Origin of Negative Thermal Expansion in Cubic ZrW_2O_8 Revealed by High Pressure Inelastic Neutron Scattering

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Isotropic negative thermal expansion has been reported in cubic ZrW_2O_8 over a wide range of temperatures (0–1050 K). Here we report the direct experimental determination of the Grüneisen parameters of phonon modes as a function of their energy, averaged over the whole Brillouin zone, by means of high pressure inelastic neutron scattering measurements. We observe a pronounced softening of the phonon spectrum at $P = 1.7$ kbar compared to that at ambient pressure by about 0.1–0.2 meV for phonons of energy below 8 meV. This unusual phonon softening on compression, corresponding to large negative Grüneisen parameters, is able to account for the observed large negative thermal expansion.

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ZrW_2O_8 has been the subject of numerous recent investigations [1–13] as it shows a large isotropic negative thermal expansion (NTE) over a wide range of temperatures (0–1050 K). This ceramic material is well suited for use as a component in composites with tailored thermal expansion coefficients [3]. The structure of ZrW_2O_8 consists [1,2] of a framework of corner linked ZrO_6 octahedral and WO_4 tetrahedral units. The NTE behavior in ZrW_2O_8 has been suggested to be due to the transverse vibration of an O atom in the W-O-Zr linkages [1,2] and rigid unit modes [8]. Specific heat [4] and inelastic neutron scattering measurements [5] have shown the importance of low energy phonons in understanding NTE.

Thermal expansion in insulating materials is related to the anharmonicity of lattice vibrations. The key parameters, known as Grüneisen parameters, are obtained from the volume dependence of phonon frequencies. In the quasiharmonic approximation each phonon mode of energy E contributes $\frac{1}{BV}\Gamma_i C_{Vi}$ to the thermal expansion [14] (where Γ_i is the mode Grüneisen parameter, V is the unit cell volume, B is the bulk modulus, C_{Vi} is the contribution of the phonon mode of energy E to the specific heat). Since C_{Vi} is positive for all modes at all temperatures, NTE would result only from large negative values of the Grüneisen parameters. Some estimates of the Grüneisen parameter have been reported [5,9] on the basis of the observed NTE and certain assumptions about the energy dependence of the Grüneisen parameters or the phonon density of states. These estimates indicated fairly large negative values of the Grüneisen parameters. Recently Grüneisen parameter of zone center modes above 5 meV have been determined [10] using high pressure Raman spectroscopic studies. However, in order to understand the NTE, one requires the Grüneisen parameters averaged over the whole Brillouin zone, which can be directly obtained from the measurement of the pressure dependence of the phonon density of states. In this Letter, we have obtained these data from inelastic neutron scattering experiments and successfully used them to explain the NTE.

The polycrystalline sample of ZrW_2O_8 is prepared from stoichiometric amounts of $ZrOCl_2 \cdot xH_2O$ and WO_3. The $ZrOCl_2$ dissolved in water is mixed with WO_3 in ammonium hydroxide. The precipitate is subsequently dried at 1200 °C for 6 h and quenched. The heating to 1200 °C is then repeated with intermittent grindings until the compound is found x-ray pure. The structure of the bulk sample in the ordered cubic phase [1] was confirmed by neutron diffraction.

The high pressure inelastic neutron scattering experiments have been carried out on a polycrystalline sample of ZrW_2O_8 using the IN6 spectrometer at the Institut Laue Langevin (ILL), France. The measurements at IN6 are performed using the time of flight technique. Pyrolitic graphite (002) is used as a monochromator. The second order reflection from the graphite monochromator is removed by a beryllium filter cooled at liquid nitrogen temperature. An incident energy of 3.12 meV with an elastic resolution of 80 μeV is chosen and the measurements are performed in the energy gain mode. The angular range of the spectrometer is from 10° to 113°. About 15 g of the ZrW_2O_8 sample are 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 the measurements at 160 K which is above its critical point. Since the cubic phase is known to irreversibly transform to the orthorhombic phase [6,7] at pressures above 2.1 kbar, the present measurements in the cubic phase were performed at ambient pressure, 0.3, 1.0, and 1.7 kbar. It was also confirmed by neutron diffraction that the pressure released sample continued to be in the original cubic phase. The inelastic neutron scattering signal is corrected for the contributions from argon at the respective pressures and for the empty cell.

The data were suitably averaged over the angular range of scattering using the available software package at ILL

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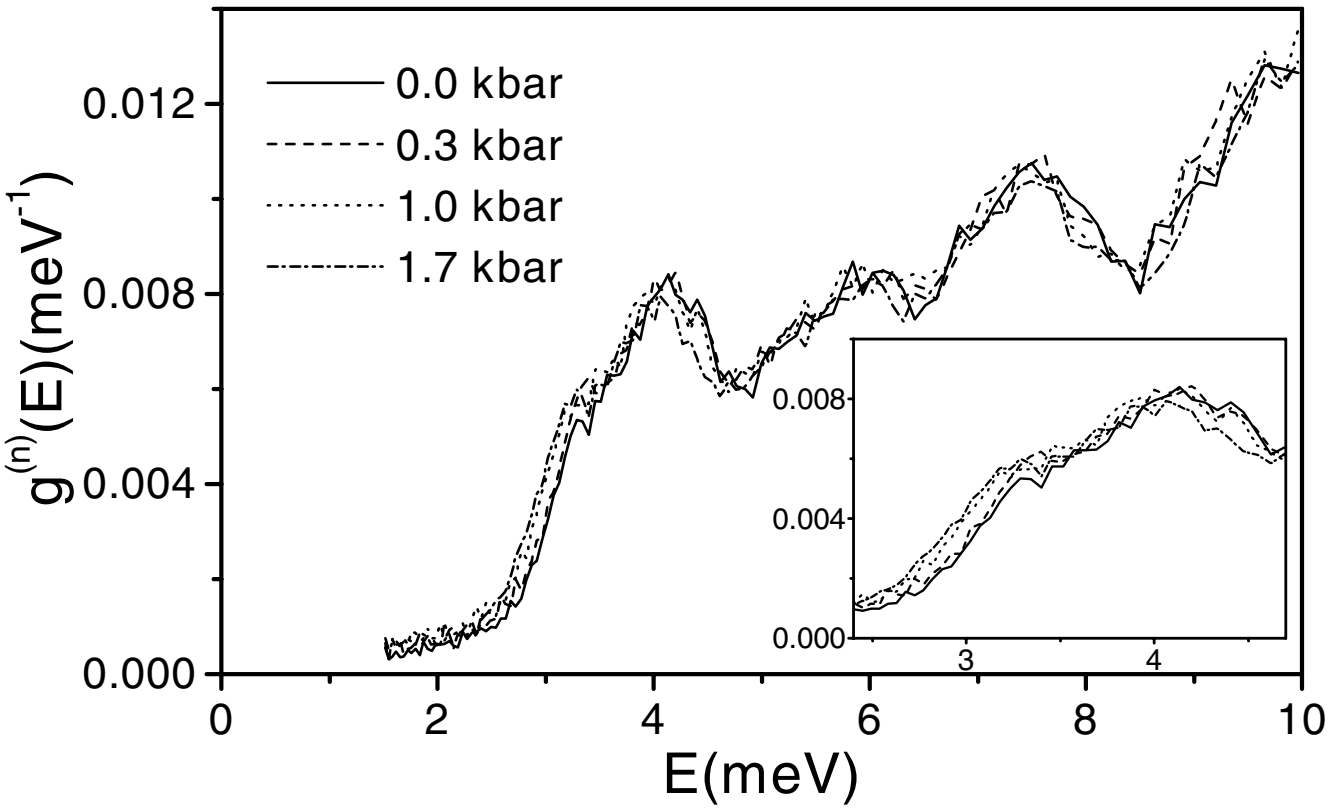

FIG. 1. The experimental phonon spectra for cubic ZrW_2O_8 as a function of pressure at a fixed temperature of 160 K: ambient pressure (full line), 0.3 kbar (dashed line), 1.0 kbar (dotted line), and 1.7 kbar (dash-dotted line). The inset shows the spectra around 4 meV on an expanded scale.

to obtain the dynamical structure factor $S(Q,E)$. In the incoherent approximation the structure factor, as observed in the neutron gain process, is related to the phonon density of states [15] as follows:

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

$$\simeq \sum_k \frac{\sigma_k}{M_k}\,g_k(E)\,, \qquad (2)$$

where $n(E,T) = [\exp(E/KT) - 1]^{-1}$, A is a constant, σ_k, M_k, and g_k are, respectively, the neutron scattering cross section, mass, and the partial density of states, respectively, for the kth atom. The quantity within $\langle\cdots\rangle$ represents the average over all Q values. $2W(Q)$ is the Debye-Waller factor.

The measured neutron-cross-section weighted phonon density of states $g^{(n)}(E)$ at 160 K and different pressures is shown in Fig. 1. The ambient pressure results are in agreement with the previous measurements [5]. The phonon spectra shift towards lower energy with increasing pressure. The shift is particularly pronounced below 5 meV where we observe a softening by about 0.15 meV at 1.7 kbar with respect to ambient pressure. These observations are in excellent agreement with our lattice dynamical calculations (Fig. 2) [11,16].

The experimental neutron weighted phonon density of states $g^{(n)}(E)$ have been converted to phonon density of states $g(E)$ using the ratio of the calculated [11] $g^{(n)}(E)$ to $g(E)$. The spectral weight up to 10 meV is about 11.2%, which corresponds to about 15 phonon modes out of the total 132 modes in cubic ZrW_2O_8 per unit cell. The Grüneisen parameter $[\Gamma(E) = \frac{B}{E}\frac{dE}{dP}$, where $B = -V\frac{dP}{dV}]$ for phonons of energy E has been obtained [Fig. 3(a)] using the cumulative distributions for the density of states.

The experimental results of Grüneisen parameters [Fig. 3(a)] are in very good agreement with predictions from lattice dynamics [11]. The large negative Grüneisen

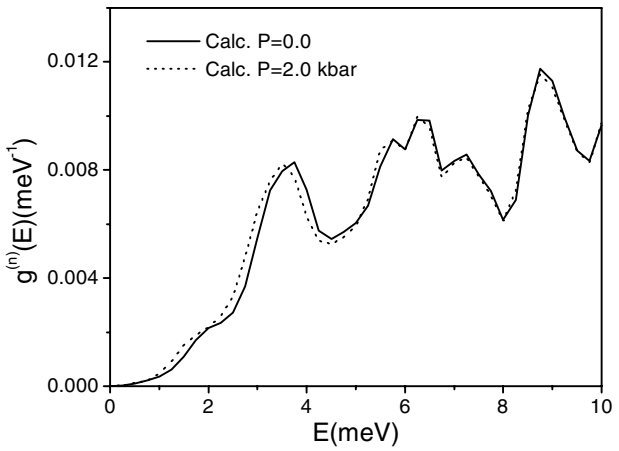

FIG. 2. The calculated phonon spectra [11] for cubic ZrW_2O_8 at ambient pressure (full line) and 2.0 kbar (dotted line) at 0 K.

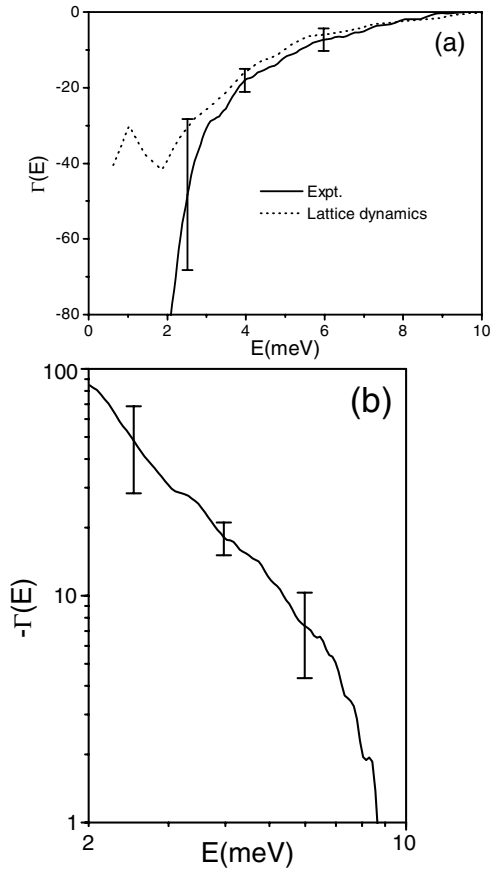

FIG. 3. (a) The experimental Grüneisen parameter $[\Gamma(E)]$ as a function of phonon energy (E) (averaged over the whole Brillouin zone). The Grüneisen parameter has been determined using the density of states at $P = 0$ and 1.7 kbar (full line) which represents the average over the whole range in this study. The calculated $\Gamma(E)$ from our lattice dynamical calculations [11] is shown by a dotted line. (b) The logarithmic plot of $-\Gamma(E)$ vs E.

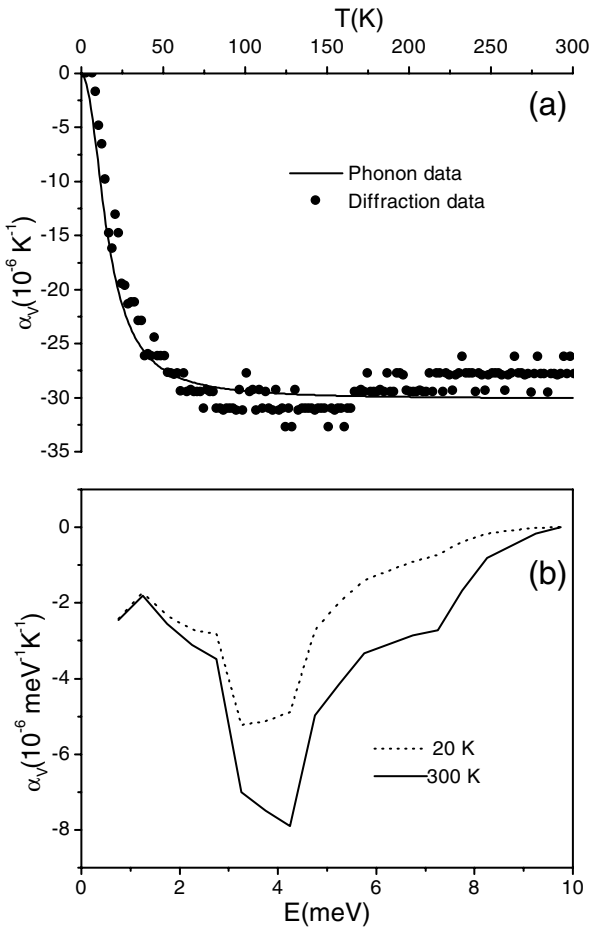

FIG. 4. (a) The comparison between the volume thermal expansion (α_V) derived from the present high pressure inelastic neutron scattering experiment (full line) and that obtained using neutron diffraction [9] (filled circles). We have used the experimental bulk modulus value [6] of 72.5 GPa in the calculation of thermal expansion. (b) The contribution of phonons of energy (E) to the volume thermal expansion as a function of E at 20 K (dotted line) and 300 K (full line). A constant $\Gamma(E)$ value of -80 has been assumed for phonons of energy below 2 meV.

parameter of low energy phonons might be understood in terms of a dynamical instability of the acoustic mode [11]. From the logarithmic plot in Fig. 3(b) we note that, for the phonon energy range of $E = 2$ to 7 meV, Γ is nearly proportional to E^{-2}, which corresponds to $E^2 = A(V - V_0)$ with A and V_0 as characteristic parameters. Indeed such a behavior may be expected near a phonon instability, as predicted in our lattice dynamical calculation. The weighted average value of Γ for 1.5 to 8.5 meV phonons is -10.6 which is in good agreement with a value of -14 ± 2 reported [5] from the analysis of the NTE and the ambient pressure phonon density of states. Again a negative Γ of -32.7, as reported [9] for an Einstein mode at 3.3 meV, is in good agreement with our experimental data of -28 at the same energy. Grüneisen parameters of some Raman active mode at the Brillouin zone center are available [10]; however, these cannot be compared with the present data which correspond to the average over the whole Brillouin zone.

The above data on $g(E)$ and $\Gamma(E)$ obtained from the phonon spectra at ambient pressure and 1.7 kbar are used to derive [11,14] a temperature dependent volume thermal expansion coefficient (α_V). The α_V thus derived from our inelastic neutron scattering data is in good agreement [Fig. 4(a)] with that directly observed by diffraction [9]. The analysis shows that the large negative Grüneisen parameters of modes below 8 meV are able to explain the low temperature thermal expansion coefficient and its nearly constant value above 70 K [17]. In Fig. 4(b) we show the contribution of phonons of energy E to the thermal expansion as a function of E at 20 and 300 K. The maximum contribution to α_V is found to be from phonon modes of energy 4 ± 1 meV which is consistent with the previous analysis of diffraction data [9].

In this paper we have provided direct experimental evidence of large phonon softening as a function of pressure and, therefore, large negative Grüneisen parameters of phonons of energies below 8 meV. These phonons include the acoustic, and librational and translational optic

modes. We have also shown that this anomalous phonon behavior is able to account for the observed large negative thermal expansion in cubic ZrW_2O_8 over the full temperature range of 0–1050 K.

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[16] The experimental and the calculated phonon density of states are compared in two respects: (i) the overall shape and (ii) the softening due to pressure. We regard the agreement on the first count as very good considering the known inherent limitations both in experiment (e.g., incoherent approximation) and theory. The second point is quantitatively better illustrated in Fig. 3 and again shows a very good agreement.

[17] Figure 4(a) shows the volume thermal expansion up to 300 K. It is nearly constant above 70 K. Above 300 K, the behavior is modified by two important contributions as noted in Ref. [11], namely, (i) an order-disorder phase transition at about 400 K which causes a volume drop of about 0.4% which is not accounted for in the lattice dynamical model and (ii) corrections due to anharmonicity of phonons. As shown in Ref. [11], the observed negative thermal expansion is accounted for over the entire range of temperature up to 1050 K by the anomalous phonon behavior by taking into account the above mentioned factors.