PHYSICAL REVIEW B **79**, 104304 (2009)

Effective semiempirical ansatz for computing anharmonic free energies

Zhongqing Wu (吴忠庆)* and Renata M. Wentzcovitch
Department of Chemical Engineering and Materials Science and Minnesota Supercomputing Institute,
University of Minnesota, Minneapolis, Minnesota 55455, USA

(Received 2 November 2008; revised manuscript received 3 February 2009; published 25 March 2009)

A semiempirical *ansatz* to compute anharmonic contributions to the free energy neglected in quasiharmonic calculations is introduced. A parametrized temperature-dependent modification of the vibrational density of states designed to be used directly with the quasiharmonic free-energy expression is proposed. An approximate relationship between the modified frequencies and the renormalized frequencies is developed. This parametrization is shown to produce the correct low and high temperature behavior of the anharmonic free energy and other thermodynamics properties. It is shown that the thermodynamics properties of α- and β-Mg_2SiO_4 (forsterite and wadsleyite) and MgO (periclase) improve considerably after inclusion of anharmonic effects. Anharmonicity is shown to have a significant effect on the phase boundary of the forsterite to wadsleyite transformation. Inclusion of anharmonic effects can reconcile discrepancies between the measurements of the Clapeyron slope of this transition and the values predicted by quasiharmonic calculations.

DOI: 10.1103/PhysRevB.79.104304 PACS number(s): 65.40.−b, 63.20.Ry, 91.60.Hg, 71.15.Dx

I. INTRODUCTION

The quasiharmonic approximation (QHA) (Ref. 1) in conjunction with first-principles vibrational density of states[2] has been successfully and widely used to compute thermodynamics properties of materials by first principles.[3] In the QHA, intrinsic temperature (anharmonic) effects caused by phonon-phonon interaction are neglected. In the most commonly used version of this approximation, the statically constrained QHA,[4] temperature effects on the crystal structure and on phonon frequencies are accounted for through extrinsic volumetric effects only. Because intrinsic temperature effects increase with temperature, the QHA becomes inadequate beyond a certain temperature located between the Debye temperature, θ_D, and the melting temperature, T_M.[5–12] The lower the pressure the more visible this effect is. For example, at 0 GPa the thermal expansion coefficient of MgO (Refs. 3 and 10) deviates strongly from experimental data above 1000 K. Anharmonicity can be computed directly by first principles and phonon lifetime and linewidth for individual modes have already been carried out.[13,14] However, calculation of the anharmonic free energy requires computation of phonon-phonon interaction for all modes sampled in the Brillouin zone and this remains a daunting task.

Several parametrized approximations to treat anharmonic effects have been proposed.[15–20] Usually, the anharmonic correction to the quasiharmonic free energy, $F_{\text{anh}}(V,T)$, is written as an expansion in powers of T at high temperatures.[15,16,18] According to perturbation theory, the lowest order term is quadratic in T,[15] i.e., $F_{\text{anh}}(V,T)=\frac{3nk_B}{2}b(V)T^2$. This expression is valid only in the high-temperature limit. It produces small but unphysical results at low temperatures such as a linear anharmonic heat capacity. Furthermore, the parameter $b(V)$ is volume sensitive since anharmonicity decreases rapidly with pressure. Unphysical low temperature results and the difficult determination of the volume dependence of b, usually achieved through molecular dynamics (MD) simulations,[20] limits the application of this method. Anharmonic effects can also be accounted for by using the measured or computed temperature-dependent frequencies, i.e., the self-consistent renormalized phonon frequencies, into the quasiharmonic formula of the entropy but not for other thermodynamics functions like the Helmholtz free energy.[16,17,21] This has been accomplished by combining Debye-type models[16,18] and experimentally measured temperature-dependent frequencies. Nevertheless, replacement of some form of temperature dependent frequencies directly into the free-energy formula has also been done as a form of parametrization.[19,20,22,23] All these methods introduce inevitably volume-sensitive parameters or require explicit knowledge of the renormalized frequencies, none of which are easy to obtain at high pressures and temperatures.

Although anharmonicity is naturally included in MD simulations,[20] it is not so straightforward to extract this information. Although phonon density of states can in principle be obtained from MD, the limited number of atoms possible in first-principles simulations limits the number of wave numbers (q vectors) that can be sampled. This limitation can be overcome by performing force field type simulations[20,24] which can handle considerably larger numbers of atoms. However, this is a laborious procedure whose outcome is not as reliable as that of a purely but prohibitively costly first-principles approach. In contrast, phonon calculations based on density-functional perturbation theory can sample as many wave numbers as necessary with the effort scaling linearly with number of q vectors. The accuracy of the final phonon density of states can easily be checked against wave number samplings used in the computation of force constants and of the phonon density of states and it is not a problem to increase either if necessary. For instance, the thermodynamics properties of MgO derived from first-principles MD (64 atoms) at room temperature plus corrections for quantum effects using a Debye-type model,[24] are still not as good as those derived by first-principles QHA calculations[10] equivalent to an MD simulation including 3456 atoms. It is therefore desirable to use QHA results as a starting point and find an effective and easy approach to augment the QHA free energy with an anharmonic contribution to extend the temperature regime of applicability of these calculations.

In this paper we introduce a semiempirical approach that builds on quasiharmonic free-energy calculations to obtain the anharmonic contribution to the free energy. The prominent advantage of this approach is that a single volume and temperature-independent parameter, c, is involved, which makes this method easily applicable. This method produces the correct low and high-temperature anharmonic behavior and reduces to the QHA when $c=0$. We show that the thermodynamics properties of α- and β-Mg_2SiO_4 (forsterite and wadsleyite) improve considerably after inclusion of anharmonic effects. We also show that anharmonic effects increase dramatically the Clapeyron slope (CS) of the phase transformation between forsterite and wadsleyite. This improves the agreement between the predicted CS and those obtained by experiments. The thermodynamics properties of MgO (periclase) also show noticeable changes at relevant mantle conditions.

II. CALCULATION DETAILS

The complete quasiharmonic calculations[16] of periclase, forsterite, and iron free wadsleyite upon which the current calculations are based have been published earlier.[3,25–28] These were plane-wave pseudopotential calculations whose details have been extensively discussed in those papers. The pseudopotential for magnesium was generated by the method of von Barth and Car,[3] while those for oxygen and silicon were generated by the method of Troullier and Martins.[29] The plane-wave cutoff energy is 70 Ry. Brillouin zone summations over electronic states were performed over $4\times4\times4$ (10 points), $4\times2\times4$ (16 points), and $4\times4\times4$ (17 points) k mesh with (1/2,1/2,1/2) shift from original for periclase, forsterite, and wadsleyite, respectively. The structures were well optimized using variable cell shape molecular dynamics.[30] Dynamical matrices were computed on $4\times4\times4$, $2\times2\times2$, and $2\times2\times2$ q mesh using density-functional perturbation theory (DFPT)[2] and then interpolated in a regular $12\times12\times12$, $12\times12\times12$, and $9\times9\times9$ q mesh to obtain the vibrational density of state for periclase, forsterite, and wadsleyite.

III. ANSATZ

The quasiharmonic free energy is expressed as

$$F_H(V,T) = U_0(V) + \frac{1}{2}\sum_{q,j}\hbar\omega_{q,j}(V) + k_BT\sum_{q,j}\ln\{1-\exp[-\hbar\omega_{q,j}(V)/k_BT]\}. \quad (1)$$

$U_0(V)$ is the internal static energy obtained by a first-principles variable cell shape type structural optimization under hydrostatic pressure. The second and third terms are the zero-point (F_H^{zp}) and thermal energies (F_H^{th}), respectively. In the statically constrained QHA, the crystal structure and phonon frequencies are unique functions of the volume.[4] Temperature effects on these quantities are accounted for through volumetric effects only. The intrinsic temperature dependence, i.e., anharmonic effects caused by phonon-phonon interactions, is neglected. For a recent discussion of some consequences of this approximation see Ref. 4.

The fully anharmonic free energy can be separated as

$$F_A(V,T) = F_H(V,T) + F_{\mathrm{anh}}(V,T), \quad (2)$$

where $F_{\mathrm{anh}}(V,T)$ is the anharmonic correction to the quasiharmonic free energy, $F_H(V,T)$. As argued by Falk,[31] Wallace,[16] and demonstrated by Hui and Allen,[17] it is possible to compute exactly the anharmonic entropy, S_A, if one replaces the harmonic frequencies, $\omega_{q,j}(V)$, by the renormalized temperature-dependent frequencies, $\Omega^S_{q,j}(V,T)$, in the harmonic formula, $S_H=-(\partial F_H/\partial T)|_V$:

$$S_A(V,T) = -k_B\sum_{q,j}\left\{\ln[1-\exp(-x^S_{q,j})] + x_{q,j}\frac{\exp(-x^S_{q,j})}{1-\exp(-x^S_{q,j})}\right\}, \quad (3)$$

where $x^S_{q,j}=\frac{\hbar\Omega^S_{q,j}(V,T)}{k_BT}$. This substitution is not valid for any other thermodynamics function. Although progress has been made in first-principles computations of individual renormalized phonon frequencies,[13,14] it is still a daunting task to renormalize the entire vibrational spectrum. Here we introduce an *ansatz* that captures the effect of anharmonicity on the free energy and permits computations of anharmonic thermodynamics properties directly from the free energy. It relies on the definition of a modified temperature-dependent vibrational spectrum, $\Omega^F_{q,j}$, that reproduces the anharmonic free energy when used directly in Eq. (1). These frequencies must reproduce the correct anharmonic behavior, i.e., anharmonicity should increase with temperature at constant pressure, and decrease with pressure at constant temperature. An approximate relationship between the modified frequencies, $\Omega^F_{q,j}$, and the renormalized frequencies, $\Omega^S_{q,j}$, will be derived below in the high temperature limit.

The temperature dependence of $\Omega^F_{q,j}$ is implicitly expressed as

$$\Omega^F_{q,j}(V,T) = \omega(V'), \quad (4)$$

where V' depends on temperature for a fixed volume V:

$$V' = V\left\{1 - c\frac{[V-V_0]}{V_0}\right\}. \quad (5)$$

V and V_0 are the predicted quasiharmonic volumes at high and zero temperature, respectively, both at the same quasiharmonic pressure, $P(V,T)$. c is a constant to be determined empirically by comparing, for instance, experimental data on the thermal expansivity, α, to predictions of quasiharmonic-like calculations using the modified spectrum of Eq. (4). This *ansatz* is suggested by the fact that in the QHA phonon frequencies depend on volume only. Therefore, if the predicted quasiharmonic volumes differ from the experimental volumes, the correction of the frequencies should be expressed through a volume-dependent term. Equation (5) expresses this idea in a more general form by introducing the constant c. More general parametrizations of V', such as a power series in $[V-V_0]$, or parametrizations depending explicitly on lattice parameters are also viable and may be useful. Notice that the expected anharmonic behavior, which increases with temperature at constant pressure and decreases with pressure at constant temperature, is embodied in Eq. (5): V' tends to V at low temperatures and constant pressure or at high pressures and constant temperatures. It is straightforward to show that $F_A(V,T)$ then is

$$F_A(V,T) = F_H(V',T) + [U_0(V) - U_0(V')]. \tag{6}$$

This is the relationship actually used in these calculations. One can see that $F_A(V,T)$ reduces to $F_H(V,T)$ at $c=0$ or at $T=0$ K.

From Eq. (5), the temperature dependence of Ω_i^F $(i \equiv q,j)$ can be expressed (see the Appendix, Sec. 1 for derivation) as

$$a_i^F = \left(\frac{\partial \ln \Omega_i^F}{\partial T}\right)_V = \gamma_i(V')\alpha(V,T)c\beta. \tag{7}$$

$\beta = \frac{V^2 K_T}{V' V_0 K_0}$, where K_0, K_T are isothermal bulk modulus at 0 K and finite T, respectively, $\gamma_i(V')$ is the mode Grüneisen parameter, $\alpha(V,T)$ is the quasiharmonic thermal expansivity, and c is the empirically determined constant. β and $\alpha(V,T)$ are always positive, $\beta \sim 1$ at low temperatures, and the product $\beta\alpha(V,T)$ increases slightly and linearly with temperature at high T (see Fig. 1). γ_is are positive in most cases, but can be negative for *harmonic* modes that soften under pressure. Therefore, the temperature dependence of Ω_i^F is proportional to $c\gamma_i$ with a positive and slightly linearly temperature-dependent prefactor at high temperatures. At low temperatures the prefactor is the thermal expansivity α (see the Appendix, Sec. 2). From Eq. (7), we see that the temperature dependence of Ω_i^F could be captured even more realistically by introducing frequency-dependent parameters, c_is. This would entail defining frequency-dependent V_is in Eq. (4) and rewriting Eq. (6) as a sum over contributions from individual modes. As is, the single parameter c is a weighted average of the c_is. Since most γ_is are positive, and this is true for all three minerals addressed here, $c>0$ implies that the predominant anharmonic effect on frequencies is to increase them with increasing temperature, while $c<0$ indicates the opposite, anharmonic frequencies in average decrease with increasing temperature. Recall, however, that Ω_i^F are not the true renormalized frequencies, Ω_i^S, but it might be quite similar to Ω_i^S (see the Appendix, Sec. 2).

An approximate relationship between Ω_i^F and Ω_i^S can be derived by recalling that the anharmonic entropy can be computed in two different ways, using Eq. (3) or using

$$S_A = -\left.\frac{\partial F_H}{\partial T}\right|_{X^F} = \sum_i \left[-k_B \ln(1-e^{-X_i^F}) + X_i^F \cdot k_B \frac{e^{-X_i^F}}{1-e^{-X_i^F}} - \hbar \frac{\partial \Omega_i^F}{\partial T} \frac{e^{-X_i^F}}{1-e^{-X_i^F}} \right], \tag{8}$$

where $X_i^F = \frac{\hbar\Omega_i^F}{k_B T}$. Imposing the equality between each term under the summations in Eqs. (3) and (8) it is possible to show (see the Appendix, Sec. 2) that

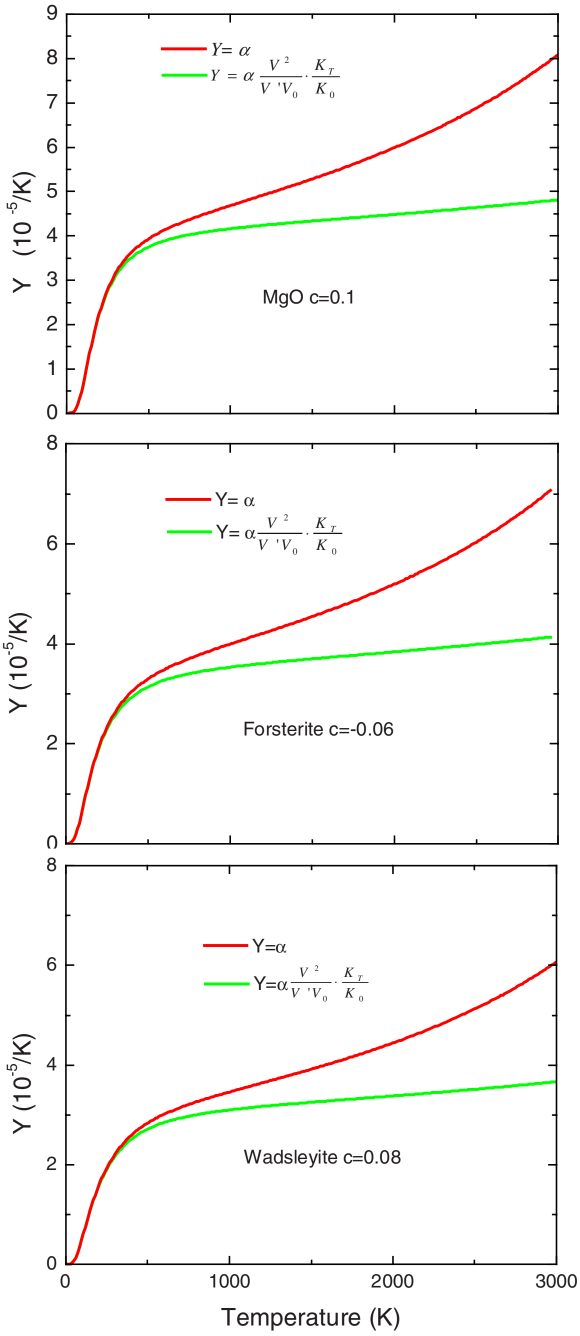

FIG. 1. (Color online) Temperature dependence of α and $\alpha\beta$ [see Eqs. (A10) and (A11)] at 0 GPa for MgO, α- and β-Mg_2SiO_4.

$$\Omega_i^S \simeq \Omega_i^F + k_B T^2 \frac{1 - e^{-(\hbar\Omega_i^F/k_B T)}}{\hbar} \frac{\partial \ln \Omega_i^F}{\partial T}, \tag{9}$$

and

$$a_i^S = \frac{\partial \ln \Omega_i^S}{\partial T} \simeq (1+\eta_i)\frac{\partial \ln \Omega_i^F}{\partial T} = (1+\eta_i)a_i^F, \tag{10}$$

where $\eta_i = \frac{2k_B T}{\hbar\Omega_i^F} - \exp(-\frac{\hbar\Omega_i^F}{k_B T})(\frac{2k_B T}{\hbar\Omega_i^F}+1)$. η_i is positive and increases quickly with temperature if $k_B T < \hbar\Omega_i^F$ and then tends to 1 when $k_B T > \hbar\Omega_i^F$. At $T=300$ K, most phonon frequen-

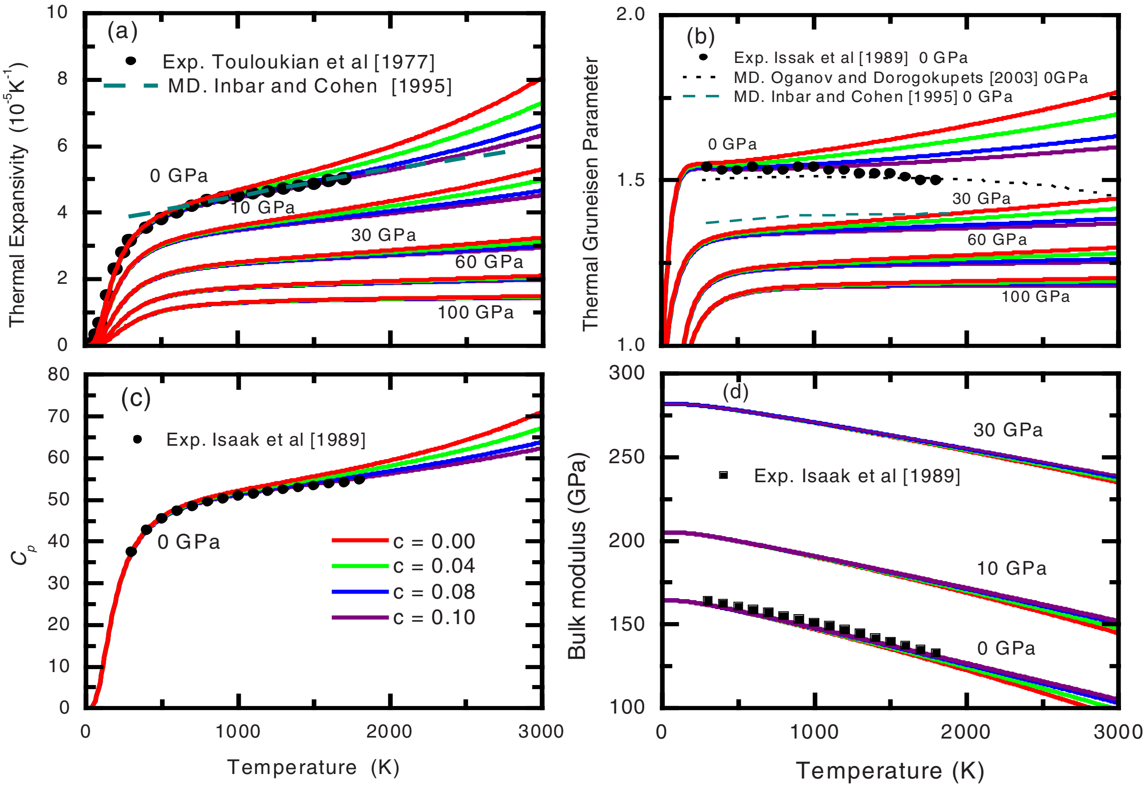

FIG. 2. (Color online) Thermodynamic properties of periclase after the anharmonic correction with various parameter c [see Eq. (5), $c=0$ corresponds to QHA]. (a) Thermal expansion α (Ref. 58), (b) thermal Grüneisen parameter γ_{th}, (c) isobaric specific heat C_p, and (d) adiabatic bulk modulus.

cies are in the range 1–3 k_BT. Correspondingly, their η_i's are in the range of 0.6–0.9. Therefore Ω^S always increases (if $c>0$) or decreases (if $c<0$) more quickly than Ω^F. The quantities with obvious temperature dependence in Eq. (10) are the product $\beta\alpha$ from Eq. (7) and η_i, both increasing rapidly with temperature at low temperatures and becoming weakly temperature dependent at high temperatures (see the Appendix, Sec. 1). Therefore we expect a noticeable nonlinearity in a_i^S at low temperatures and a nearly linear behavior at high temperatures. In fact, this behavior has been observed in the renormalized frequencies of diamond by Raman scattering experiments.[32,33]

IV. PREDICTIONS AND COMPARISONS WITH EXPERIMENTS

MgO (periclase) is an important mineral of Earth's lower mantle. Its thermodynamics properties above 2000 K are important to understanding the state of this region.[11] It is also a very important material in high pressure technology. Because of its large stability field, it lends itself as a high pressure and high temperature calibrant. Its equation of state at multi-Mbars and several thousands of Kelvin is often used as pressure standard in high temperature diamond anvil cell experiments.[34–37] α- and β-Mg_2SiO_4 (forsterite and wadsleyite) are important minerals of Earth's upper mantle and transition zone, respectively. The phase transformation between α- and β-Mg_2SiO_4 is responsible for the seismic wave velocity discontinuity at 410 km depth. Understanding the nature of this transformation is important for the interpretation of seismic data and for geodynamic modeling of mantle convection. Recently it was pointed out by Yu *et al.*[29] that the QHA is in the borderline limit of validity at the conditions in which this transformation takes place in the mantle, i.e., ~1700 K and 13.5 GPa. It is therefore desirable to reinvestigate this transformation including anharmonic effects in the free energy of these phases.

A. Anharmonic effects in periclase (MgO)

Periclase has been extensively investigated experimentally and theoretically. Its anharmonic behavior has also been previously discussed in the literature.[24,37,38] Several thermodynamics properties of MgO derived from anharmonic free energies computed using Eqs. (4)–(6) are shown in Fig. 2 for various values of c. As expected, at low temperatures, i.e., before quasiharmonic results ($c=0$) start deviating from experimental values, anharmonic effects are negligible for any c. Anharmonic effects also become less and less significant with increasing pressure. At $P=100$ GPa anharmonicity can be almost entirely overlooked up to 3000 K. This is consistent with conclusions by Inbar and Cohen[7] obtained using the VIB method. They have showed no significant differences between MD results and quasiharmonic results at such pressures and temperatures. In general, the correction becomes increasingly significant with increasing temperature. Our results show great improvement in the agreement with experimental thermodynamics data at high temperatures with increasing c. Comparison of predicted and measured thermal expansivity indicates that the optimum value of c is ~ 0.1. For this value of c, the predicted thermal expansivity differs from measured values by less than 1% up to the highest measured temperature, $T = 1700$ K at 0 GPa. γ_{th} and C_p are also very well predicted for this value. For $c = 0.1$, γ_{th} is nearly temperature independent, which is consistent with results by Inbar and Cohen[7] as well. The predicted γ_{th} is also in good agreement with experimental values.[39] For $c = 0.1$, C_p is also in excellent agreement with experimental data.[39] Therefore, anharmonic effects described by Eq. (5) are very close to the expected ones. The fact that this anharmonic calculation builds on quasiharmonic ones that are already in excellent agreement with experiments at low temperatures leads to better agreement with experiments at high temperatures than MD simulations alone. Those excellent agreements also ensure that the pressure scale of MgO (Ref. 37) based on current anharmonic correction has very precise thermal pressure.

From Fig. 2(d) one sees that anharmonic effects on the adiabatic bulk modulus, K_S, at 0 GPa begins to be noticeable above 1000 K. Predictions of K_S of minerals at relevant mantle conditions are extremely important. Table I shows the effect of anharmonicity on the properties displayed in Fig. 2, at some relevant conditions. The property most affected by anharmonicity is the thermal expansivity, α, followed by γ_{th} and C_P, with K_S being the least sensitive. At conditions of the uppermost lower mantle anharmonicity changes the quasiharmonic K_S by 0.8%. Anharmonicity decreases with increasing pressure and at core-mantle-boundary conditions the quasiharmonic predictions for K_S should be correct within −0.09%.

TABLE I. Thermodynamics properties at relevant mantle conditions before and after inclusion of the anharmonic free-energy contribution.

MgO at 2000 K and 23 GPa

C	α (10^{-5}/K)	γ	C_p (J mol^{-1} K^{-1})	K_S (GPa)
0	3.25	1.437	54.07	224.917
0.1	3.04	1.38	52.79	226.822
Change (%)	−6.5	−4.0	−2.4	0.8

MgO at 4000 K and 135 GPa

C	α (10^{-5}/K)	γ	C_p (J/mol K)	K_S (GPa)
0	1.31	1.202	52.769	598.19
0.1	1.268	1.178	52.025	597.64
Change (%)	−3.2	−2.2	−1.4	−0.09

Forsterite at 1700 K and 13.5 GPa

C	α (10^{-5}/K)	γ	C_p (J/mol K)	K_S (GPa)
0	2.862	1.078	180.549	164.267
−0.06	2.96	1.102	182.008	163.763
Change (%)	3.5	2.2	0.8	−0.3

Wadsleyite at 1700 K and 13.5 GPa

C	α (10^{-5}/K)	γ	C_p (J/mol K)	K_S (GPa)
0	2.674	1.173	180.77	202.105
0.08	2.564	1.141	178.85	203.01693
Change (%)	−4.1	−2.7	−1.0	0.45

B. Anharmonic effects on the forsterite→wadsleyite transition

Precise knowledge of the phase boundary between forsterite and wadsleyite is needed to constrain the thermal structure and mineralogy of the mantle, particularly of the upper mantle, transition zone, and the velocity discontinuity of the seismic wave at depth about 410 km. Given its importance, this transformation has been extensively investigated by both experiments and theory.[28,40–46] Quasiharmonic calculations of this phase boundary have consistently shown similar Clapeyron slopes (CS),[28,45,46] 2.5–2.7 MPa/K. These values are smaller than the values determined directly from high pressure and temperature crystallographic data[41,42] or from semiempirical thermodynamics calculations,[47] 3.6–4.0 MPa/K. Anharmonic effects have long been recognized in forsterite as well. Its heat capacity at constant volume, C_v, can exceed the Dulong-Petit limit between 1400 and 1800 K at 0 GPa.[48–51] It has also been recognized that the conditions at the 410 km discontinuity is at the borderline limit of validity of the QHA.[25,28] Therefore, anharmonicity could be the source of the discrepancy between quasiharmonic predictions and measured or semiempirical CSs. As far as we know, the effect of anharmonicity on phase boundary computations has not been discussed so far because of the difficulty in addressing anharmonic free energies. With the current approach we are in position to discuss this effect on phase transformations also. We find that anharmonic effects are quite different in forsterite and in wadsleyite. Actually they are opposite and this enhances anharmonic effects on the phase boundary. Before we discuss this effect we analyze anharmonicity in forsterite and wadsleyite separately.

1. Forsterite

The most consistent experimental thermodynamics data for forsterite is C_p. Measurements of other thermodynamics properties, such as thermal expansivity and C_v, by different groups differ significantly from each other. Therefore we use C_p to determine the anharmonic constant c. Figure 3(a) shows the anharmonic C_p computed for several values of c. At low temperatures, the QHA result ($c = 0$) is in good agreement with experimental values.[49,50,52] But with increasing temperature, the quasiharmonic C_p increases more slowly than the experimental values. This behavior is opposite to that in MgO, where the QHA overestimates C_p [see Fig. 2(c)]. It is apparent that the anharmonic free-energy contribution in forsterite requires a negative c. The root-mean-

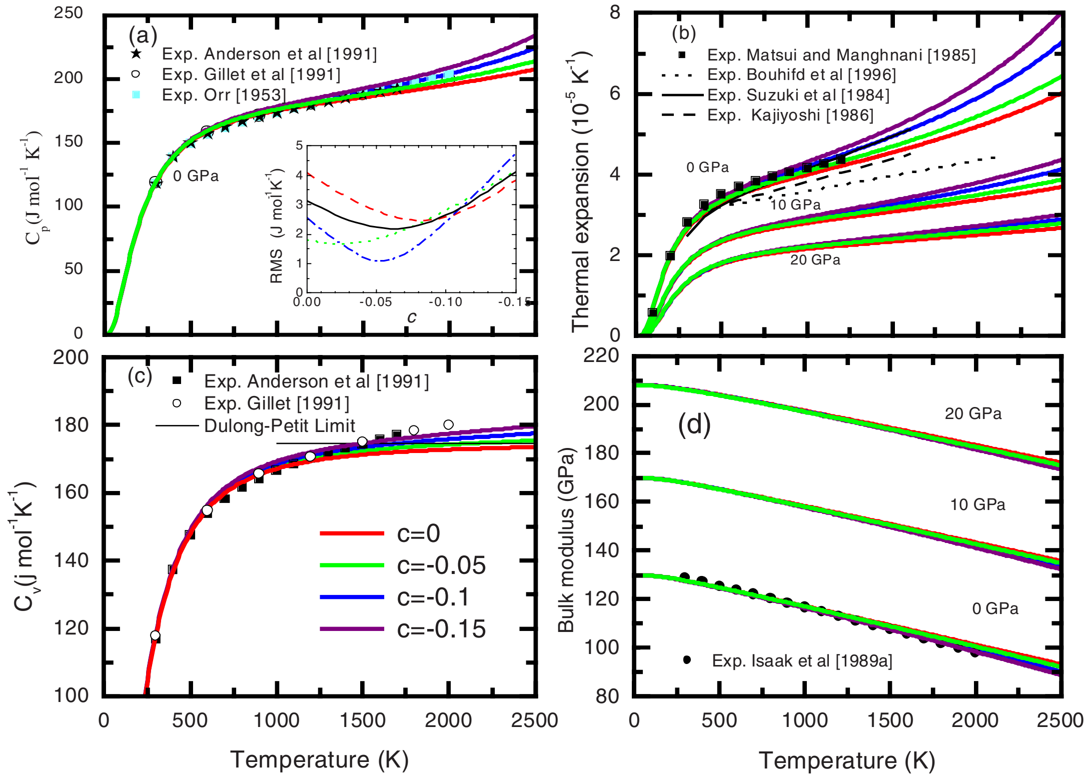

FIG. 3. (Color online) Thermodynamic properties of forsterite after the anharmonic correction with various parameter c. (a) Isobaric specific heat C_p at 0 GPa. The inset shows the RMS of the difference between our calculated and experimental C_p from Orr (Ref. 52) (dashed line), Anderson *et al.* (Ref. 49) (dotted line), Gillet *et al.* (Ref. 50) (dashed dotted line), and all above data (solid line). (b) Thermal expansion α, (c) specific heat at constant volume C_V at 0 GPa, and (d) adiabatic bulk modulus.

square (RMS) of the difference between the calculated and experimental C_p versus c should be a good indicator the best value of this constant. This RMS is shown in the inset in Fig. 3(a) versus c. The four curves in this inset represent comparisons with different experimental data sets. c should be between −0.085 and −0.055 based on comparisons with data by Orr[52] and Gillet *et al.*,[50] respectively. c is about −0.006 if we use simultaneously data from all three experimental groups.[49,50,52]

As discussed in Sec. II, c reflects the intrinsic temperature effect (anharmonicity) on phonon frequencies. $c>0$ ($c<0$) implies anharmonicity increases (decreases) the average phonon frequencies at fixed volume. $c<0$ in forsterite is consistent with Raman measurements by Gillet *et al.*,[50] who indicate that all a_i's for 21 Raman modes are negative. Since the product $\alpha\beta$ is approximately 3.2×10^{-5}/K at 600 K (see Fig. 1), $\eta_i \sim 1$, and $0.4<\gamma_i<2.1$, we obtain a_i^S in the range -0.2 to -0.9×10^{-5}/K. Considering that experiments were carried out at constant pressure and the approximations involved in the calculation of a_is, these are close to the measured values of -1 to -2×10^{-5}/K.[50] From this analysis [see Eqs. (7) and (10)] we expect the vibrational modes with smaller γ_is to have smaller absolute values of a_i. This behavior of a_is was indeed observed by Gillet *et al.*[50] at constant pressure. They found that the absolute value of a_i's involving tetrahedral Si-O bond stretching with smaller γ_is[25] are smaller than for other lattice modes.

Thermal expansion data for forsterite from different reports[51,53–55] are considerably different, especially at high temperatures [Fig. 3(b)]. Our prediction for thermal expansivity α using the optimum c determined from C_P, −0.06, agrees best with data by Matsui and Manghnan[55] and by Suzuki *et al.*[53] These data sets show that the QHA underestimates α at high temperatures. Consistently, the constant c derived from comparisons between predicted α and measurements from these experimental data sets are $c=-0.09$ (from Suzuki *et al.*[53]) −0.10 (from Matsui and Manghnani[55]) [see Fig. 3(b)] which are close to the value of −0.06 determined from C_p.

Anharmonic corrections with negative c raise C_v beyond the Dulong-Petit limit at high temperatures. The crossing of the Dulong-Petit limit is at ~2000 K (1800 K) for $c=-0.06$ (−0.085). The experimental crossing temperatures are 1300 K,[50] 1400 K,[48] and 1500 K.[49,51] It appears that differences in the crossing temperatures are mainly caused by the difference in thermal expansion data used to calculate C_v. C_P is the measured quantity and C_V is obtained from thermal expansivity α, γ_{th}, and C_P. The thermal expansivity data adopted in these experiments are smaller than ours. Therefore C_v in these experiments are larger than ours obtained with $c=-0.06$ and −0.085, even though our calculated C_p agrees well with the experimental data.

Table I displays the effect of anharmonicity on thermodynamics properties at relevant mantle conditions, i.e., 1700 K and 13.5 GPa. Unlike in MgO, anharmonicity increases the values of thermodynamics properties. As in MgO, the most affected property is thermal expansivity α followed by γ_{th}, C_P, and K_S.

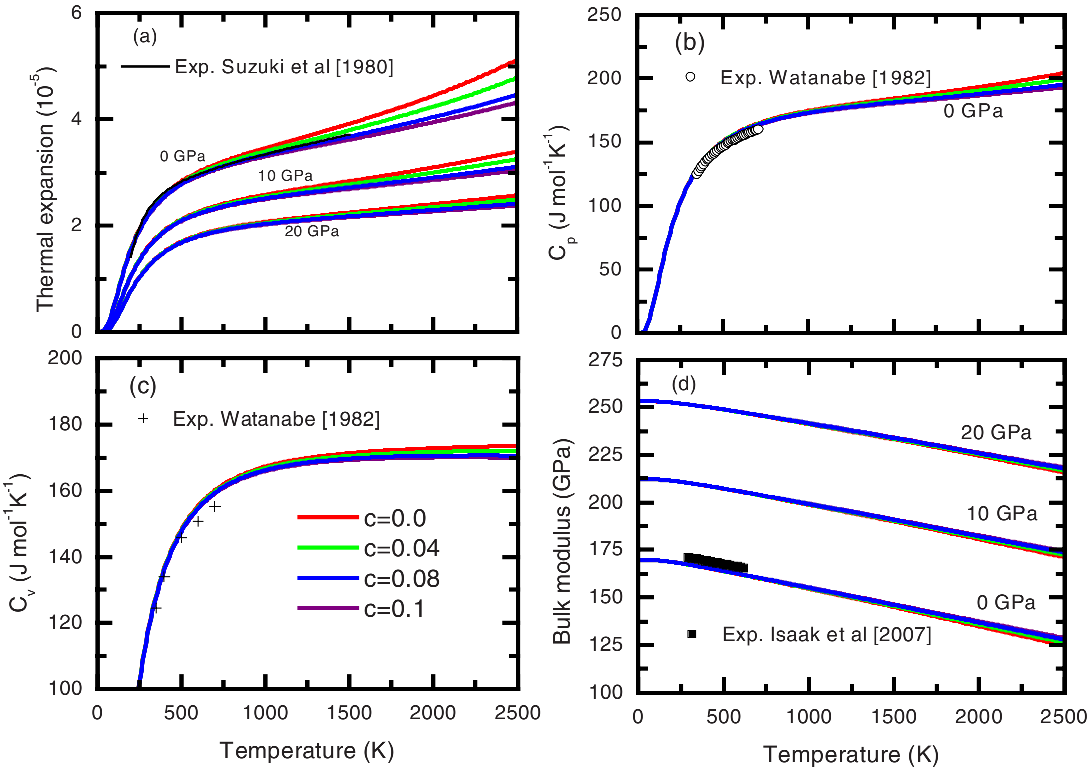

FIG. 4. (Color online) Thermodynamic properties of wadsleyite with the anharmonic correction. (a) Thermal expansion α. (b) Isobaric specific heat C_p (Ref. 59), (c) specific heat at constant volume C_V at 0 GPa (Ref. 59), and (d) adiabatic bulk modulus.

2. Wadsleyite

Figure 4 shows the variation in thermal expansivity α, C_p, and C_v, with c in wadsleyite. At low temperatures, all properties agree well with experimental data irrespective of c. At high temperatures, the nature of anharmonic effects is opposite to that in forsterite and similar to that in MgO. Therefore, $c>0$ in wadsleyite. Using α from Suzuki *et al.*[56] to determine c we get $c\sim 0.08$ [see Fig. 4(a)]. This value for the anharmonic constant c also improves the temperature dependence of C_p and C_v, even though it is difficult to determine a reasonable value of c from C_p and C_v due to the absence of sufficiently high temperature data at low pressure (wadsleyite is metastable at 0 GPa). However, it should be clear from all these thermodynamics properties of wadsleyite that its anharmonic constant c should be positive.

Table I also displays the effect of anharmonicity on thermodynamics properties of wadsleyite at relevant mantle conditions. Like in MgO, anharmonicity decreases the thermodynamics properties and, again, the most affected property is thermal expansivity α, followed by γ_{th}, C_P, and K_S.

3. The Clapeyron slope (CS)

The CS can be directly measured by high temperature and high pressure experiments ("direct measurements" henceforth), calculated from thermochemical data, or by combining vibrational spectroscopy data or calculated vibrational density of states in conjunction with the QHA ("calculations" henceforth). As shown in Table II, there are discrepancies between the CSs of the forsterite-wadsleyite transformation determined by direct measurements and by calculations. With the exception of a CS of 2.5 MPa/K determined by the quench method,[43] which has been argued to underestimate the slope in several phase transformation studies,[42] direct measurements of the phase boundary show steeper phase boundaries, e.g., CSs such as 3.5 MPa/K,[40] 3.6 MPa/K,[41] and 4.0 MPa/K.[42] By contrast, calculations show less steep slopes: 2.7 MPa/K from quasiharmonic calculations based on spectroscopic data,[45] 2.7 MPa/K from quasiharmonic calculations using interatomic potentials[46] and 2.7 MPa/K (2.5 MPa/K) using first-principles LDA (GGA) vibrational density of states.[28] Thermochemical calculations by Akaogi *et al.*[44] displaying the Dulong-Petit limit[57] also show a small value of the CS, 1.8 MPa/K. This consistency between quasiharmonic results seems to indicate that something in the QHA produces a smaller CS. Therefore the most likely cause

TABLE II. Measured and calculated Clapeyron slopes (MPa/K) of the thermodynamic boundary between forsterite and wadsleyite.

High pressure experiment	2.5	Katsura and Ito (Ref. 43)
	3.5	Suito (Ref. 40)
	3.6	Morishma *et al.* (Ref. 41)
	4.0	Katsura *et al.* (Ref. 42)
QHA calculation	1.8	Akaogi *et al.* (Ref. 44)
	2.7	Price *et al.* (Ref. 46); Chopelas (Ref. 45); Yu *et al.* (Ref. 28)
This study	3.6	Using $c=-0.06$ (forsterite) and 0.08 (wadsleyite)

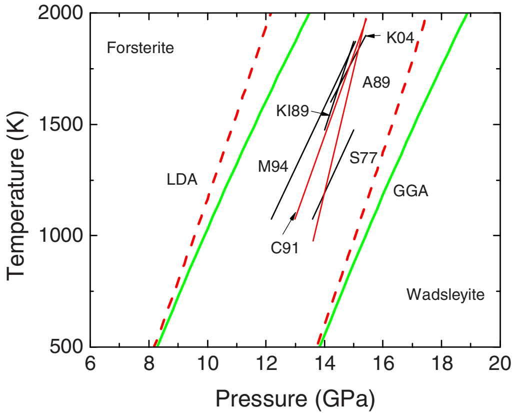

FIG. 5. (Color online) Phase boundary of the forsterite-to-wadsleyite transformation predicted by LDA (left) and GGA (right) quasiharmonic calculations (red dashed lines) and including anharmonic contributions to the free energy according to Eqs. (1)–(6) using $c_\alpha=-0.06$ and $c_\beta=0.08$ (green solid line). Other boundaries are from Katasura *et al.* (Ref. 42), Katasura and Ito (Ref. 43), Morishima *et al.* (Ref. 41) (M94), Suito (Ref. 40), Chopelas (Ref. 45) (C91), and Akaogi *et al.* (Ref. 44) (A89).

of the discrepancy between the slopes obtained by direct measurements and by calculations is anharmonic effects not include in the calculations.

As discussed above, anharmonic effects on forsterite and wadsleyite are completely different. The anharmonic constant in forsterite, c_α, is negative, while in wadsleyite, c_β, is positive. The anharmonic free energy is negative for forsterite and positive for wadsleyite (see Figs. 7 and 8). This leads to further anharmonic stabilization of forsterite at high temperatures, and to an increase in the CS. As shown in Fig. 5, the phase boundary changes substantially after anharmonic corrections. $c_\alpha=-0.06$ and $c_\beta=0.08$ change the transformation pressure by ~1 GPa at 1700 K and the CS increases from 2.7 MPa/K ($c_\alpha=c_\beta=0$) to 3.6 MPa/K. Figure 6 shows the calculated CS at 1700 K versus c_α for $c_\beta=0$ and $c_\beta=0.08$. The CS varies quite linearly with c_α and c_β and can be expressed as

$$\mathrm{CS}=\mathrm{CS}_0+7.82(c_\beta-c_\alpha), \tag{11}$$

where CS_0 is the slope given by a quasiharmonic calculation ($c_\alpha=0$). Therefore, anharmonicity may affect the CS particularly strongly when the CS is positive and the low pressure phase has a negative anharmonic constant c and the high pressure phase has positive c, or when the CS is negative and the low pressure phase has positive c and the high pressure phase has negative c. In the present case, the discrepancy between direct measurements and calculations of the CS are reconciled after inclusion of anharmonicity in the calculations (see Table II).

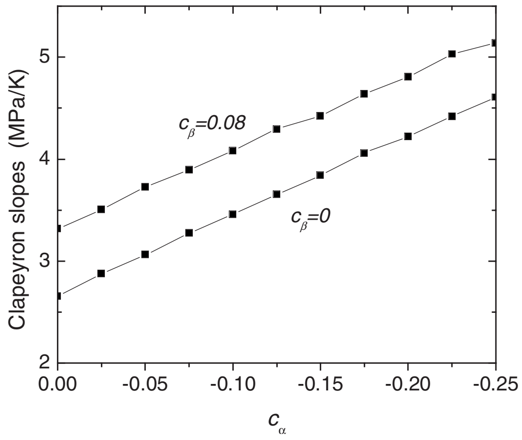

FIG. 6. The Clapeyron slope at 1700 K versus the anharmonic constants for forsterite (c_α) and wadsleyite (c_β). Their relations can be well described by Eq. (11).

V. ANHARMONIC CONTRIBUTION TO THE FREE ENERGY

Based on perturbation theory, the lowest order term of the anharmonic free energy contribution is proportional to T^2 at high temperatures.[15] Namely,

$$F_{\mathrm{anh}}=b(V)T^2. \tag{12}$$

The third- and higher-order correction terms may be necessary in some cases. For MgO, molecular dynamic simulations indicate that, although the third- and fourth-order terms become non-negligible at very high temperatures, the anharmonic free energy still can be well fitted by a quadratic function in T at high temperatures.[20] The anharmonic free-energy correction based on Eqs. (1)–(6) at various volumes is displayed in Fig. 7. Similarly to the correction extracted from MD simulations,[20] the present anharmonic free-energy correction in MgO can be well fitted by a quadratic function [Fig. 7(a)]. This is also true for forsterite and wadsleyite [Figs. 7(b) and 7(c)].

Equation (12) is valid only in the high temperature limit and produces unphysical results at low temperatures, such as a linear temperature dependence of C_V. The present *ansatz* produces an appropriate anharmonic free-energy correction at low temperatures as well. As shown in Fig. 8, the anharmonic free-energy contribution in MgO, and in α- and β-$\mathrm{Mg_2SiO_4}$ exhibit the typical T^4 behavior at low temperatures.[16] The present *ansatz* therefore reproduces the correct high and low temperature behaviors of the anharmonic contribution to the free energy and improves significantly the thermodynamics properties of these phases. This suggests that it must capture quite well the essence of anharmonic effects on the free energy of solids.

VI. CONCLUSION

We introduced a simple and effective semiempirical approach to compute anharmonic free energy in solids. The modified temperature-dependent frequencies to be used directly in the quasiharmonic free-energy formula are expressed implicitly through a dependence on the quasiharmonic (temperature dependent) volume. Only one constant, c, needs to be determined by comparing predicted properties with experimental data. $c=0$ reduces the free energy to the quasiharmonic formula. The approach produces the correct low and high temperature anharmonic behaviors. The pre-

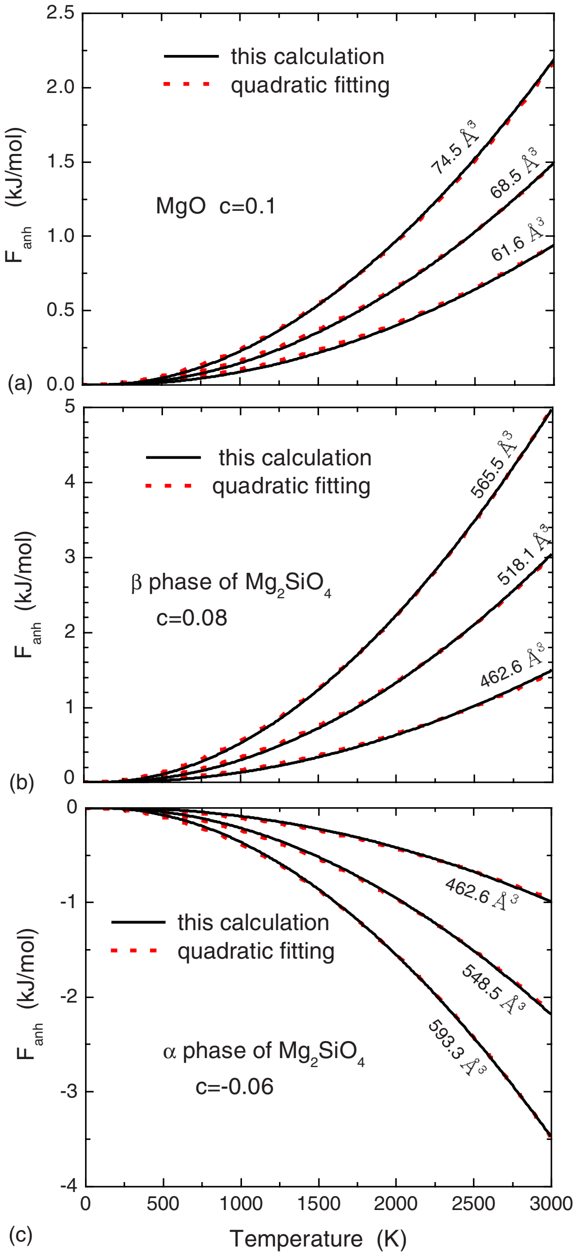

FIG. 7. (Color online) Temperature dependence of the anharmonic contribution to the free energy at various volumes. (a) Periclase, (b) wadsleyite (β phase of Mg_2SiO_4), (c) forsterite (α phase of Mg_2SiO_4). Red dotted lines are the fitting curve using quadratic function Eq. (12).

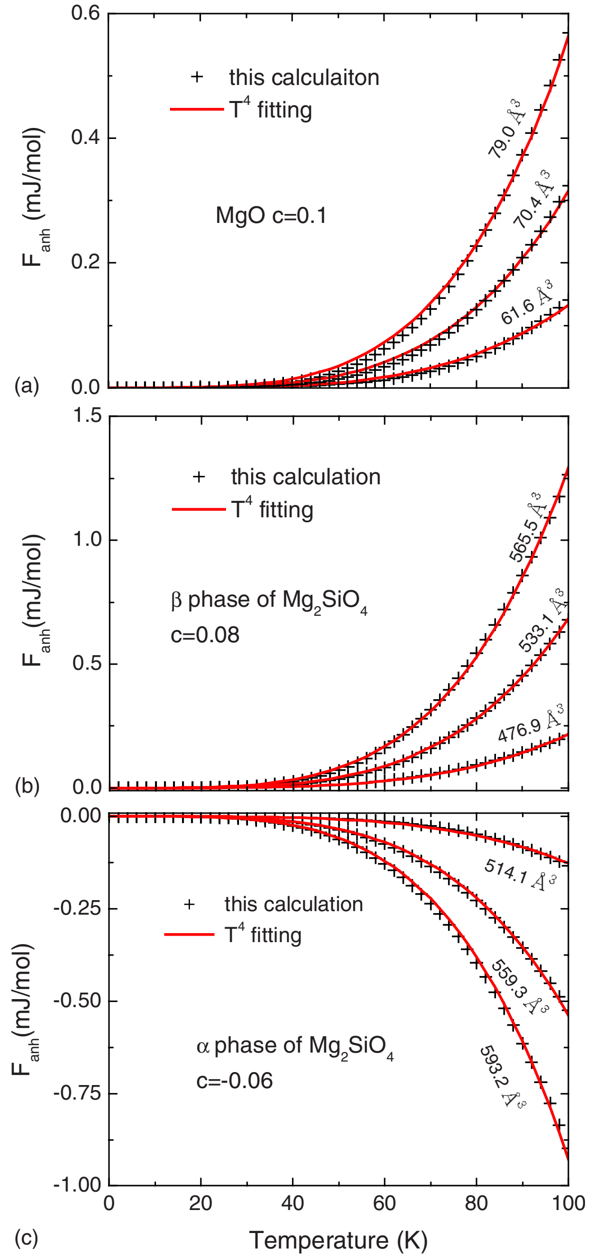

FIG. 8. (Color online) Low temperature anharmonic free energy at various volumes. (a) Periclase, (b) wadsleyite (β phase of Mg_2SiO_4), (c) forsterite (α phase of Mg_2SiO_4).

dicted thermodynamics properties of MgO are in excellent agreement with experimental data over a wide temperature range after the anharmonic free-energy correction is included. The thermodynamics properties of forsterite and wadsleyite also improve much with this correction.

According to our analysis, there are two clearly distinct types of anharmonic effects in crystals: those for which $c > 0$ and those for which $c < 0$. For cases with $c < 0$, such as forsterite, the QHA underestimates the thermodynamics properties. Experimentally C_v can exceed the Dulong-Petit limit in this case. In contrast, for cases with $c > 0$, such as periclase and wadsleyite, the QHA overestimates the thermodynamics properties and C_v is always below the Dulong-Petit limit.

Our results also confirm that anharmonic effects may play an important role in the Earth's upper mantle and transition zone. Most striking is the effect of anharmonicity on the thermodynamics phase boundary between forsterite and wadsleyite. The effect moves the phase boundary to higher pressures at higher temperatures and increases the Clapeyron slope of this transformation. The discrepancy between the measurements of this slope and those predicted by quasiharmonic calculations is reconciled after inclusion of anharmonic effects. At lower mantle conditions, anharmonic effects in MgO are noticeable in the uppermost part of the lower mantle, but decrease rapidly with increasing depth (pressure). For all the minerals investigated, anharmonic effects are most noticeable in the thermal expansivity, followed by the thermal Grüneisen parameter, constant pressure specific heat, and adiabatic and isothermal bulk moduli.

ACKNOWLEDGMENTS

Calculations were performed with the QUANTUM ESPRESSO package (http://www.pwscf.org). Work was supported by NSF/EAR Grants No. 0230319 and No. 0635990, and NSF/ITR Grant No. 0428774 (VLab). Z.W. thanks Yonggang Yu and Ningdong Huang for helpful discussions. R.M.W. acknowledges the Humboldt Foundation for support. She also thanks Bjoern Winkler and Goethe University for hospitality during the final stages of this work.

APPENDIX

1. Derivation of Eq. (7)

The temperature dependence of the phonon frequencies is usually expressed as

$$a_i = \left(\frac{\partial \ln \omega_i}{\partial T} \right)_V . \tag{A1}$$

Let a_i^F be the anharmonic parameter associated with the modified frequencies used in the free-energy formula

$$a_i^F = \left(\frac{\partial \ln \Omega_i^F}{\partial T} \right)_V , \tag{A2}$$

where

$$\Omega_{q,j}^F(V,T) = \omega(V') \tag{A3}$$

and

$$V' = V\left\{ 1 - c\frac{[V - V_0]}{V_0} \right\} . \tag{A4}$$

For short, we adopted $V=V(P,T)$ and $V_0=V(P,0)$ above. Then

$$a_i^F = \left(\frac{\partial \ln \omega_i}{\partial V'} \right)\left(\frac{\partial V'}{\partial T} \right)_V . \tag{A5}$$

But

$$\left(\frac{\partial \ln \omega_i}{\partial V'} \right) = -\frac{\gamma_i}{V'} \tag{A6a}$$

and

$$\left(\frac{\partial V'}{\partial T} \right)_V = c\left(\frac{V}{V_0} \right)^2 \left(\frac{\partial V_0}{\partial T} \right)_V . \tag{A6b}$$

Although V_0 is defined at $T=0$ K, it is a function of $P(V,T)$. Therefore,

$$\left(\frac{\partial V'}{\partial T} \right)_V = c\left(\frac{V}{V_0} \right)^2 \left(\frac{\partial V_0}{\partial P} \right)\left(\frac{\partial P}{\partial T} \right)_V . \tag{A7}$$

Recall that

$$\left(\frac{\partial P}{\partial T} \right)_V = \alpha K_T \tag{A8a}$$

and

$$\frac{1}{V_0}\left(\frac{\partial V_0}{\partial P} \right) = -\frac{1}{K_0} . \tag{A8b}$$

Therefore

$$\left(\frac{\partial V'}{\partial T} \right)_V = -c\alpha\frac{V^2}{V_0}\frac{K_T}{K_0} \tag{A9}$$

and

$$a_i^F = \alpha(V,T)\beta\gamma_i(V')c \tag{A10}$$

with

$$\beta = \frac{V^2}{V' V_0}\frac{K_T}{K_0} . \tag{A11}$$

The temperature dependences of α and $\alpha\beta$ are shown in Fig. 1 for MgO at 0 GPa with $c=0.1$. Below room temperature, β is close to 1 and the temperature behavior of a_i^F is mainly determined by α. However, at high temperatures β decreases with T and cancels the divergent temperature effect in α, leading to a small and linearly dependent temperature product $\alpha\beta$. This produces a small temperature dependence in a_i^F, since γ_is and c are quite small too (~ 1 and 10^{-1}–10^{-2}, respectively). In MgO, α- and β-Mg_2SiO_4, $\frac{\partial a_i^F}{\partial T} \approx 5\times 10^{-10}/K^2$, $-3\times 10^{-10}/K^2$, and $4\times 10^{-10}/K^2$, respectively, above 1000 K. This small value will be exploited in the next section.

2. Deviation of the relation between Ω^F and Ω^S

An approximate relationship between the renormalized frequencies to be used in the quasiharmonic entropy formula, Ω_i^S, and the modified frequencies to be used directly in the quasiharmonic free-energy formula, Ω_i^F, is obtained by writing

$$S_A = S_H(X^S) = \sum_i \left[-k_B \ln(1 - e^{-X_i^S}) + X_i^S k_B \frac{e^{-X_i^S}}{1 - e^{-X_i^S}} \right], \tag{A12}$$

$$S_A = -\left.\frac{\partial F_H}{\partial T}\right|_{X^F} = \sum_i \left[-k_B \ln(1 - e^{-X_i^F}) + X_i^F k_B \frac{e^{-X_i^F}}{1 - e^{-X_i^F}} - \hbar\frac{\partial \Omega_i^F}{\partial T}\frac{e^{-X_i^F}}{1 - e^{-X_i^F}} \right], \tag{A13}$$

where $X_i^S = \frac{\hbar\Omega_i^S}{k_B T}$ and $X_i^F = \frac{\hbar\Omega_i^F}{k_B T}$. The equivalence of corresponding terms under the summations can be used to derive a relationship between these frequencies. The last term in Eq. (A13) is related to the difference $\Delta X_i = X_i^F - X_i^S$ by

$$\left.\frac{\partial S_H}{\partial X}\right|_{X_i^S} \Delta X_i = \hbar \frac{\partial \Omega_i^F}{\partial T} \frac{e^{-x_i^F}}{1 - e^{-x_i^F}}. \tag{A14}$$

We also have

$$\frac{\partial S_H}{\partial X} = - k_B \frac{e^{-X}}{1 - e^{-X}} + k_B \frac{e^{-X}}{1 - e^{-X}} - X \cdot k_B \frac{e^{-X}}{(1 - e^{-X})^2}$$
$$= - X \cdot k_B \frac{e^{-X}}{(1 - e^{-X})^2}. \tag{A15}$$

Replacing

$$\left(\frac{\partial S_H}{\partial X}\right)_{x=x_i^S} = \left(\frac{\partial S_H}{\partial X}\right)_{x=x_i^F} - \left(\frac{\partial^2 S_H}{\partial X^2}\right)_{x=x_i^F} dX_i \tag{A16}$$

in Eq. (A14) we have

$$\left(\frac{\partial S_H}{\partial X}\right)_{x=x_i^F} \Delta X_i - \left(\frac{\partial^2 S_H}{\partial X^2}\right)_{x=x_i^F} \Delta X_i^2 = \hbar \frac{\partial \Omega_i^F}{\partial T} \frac{e^{-x_i^F}}{1 - e^{-x_i^F}}. \tag{A17}$$

The second term on the left-hand side (lhs) of Eq. (A17) is of second order in ΔX_i^F and will be neglected. Therefore

$$\left(\frac{\partial S_H}{\partial X}\right)_{x=x_i^F} \Delta X_i = \hbar \frac{\partial \Omega_i^F}{\partial T} \frac{e^{-x_i^F}}{1 - e^{-x_i^F}}. \tag{A18}$$

Using Eq. (A15) we have

$$X_i^S = X_i^F + \frac{\hbar}{k_B X_i^F}(1 - e^{-X_i^F}) \frac{\partial \Omega_i^F}{\partial T} \tag{A19}$$

or in terms of frequencies

$$\Omega_i^S = \Omega_i^F + \frac{k_B T^2}{\hbar}(1 - e^{-(\hbar\Omega_i^F/k_B T)}) \frac{\partial \ln \Omega_i^F}{\partial T}. \tag{A20}$$

A relationship between the anharmonic parameters a_i^S and a_i^F at high T, where the anharmonic parameters c are non-negligible can now be derived. From Eq. (A20) we have

$$\frac{d\Omega_i^S}{dT} = \frac{d\Omega_i^F}{dT} + \left[\frac{2k_B T}{\hbar}(1 - e^{-(h\Omega_i^F/k_B T)}) - e^{-(h\Omega_i^F/k_B T)} \Omega_i^F\right] \frac{\partial \ln \Omega_i^F}{\partial T} + \Delta, \tag{A21}$$

where

$$\Delta = \frac{k_B T^2}{\hbar}(1 - e^{-\hbar\Omega_i^F/k_B T}) \frac{\partial a_i^F}{\partial T}. \tag{A22}$$

Now we divide Eq. (A21) by Ω_i^S on the lhs and, since temperature effects on frequencies are relatively very small, we assume $\Omega_i^S \approx \Omega_i^F$ and divide by Ω_i^F on the right-hand side (rhs). The last term then is

$$\frac{\Delta}{\Omega_i^F} = \frac{k_B T}{\hbar \Omega_i^F}(1 - e^{-(h\Omega_i^F/k_B T)}) T \frac{\partial a_i^F}{\partial T}. \tag{A23}$$

This term is small compared to the others. For instance, from Eq. (A10) we have

$$\frac{\partial a_i^F}{\partial T} = \frac{\partial(\alpha\beta\gamma_i c)}{\partial T}. \tag{A24}$$

The product $\alpha\beta$ is linear in T and changes by $\sim 10^{-5}$/K each 3000 K at high T (see Fig. 1). Therefore

$$\frac{\partial a_i^F}{\partial T} \approx 3.3 \times 10^{-9} \gamma_i c / K^2. \tag{A25}$$

Besides $\frac{k_B T}{\hbar \Omega_i^F}(1 - e^{h\Omega_i^F/k_B T})$ is always less than 1.

$$\frac{k_B T}{\hbar \Omega_i^F}(1 - e^{-(h\Omega_i^F/k_B T)}) = \begin{cases} 0.43 & \text{when } \dfrac{k_B T}{\hbar \Omega_i^F} = 0.5 \\ 0.63 & \text{when } \dfrac{k_B T}{\hbar \Omega_i^F} = 1 \\ 0.79 & \text{when } \dfrac{k_B T}{\hbar \Omega_i^F} = 2. \end{cases}$$

In contrast, $a_i^F = \frac{\partial \ln \Omega_i^F}{\partial T} \approx 4.5 \times 10^{-5} \gamma c / K$ at high T. Therefore the term ignored, i.e., Eq. (A23), is small. For example, at 1500 K it is only about one tenth of a_i^F. Therefore,

$$a_i^S = \frac{\partial \ln \Omega_i^S}{\partial T} \sim (1 + \eta_i) \frac{\partial \ln \Omega_i^F}{\partial T} = (1 + \eta_i) a_i^F, \tag{A26}$$

where

$$\eta_i = \frac{2k_B T}{\hbar \Omega_i^F} - \left(1 + \frac{2k_B T}{\hbar \Omega_i^F}\right) e^{[-(\hbar\Omega_i^F/k_B T)]}. \tag{A27}$$

---

*Corresponding author. zqwu00@gmail.com

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[2] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[3] B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, Science **286**, 1705 (1999).

[4] P. Carrier, R. Wentzcovitch, and J. Tsuchiya, Phys. Rev. B **76**, 064116 (2007).

[5] M. Matsui, G. D. Price, and A. Patel, Geophys. Res. Lett. **21**, 1659 (1994).

[6] S. M. Foiles, Phys. Rev. B **49**, 14930 (1994).

[7] I. Inbar and R. E. Cohen, Geophys. Res. Lett. **22**, 1533 (1995).

[8] B. Bertheville, H. Bill, and H. Hagemann, J. Phys.: Condens.

Matter **10**, 2155 (1998).

[9] G. Kern, G. Kresse, and J. Hafner, Phys. Rev. B **59**, 8551 (1999).

[10] B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, Phys. Rev. B **61**, 8793 (2000).

[11] R. M. Wentzcovitch, B. B. Karki, M. Cococcioni, and S. de Gironcoli, Phys. Rev. Lett. **92**, 018501 (2004).

[12] T. Sun, P. B. Allen, D. G. Stahnke, S. D. Jacobsen, and C. C. Homes, Phys. Rev. B **77**, 134303 (2008).

[13] M. Lazzeri, M. Calandra, and F. Mauri, Phys. Rev. B **68**, 220509(R) (2003).

[14] N. Bonini, M. Lazzeri, N. Marzari, and F. Mauri, Phys. Rev. Lett. **99**, 176802 (2007).

[15] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Course of Theoretical Physics Vol. 5 (Butterworth & Heinemann, Oxford, 1980), Pt. I.

[16] D. C. Wallace, *Thermodynamics of Crystal* (Wiley, New York, 1972).

[17] J. C. K. Hui and P. B. Allen, J. Phys. C **8**, 2923 (1975).

[18] P. Gillet, J. Matas, F. Guyot, and Y. Ricard, in *Thermodynamic Properties of Minerals at High Pressures and Temperatures from Vibrational Spectroscopic Data, Microscopic Properties and Processes in Minerals*, edited by K. Wright and R. Catlow, NATO Advanced Studies Institute, Series C: Mathematical and Physical Sciences (Kluwer, Dordrecht, 1999), Vol. 543, pp. 71–92.

[19] W. B. Holzapfel, M. Hartwig, and W. Sievers, J. Phys. Chem. Ref. Data **30**, 515 (2001).

[20] A. R. Oganov and P. I. Dorogokupets, J. Phys.: Condens. Matter **16**, 1351 (2004).

[21] T. H. K. Barron, *Proceedings of the International Conference on Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1963), pp. 247–253.

[22] J. L. Feldman, G. K. Horton, and J. B. Lurie, J. Phys. Chem. Solids **26**, 1507 (1965).

[23] W. C. Overton, Jr., J. Phys. Chem. Solids **29**, 711 (1968).

[24] A. R. Oganov and P. I. Dorogokupets, Phys. Rev. B **67**, 224110 (2003).

[25] L. Li, R. M. Wentzcovitch, D. J. Weidner, and C. R. S. Da Silva, J. Geophys. Res. **112**, B05206 (2007).

[26] Z. Wu and R. M. Wentzcovitch, J. Geophys. Res. **112**, B12202 (2007).

[27] Y. G. Yu and R. M. Wentzcovitch, J. Geophys. Res. **111**, B12202 (2006).

[28] Y. G. Yu, Z. Wu, and R. M. Wentzcovitch, Earth Planet. Sci. Lett. **273**, 115 (2008).

[29] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[30] R. M. Wentzcovitch, J. L. Martins, and G. D. Price, Phys. Rev. Lett. **70**, 3947 (1993).

[31] H. Falk, Am. J. Phys. **38**, 858 (1970).

[32] E. S. Zouboulis and M. Grimsditch, Phys. Rev. B **43**, 12490 (1991).

[33] E. Anastassakis, H. C. Hwang, and C. H. Perry, Phys. Rev. B **4**, 2493 (1971).

[34] M. S. Vassiliou and T. J. Ahrens, Geophys. Res. Lett. **8**, 729 (1981).

[35] S. Speziale, C. Zha, T. S. Duffy, R. J. Hemley, and H. K. Mao, J. Geophys. Res. **106**, 515 (2001).

[36] P. I. Dorogokupets and A. R. Oganov, Phys. Rev. B **75**, 024115 (2007).

[37] Z. Wu *et al.*, J. Geophys. Res. **113**, B06204 (2008).

[38] F. D. Stacey and D. G. Isaak, J. Geophys. Res. **108**, 2440 (2003).

[39] D. G. Isaak, O. L. Anderson, and T. Goto, Phys. Chem. Miner. **16**, 704 (1989).

[40] K. Suito, *High-Pressure Research—Applications to Geophysics* (Academic, New York, 1977), pp. 255–266.

[41] H. Morishima *et al.*, Science **265**, 1202 (1994).

[42] T. Katsura *et al.*, J. Geophys. Res. **109**, B02209 (2004).

[43] T. Katsura and E. Ito, J. Geophys. Res. **94**, 15663 (1989).

[44] M. Akaogi, E. Ito, and A. Navrotsky, J. Geophys. Res. **94**, 15671 (1989).

[45] A. Chopelas, J. Geophys. Res. **96**, 11817 (1991).

[46] G. D. Price, S. C. Parker, and M. Leslie, Phys. Chem. Miner. **15**, 181 (1987).

[47] L. Stixrude and C. Lithgow-Bertelloni, J. Geophys. Res. **110**, B03204 (2005).

[48] H. Cynn, J. D. Carnes, and O. L. Anderson, J. Phys. Chem. Solids **57**, 1593 (1996).

[49] O. L. Anderson, D. L. Isaak, and H. Oda, J. Geophys. Res. **96**, 18037 (1991).

[50] P. Gillet, P. Richet, F. Guyot, and G. Fiquet, J. Geophys. Res. **96**, 11805 (1991).

[51] M. A. Bouhifd, D. Andrault, G. Fiquet, and P. Richet, Geophys. Res. Lett. **23**, 1143 (1996).

[52] R. L. Orr, J. Am. Chem. Soc. **75**, 528 (1953).

[53] I. Suzuki, H. Takei, and O. L. Anderson, in *Proceedings of the 8th International Thermal Expansion Symposium, Gaithersburg, 1981*, edited by Thomas A. Hahn (Plenum, New York, 1984), pp. 79–88.

[54] K. Kajiyoshi, M.S. thesis, Okayama University, Okayama, Japan, 1986.

[55] T. Matsui and M. H. Manghnani, Phys. Chem. Miner. **12**, 201 (1985).

[56] I. Suzuki, E. Ohtani, and M. Kumazawa, J. Phys. Earth **28**, 273 (1980).

[57] R. G. Berman and T. H. Brown, Contrib. Mineral. Petrol. **89**, 168 (1985).

[58] Y. S. Touloukian, R. K. Kirdby, E. E. Taylor, and T. Y. R. Lee, *Thermophysical Properties of Matter* (Plenum, New York, 1977), Vol. 13.

[59] H. Watanabe, *High-Pressure Research in Geophysics* (Center for Academic Publications, Tokyo, 1982), p. 441.