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First-principles calculations of the thermal expansion of metals

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We present first-principles calculations of the thermal expansion of several simple metals (Al, Li, and Na) within the quasiharmonic approximation. Linear-response theory is used to determine the volume-dependent phonon frequencies within the density-functional framework. Our results indicate that the treatment of anharmonic effects at the quasiharmonic level provides a remarkably good description of the structural and elastic properties of these materials up to their melting points. [S0163-1829(97)02434-X]

Electronic-structure calculations based on density-functional theory (DFT) in the local-density approximation (LDA) have proved to be effective tools for studying the zero-temperature energetics of many systems, ranging from bulk materials to surfaces, interfaces, and clusters.[1] With increasingly powerful computers and efficient algorithms, very large systems can now be handled, and problems in the material science arena are within reach. However, the application of *ab initio* methods to the study of thermodynamic properties such as phase diagrams,[3] defect energetics,[4] nucleation, and growth, for example, remains challenging.

For ordered solids, the free energy at finite temperature has contributions from both the lattice vibrations and the thermal excitation of electrons. Within the density-functional framework, the latter contribution can be taken into account by using the Mermin functional rather than the ordinary DFT energy functional.[2] The treatment of phonon contributions to the free energy on an equal footing is less straightforward. First-principles molecular-dynamics methods such as the Car-Parrinello method[5] can be used to determine thermal properties that can be expressed as statistical averages. However, since the ionic degrees of freedom are treated classically, these simulations are not valid at temperatures comparable to or lower than the Debye temperature. A further drawback is that the entropy, and hence the free energy, cannot be expressed as an ensemble average. To calculate these quantities, more elaborate techniques such as thermodynamic integration schemes are needed, which significantly increases the computational effort required.[6]

The quasiharmonic approximation[7] provides an alternative approach for determining the lattice contributions to the free energy. In this approximation, the Helmholtz free energy F is given by

$$F(V,T)=E_{\mathrm{LDA}}(V)+k_BT\sum_{\mathbf{q}j}\ln\left(2\sinh\frac{\hbar\omega_{\mathbf{q}j}(V)}{2k_BT}\right), \quad (1)$$

where $E_{\mathrm{LDA}}(V)$ is the energy of the static lattice at a given volume V, and $\omega_{\mathbf{q}j}(V)$ is the frequency of the jth phonon band at the point $\mathbf{q}$ in the Brillouin zone. Vibrational modes are treated quantum mechanically, but the full Hamiltonian is approximated by a harmonic expansion about the equilibrium atomic positions. Anharmonic effects are included through the explicit volume dependence of the vibrational frequencies. Calculations based on various semiempirical methods suggest that the quasiharmonic approximation provides a reasonable description of the thermodynamic properties of many bulk materials below the melting point.[6,8–11] However, because of the large computational cost of determining the complete phonon spectrum as a function of volume, few first-principles investigations have been carried out.

With recently developed DFT-based linear-response methods,[12,13] vibrational modes with wave vectors at arbitrary points in the Brillouin zone (BZ) can be accurately and efficiently computed without using large supercells. These methods can be used to assess the accuracy of the quasiharmonic approximation for describing the thermodynamics of different physical systems. Studies of the thermal properties of C (Ref. 14) and Si (Refs. 15 and 16) based on phonon spectra calculated using the linear-response approach or other first-principles methods have found that the treatment of anharmonic effects at the quasiharmonic level is sufficient for describing these materials, at least up to temperatures of several hundred kelvin. In this paper, we assess the applicability of the quasiharmonic approximation to simple s-p metals. Using the linear-response method for computing phonon spectra, we study the thermal expansion of Li, Na, and Al up to their melting points. Our results indicate that the quasiharmonic approximation provides a remarkably good description of the structural and elastic properties of these metals even near their melting points, where anharmonic effects are expected to be large. With regard to the equilibrium structural properties of the alkali metals, it is well known that there are large discrepancies between LDA results and experimental values. These discrepancies are reduced when phonon contributions to the free energy are included in the calculations.

All of our calculations are performed using plane-wave basis sets with norm-conserving pseudopotentials[17] representing the ion-electron interaction. For Li and Na the Wigner interpolation formula[18] for correlation is used, while for Al the Perdew-Zunger (PZ) parametrization[19] is used. In all cases a core correction is included to account for the

TABLE I. Calculated ground-state properties at $T=0$, without vibrational effects. Also shown are experimental values for the lattice constants at low temperatures (Ref. 23) and the room-temperature bulk moduli (Ref. 24).

System	a_0 (Å)		B (GPa)	
	Calc.	Expt.	Calc.	Expt.
Li	3.41	3.49	15.4	11.6
Na	4.11	4.23	9.0	6.8
Al	3.98	4.02	85.0	72.2

nonlinearity of the exchange and correlation potential between core and valence charge densities.[20] Sums over the BZ are performed on a mesh of **k** points generated with the scheme of Monkhorst and Pack.[21] The dynamical matrix is calculated using the method described in Ref. 13, where the self-consistent change to the Hamiltonian caused by displacing an ion is obtained by solving a Bethe-Saltpeter equation for the change in the charge density. For the bcc structure, the dynamical matrix is calculated for 140 phonon wave vectors in the irreducible element of the BZ, while for the fcc structure, 89 wave vectors in the irreducible BZ are considered. The Helmholtz free energy, given by Eq. (1), is calculated by summing over these wave vectors. Note that because we are considering temperatures well below electronic energy scales, and since the electronic density of states varies slowly and smoothly with lattice constant, the contribution of the thermal excitation of electrons to the thermal expansion coefficient is negligible and is not included in the results presented here.

The ground-state properties obtained for the static lattice are listed in Table I. In all cases the LDA underestimates the lattice constant and overestimates the bulk modulus.[22] For Al, the lattice constant is underestimated by about 1%, which is typical for LDA calculations. For the alkali metals, the error in the calculated lattice constant is significantly larger: 2.7% for Na and 2.3% for Li. If the PZ parametrization of the correlation potential is used for the alkalis, the lattice constants are even more severely underestimated. We use the Wigner formula for the alkali metals in order to minimize this discrepancy. The calculated bulk moduli, found by differentiating the fitted equations of state at the equilibrium volumes, are significantly larger than the experimental values. This is related to the underestimation of the lattice constant. At larger lattice constants, the calculated bulk modulus decreases. It has been suggested that calculations of elastic constants should be carried out at the experimental lattice constant.[25] However, as shown in Table II, such a scheme would produce too large a correction for these materials.

TABLE II. Bulk moduli calculated at experimental room-temperature lattice constants using static LDA equations of state. Experimental values are from Ref. 24.

System	a_0 (Å)	B (GPa)	
	Expt.	Calc.	Expt.
Li	3.52	9.4	11.6
Na	4.28	4.6	6.8
Al	4.05	64.2	72.2

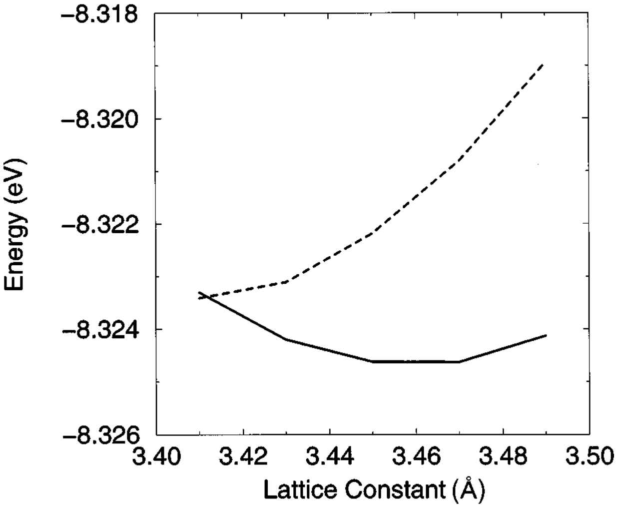

FIG. 1. Equations of state for Li. The solid curve is the Helmholtz free energy at 298 K and the dashed curve is the electronic energy (LDA) at $T=0$.

To obtain the temperature dependence of the lattice constant and bulk modulus, we use Eq. (1) to compute the Helmholtz free energy at temperature T for several volumes. The corresponding energy-volume points are fitted to a Murnaghan equation of state,[26] from which the equilibrium lattice constant and the bulk modulus are determined. In Fig. 1, the energy-volume curves are plotted for Li over a small temperature range. The solid curve corresponds to $T=298$ K, while the dashed curve shows the static $T=0$ LDA results. The inclusion of vibrational effects significantly alters the equation of state—changes are seen in both the position of the minimum and the local curvature at the minimum.

In Table III we list the lattice constants calculated from the room-temperature equations of state. For the alkali metals, the inclusion of phonon contributions to the free energy significantly improves the agreement between the calculated and measured lattice parameters. The primary source of improvement comes from the phonon zero-point contributions to the free energy at $T=0$. We deduce this from the observation that the calculations provide a good account of the relative changes in lattice constant as a function of temperature, as discussed below.

The inclusion of vibrational effects also improves the elastic properties compared to room-temperature experimental values. In Table III we have listed the bulk moduli for the

TABLE III. Room-temperature lattice constants and bulk moduli calculated using the Helmholtz free energy. Experimental data are obtained from Ref. 23. For Li, the experimental value for the lattice parameter is extrapolated from 78 K using the experimental coefficient of linear expansion (Ref. 27).

System	a_0 (Å)		B (GPa)	
	Calc.	Expt.	Calc.	Expt.
Li	3.48	3.52	11.5	11.6
Na	4.19	4.28	6.8	6.8
Al	4.00	4.05	75.2	72.2

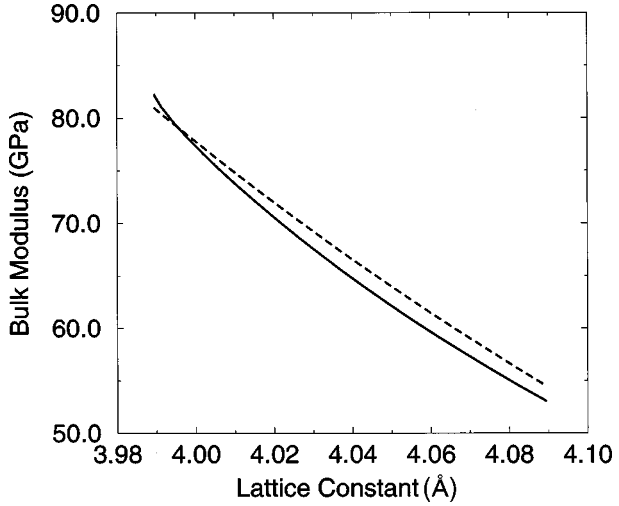

FIG. 2. Calculated bulk modulus as a function of lattice parameter. The solid curve is obtained from the temperature-dependent Helmholtz free energy and the dashed curve is obtained from the $T=0$ electronic energy.

different materials at room temperature, and as can be seen the agreement between theory and experiment is quite remarkable. In all cases the theoretical bulk moduli are within 2% of the experimental values, which is significantly better than the results obtained using the static equation of state at either the equilibrium LDA lattice parameter or the room-temperature experimental lattice parameter. To identify the source of improvement, we have plotted in Fig. 2 the bulk modulus of Al as a function of lattice parameter for two cases. The solid curve is that obtained from the temperature-dependent equations of state, and the dashed curve is obtained by looking at the local curvature of the static $T=0$ equation of state at a given volume. The closeness of the two curves indicates that the improvement of the bulk modulus as a function of temperature is primarily due to the change in the lattice constant. This suggests that static LDA calculations carried out at the room-temperature lattice constant determined within the quasiharmonic approximation can yield reasonably accurate elastic constants, while requiring significantly less computational effort than a full quasiharmonic calculation of finite-temperature elastic constants.

Using the results obtained for the lattice constant as a function of temperature, we can determine the thermal expansion as

$$\frac{\Delta l}{l}=\frac{a_0(T)-a_0(\mathrm{RT})}{a_0(\mathrm{RT})}, \tag{2}$$

where $a_0(T)$ is the lattice constant at a given temperature and RT is room temperature. The results are plotted in Fig. 3 as solid curves with the experimental data[27] plotted as squares. The agreement between theoretical and experimental results is remarkably good. Even with the small errors in the equilibrium lattice constant, the present calculations correctly describe the temperature dependence of the relative volume changes very accurately. Even more surprising is the accuracy of the quasiharmonic approximation in these tests. The agreement between theory and experiment holds not only at low temperatures, where the atomic motions are small and likely to be harmonic, but also at temperatures close to the melting point, where the amplitude of atomic motions is large.

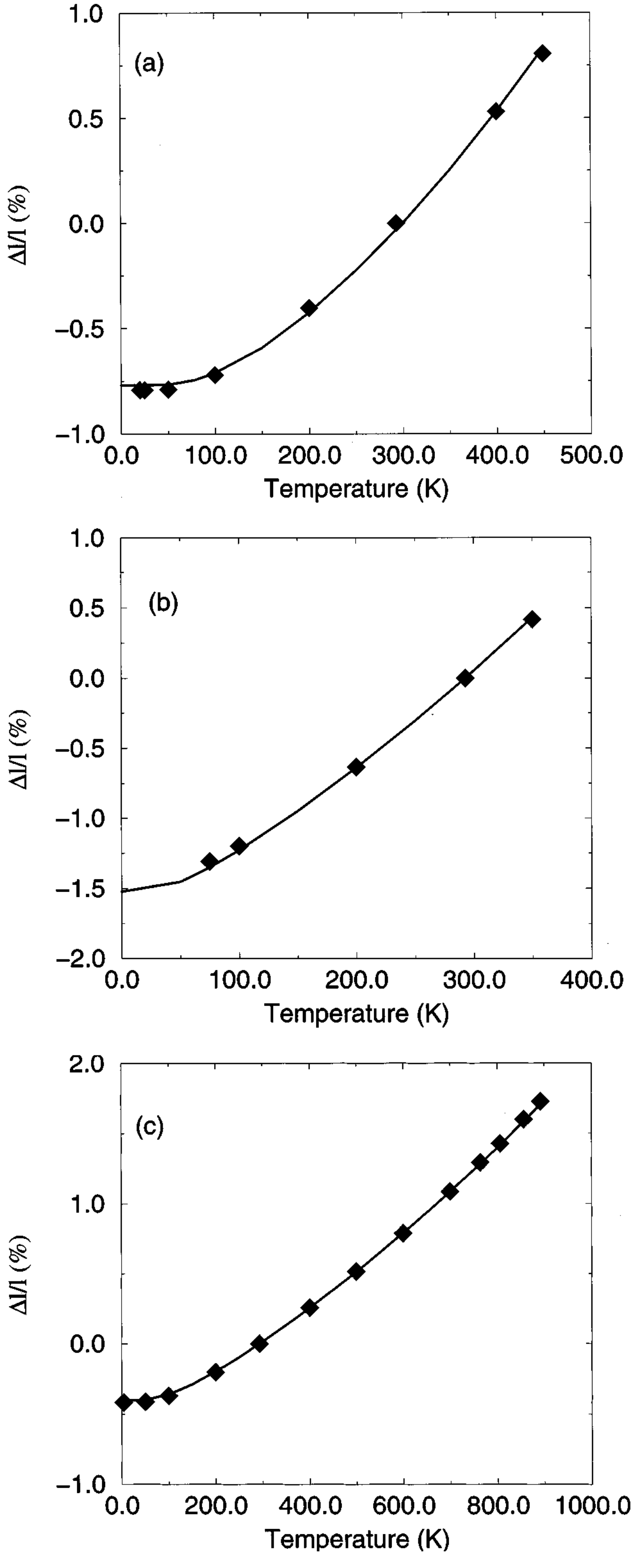

FIG. 3. Temperature dependence of the thermal linear expansion for (a) Li, (b) Na, and (c) Al. Solid curves connect calculated values and symbols represent experimental data from Ref. 27.

In conclusion, we have shown that by including the effects of lattice vibrations, structural and elastic properties of several s-p bonded metals can be more accurately calculated. The improvement in the elastic properties is primarily related to the improvement in the lattice parameter. However, using the experimental lattice parameter to determine the bulk modulus from the static equation of state results in large errors. When the static equation of state is used, the best results for the bulk modulus are found when the lattice parameter is chosen to minimize the Helmholtz free energy at the temperature where the experiments are performed (room temperature). This suggests an approach for the accurate determination of other elastic constants: Determine the theoretical room-temperature lattice constant and use this value for calculating the elastic constants based on static LDA energies. This procedure removes the reliance on experimental data, and may significantly improve the calculated elastic constants. The accuracy of the combination of the linear-response methods with the quasiharmonic approximation is demonstrated by the excellent agreement between the calculated and measured linear coefficients of thermal expansion. This first-principles approach can be used to investigate other materials properties such as phase diagrams, stability, and growth. Temperature-dependent defect energetics, which are crucial for understanding mechanical properties, can also be studied.

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