

***Ab initio* calculation of the thermal properties of Cu: Performance of the LDA and GGA**

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The thermal properties of bulk copper are investigated by performing *ab initio* density functional theory and density functional perturbation theory calculations and using the quasiharmonic approximation for the free energy. Using both the local density approximation (LDA) and generalized gradient approximation (GGA) for the exchange-correlation potential, we compute the temperature dependence of the lattice constant, coefficient of thermal expansion, bulk modulus, pressure derivative of the bulk modulus, phonon frequencies, Grüneisen parameters, and the electronic and phonon contributions to the specific heats at constant volume and constant pressure. We obtain answers in closer agreement with experiment than those obtained from more approximate earlier treatments. The LDA and GGA errors in computing anharmonic quantities are significantly smaller than those in harmonic quantities. We argue that this should be a general feature and also argue that LDA and GGA errors should increase with temperature.

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I. INTRODUCTION

In any study of the properties of metals, it is obviously crucial to include the effects of temperature. Thermal expansion results from the anharmonicity of the interatomic potentials, and this change in the lattice constant upon heating a metal is accompanied by changes in the elastic and vibrational properties. Experimental measurements of the temperature dependence of the lattice constant, elastic moduli, phonon frequencies, Grüneisen parameters, etc., of most elemental metals have been available for a few decades now. However, it has become possible to calculate these thermal properties from first principles only in the last few years.

There are two main issues to be resolved when trying to compute the thermal properties of metals: one is how to describe the interatomic interactions accurately, and the other is how to incorporate the effects of temperature into this description.

To date, most computations of the thermal properties of metals have made use of parametrized interatomic potentials. This necessarily introduces errors, even when the potentials are semiempirical and include both theoretical and experimental values in the fitting database. Self-consistent density functional theory (DFT) calculations provide the most accurate way of computing interatomic interactions from first principles. Using the DFT prescriptions to obtain the energies as a function of nuclear coordinates avoids the errors introduced by assuming parametrized forms of interatomic potentials.

As for computing the effects of temperature, one possible approach is to perform molecular dynamics simulations at finite temperatures. This approach has, for example, been combined with empirical and semiempirical potentials to calculate the thermal properties of metals. In principle, this approach can be extended by performing *ab initio* molecular dynamics calculations at finite temperatures for large unit

cells containing many metal atoms. However, the amount of computational effort required in order to obtain reliable thermodynamic averages makes this difficult, especially for the noble metals and transition metals, which contain tightly bound valence electrons. Also, since such simulations treat the ionic degrees of freedom classically, the results are not valid at very low temperatures, when zero-point effects are important.

An alternative approach is to compute the vibrational free energy using the quasiharmonic approximation, in which anharmonic effects are included via the volume dependence of phonon frequencies, which can be determined by performing *ab initio* calculations. Here too, in order to perform reliable averages, it is necessary to compute the frequencies for many wave vectors in the Brillouin zone (BZ), which is computationally expensive, especially if the phonon frequencies are calculated using the “frozen-phonon” method. The development of density functional perturbation theory¹ (DFPT) has considerably reduced the computational cost of obtaining phonon frequencies throughout the BZ, since unlike the frozen-phonon method, this technique does not require using large supercells to access wave vectors away from the zone center.

Thus combining *ab initio* DFPT calculations with a quasiharmonic treatment of the anharmonicity of vibrations currently offers us the most reliable yet practicable approach towards calculating averaged thermal properties, at least up to temperatures not too close to the melting point. In recent years, this combined approach has been shown to be quite successful in predicting the bulk thermal properties of the simple metals Al, Li, and Na,² and the noble metal Ag.³

However, there remains one important issue that has to be decided when performing *ab initio* calculations: how to describe the exchange and correlation effects in the electron-electron interactions. The exact form of the exchange-correlation functional is not known, and one has to use

various approximate schemes; the most widely used ones being the local density approximation (LDA) and various versions of generalized gradient approximations (GGA's). The GGA's are intended to be an improvement on the conventional LDA and do indeed perform better in certain situations, such as transition states in chemical reactions or systems containing "weak" bonds. Unfortunately, however, the GGA's do not always give answers that are in better agreement with experiment.

Improving the treatment of exchange and correlation effects is the holy grail in the field of electronic structure calculations, and as an aid towards achieving this goal, it is desirable to have a clear picture of the comparative merits of the LDA and GGA in various situations. It has been known for a long time now that the LDA tends to "overbind," giving lattice constants that are too small and bulk moduli, phonon frequencies, and cohesive energies that are too large. The GGA's seem to overcorrect these errors, giving lattice constants that are too large. A recent study⁴ showed that this overcorrection is manifested also in the harmonic properties: the GGA gives bulk moduli and phonon frequencies that are systematically lower than the experimental ones. We are not aware of any detailed studies comparing the performance of the LDA and GGA in describing anharmonic effects, which manifest themselves in the temperature dependence of the lattice constant, elastic and vibrational properties, and specific heat capacities, and in the values of anharmonic quantities such as the Grüneisen parameters.

To this end, in this paper, we have performed *ab initio* calculations to study the thermal properties of bulk copper, using both the LDA and GGA. We have computed the temperature dependence of the lattice constant, the coefficient of thermal expansion, the isothermal bulk modulus, the phonon frequencies, the individual and overall Grüneisen parameters, and the specific heat capacities at constant volume and constant pressure.

II. AB INITIO CALCULATIONS

The *ab initio* calculations were performed using the PWSCF and PHONON codes.⁵ Total energies were computed using DFT, and phonon frequencies using DFPT. The interaction between the ions and valence electrons was described using an ultrasoft pseudopotential.⁶ A plane-wave basis set with a cutoff of 30 Ry was used; a cutoff of 300 Ry was used in the expansion of the augmentation charges necessitated by the use of the ultrasoft (non-norm-conserving) pseudopotential. Brillouin-zone integrations were performed using 60 \mathbf{k} points in the irreducible part of the BZ. Phonon dynamical matrices were computed *ab initio* for a $4 \times 4 \times 4$ \mathbf{q} -point mesh; Fourier interpolation was then used to obtain the dynamical matrices on a $24 \times 24 \times 24$ \mathbf{q} -point mesh. This latter set was used to evaluate all quantities that involve an integration over phonon wave vectors \mathbf{q} .

In order to deal with the possible convergence problems for metals, a smearing technique was employed using the Methfessel-Paxton (MP) scheme,⁷ with the smearing parameter σ set equal to 0.05 Ry. However, when evaluating the electronic contribution to the specific heat capacity (as ex-

plained below) we instead used a Fermi-Dirac (FD) smearing, with the electronic levels occupied according to the FD distribution appropriate to the temperature of interest T . (Incidentally, with this latter scheme, we did not face convergence problems even at low values of T .)

When using the LDA, we used the parametrization by Perdew and Zunger of the results of Ceperley and Alder.⁸ For the GGA, we used the Perdew-Burke-Ernzerhof form;⁹ this choice was made in part because it is easier to implement in the DFPT calculations and because it gives a good description of the linear response of the uniform electron gas.

To summarize, the following were obtained from DFT and DFPT calculations: (i) Total energies at a range of lattice constants, using (a) MP smearing and (b) FD smearing, for a range of temperatures between 1 and 1400 K. (ii) For each lattice constant, the dynamical matrices (and thus phonon frequencies) for the $4 \times 4 \times 4$ set of \mathbf{q} points, using MP smearing; Fourier interpolation was then used to obtain the dynamical matrices on the $24 \times 24 \times 24$ set of \mathbf{q} points. (It was verified that replacing the MP smearing by the FD smearing did not make an appreciable difference to the phonon frequencies: i.e., the latter are not sensitive to the electronic temperature.) All of the above quantities were computed using both the LDA and GGA. This set of results was then used to calculate the thermal behavior, as described below.

III. RESULTS AND ANALYSIS

The static results for lattice constant a_0 , the bulk modulus B_0 , and the pressure derivative of the bulk modulus B' are obtained by fitting the results for the static total energies (using MP smearing) versus lattice constant to the fourth-order Birch-Murnaghan equation of state.¹⁰ Using the LDA, we obtain $a_0 = 6.71$ bohrs, $B_0 = 1.72$ Mbar, and $B' = 5.0$. The corresponding results with the GGA are $a_0 = 6.94$ bohrs, $B_0 = 1.28$ Mbar, and $B' = 5.11$. As expected, the experimental values for the lattice constant ($a_0 = 6.82$ bohrs) (Ref. 11) and bulk modulus (1.37 Mbar) (Ref. 12) lie sandwiched between the LDA and GGA values; it should, however, be noted that the experimental values are at room temperature, and the calculated values listed above do not yet include the effects of temperature. For B' , there does not seem to be a consensus on the experimental value, with several values reported in the literature. Listed in chronological order, these are 3.91,¹³ 5.3,¹⁴ 4.8,¹⁵ 4.1,¹⁶ 5.59,¹⁷ and 5.44.¹⁸

To study the effects of changing temperature, one has to look at the free energy, incorporating the effects of thermal vibrations (phonons). The free energy at temperature T and lattice constant a is given, within the quasiharmonic approximation, by

$$F(a, T) = E_{\text{stat}}(a) + k_B T \sum_{\mathbf{q}\lambda} \ln \left\{ 2 \sinh \left(\frac{\hbar \omega_{\mathbf{q}\lambda}(a)}{2k_B T} \right) \right\}. \quad (1)$$

Here, the first term on the right-hand side is the static energy $E_{\text{stat}}(a)$, and the second term is the vibrational free energy. The sum is over all three phonon branches λ and over all

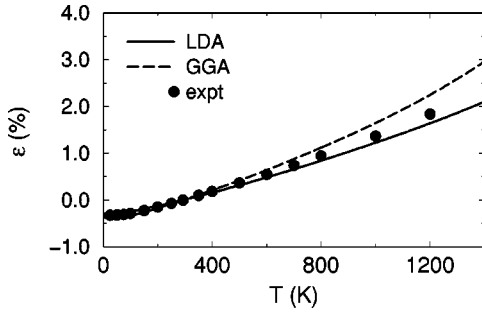


FIG. 1. Linear thermal expansion ϵ as a function of temperature, referred to a reference temperature T_c of 298.15 K. The experimental values are from Ref. 19. It is seen that both the LDA (solid line) and GGA (dashed line) results are close to the experimental values.

wave vectors \mathbf{q} in the BZ (we will use the $24 \times 24 \times 24$ \mathbf{q} mesh in evaluating this), \hbar is Planck's constant, k_B is Boltzmann's constant, and $\omega_{\mathbf{q}\lambda}(a)$ is the frequency of the phonon with wave vector \mathbf{q} and polarization λ , evaluated at lattice constant a .

The lattice constant at temperature T , $a_0(T)$, is obtained by minimizing $F(a, T)$ with respect to a . The linear expansion $\epsilon(T)$ is then given by

$$\epsilon(T) = \frac{a_0(T) - a_0(T_c)}{a_0(T_c)}, \quad (2)$$

where T_c is the reference temperature of 298.15 K.

Figure 1 shows the results for $\epsilon(T)$ (expressed as a percentage) using both the LDA and GGA, compared to the experimental value.¹⁹ It is seen that the agreement with experiment is quite good, though the LDA slightly underestimates the expansion and the GGA slightly overestimates it. This becomes more obvious upon differentiating the results for $a_0(T)$ to obtain the coefficient of linear expansion:

$$\alpha(T) = \frac{1}{a_0(T_c)} \left(\frac{da_0(T)}{dT} \right). \quad (3)$$

[Note that this definition of $\alpha(T)$ is the one used for experimental data. When using $\alpha(T)$ in thermodynamic relations, $a_0(T_c)$ should be replaced by $a_0(T)$ in the right-hand side of the above equation.] Figure 2 compares the calculated and

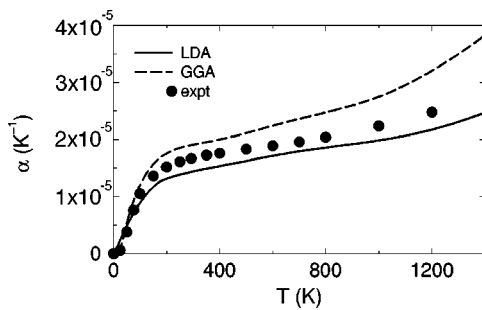


FIG. 2. Coefficient of linear thermal expansion α as a function of temperature. Both the LDA and GGA values are reasonably close to the experimental values; however, the LDA underestimates and the GGA overestimates the thermal expansion. Experimental values are from Ref. 19.

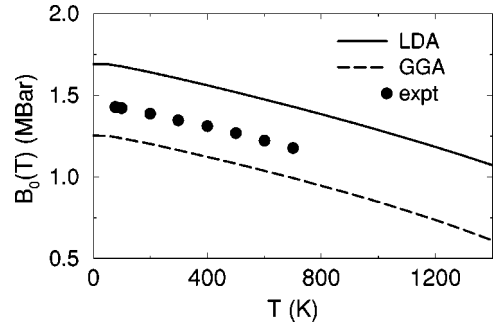


FIG. 3. Variation with temperature of the bulk modulus B_0 . At all temperatures, the LDA (solid line) overestimates B_0 and the GGA (dashed line) underestimates it; however, $\partial B_0 / \partial T$ is approximately the same for the LDA, GGA, and experimental values. The experimental values are from Ref. 21.

experimental values¹⁹ for $\alpha(T)$ up to a temperature of 1400 K (the experimental value for the bulk melting temperature is 1357 K). Once again, it is clear that the experimental values lie sandwiched between the LDA and GGA values, though they lie somewhat closer to the LDA values, especially at high temperature. However, it should be pointed out that the calculated values may be inaccurate at very high temperatures for two reasons: (i) The use of the quasiharmonic approximation may not be justified at temperatures just below the melting point, as this is expected to be a region of high anharmonicity. (ii) A part of the experimentally measured thermal expansion at high temperatures results from the formation of vacancies; this effect is not included in our calculations, where we assume that the crystal remains defect free at all temperatures.

By fitting the results for the free energy from Eq. (1) to the fourth-order Birch-Murnaghan equation of state,¹⁰ we also obtain the variation in temperature of the bulk modulus B_0 and the pressure derivative of the bulk modulus B' . We find that the quality of the fit is noticeably better with the fourth-order equation of state than with the Murnaghan equation of state²⁰ or with the third-order Birch-Murnaghan equation, especially at higher temperatures. The results for $B_0(T)$ are plotted in Fig. 3, from which it can be seen that though, at all temperatures, the absolute value of $B_0(T)$ is overestimated by the LDA and underestimated by the GGA, the rate of change of B_0 with temperature is approximately the same for both, and moreover, this rate agrees well with that measured experimentally.²¹ Figure 4 shows the results for $B'(T)$; it can be seen that B' depends noticeably on the temperature. (Incidentally this temperature dependence is considerably underestimated if one uses the Murnaghan equation or the third-order Birch-Murnaghan equation.) At 300 K, the LDA and GGA values for B' are 5.21 and 5.40, respectively, compared to the static values of 5.00 and 5.11. These values agree well with some of the room-temperature experimental values cited above,¹³⁻¹⁸ though there is a considerable scatter in the experimentally reported values.

Since we know how the phonon frequencies vary with a_0 and how a_0 varies with T , it is now a simple matter to get the phonon frequencies at any desired temperature. In Fig. 5, the calculated and measured²² phonon frequencies, at a tempera-

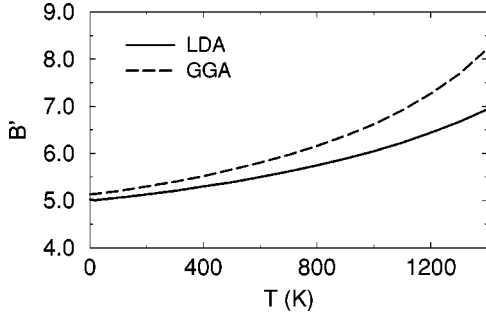


FIG. 4. Variation with temperature of the pressure derivative of the bulk modulus B' . The solid line is the LDA result, and the dashed line is the GGA result.

ture $T = 80$ K, are plotted along several high-symmetry directions in the Brillouin zone. At this temperature, the LDA gives $a_0 = 6.73$ bohrs and the GGA gives $a_0 = 6.96$ bohrs (since the temperature is relatively low, there is not an appreciable change from the static values). Yet again, it can be seen that the experimental values lie in between the LDA and GGA values. The overestimation (underestimation) of the frequencies by the LDA (GGA) can be traced back to the underestimation (overestimation) of the lattice constant. In fact, if the phonon frequencies are computed at the *experimental* lattice constant, the situation is reversed, and the GGA frequencies are *higher* and the LDA frequencies *lower* than experiment, though the latter are closer to the experimental values than the former.

We can also compute the temperature dependence of the specific heat capacities at constant volume and constant pressure, as described below. The specific heat at constant volume has two contributions: one from the phonons and the other from the electrons. The former is given by

$$C_V^{\text{ph}}(T) = \sum_{\mathbf{q}\lambda} C_v(\mathbf{q}\lambda) \\ = k_B \sum_{\mathbf{q}\lambda} \left(\frac{\hbar \omega_{\mathbf{q}\lambda}(a_0(T))}{2k_B T} \right)^2 \sinh^{-2} \left(\frac{\hbar \omega_{\mathbf{q}\lambda}(a_0(T))}{2k_B T} \right). \quad (4)$$

The electronic contribution to the specific heat, $C_V^{\text{el}}(T)$, is obtained from the self-consistent DFT calculations using FD

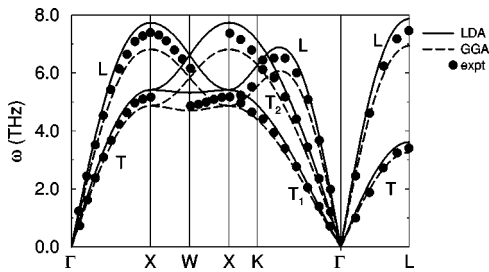


FIG. 5. Phonon dispersion along high-symmetry directions in the BZ, at 80 K. The solid and dashed lines are the results obtained using the LDA and GGA, respectively, and the solid circles are the experimental values from Ref. 22. “L” and “T” denote the longitudinal and transverse branches, respectively.

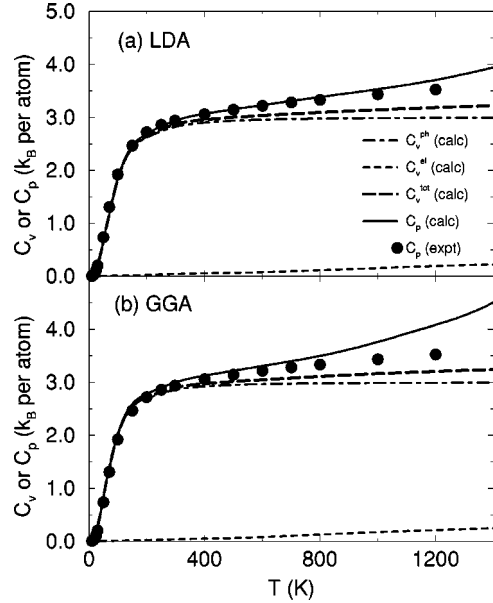


FIG. 6. Calculated values of C_p and C_v , in units of k_B per atom, obtained using the (a) LDA and (b) GGA. The dot-dashed lines show C_V^{ph} , the thin dashed lines show C_V^{el} , and the thick dashed lines show their sum C_V^{tot} . The solid lines show the calculated values for C_p , obtained from C_V^{tot} by using Eq. (5). The dots show the experimental results for C_p , as given in Ref. 19.

smearing corresponding to a temperature T , by computing the derivative with respect to the smearing temperature T of the electronic entropy, evaluated at the corresponding lattice constant $a_0(T)$. The total specific heat at constant volume is then $C_V^{\text{tot}}(T) = C_V^{\text{ph}}(T) + C_V^{\text{el}}(T)$.

C_p , the specific heat at constant pressure, can then be computed by using the relation

$$C_p(T) = C_V^{\text{tot}}(T) + \frac{9}{4} \alpha^2(T) B_0(T) a_0(T) T. \quad (5)$$

Figures 6(a) and 6(b) show the results thus obtained for $C_V^{\text{ph}}(T)$, $C_V^{\text{el}}(T)$, $C_V^{\text{tot}}(T)$, and $C_p(T)$, computed using the LDA and GGA, respectively. As expected, the electronic contribution to the specific heat, $C_V^{\text{el}}(T)$, is much smaller than the phonon contribution $C_V^{\text{ph}}(T)$, though not negligible. The experimental values for $C_p(T)$ (Ref. 19) are also plotted. It is seen that for both the LDA and GGA the agreement with experiment is excellent up to about 600 K. Above this temperature, the agreement remains very good for the LDA, but is poorer for the GGA. Note that at these high temperatures, $C_V^{\text{ph}}(T)$ has reached its saturation value of $3k_B$ per atom, and the LDA and GGA values for $C_V^{\text{ph}}(T)$ are therefore identical. For the difference between C_p and C_V , the error due to the underestimation (overestimation) of α by the LDA (GGA) is to some extent canceled out by the overestimation (underestimation) of B_0 .

The anharmonicity of the vibrations can be examined by computing the mode Grüneisen parameters, defined by

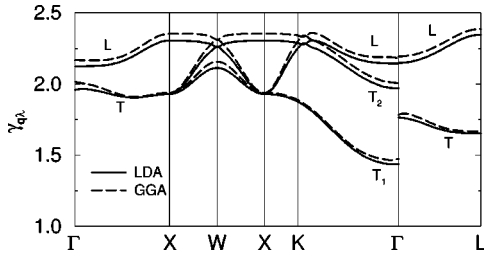


FIG. 7. Calculated dispersion curves for the individual mode Grüneisen parameters $\gamma_{q\lambda}$ for the same high-symmetry directions in the BZ as in Fig. 5. The values have been evaluated at the static lattice constant; the discrepancy between the LDA (solid lines) and GGA (dashed lines) results is small. “L” and “T” denote the longitudinal and transverse branches, respectively.

$$\gamma_{q\lambda} = - \frac{V}{\omega_{q\lambda}(V)} \frac{\partial \omega_{q\lambda}(V)}{\partial V}, \quad (6)$$

where $V = a^3/4$ is the volume of the unit cell. Figure 7 shows the results for the Grüneisen parameters for the same high-symmetry modes for which the frequencies were plotted in Fig. 5. They have been evaluated at the static lattice constants. Though the LDA and GGA static lattice constants are different, it can be seen that the discrepancy in the corresponding Grüneisen parameters is small, considerably smaller than the differences in phonon frequencies. For example, at the X point (zone edge along $[100]$), the discrepancy between the LDA and GGA results for the phonon frequencies is 10.7% and 12.5% for the transverse and longitudinal branches, respectively, whereas the corresponding Grüneisen parameters differ by only 0.4% and 2.1%, respectively. It is interesting to compare Fig. 7 with Fig. 3 of Ref. 3, which shows the corresponding result for Ag. Though the phonon dispersion curves of Ag and Cu are very similar in shape and structure, our curves for the Grüneisen parameters of Cu look quite different, in some areas of the BZ, from those reported earlier for Ag.

We also compute the overall Grüneisen parameter γ , which is obtained by averaging over the individual Grüneisen parameters $\gamma_{q\lambda}$ of all the modes, using the equation

$$\gamma(T) = \frac{\sum_{q\lambda} \gamma_{q\lambda} C_V(\mathbf{q}\lambda)}{\sum_{q\lambda} C_V(\mathbf{q}\lambda)}, \quad (7)$$

where the contribution from each mode ($\mathbf{q}\lambda$) is weighted by $C_V(\mathbf{q}\lambda)$, its contribution to the specific heat, as defined in Eq. (4). This quantity is of interest because it appears in some useful thermodynamic relations (as discussed below), and experimental papers often report this overall value. The temperature dependence of γ comes from the temperature dependence of both the individual Grüneisen parameters $\gamma_{q\lambda}$ (which depend on the lattice constant and hence on T) and that of the specific heat.

Figure 8 shows the results for the variation of the overall Grüneisen parameter γ as a function of temperature. It is seen that the percentage difference between the LDA and GGA results is small, ranging from 2.5% at 100 K to 5.3% at 1300 K. The discrepancy with experiment is also quite small, with the LDA and GGA errors being 2.8% and

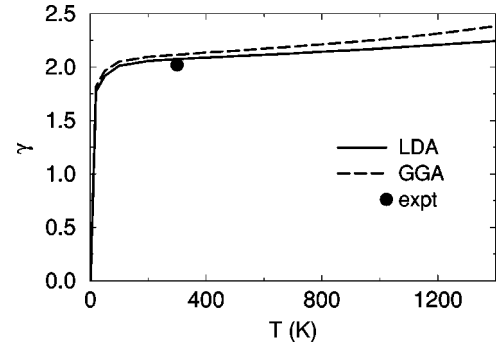


FIG. 8. Overall Grüneisen parameter γ as a function of temperature. The solid and dashed lines are the results obtained using the LDA and GGA, respectively. The experimental value is taken from Ref. 24.

4.8%, respectively, at room temperature. In comparison, the LDA and GGA results for the bulk modulus (plotted in Fig. 3) differ from each other by 30%–50% over the same temperature range, with the LDA and GGA errors (with respect to experiment) being 18.8% and 13.7%, respectively, at room temperature.

IV. COMPARISON WITH EARLIER CALCULATIONS

We compare our results to those of three previous calculations. In the first, interatomic potentials are described by a pair potential fit to experimental data, and thermal effects are treated by formulas that are valid in the high-temperature limit. In the second, the static energies at zero temperature are computed *ab initio*. However, thermal effects are computed using a Debye model and various approximate relations; i.e., the phonon frequencies are not calculated *ab initio*. In the third calculation, the interatomic potentials are described by an empirical form that includes some many-body effects, and thermal effects are treated using finite-temperature molecular dynamics simulations.

In their study of the thermodynamic properties of face-centered-cubic (fcc) metals, MacDonald and MacDonald²³ have described the interatomic interactions using a modified Morse potential fit to experimental data such as the Debye temperature Θ_D , the sublimation energy, and the thermal expansion in the neighborhood of Θ_D (342 K). The electronic contribution to C_V is estimated using free-electron theory. Though the thermal expansion is fit to agree with experiment at low temperatures, α is underestimated by about 20% at 1200 K (in comparison, our results for α at 1200 K, with no fit to data on thermal expansion, differ from experiment by -12% when using the LDA and $+29\%$ when using the GGA). The absolute value of B_0 agrees well with experiment (which is to be expected, given the fitting to Θ_D); however, $\partial B_0(T)/\partial T$ is underestimated. The magnitude of the electronic contribution to C_V , estimated from free-electron theory, is similar to what we obtain from our more exact approach, and the agreement between the calculated and experimental values for C_p is fairly good, similar to that obtained by us. The value of γ changes from 1.947 at 100 K to 2.127 at 1000 K, which is comparable to our results. How-

ever, it should of course be kept in mind that in our calculations we do not fit to any empirical data at all.

Moruzzi, Janak, and Schwarz²⁴ have computed the bulk binding curve [i.e., $E_{\text{stat}}(a)$] by performing *ab initio* augmented-spherical-wave method calculations. They use this to obtain B_0 (and thus an approximate Θ_D) and γ (independent of T). The free energy is then evaluated in the Debye model, with the volume dependence of the frequencies being determined by γ . They evaluate α only up to $T=300$ K, getting a value of α that is too low at 300 K by 20%. Our calculation improves upon this one in that we do not use a Debye model and do not assume that all modes have the same degree of anharmonicity, since we calculate individually and exactly the values of $\omega_{\text{q}\lambda}(a)$. This is probably why our calculated values for α are closer to experiment: at 300 K, our errors in the calculated α are -14% (LDA) and $+14\%$ (GGA).

Çağın *et al.*²⁵ have used the empirical Sutton-Chen potential to describe the interatomic interactions. The potential parameters are fit to the cohesive energy, bulk modulus, etc., at 0 K. Temperature effects are determined by performing molecular dynamics simulations. As a comparison, let us consider the values for the thermal expansion ϵ at 1000 K: they obtain a result of 2.42%, compared to our values of 1.22% (LDA) and 1.64% (GGA), and the experimental value of 1.37%. Our values are clearly closer to experiment; in this case, their larger errors presumably arise from deficiencies in their interatomic potential.

To summarize, though our results do not agree exactly with experiment, we still do a better job than earlier calculations. This is because we have eliminated the errors due to the utilization of parametrized interatomic potentials and an approximate treatment of the lattice vibrations. The (smaller) errors that remain in our calculations are due to the choice of exchange-correlation potential (and, possibly, the use of the quasiharmonic approximation, though we believe these errors to be small).

V. DISCUSSION OF RESULTS

From the results presented in Sec. III, it is clear that the approximations used for the exchange-correlation potentials introduce much smaller errors in anharmonic quantities such as γ , B' , and $\partial B_0(T)/\partial T$ than in harmonic properties like the bulk modulus and phonon frequencies.

At first sight, the relatively large discrepancy between the LDA and GGA values for the coefficient of thermal expansion α may seem to contradict this statement. However, α is not a purely anharmonic quantity. For example, in a one-dimensional anharmonic potential given by $V(x) = \frac{1}{2}cx^2 - \frac{1}{6}gx^3$, we have $\alpha \propto g/c^2$ (Ref. 12); i.e., α depends on both the harmonic coefficient c and the anharmonic coefficient g , and an error in the former will be manifested as an even larger error in α . For the present case, where we have to average over a number of normal modes in three dimensions, it is possible to derive¹¹ a corresponding equation relating α to the averaged anharmonic quantity γ and harmonic quantity B_0 :

$$\alpha(T) = \frac{\gamma(T)C_V(T)}{3B_0(T)}. \quad (8)$$

From Fig. 8, it is seen that the discrepancy between the LDA and GGA values of $\gamma(T)$ is small and that both are close to experiment. Any error in $C_V(T)$ is negligible, especially at temperatures above the Debye temperature, where C_V has reached its saturation value of $3k_B$ per atom. There remains the large error in $B_0(T)$. At a temperature of 1000 K, for example, the LDA and GGA values for γ , B_0 , and α differ by 4%, 41%, and 32%, respectively, which is consistent with our argument that the discrepancy in α arises almost entirely from the discrepancy in B_0 .

If we assume that the main source of the LDA and GGA errors in the values of physical quantities is the wrong value obtained for the lattice constant, then it is indeed consistent that the errors in anharmonic quantities should be smaller than those in harmonic quantities. If the energy of a crystal is expanded as a Taylor series in powers of the lattice constant, then the error arising from evaluating derivatives at the wrong lattice constant get progressively less for higher derivatives. (For example, if the expansion were truncated at cubic order, then the error in the second derivative is proportional to the error in the lattice constant, whereas there would be no error in the third derivative.) Thus errors arising from using a wrong lattice constant are manifested to lesser and lesser degrees as one goes to higher-order anharmonic properties.

One can also argue that the LDA and GGA errors made in computing physical properties should increase with temperature: At $T=0$, the LDA underestimates a_0 and the GGA overestimates it. Upon heating, the LDA underestimates the thermal expansion (because of the overestimation of B_0) and the GGA overestimates it (because of the underestimation of B_0). Thus, as the temperature is increased, the underestimation by the LDA and the overestimation by the GGA of the lattice constant are both aggravated further, resulting in increasingly unreliable results for physical properties, though the errors are smaller for anharmonic properties than harmonic ones. To avoid this, we suggest that when performing *ab initio* DFT calculations at high temperatures in systems that display large errors in the calculated bulk modulus, it is perhaps a good idea to use the experimental values of the thermal expansion, regardless of whether one is using the LDA or GGA. It is also useful to keep in mind that the error in the static value for the bulk modulus is already a good indicator of the magnitude of the error that will be made in the coefficient of thermal expansion; thus, if in a particular case, either the LDA or GGA gives a better value for the static value of a_0 and B_0 , it will probably also give a better description of finite-temperature properties.

VI. SUMMARY

To summarize, we have performed *ab initio* calculations to study the thermal properties of bulk copper, using phonon frequencies computed using DFPT, and the quasiharmonic approximation for the vibrational free energy. We have calculated the temperature dependence of the lattice constant

a_0 , the thermal expansion ϵ , the coefficient of thermal expansion α , the bulk modulus B_0 , the pressure derivative of the bulk modulus B' , the overall Grüneisen parameter γ , and the lattice and electronic contributions to the specific heat capacities at constant volume and pressure, C_V and C_p . We have also presented results for the dispersion, along high-symmetry directions in the BZ, of the phonon frequencies and mode Grüneisen parameters. All of the above have been computed using both the local density approximation and generalized gradient approximation.

Neither the LDA nor GGA is clearly to be preferred in this case, with both giving errors of comparable magnitude (though generally of opposite sign). At all temperatures, the LDA systematically underestimates the lattice constant and the coefficient of thermal expansion, and the GGA overestimates these. In contrast, the LDA always overestimates the bulk modulus and phonon frequencies, and the GGA underestimates them. The electronic contribution to the specific heat is found to be considerably smaller than the phononic contribution, though not negligible. The results for C_p agree very well with experiment, except for the GGA results at high temperatures. However, the discrepancy between the LDA and GGA results (and their discrepancy with experi-

ment) is considerably lower for anharmonic quantities such as γ , B' , and $\partial B_0(T)/\partial T$ than for the harmonic properties. In any event, our results are closer to experiment than those of earlier calculations in which the interatomic interactions and/or thermal effects were treated approximately.

We have argued that if the main source of errors can be attributed to the wrong value obtained for the lattice constant resulting from the approximate nature of the exchange-correlation potential, then it is indeed reasonable that the errors in anharmonic quantities should be smaller than those in harmonic quantities. We have also argued that the LDA and GGA errors should increase with temperature, suggesting the need for care and caution when performing *ab initio* calculations at high temperatures.

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