Low-temperature properties of fcc Al from modified Debye theory

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Abstract
The value of the lattice parameter of fcc Al at low temperatures, $a(T)$, is shown to be accurately determined by the Debye theory of lattice vibrations and first-principles total energy band calculations. The Debye theory uses the well-known generalization to direction-dependent elastic mode frequencies and is further modified by introducing a parameter β_z, which gives the fraction of the full Debye zero-point energy that is possessed by the actual dispersive mode frequencies. The calculation of $a(T)$ is simplified by minimizing the Gibbs free energy of the vibrating lattice rather than the usual procedure of minimizing the total energy at constant volume. The parameter β_z is shown to affect the value of $a(T)$, but comparison of $a(T)$ with experiment is not able to evaluate β_z because of the inherent inaccuracy of the band calculations (the GGA value is 0.7% high, and the LSDA value is 1.2% low for $a(T)$). By using experimental values of $a(T)$ and elastic constants $c_{ij}(T)$, $ij = 11, 12, 44$ and modified Debye theory, β_z is evaluated as 0.48 without band calculations. From β_z the rigid lattice of a is shown to be 4.01 Å, midway between the GGA and LSDA values.

1. Introduction

This work shows that the Debye theory of lattice vibrations combined with first-principles total-energy band calculations can accurately find the temperature dependence of the lattice parameter $a(T)$ of fcc Al from 0 K to at least 300 K. Hence Debye theory is shown to be an alternative procedure for calculating $a(T)$ at low temperatures that is simpler than the computationally intensive complete phonon spectra usually used to compute thermal expansion from first principles.

The Debye theory of lattice vibrations derives a one-parameter formula for the free energy of lattice vibrations as a function of temperature $F(\theta_D, T)$. The parameter θ_D depends just on volume for cubic materials, but in the quasi-harmonic approximation it does not depend on T. The original form of Debye theory [1] had three defects:

(1) it assumed that the elastic waves that were used to describe the lattice vibration modes were isotropic,

(2) it neglected dispersion of the actual lattice modes, which have frequencies that differ from the frequencies of elastic waves as functions of wavenumber,

(3) it assumed that the zero-point energy (ZPE) was a sum of elastic wave contributions over the entire phonon spectrum, thereby neglecting the fact that dispersion would change the contributions of all the higher frequencies.

The first two defects were remedied for low-temperature applications in the 1930s and 1940s (for a review see [2]) by obtaining elastic wave velocities as functions of direction from solutions of the elastic equations of motion. This generalized Debye theory thus made the temperature dependence of $F(\theta_D, T)$ accurate at sufficiently low temperatures and exact approaching 0 K. Also, at temperatures sufficiently low that only elastic waves are excited, the second defect, neglect of dispersion, could be ignored. However, the third defect, the wrong estimate of the ZPE, is not remedied by using directionally correct elastic wave velocities at low temperatures because all modes enter the ZPE, including dispersive ones.

In application of the Debye theory to the calculation of lattice dimensions, the ZPE is important. This work attempts to remedy the third defect for low-temperature applications by introducing a parameter β_z that fractionally reduces the Debye values of the ZPE in $F(\theta_D, T)$. In the first part (sections 2 and 3) of the paper we find the equilibrium lattice dimension $a(T)$ of fcc Al by minimizing with respect to structure the Gibbs free energy G at zero pressure obtained by adding the modified Debye free energy of lattice vibration $F_m(\theta_D, T)$ (modified by β_z) to the rigid-lattice band energy $E(a)$. The resulting theoretical equilibrium lattice dimensions can then be compared to measured lattice dimensions, which of course contain the vibrational effects. But due to the inherent inaccuracy of the band energy calculation, we show that no value of β_z can be established.

The first part of the paper carries out the calculation based on first-principles band calculations of the cubic elastic constants at particular a values, which give $\theta_D(a)$, $F_m(\theta_D(a), T)$ at these a values. This part of the paper establishes some important results: that Debye theory gives $a(T) - a(0)$ accurately up to at least 300 K (necessary for the second part of the paper which fits measured $a(T)$ between 100 and 200 K); that the limiting T^4 term for $F_m(\theta_D, T)$ is not adequate to fit experiment; that the use of the Gibbs free energy at zero pressure is simpler than the usual procedure of calculating the internal energy at constant volume from complete phonon spectra at many volumes (to find the volume of zero pressure); that the band calculation with the generalized-gradient approximation (GGA) gives high values of a compared to experiment and the local-spin-density approximation (LSDA) gives low values; hence, although β_z affects the value of a, the inaccuracies are too large to permit evaluation of β_z.

In the second part of the paper we avoid the inherent inaccuracies of the GGA and LSDA by using experimental values of $a(T)$ and $c_{ij}(T), ij = 11, 12, 44$ to find θ_D and $F_m(\theta_D, T)$; $F_m(\theta_D, T)$ is then fitted to the experimental change in $a(T)$ between 100 and 200 K to determine β_z and a_R, the rigid-lattice value of a, which can be compared directly with the results of rigid-lattice band calculations. The measured $a(T)$ and $c_{ij}(T)$ also give a value of a Grüneisen-type parameter γ_{DG} describing the volume dependence of the Debye parameter θ_D, which in the quasi-harmonic approximation depends on volume but not on temperature. The values of β_z, γ_{DG} and a_R do not require band calculations and their accuracy rests on the accuracy of measured dimensions and elastic constants at several temperatures and on the accuracy of generalized and modified Debye theory near 0 K.

2. Procedures of band calculations

First-principles band calculations of fcc Al were performed using the full-potential augmented-plane-wave plus local orbitals (APW + lo) method together with either the generalized-gradient approximation (GGA) or the local-spin-density approximation (LSDA) as implemented in the WIEN2k_05 package [3]. A plane-wave cutoff $R_{MT}K_{max} = 7$, $R_{MT} = 1.6$ au, $G_{max} = 14$, mixer $= 0.05$ and 1000 k-points in the irreducible Brillouin zone were used in all the band calculations. The k-space integration was done by the modified tetrahedron method. Tests with larger basis sets and different Brillouin zone samplings yielded only very small changes in the results. The convergence criterion on the energies is set at 1×10^{-3} mRyd (10^{-6} Ryd).

The band calculation program WIEN2k_05 is called by a minimum path program MNP [4] which makes a series of jumps in structure based on the local slope and curvature of the Gibbs free energy $G = E + pV$ (at $T = 0$) at a point in structure space (whose coordinates are the components of the unit cell lattice vectors in orthogonal coordinates). The calculation rapidly approaches the structure at the minimum of G and simultaneously finds the Gibbs free energy, the lattice structure and the elastic constants at rigid-lattice equilibrium at a given pressure p.

At given temperature T and pressure p the Gibbs free energy

$$G = E^{elec} + pV + F(\theta_D, T), \tag{1}$$

where $E^{elec} + pV$ is the rigid-lattice Gibbs free energy (Ryd/atom) from the MNP calculation, V is the volume per atom; $F(\theta_D, T)$ is the free energy of lattice vibrations (Ryd/atom), which is given in generalized Debye theory by [5, pages 53, 213]

$$F(\theta_D, T) = \frac{9}{8}k_B\theta_D + \frac{9k_B\theta_D}{x^4}\int_0^x z^2 \ln\left(1 - e^{-z}\right) dz, \qquad x \equiv \frac{\theta_D}{T}, \tag{2}$$

where k_B is Boltzmann's constant and $\frac{9}{8}k_B\theta_D$ is the full Debye zero-point energy (ZPE).

The first two terms of the expansion of $F(\theta_D, T)$ as powers of T [5, page 213] are

$$F(\theta_D, T) \simeq \frac{9}{8}k_B\theta_D - \frac{\pi^4}{5}\frac{k_B T^4}{\theta_D^3}. \tag{3}$$

To determine the temperature dependence of the equilibrium lattice constant $a(T)$ we select three reference values of the lattice parameter a which bracket $a(T)$, the equilibrium value of a at T. We then evaluate $E^{elec}(a) + pV$, $\theta_D(a)$ and $F(\theta_D, T)$ at each reference value of a using (2); hence we can evaluate $G(a, T)$ using (1) (here we only consider the zero-pressure case). We evaluate $\theta_D(a)$ at the reference values of a using the elastic constants $c_{ij}(a)$ ($ij = 11, 12, 44$) determined from $(\partial^2 G/\partial\varepsilon_i\partial\varepsilon_j)/V$. Fitting of the G values at the three reference points at a given temperature T with a second-order polynomial and finding the a that minimizes $G(a, T)$ gives the equilibrium lattice constant $a(T)$.

We make the calculated $a(T)$ depend on a factor β_z in the ZPE by using a modified free energy of vibration $F_m(\theta_D, T)$ in (1), namely

$$F_m(\theta_D, T) = \frac{9}{8}\beta_z k_B\theta_D + \frac{9k_B\theta_D}{x^4}\int_0^x z^2 \ln\left(1 - e^{-z}\right) dz, \qquad x \equiv \frac{\theta_D}{T}. \tag{4}$$

3. Results of band calculations

Table 1 lists the calculated values of the Debye temperature θ_D, the electronic energy E^{elec} and the Gibbs free energy $G(a, T) = E^{elec} + F_m(\theta_D, T)$ (at $p = 0$) of fcc Al at the three reference points a_1, a_2, a_3. The modified free energy of lattice vibrations $F_m(\theta_D, T)$ is calculated from (4) using the GGA at $T = 0$, 50 and 100 K with both $\beta_z = 0$ and 1 in each case. Fittings of the
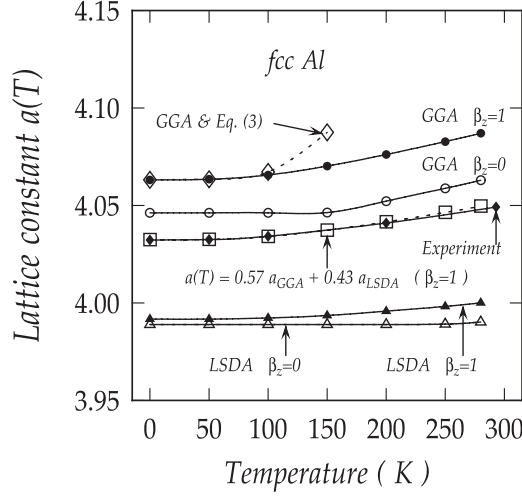
Figure 1. Temperature dependence of the equilibrium lattice constant of fcc Al. The solid diamonds are the experimental data from [6]. The open and solid circles are calculated from (4) using the GGA with $\beta_z = 0$ and 1 respectively. The open and solid triangles are calculated from (4) using the LSDA with $\beta_z = 0$ and 1 respectively. The open squares are the linear combination of the GGA and LSDA results with $a(T) = 0.57a^{\mathrm{GGA}} + 0.43a^{\mathrm{LSDA}}$ at $\beta_z = 1$ to fit the experimental data. The open diamonds are calculated from (3) using the GGA with $\beta_z = 1$. The solid and dashed lines interpolate between the data points.

Table 1. Debye temperature θ_{D}, electronic energy E^{elec} and Gibbs free energy $G(a, T) = E^{\mathrm{elec}} + F_{\mathrm{m}}(\theta_{\mathrm{D}}, T)$ (at $p = 0$) of fcc Al at the three reference points a_1, a_2, a_3. The modified free energy of lattice vibrations $F_{\mathrm{m}}(\theta_{\mathrm{D}}, T)$ in $G(a, T)$ is calculated from (4) using the GGA with $\beta_z = 1$ and 0 respectively.

	$a_1 = 4.046\,197$ Å	$a_2 = 4.070\,474$ Å	$a_3 = 4.094\,751$ Å
θ_{D} (deg)	433.91	409.13	385.23
E^{elec} (Ryd/atom)	$-485.638\,978$	$-485.638\,839$	$-485.638\,519$
$G(T = 0$ K) (Ryd/atom) $\beta = 1$	$-485.635\,887$	$-485.635\,924$	$-485.635\,774$
$\beta = 0$	$-485.638\,978$	$-485.638\,839$	$-485.638\,519$
$G(T = 50$ K) (Ryd/atom) $\beta = 1$	$-485.635\,896$	$-485.635\,935$	$-485.635\,788$
$\beta = 0$	$-485.638\,987$	$-485.638\,850$	$-485.638\,533$
$G(T = 100$ K) (Ryd/atom) $\beta = 1$	$-485.636\,011$	$-485.636\,067$	$-485.635\,938$
$\beta = 0$	$-485.639\,102$	$-485.638\,982$	$-485.638\,683$

values of the Gibbs free energies $G(a, T)$ at the three reference points with a second-order polynomial give at the minimum of G the equilibrium lattice constants $a^{\mathrm{GGA}}(T)$ with $\beta_z = 0$ and 1. The equilibrium lattice constants $a^{\mathrm{LSDA}}(T)$ with $\beta_z = 0$ and 1 are found similarly.

Figure 1 shows the comparison of calculated $a(T)$ with the experimental result for fcc Al. The solid diamonds are the experimental data from [6]. The open and solid circles are calculated from (4) using the GGA with $\beta_z = 0$ and 1 respectively. The open and solid triangles are calculated from (4) using the LSDA with $\beta_z = 0$ and 1 respectively. The open squares are the linear combination of the GGA and LSDA results with $a(T) = 0.57\,a^{\mathrm{GGA}} + 0.43\,a^{\mathrm{LSDA}}$ at $\beta_z = 1$ to fit the experimental data. The open diamonds are calculated from (3) using the GGA with $\beta_z = 1$. At low temperatures ($T \leqslant 50$ K) the calculated $a(T)$ are the same from

both (3) and (4). However, at $T > 50$ K the term $\frac{\pi^4}{5}\frac{k_B T^4}{\theta_D^3}$ in (3) increases with increasing T much faster than the integral term in (4). As shown in figure 1 at $T = 150$ K the value of $a(T)$ calculated from (3) is much larger than that from (4) (the open diamond versus the solid circle). Calculations of $a(T)$ from (3) at $T > 150$ K would require more reference points with larger a.

4. Vibrational parameters evaluated without band calculations

Section 3 showed two features of Debye theory:

(1) Debye theory can describe the temperature dependence of the lattice parameter rather well up to at least 300 K;
(2) Debye theory does not find the lattice parameter at 0 K accurately because of the inherent inaccuracy of the band calculations, even when the full range of zero-point energy for $\beta_z = 0$ to 1 is considered.

To evaluate β_z we need a procedure which does not require band calculations.

To evaluate β_z we consider using the first feature of the Debye theory given above, namely the accurate evaluation of the thermal expansion. We tried first a procedure which assumed that θ_D had an exponential dependence on volume with one parameter, $\theta_D \propto V^{-\gamma_{DG}}$; γ_{DG} is a Grüneisen-type parameter which we shall call the Debye–Grüneisen parameter. If $\theta_D(V_0)$ is known from measurement, where V_0 is the volume at 0 K, then θ_D and $F_m(\theta_D, T)$, the modified (by factor β_z) Helmholtz free energy of vibration, would be known as functions of V and T. We expand E around $a(0)$ (the lattice parameter at $T = 0$ including the ZPE effect) as a function of a in terms of the known bulk modulus B_0 and minimize the Gibbs free energy (at $p = 0$) with respect to a at several T, where

$$G(a, T) = E(a) + F_m(\theta_D(a), T). \tag{5}$$

This procedure expresses the equilibrium a at T in terms of B_0, γ_{DG} and β_z. We tried to evaluate β_z and γ_{DG} by fitting $a(T)$. It proved possible to fit measured $a(T)$ values [6] at $T = 50$, 100 and 200 K with $\beta_z = 0$–1 over narrow non-overlapping range of γ_{DG} ($\gamma_{DG} = 2.30$–2.39 at 50 K, 2.62–2.70 at 100 K and 2.99–3.20 at 200 K), but no unique values of β_z and γ_{DG} would fit even two values of T. Hence a single γ_{DG} parameter would not represent $\theta_D(V)$ adequately.

To evaluate β_z we then added to the measured $a(T)$ values the measured values of $c_{11}(T)$, $c_{12}(T)$, $c_{44}(T)$ for fcc Al [7]. The values of $a(T)$ and $c_{ij}(T)$ give $\theta_D(T)$. We now use Debye theory to develop an equation containing β_z for the thermal expansion between two temperatures T_1 and T_2 at which we have the measured lattice parameter values a_1, a_2 and values of θ_D. The numerical procedure is as follows. Results are in table 2.

At each T the equilibrium equation

$$\left(\frac{\partial G(a, T)}{\partial a}\right)_T = \frac{dE(a)}{da} + \left[\frac{\partial F_m(\theta_D(a), T)}{\partial a}\right]_T = 0 \tag{6}$$

relates dE/da to $(\partial F/\partial a)_T$. Then the difference in dE/da between T_1 and T_2 can be expressed in two ways:

$$\left(\frac{dE}{da}\right)_2 - \left(\frac{dE}{da}\right)_1 = \frac{\overline{d^2 E}}{da^2}(a_2 - a_1) = \left(\frac{\partial F}{\partial a}\right)_1 - \left(\frac{\partial F}{\partial a}\right)_2. \tag{7}$$

In (7), $\overline{d^2 E}/da^2$ is an average value over the range a_1–a_2 which can be expressed in terms of the bulk modulus

$$\left(\frac{d^2 E}{da^2}\right)_i = \frac{9}{4}a_i B_i + \frac{2}{a_i}\left(\frac{dE}{da}\right)_i, \qquad i = 1, 2 \tag{8}$$

Table 2. Parameter values for fcc Al at 100, 200 K and zero pressure leading to values of β_z, γ_{DG} and a_R.

	100 K	200 K
T (deg)	100 K	200 K
a (Å) [6]	4.034 195	4.040 980
c_{11} (Mbar) [7]	1.1333	1.1040
c_{12} (Mbar) [7]	0.6185	0.6130
c_{44} (Mbar) [7]	0.3104	0.2064
B (Mbar)	0.7901	0.7767
θ_D (deg)	426.87	417.62
$d\theta_D/dT$ (no dimension)	$-0.078\,23$	$-0.102\,23$
da/dT (Bohr/deg)	0.4790×10^{-4}	0.8305×10^{-4}
$d\theta_D/da$ (deg/Bohr)	-1.6332×10^3	-1.2309×10^3
γ_{DG} (no dimension)	5.14	3.97
$(\partial F/\partial\theta_D)_T$ (Ryd/deg)	0.4132×10^{-5}	0.7304×10^{-5}
$(\partial F/\partial a)_T$ (Ryd/Bohr)	0.3571×10^{-2}	0.4756×10^{-2}

In (8) B is the bulk modulus $V d^2E/dV^2$ at a_1 and a_2 and the second term is needed in transforming variables from $V = a^3/4$ to a when $dE/da \neq 0$.

To complete (7), we need the relations

$$\left(\frac{\partial F}{\partial a}\right)_T = \left(\frac{\partial F}{\partial \theta_D}\right)_T \frac{d\theta_D}{da}, \tag{9}$$

$$\left(\frac{\partial F}{\partial \theta_D}\right)_T = k_B \left(\frac{9}{8}\beta_z + J(x)\right), \qquad x \equiv \frac{\theta_D}{T}, \tag{10}$$

$$J(x) \equiv I(x) + x\frac{dI(x)}{dx}, \tag{11}$$

$$I(x) \equiv \frac{9}{x^4} \int_0^x z^2 \ln\left(1 - e^{-z}\right) dz. \tag{12}$$

Putting (8)–(12) in (7) gives a linear equation for β_z:

$$\frac{9}{8}(a_2 - a_1)(a_1B_1 + a_2B_2) - \frac{a_2}{a_1}\left(\frac{\partial F}{\partial a}\right)_1 + \frac{a_1}{a_2}\left(\frac{\partial F}{\partial a}\right)_2 = 0. \tag{13}$$

Equation (13) with the use of (9)–(12) is now applied at $T_1 = 100$ K and $T_2 = 200$ K. The five values of $a(T)$ given in [6], plotted in figure 2(a), are used to find the best-fit cubic, which gives da/dT at $T = 100$ and 200 K (table 2). The measured $c_{11}(T)$, $c_{12}(T)$, $c_{44}(T)$ values in [7] and $a(T)$ values in [6] were used to find $\theta_D(T)$ (figure 2(b)). The best-fit cubic to five consecutive values of $\theta_D(T)$ were then used to find $d\theta_D/dT$ at 100 and 200 K (table 2). Then

$$\frac{d\theta_D}{da} = \frac{d\theta_D/dT}{da/dT} \tag{14}$$

was evaluated at 100 and 200 K (table 2). The a and θ_D values at low values of T (50 K and below) varied too slowly to give accurate derivatives, but the variations were reasonable at 100 and 200 K. Then $(\partial F/\partial a)_T$ was found from (9) and (10) at 100 and 200 K (table 2) using interpolation in a large table of $J(x)$, and inserted in (13) to find $\beta_z = 0.48$. The bulk moduli B_1 and B_2 were found from the measured c_{11} and c_{12} at 100 and 200 K (table 2).

From θ_D, $d\theta_D/da$ and a at 100 and 200 K, the Debye–Grüneisen parameter γ_{DG} can be evaluated (table 2); it is defined by

$$\gamma_{DG} \equiv -\frac{\partial \ln \theta_D}{\partial \ln V} = -\frac{a}{3\theta_D}\frac{d\theta_D}{da}. \tag{15}$$
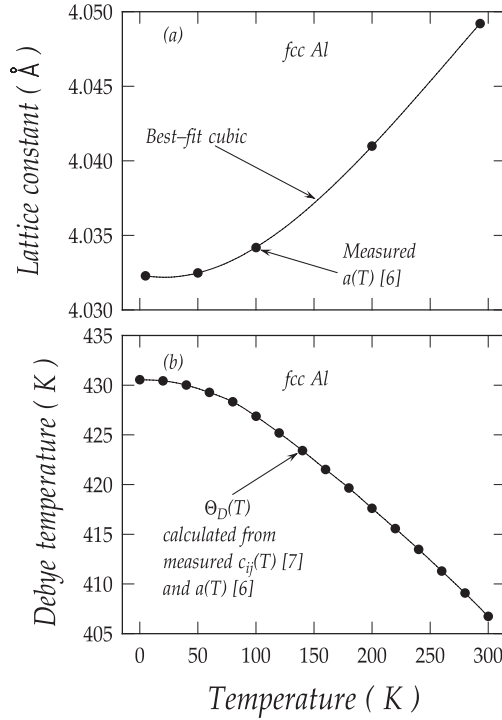
Figure 2. (a) Experimental lattice constant (solid circles, from [6]) and its best-fit cubic (solid line) as a function of temperature. (b) Debye temperature $\theta_D(T)$ (solid circles) calculated from the measured $c_{11}(T)$, $c_{12}(T)$, $c_{44}(T)$ [7] and $a(T)$ values [6] as a function of temperature. The solid line interpolates between the data points.

Finally a_R, the rigid-lattice value of a, can be estimated as the a value at which $dE/da = 0$, where

$$\left(\frac{dE}{da}\right)_R = \left(\frac{dE}{da}\right)_1 + (a_R - a_1)\left(\frac{d^2E}{da^2}\right)_1 = 0. \tag{16}$$

Then using (6) and (8)–(12) in (16) gives $a_R = 4.01$ Å, which may be compared to the GGA value of 4.05 Å and the LSDA value 3.98 Å (figure 1 at $\beta_z = 0$, $T = 0$).

5. Discussion

Section 3 uses the Debye theory of lattice vibrations, generalized by direction-dependent elastic waves and modified by a fractional factor β_z in the ZPE combined with first-principles full-potential total-energy band calculations. The combined theories are applied to calculation of the equilibrium lattice parameter $a(T)$ of fcc Al as a function of temperature (only $p = 0$ is considered).

The following features of this form of Debye theory are shown.

(1) The calculated $a(T)$ differs from measured values over the full range of β_z for both the GGA and the LSDA; hence β_z cannot be evaluated. The GGA results are high by an average 0.7% and the LSDA results are low by 1.2%. These results on the band theory errors are similar to those found by Narasimhan and Gironcoli for thermal parameters of Cu [8].

(2) The calculated thermal expansion from 0 to 300 K fits the measured thermal expansion rather well.

(3) The frequently quoted lowest-order term in the low-T expansion of $F(V, T)$, the T^4 term, is of little value. It is a poor approximation where the thermal expansion is large enough to be measured with good accuracy, and where the term applies a and θ_D vary too little to give accurate derivatives.

The procedure used to find $a(T)$ is another application of the thermodynamic theorem that the equilibrium structure is found at a given p and T by minimizing the Gibbs free energy $G = E + pV + F$. By use of G at reference structures, which are not in general in equilibrium states, the structure at the minimum can be found by fitting a smooth function to the G values and finding the a of the minimum. In previous work [9] we have varied p at $T = 0$; here we vary T at $p = 0$, but the procedure could be used at any p and T.

An alternative procedure finds the equilibrium for cubic materials (which have only one structure parameter V or a) from $p = -\mathrm{d}(E + F)/\mathrm{d}V$, which is equivalent to $\mathrm{d}G/\mathrm{d}V = 0$. In the alternative procedure E is evaluated as a function of V, F as function of V and T, and $p(V, T)$ is found by differentiating with respect to V. It is then necessary to solve $p(V, T) = p_0$ to find $V(T)$ at p_0. This procedure was used for the thermal expansion of Ag by Xie *et al* [10], who found complete phonon spectra calculated at constant V as a function of V, which gave $F(V, T)$ to high values of T. Here we fix p and T first, evaluate E and F at a few reference values of V and interpolate $G(V)$ to find equilibrium at the minimum of G. The process is repeated at each T (and p if wanted) to find $a(T)$. Over a range of T (and p) the E values do not have to be recalculated, and θ_D in $F(\theta_D(V), T)$ also does not have to be recalculated; only T and p are varied. The expansion in $a(T)$ as T increases is driven by the decrease of θ_D due to the decrease of elastic constants as a increases (an anharmonic effect). Decrease of θ_D decreases F and favours increase of a until the increase of strain energy as $E(a)$ increases balances the decrease in F.

We note some consequences of the calculations in section 4, which evaluated β_z, the fraction by which the ZPE in Debye theory should be reduced, and found to be about one half for fcc Al. Note that use of the full Debye ZPE (at $\beta_z = 1$) to take account of the ZPE effect on transition pressure, such as is done in [11, figure 1] for the transition from fcc Al to hcp Al, is an overestimate. Note that the value of β_z was used to estimate that purely theoretical quantity a_R, the rigid-lattice value of a, which came out midway between the GGA and LSDA estimates. The evaluations of a_R directly from measurements provides a useful check on the accuracy of band calculations. In the evaluation of β_z from (13), values of the bulk moduli B_1 at 100 K and B_2 at 200 K were taken from measurements. These values of B_1 and B_2 given by $V(\partial^2 G/\partial V^2)_T$ then included a contribution from $V(\partial^2 F/\partial V^2)_T$ added to $V\,\mathrm{d}^2 E/\mathrm{d}V^2$, whereas (7) and (13) require just the contribution from E. However the F contribution to B is only a few per cent of the contribution from E and can be neglected. In [12, page 6] the contribution from F at 0 K, which is just the ZPE, is evaluated from complete phonon spectra of fcc Al to be 1.8% of the total B.

The calculation of β_z from complete phonon spectra has a complication because mode frequencies are calculated at constant volume, whereas the experiment is at constant pressure. To use complete phonon spectra at constant volume the total energy must be calculated at enough volumes to find the volume and frequencies corresponding to the pressure of the experiment (here zero); moreover, the calculation must be repeated at each temperature, since the volume changes with temperature. The use of Debye theory avoids this complication because the elastic constants that determine θ_D are at constant pressure.

Finally, we note that the values of the Debye–Grüneisen parameter γ_{DG}, 5.1 at 100 K and 4.0 at 200 K, are larger than the values for the standard Grüneisen parameter, e.g., $\gamma_G = 2.2$ at 100 and 200 K for fcc Al [5, page 57]; in addition γ_{DG} varies strongly with T. The accuracy of γ_{DG} depends directly on the accuracy of measured $a(T)$ and $c_{ij}(T)$, and does not involve any thermodynamic or electronic theory.

Acknowledgments

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