Lattice dynamical calculation of isotropic negative thermal expansion in ZrW_2O_8 over $0-1050$ K

R. Mittal and S. L. Chaplot*

Condensed Matter Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

(Received 1 June 1999)

We report detailed lattice dynamical calculations of the large isotropic negative thermal expansion (NTE) over 0–1050 K in ZrW_2O_8 in its cubic phase. The results bring out the unusually dominant quantitative contributions to NTE of the transverse acoustic, and librational and translational optic phonons below 8 meV. The contributions of these phonons are reduced in the high pressure orthorhombic phase which therefore shows NTE only below 270 K. The calculations show a fair agreement with the published thermal expansion data in both phases. [S0163-1829(99)14233-4]

Anomalous behavior in material properties has generally attracted special attention. Negative thermal expansion has been known for a long time in several elemental solids (e.g., Si, Ge, diamond)[1(a)–1(c)] at low temperatures and other compounds in certain crystallographic directions.[1(d)] A negative poisson ratio in quartz has been studied.[1(e)] However, the observation[1(f)] of large isotropic negative thermal expansion (NTE) in cubic ZrW_2O_8 has been very intriguing. This also opens up new possibilities of preparing composite materials with a required value of the thermal expansion. The ZrW_2O_8 crystal structure[1(f)] consists of a framework of corner linked ZrO_6 octahedral and WO_4 tetrahedral units. The NTE has been associated with the presence of Zr-O-W transverse vibrational modes.[1(f)] From a lattice dynamical calculation Pryde *et al.*[2(a)] predicted a non-Debye-like continuum of low-energy librational modes extending to almost zero energy and attributed these modes to NTE. Such modes are known to occur in glasses but are unusual in crystalline materials. Recent accurate specific heat measurements[3(a)] and neutron inelastic scattering measurements[3(b)] reveal the presence of the usual Debye E^2 spectrum at low energies which is inconsistent with the theoretical prediction.[2(a)] Reference 2(a) also predicted extremely small unusual values of the elastic constants which yield a bulk modulus of 1.7 GPa; the value is about 40 times smaller than the experimental value of 72 GPa.[4(b)] Here we report a lattice dynamical calculation which shows a very good agreement with the neutron experiment and the observed specific heat, bulk modulus, and thermal expansion. Further, our model calculation also reproduces the observed anomalous NTE in the high pressure orthorhombic phase[4] of ZrW_2O_8. Our analysis brings out the dominant contribution especially of the transverse acoustic phonons and also the role of a number of low-energy translational and librational optic phonons in leading to a large NTE.

In the quasiharmonic approximation (QHA) each of the phonon modes $\omega(\mathbf{q},j)$, where, $\omega(\mathbf{q},j)=$ frequency, $\mathbf{q}$ = wave vector, $j=$ mode index, $j=1,3N$; N being the number of atoms in the crystallographic primitive unit cell, contribute to the thermal expansion[5] equal to $(1/BV)\Gamma(\mathbf{q},j)C_V(\mathbf{q},j,T)$, where $\Gamma(\mathbf{q},j)=-\partial\ln\omega(\mathbf{q},j)/\partial\ln V$ is the mode Gruneisen parameter, V is the cell volume, B is the bulk modulus, $C_V(\mathbf{q},j,T)=\partial E(\mathbf{q},j)/\partial T$ is the contribution of the phonon mode

to the specific heat, $E(\mathbf{q},j)=(n+\frac{1}{2})\hbar\omega(\mathbf{q},j)$, $n=[\exp(\hbar\omega(\mathbf{q},j)/kT)-1]^{-1}$. Since $C_V(\mathbf{q},j,T)$ is positive for all modes at all temperatures, it is clear that the NTE would result only from large negative values of the Gruneisen parameter for certain phonons; the values should be large enough to compensate for the normal positive values of all other phonons. The frequencies of such phonons should decrease on compression of the crystal rather than increase which is the usual behavior. It is very interesting to note that the quantization of the finite phonon energies is important to the phenomena of NTE, just as in the case of specific heat. The QHA includes the effect of implicit anharmonicity of phonons due to the change of unit cell volume. However, the effect of explicit anharmonicity due to large thermal amplitudes may also be significant at high temperature.[5] We have calculated this effect using the formalism of Ref. 5(d).

A first principles calculation of the phonon spectrum would be too tedious due to the complexity of the structure; there are 44 and 132 atoms per unit cell in the cubic and orthorhombic phases, respectively. As we need to calculate the volume dependence of the frequencies, a usual mass and spring approach based on fixed values of the force constants would not be useful. We therefore resort to an approach using an interatomic potential function. The binding energy of oxides such as ZrW_2O_8, silicates or quartz SiO_2 largely comes from the ionic interaction although it also involves some covalent bonding. Thus ionic and short-ranged pair-potentials derived from *ab initio* Hatree-Fock calculations of the energy surfaces have been found to be highly successful for SiO_2, $AlPO_4$ (Ref. 6), etc., in their many polymorphic forms over a range of pressures and temperatures. Since *ab initio* potentials are not yet available for ZrW_2O_8, we have derived empirical interatomic potentials. Our procedure,[7(a)] essentially making use of the static and dynamic equilibrium conditions of the crystal structure, has been very successful and useful in case of several materials including the high-temperature oxide superconductors. We use the following form of potential:

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

$$(1)$$

TABLE I. Comparison of the experimental structural parameters [Ref. 1(f)] and the bulk modulus Ref. 4(b) at 293 K in the cubic phase of ZrW_2O_8 with the calculations. The units used are Å for the lattice constant a, Å^2 for mean squared amplitudes u^2, and GPa for the bulk modulus B.

		Expt.	Calc.
	a	9.15993	9.2188
	B	72.5	88.4
Zr	x	0.0003	0.0020
	u^2	0.010	0.012
W1	x	0.3412	0.3547
	u^2	0.012	0.011
W2	x	0.6008	0.6018
	u^2	0.010	0.011
O1	x	0.2071	0.2071
	y	0.4378	0.4382
	z	0.4470	0.4475
	u^2	0.022	0.026
O2	x	0.7876	0.7863
	y	0.5694	0.5674
	z	0.5565	0.5599
	u^2	0.020	0.018
O3	x	0.4916	0.4905
	u^2	0.023	0.021
O4	x	0.2336	0.2429
	u^2	0.037	0.045

where r is the separation between the atoms of type k and k', $Z(k)$ and $R(k)$ are empirical charge and radii parameter of the atom type k, $a = 1822$ eV, $b = 12.364$, and $C = 100$ eV Å.[6] The last term in Eq. (1) is applied only between oxygen atoms. The parameters values derived are $Z(Zr) = 2.2$, $Z(W) = 3.3$, $Z(O) = -1.1$, $R(Zr) = 1.13$ Å, $R(W) = 1.21$ Å, $R(O) = 2.045$ Å. As a further improvement we included a covalent potential[7(b)] between the nearest W and O atoms

$$V(r) = -D \exp[-n(r-r_0)^2/(2r)] \qquad (2)$$

($D = 5.0$ eV, $n = 29.4$ Å^{-1}, $r_0 = 1.79$ Å) and introduced polarizibility of the oxygen atom in the framework of the shell model[5(a),7(c)] with the shell charge $Y(O) = -1.6$ and shell-core force constant $K(O) = 70$ eV/Å^2. As in Refs. 6,7, many-body forces are included implicitly through the two-body potential, which is justified from the ability of the potential to reproduce the equilibrium crystal structural parameters of the cubic phase (Table I) and other dynamical properties quite satisfactorily as discussed later.

The phonon frequencies as a function of wave vectors in the entire Brillouin zone and its volume and pressure dependence in QHA are calculated using a program[8] developed by us, where the crystal structure at each pressure is obtained by minimization of the free energy.[9] The phonon density of states and the thermal expansion $\alpha(T)$ in the cubic phase are calculated by integrating over the contribution of phonons of wave vectors on a $9 \times 9 \times 9$ mesh in an octant of the cubic Brillouin zone. Variation of the calculated phonon spectrum
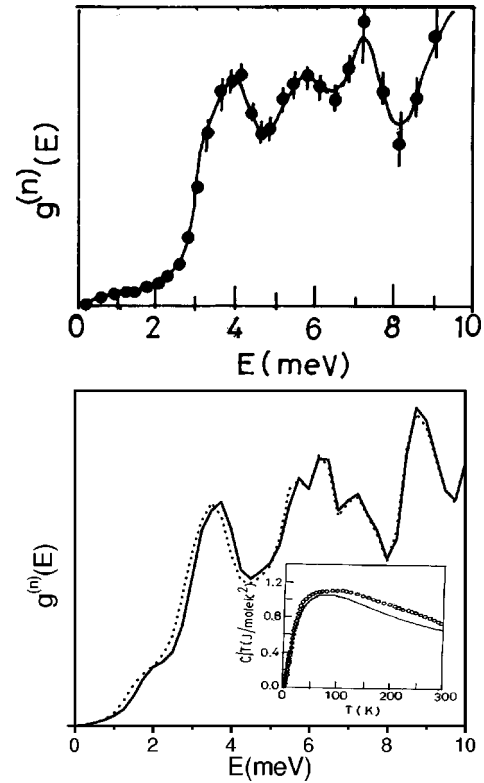

FIG. 1. The neutron-cross section weighted phonon density of states (in arbitrary units) for energies $E = 0-10$ meV; experimental Ref. 3(b) (upper) and calculated (lower). The calculated spectrum is shown at two volumes corresponding to the ambient pressure (full line) and at 0.18% compression (dotted line). The calculated curves have been broadened with a Gaussian function (FWHM $= 0.5$ meV) in order to correspond to the experiment. The inset shows the comparison of the calculated (line) and experimental (circles) [Ref. 3(a)] specific heat.

with volume (Fig. 1) as well as the calculated Gruneisen parameter (inset in Fig. 2) show that the phonons of energies below 8 meV are the most relevant to NTE, which is consistent with the analysis[3(b)] based on the neutron results. The
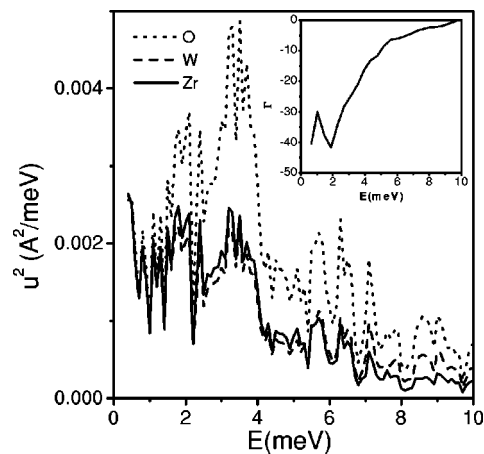

FIG. 2. The calculated contribution to the mean squared amplitude of various atoms arising from phonons of energy E at $T = 293$ K in the cubic ZrW_2O_8. The inset shows the calculated mode Gruneisen parameter (Γ) averaged for phonons of energy (E).
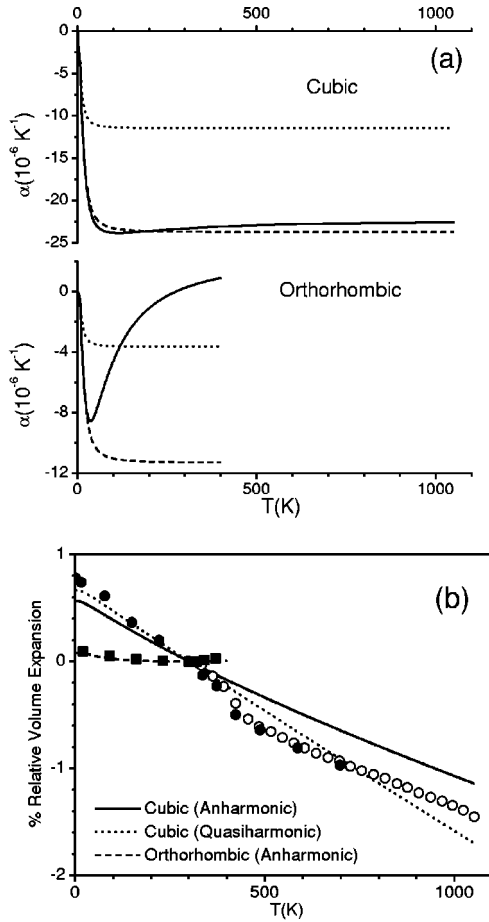
FIG. 3. (a) The calculated volume thermal expansion (solid line) in QHA in the cubic and orthorhombic phases along with separate contributions from the two transverse acoustic phonon branches (dotted line) and all the phonons below 8 meV (dashed line). (b) Calculated percentage relative volume expansion in the two phases $(V_T/V_{300}-1)\times100\%$, V_T and V_{300} being the cell volumes at temperatures T and 300 K, respectively. The quasiharmonic calculation includes the effect of implicit anharmonicity due to volume changes only while the fully anharmonic calculation includes also the effect of explicit anharmonicity due to large thermal amplitudes. The latter effect is negligible in the calculation for the orthorhombic phase. Experimental data; cubic [Ref. 1(f)] (solid and open circles are neutron scattering and dilatometer data respectively) and orthorhombic [Ref. 4(b)] (solid squares are neutron scattering data).

calculated neutron-cross section weighted phonon spectrum and the specific heat are in excellent agreement with experiment (Fig. 1). In our calculated one phonon density of states, the first low energy peak occurs at 3.5 meV and the spectral weight upto 8 meV is 7.7% of the total spectrum, which is quite consistent with the interpretation[3(a)] of the specific heat data. Figure 3(a) shows the quasiharmonic calculation of the thermal expansion. This reveals a very interesting result, namely, that nearly 40% of the NTE in the cubic phase arises from just the two transverse acoustic modes and almost all the NTE is contributed from the modes below 8 meV. The calculated relative expansion including both the effects of implicit and explicit anharmonicity is shown in Fig. 3(b), which indicates an excellent agreement with the experimental data.[1(f)] The latter includes a small sharp drop in volume

at about 400 K associated with a disordering phase transition which also has some impact on the overall NTE. The contribution of the explicit anharmonicity is small in the cubic phase and negligible in the orthorhombic phase.

We find that the largest negative Gruneisen parameter (Γ) occurs for the transverse acoustic phonons around the Brillouin zone center, which may be associated with an elastic instability of the transverse acoustic branch at about 0.30 GPa as discussed below. It is because of the large negative Γ value of several phonons below 8 meV that the $\alpha(T)$ reaches a large negative value at very low temperature. For energies above 8 meV and up to the maximum phonon energies of 140 meV, the Γ values are very small in the range of about -1 to 1. Therefore $\alpha(T)$ continues to be negative and maintained at a high level.

We may gain some insight into the polarization of phonons of energies below 8 meV from their contribution to the mean square vibrational amplitude of various atoms. Figure 2 shows that the modes up to 1.5 meV involve equal displacements of all the atoms, which corresponds to the acoustic modes. However, from 1.5–8 meV a larger amplitude of the oxygen atoms indicates the presence of librations in addition to the translational vibrations of the ZrO_6 octahedral and WO_4 tetrahedral units. The oxygen vibrations involving bond-angular distortions of the polyhedra occur at much higher energies.

Our calculations in the cubic phase at about 0.30 GPa reveal a softening in one of the transverse acoustic branch near the Brillouin zone center. This elastic instability of the cubic phase appears to concide with the observed[4] cubic to orthorhombic phase transition in ZrW_2O_8 at about 0.3 GPa. The latter phase is retained on decompression to ambient pressure. Reference 2(b) reports an instability in the acoustic phonon branch at a larger pressure of 1.5 GPa. The thermal expansion of the orthorhombic phase is observed[4] to be anomalous; it is negative below 300 K and positive above 300 K. Above 400 K, the orthorhombic phase transforms to another cubic phase. Our calculation of thermal expansion in the orthorhombic phase is compared with the experiments in Fig. 3(b) which shows 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.

In conclusion, through detailed lattice dynamical calculations of ZrW_2O_8 we have demonstrated the dominant quantitative contributions of the transverse acoustic phonons and other low-energy rotational and translational optic phonons of energies below 8 meV towards the isotropic large negative thermal expansion. We have shown that the same phonons were also identified from their dominant contribution to the observed[3(a)] specific heat at low temperatures. These phonons yield negative thermal expansion upto very high temperature due to their unusual large softening on compression of the crystal. It is noted that the quantization of certain acoustic and other finite energy translational and librational phonons is important to the phenomenon of NTE. This is in contrast to the explanation in terms of the prediction of a continuum of very low-energy modes[2(a)] which is not borne out by neutron and specific heat experiments.[3]

*FAX: 91-22-5505151. Electronic address: chaplot@magnum.barc.ernet.in

[1] (a) R. D. McCammon and G. K. White, Phys. Rev. Lett. **10**, 234 (1963); (b) D. F. Gibbons, Phys. Rev. **112**, 136 (1958); (c) S. I. Novikova, Sov. Phys. Solid State **2**, 1465 (1961); (d) M. A. Carpenter, E. K. H. Salje, A. Graeme-Barber, B. Wruck, M. T. Dove, and K. S. Knight, Am. Mineral. **83**, 2 (1998); (e) N. R. Keskar and J. R. Chelikowsky, Nature (London) **358**, 222 (1992); (f) T. A. Mary, J. S. O. Evans, T. Vogt, and A. W. Sleight, Science **272**, 90 (1996).

[2] (a) A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, and M. C. Warren, J. Phys.: Condens. Matter **8**, 10 973 (1996); (b) A. K. A. Pryde, M. T. Dove, and V. Heine, *ibid.* **10**, 8417 (1998).

[3] (a) A. P. Ramirez and G. R. Kowach, Phys. Rev. Lett. **80**, 4903 (1998); (b) G. Ernst, C. Broholm, G. R. Kowach, and A. P. Ramirez, Nature (London) **396**, 147 (1998).

[4] (a) J. S. O. Evans, Z. Hu, J. D. Jorgensen, D. N. Argyriou, S.

Short, and A. W. Sleight, Science **61**, 275 (1997); (b) Z. Hu, J. D. Jorgensen, S. Teslic, S. Short, D. N. Argyriou, J. S. O. Evans, and A. W. Sleight, Physica B **241-243**, 370 (1998).

[5] (a) P. Bruesch, *Phonons: Theory and Experiments* (Springer, Berlin, 1982), Vol. 1; (b) R. A. Cowley, Rep. Prog. Phys. **31**, 123 (1968); (c) D. Acocella, G. K. Horton, and E. R. Cowley, Phys. Rev. Lett. **74**, 4887 (1995); (d) V. K. Jindal and J. Kalus, Phys. Status Solidi B **133**, 89 (1986); R. Bhandari and V. K. Jindal, J. Phys.: Condens. Matter **3**, 899 (1991).

[6] (a) B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990); (b) S. Tsuneyuki, M. Tsukada, H. Aoki, and Y. Matsui, *ibid.* **61**, 869 (1988).

[7] (a) S. L. Chaplot, Phys. Rev. B **37**, 7435 (1988); (b) **45**, 4885 (1992); (c) S. L. Chaplot, W. Reichardt, L. Pintschovius, and N. Pyka, *ibid.* **52**, 7230 (1995).

[8] S. L. Chaplot (unpublished).

[9] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).