³ The measurements were performed in the neutron energy loss mode. In order to reduce multiphonon scattering, the phonon measurements were carried out at low temperatures at 7 K. Background scattering was subtracted from the data using an empty-container run. Measurements of the elastic incoherent scattering from a vanadium standard provided for detector calibration and intensity normalization.

The data were suitably averaged over the angular range of scattering to obtain the dynamical structure factor $S(Q, E)$. In the incoherent approximation²³ the structure factor $S(Q, E)$ is related to the neutron-cross-section-weighted phonon density of states $g^{(n)}(E)$ as follows:

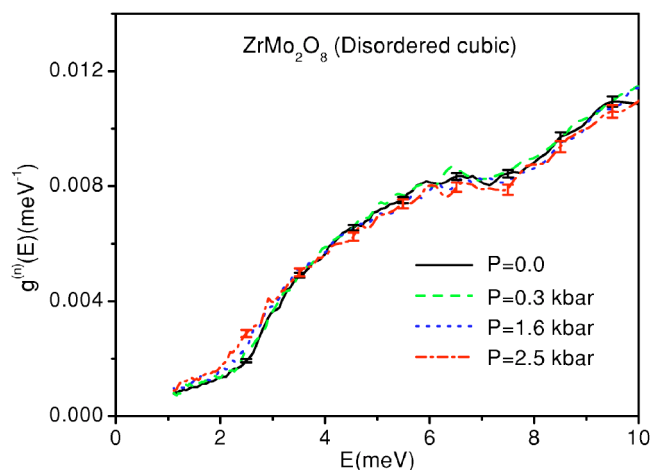


FIG. 2. (Color online) The experimental phonon spectra for the disordered cubic $ZrMo_2O_8$ as a function of pressure at 160 K.

$$g^{(n)}(E) = A \left\langle \frac{e^{2W(Q)} E}{Q^2 n(E, T) + \frac{1}{2} \pm \frac{1}{2}} S(Q, E) \right\rangle \quad (1)$$

$$= B \sum_k \frac{\sigma_k}{M_k} g_k(E), \quad (2)$$

where $n(E, T) = [\exp(E/KT) - 1]^{-1}$, A and B are normalization constants, and σ_k , M_k , and $g_k(E)$ are, respectively, the neutron scattering cross section, mass, and partial density of states of the k th atom in the unit cell. The factor σ_k/M_k for the Zr, Mo, and O atoms is 0.069, 0.060, and 0.265 b/amu, respectively. The quantity within $\langle \dots \rangle$ represents an average over all Q values. $2W(Q)$ is the Debye-Waller factor. The $+(-)$ sign indicates neutron energy loss or gain in the scattering process. The true one phonon density is simply given by

$$g(E) = \sum_k g_k(E). \quad (3)$$

III. LATTICE DYNAMICAL CALCULATIONS

The calculations have been carried out for the ordered phase of cubic ZrMo_2O_8 , which has not yet been synthesized. We assumed that the crystal structure of ZrMo_2O_8 would be similar to that of ZrW_2O_8 and that the lattice constant for the disordered phase would be about 1% lower than that for the ordered phase by analogy with ZrW_2O_8 (space group $P2_13$). The empirical interatomic potential¹⁶ as used consists of Coulombic and short-ranged terms and a van der Waals—type attractive interaction between the oxygen atoms. A shell model¹⁰ was used to describe the polarisability of the oxygen atoms. The parameters of the interatomic potential are the effective charges and radii of the atoms. The values of the empirical parameters for Zr and O were taken from our previous work¹⁶ on ZrW_2O_8 . The radius parameter for the Mo atom ($R_{\text{Mo}} = 1.18 \text{ \AA}$) was determined so that it gave the expected lattice parameter for ordered ZrMo_2O_8 . The potential parameters also satisfied the conditions of static and dynamic equilibrium of the crystal structure. The structure of ordered ZrMo_2O_8 at the minimum of the potential is given in Table I. The contributions of a $9 \times 9 \times 9$ mesh of wave vectors in one octant of the cubic reciprocal-space unit cell were used for calculations of the phonon spectrum and thermal expansion. The calculations were carried out using a current version of the computer program²⁴ DISPR developed at Trombay. The procedure for the thermal expansion calculations is given in our previous publications.^{16,17}

IV. RESULTS AND DISCUSSION

A. Experimental observation of large phonon softening in disordered cubic ZrMo_2O_8

The measured neutron-cross-section-weighted phonon densities of states $g^{(n)}(E)$ for energies of up to 10 meV at a temperature of 160 K are shown as a function of pressure in

TABLE I. The structural parameters for ordered phase (space group $P2_13$) of cubic ZrMo_2O_8 at the minimum of the interatomic potential. The units used are \AA for the lattice constant a (at $T=0$ K), \AA^2 for mean-squared amplitudes $u^2 (= \langle U^2 \rangle / 3)$ (at 300 K).

| | | |
|-------|-------|--------|
| | a | 9.1643 |
| Zr | x | 0.0016 |
| | u^2 | 0.010 |
| Mo(1) | x | 0.3526 |
| | u^2 | 0.009 |
| Mo(2) | x | 0.6028 |
| | u^2 | 0.009 |
| O(1) | x | 0.2083 |
| | y | 0.4362 |
| | z | 0.4467 |
| | u^2 | 0.021 |
| O(2) | x | 0.7857 |
| | y | 0.5680 |
| | z | 0.5619 |
| | u^2 | 0.016 |
| O(3) | x | 0.4927 |
| | u^2 | 0.019 |
| O(4) | x | 0.2419 |
| | u^2 | 0.035 |

Fig. 2. Comparison of the present $g^{(n)}(E)$ spectrum for disordered ZrMo_2O_8 and our earlier measurements¹⁹ on ordered ZrW_2O_8 shows that the three peaks at about 3.5 meV, 6 meV, and 8 meV in the latter compound broaden into a single broad peak centered at about 6 meV in the former. The spectra of ZrMo_2O_8 at high pressures show an unusually large softening. At 2.5 kbar, phonon softening of about 0.1–0.3 meV is observed for phonons below 8 meV. The phonon softening is maximum below 3.5 meV, while above 3.5 meV the softening is much less. The observed softening of low-frequency phonon modes of 2.5 meV is 0.35 ± 0.11 meV at 2.5 kbar. For cubic ZrW_2O_8 phonon softening of about 0.1–0.2 meV was observed¹⁹ at 1.7 kbar.

B. Thermal expansion in disordered cubic ZrMo_2O_8 from the phonon data

While the Grüneisen parameter can be obtained from the $g(E)$ spectra, neutron scattering measurements provide $g^{(n)}(E)$. The experimental $g^{(n)}(E)$ have been converted to phonon density of states $g(E)$ using the ratio of the calculated²⁵ $g^{(n)}(E)$ to $g(E)$. The cumulative distributions of $g(E)$ spectra at ambient pressure and 2.5 kbar have been used for obtaining the Grüneisen parameter for phonons of energy E (Fig. 3). The average value of Γ for phonons of energy 1.5–8.5 meV in disordered ZrMo_2O_8 obtained from present experiment is -6.4 . For comparison, we note that for ordered ZrW_2O_8 the average values obtained from our previous experiment¹⁹ and the analysis¹¹ of the NTE and phonon density-of-states data are -10.6 and -14 , respectively.

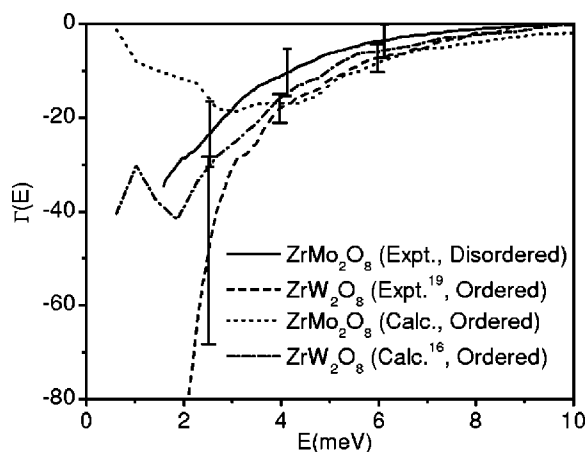


FIG. 3. The Grüneisen parameter [$\Gamma(E)$] averaged over phonons of energy E . The experimental values have been determined using the neutron data of phonon density of states as a function of pressure.

Figure 4(a) shows a comparison of thermal expansion as derived²⁶ from the phonon measurements with that obtained from diffraction⁵ data, which indicates that large negative Grüneisen parameters of modes below 10 meV are able to reproduce the NTE behavior in disordered ZrMo_2O_8 up to 100 K. Diffraction data⁵ show that α_V [inset in Fig. 4(a)] is less negative above 100 K which may be due to positive contributions from phonon modes above 10 meV. The large contributions to the measured spectra from the pressure cell (above 10 meV) does not allow us to obtain the experimental Γ values beyond 10 meV. Our calculations (Sec. IV D) for ordered cubic ZrMo_2O_8 indeed show that the positive contribution to the thermal expansion coefficient from modes above 8 meV is significant and that it reduces the overall negative contributions from modes below 8 meV. In order to identify the contribution of various phonons to the thermal expansion coefficient α_V at a particular temperature, we have calculated [using the observed $\Gamma(E)$] the contribution from phonons of various energies to the total thermal expansion at 20 K and 100 K [Fig. 4(b)]. The maximum contribution to α_V is found to be from phonon modes of energy 3.5 ± 1 meV. This is comparable to the case of ZrW_2O_8 where the maximum contribution¹⁹ to α_V is from phonon of energies 4 ± 1 meV.

C. Phonon density of states in disordered cubic ZrMo_2O_8

The experimental neutron-weighted one-phonon density of states for the disordered phase of cubic ZrMo_2O_8 in the full energy range of 150 meV is shown in Fig. 5 along with that for ordered HfW_2O_8 measured¹⁷ using the same instrument. For disordered cubic ZrMo_2O_8 the phonon bands are slightly broader when compared to those for ordered HfW_2O_8 . The peak at 25 meV in ordered HfW_2O_8 is not present in disordered ZrMo_2O_8 . In ordered HfW_2O_8 there is a band gap from 60 to 90 meV which is smeared out in disordered ZrMo_2O_8 due to the broadening of peak around 95 meV.

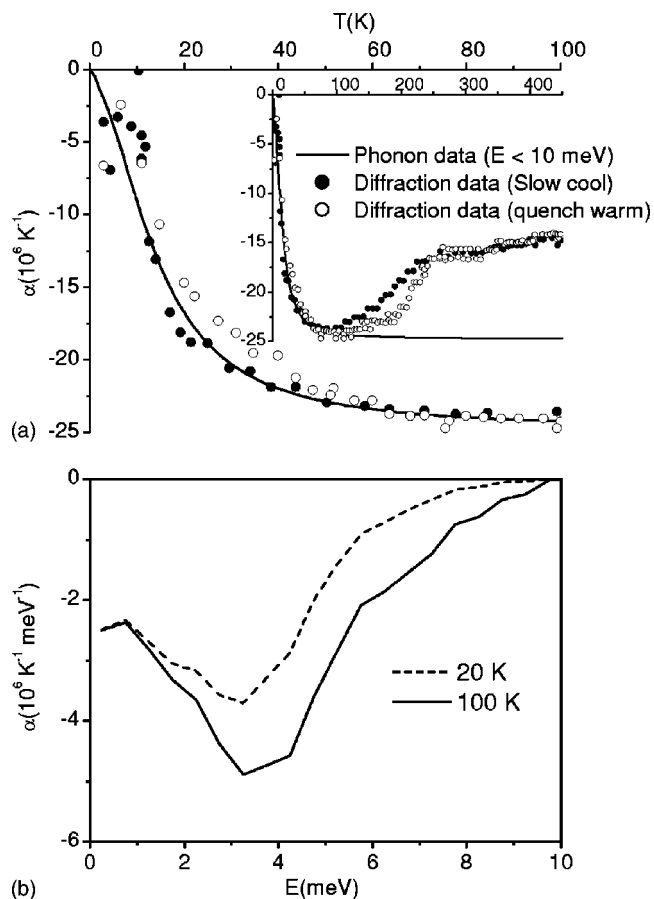


FIG. 4. (a) The comparison between the volume thermal expansion (α_V) of disordered cubic ZrMo_2O_8 derived from the present high-pressure neutron inelastic scattering experiment (solid line) and that obtained using neutron diffraction (Ref. 5) (circles) up to 100 K. The inset shows the comparison up to 450 K. (b) The contribution of phonons of energy (E) to the volume thermal expansion as a function of E at 20 K (dotted line) and 100 K (solid line). A constant $\Gamma(E)$ value of -35 has been assumed for phonons of energy below 1.5 meV.

D. Phonon density of states and thermal expansion in ordered cubic ZrMo_2O_8

Our calculation of how the phonon spectrum varies with volume for the ordered cubic phase at low energies (Fig. 6) shows that phonons of these energies are important for understanding the NTE. Similar behaviour was calculated^{16,17} for cubic ZrW_2O_8 and HfW_2O_8 . The calculated Grüneisen parameter (Fig. 3) has large negative values for phonons below 8 meV. Above 8 meV, Γ values are very small and lie in the range of about -1 to 1 . The largest negative Grüneisen parameter (Γ) occurs for the phonon modes of energy around 3 meV. The large negative Γ values of several phonons below 8 meV are responsible for $\alpha(T)$ remaining negative up to high temperatures. It can be seen from Fig. 3 that for ordered cubic ZrMo_2O_8 , Γ values are less negative for phonons of energy below 3 meV when compared with our calculated^{16,17} Γ values for cubic ZrW_2O_8 and HfW_2O_8 . Our calculations show (Fig. 7) that the contribution to NTE from the two lowest modes is about 40%. Phonons below 8 meV make the

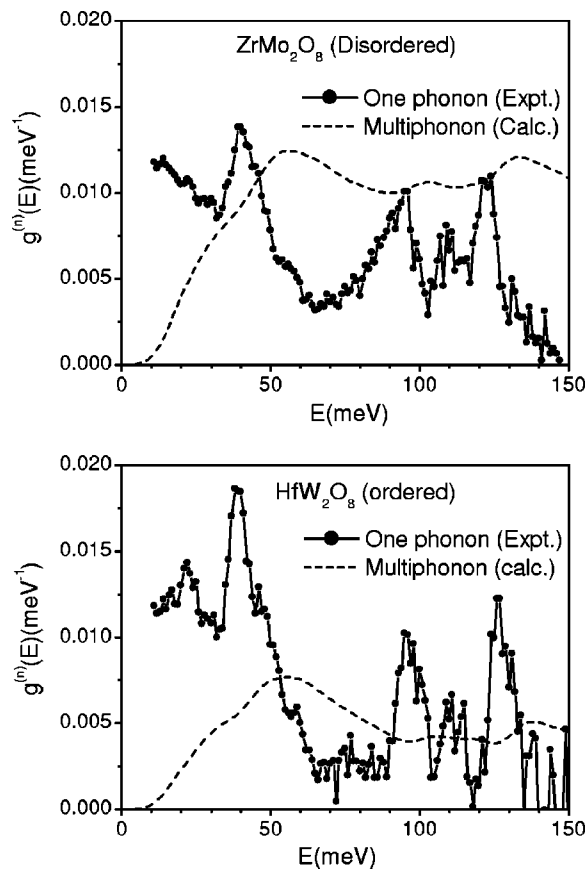


FIG. 5. The experimental neutron-weighted phonon density of states of disordered cubic ZrMo_2O_8 (at 7 K) and ordered HfW_2O_8 (at 7 K, Ref. 17). The multiphonon contribution has been estimated in the monatomic approximation and subtracted from the experimental data to obtain the one-phonon density of states. The one-phonon data for HfW_2O_8 differ slightly at high energies (around 140 meV) from our previously published data (Ref. 17) due to different estimates of multiphonon contribution.

thermal expansion coefficient negative and a smaller positive contribution from phonons above 8 meV reduces the magnitude of the negative α_V above 70 K. Ordered cubic ZrMo_2O_8 has a smaller magnitude of negative α_V in comparison^{16,17} of

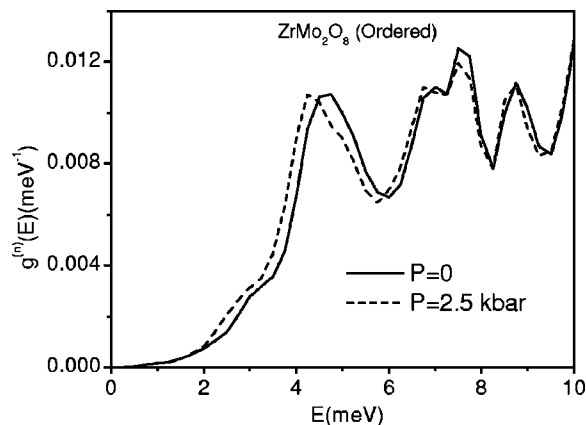


FIG. 6. The pressure variation of the calculated neutron-weighted phonon density of states below 10 meV in the ordered phase (space group $P2_13$) of cubic ZrMo_2O_8 .

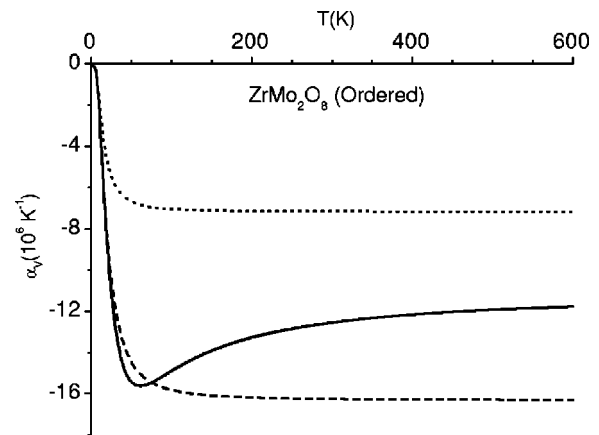


FIG. 7. The calculated volume thermal expansion (solid line) in the ordered phase (space group $P2_13$) of cubic ZrMo_2O_8 along with separate contributions from the two lowest phonon branches (dotted line) and all the phonons below 8 meV (dashed line). The calculated bulk modulus value of 86.6 GPa is used in the lattice dynamical calculation of thermal expansion of ordered ZrMo_2O_8 .

ordered cubic ZrW_2O_8 and HfW_2O_8 . For ZrMo_2O_8 the positive contribution to NTE from modes above 8 meV is significant when compared^{16,17} to ZrW_2O_8 and HfW_2O_8 .

V. CONCLUSIONS

Applying a combination of experimental phonon studies and lattice dynamical calculations to both the W and Mo families of AX_2O_8 compounds leads to a comprehensive understanding of the negative thermal expansion behavior. In this paper we have reported the experimental determination of the Grüneisen parameters of phonon modes for disordered cubic ZrMo_2O_8 as a function of their energy. These measurements provide values of Γ averaged over the whole Brillouin zone. In disordered ZrMo_2O_8 at 2.5 kbar, phonon softening of about 0.1–0.3 meV is observed for phonons below 8 meV. For cubic ZrW_2O_8 phonon softening of about 0.1–0.2 meV was observed¹⁹ at 1.7 kbar. The difference in observed mode softening between the molybdate and tungstate is able to account for the observed difference in the negative volume thermal expansion coefficient (below 100 K). The $g^{(n)}(E)$ spectrum for the disordered phase of cubic ZrMo_2O_8 has also been measured in the full energy range up to 150 meV. The phonon spectrum and thermal expansion behaviour have been calculated in the ordered phase of cubic ZrMo_2O_8 . Although the ordered phase has not yet been synthesized for the molybdate, our predictions are useful for comparison with the known ordered phase of ZrW_2O_8 .

ACKNOWLEDGMENTS

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- ²⁵The ratio $g^{(n)}(E)/g(E)$ is obtained from the calculations in the ordered phase. The same ratio is then used in the data analysis of the disordered phase.
- ²⁶The contribution of mode of energy E_i to the volume thermal expansion coefficient is given by $\alpha_V(T) = \Gamma_i C_{V_i}(T)/(BV) = [C_{V_i}(T)/V] \partial \ln E_i / \partial P$. From high-pressure inelastic neutron scattering experiments we have experimentally determined $\partial \ln E_i / \partial P (= \Gamma_i/B)$ at 160 K. Although it is known (Ref. 27) that there is a significant temperature dependence of bulk modulus, the temperature dependence of Γ_i/B is not yet determined experimentally.
- ²⁷(a) F. R. Drymiotis, H. Ledbetter, J. B. Betts, T. Kimura, J. C. Lashley, A. Migliori, A. P. Ramirez, G. R. Kowach, and J. Van Dujin, *Phys. Rev. Lett.* **93**, 025502 (2004). (b) The bulk modulus in ZrW_2O_8 is found [Ref. 27(a)] to decrease by about 40% with increase of temperature from 0 to 300 K. The temperature dependence of bulk modulus for $ZrMo_2O_8$ may be expected to be similar to the case of ZrW_2O_8 .