## Comment on "High Pressure Behavior of $ZrW_2O_8$: Grüneisen Parameter and Thermal Properties"

Ravindran *et al.* [1] have reported important data on pressure dependence of Raman frequencies in $ZrW_2O_8$ which indicate negative Grüneisen parameters of most modes below 50 meV. The authors calculated the negative thermal expansion (NTE) coefficient and specific heat at 300 K using a model based on the Raman data, and thereby concluded that, in contrast to the earlier results [2–4], modes of energies much higher than 10 meV also contribute substantially to the NTE. In this Comment, using the temperature dependence of the NTE, we show that the observed [3] nearly constant NTE above 70 K could arise only from the modes below 10 meV.

The contribution to the linear thermal expansion $\alpha_i$ arising from an Einstein oscillator of energy $E_i$ is given by $\frac{1}{3BV}\Gamma_i C_{Vi}$, where $\Gamma_i$ is the mode Grüneisen parameter, $C_{Vi}$ is the contribution of the mode to the specific heat, $B$ is the bulk modulus, and $V$ is the unit cell volume. While $C_{Vi}$ has significant temperature dependence at low temperature ($k_bT \leq E_i$), the temperature variation in $B$ and $V$ are relatively much smaller and may be ignored in the discussion here. Similarly, we may also ignore the effect of explicit anharmonicity which may lead to a variation in $\Gamma_i$ at high temperatures. Thus, to a very good approximation, the temperature dependence of $\alpha_i$ follows that of $C_{Vi}$ (inset in Fig. 1), and that both of these quantities, starting from zero at $T = 0$, reach within about 92% of their high temperature values at $T = E_i/k_b$. Thus, while a mode of 20 meV would contribute an almost constant (within 8%) thermal expansion only above 232 K, a mode of 6 meV would do so above 70 K. The experimental thermal expansion coefficient in $ZrW_2O_8$ is shown in Fig. 1 which shows a nearly constant value above 70 K. Such a behavior could only arise from a combination of modes below about 10 meV. Figure 1 shows the calculated NTE from our lattice dynamical model [2] as well as the model of [1]. Clearly a model [2] that emphasizes the contribution of low energy modes is essential to describe the observed behavior.

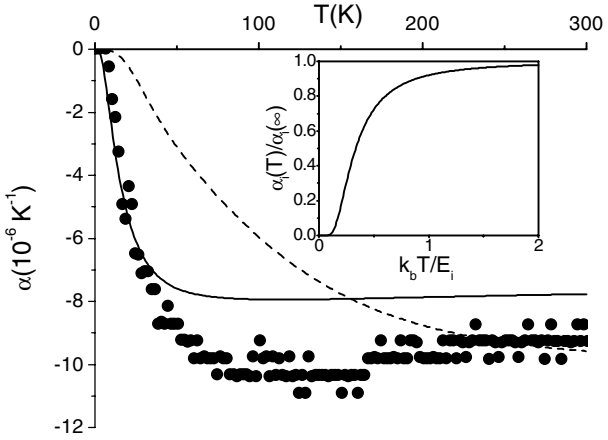


FIG. 1. Comparison of the experimental [3(a)] (symbols) linear thermal expansion coefficient with our lattice dynamical model [2] (continuous line) as well as the model of Ref. [1] (dashed line). We used the experimental bulk modulus value of 72.5 GPa [5] in the calculation with the model of Ref. [1]. The inset shows the normalized contribution to the thermal expansion coefficient as a function of temperature from an Einstein mode of energy $E_i$.

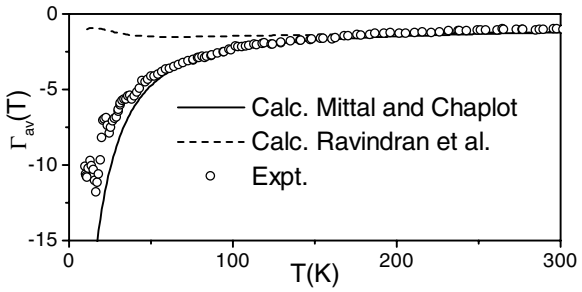


FIG. 2. Comparison of the experimental data of temperature dependent average Grüneisen parameter with our lattice dynamical model [2] as well as the model of Ref. [1]. The experimental data are derived from the observed thermal expansion [3(a)] and specific heat [4].

In Fig. 2 we convert the NTE data into a temperature dependent average $\Gamma_{av}(T)$ $(= 3BV\alpha/C_V)$. Ravindran *et al.* [1] have calculated a value of $-0.83 \pm 0.16$ at 300 K, which is in good agreement with experiment as well as our lattice dynamical calculation. However, a larger negative $\Gamma_{av}(T)$ occurs at low temperatures which has contributions essentially from low energy modes. These modes, especially below 5 meV, have not been probed in the Raman experiment [1].

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