Thermodynamic properties of FCC metals: Cu and Al

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Abstract. Isothermal bulk modulus, linear coefficient of thermal expansion, thermodynamic Grüneisen parameter and constant pressure specific heat have been computed for Cu and Al throughout a wide range of temperatures. We use a perturbative Helmholtz free energy as a function of the strain parameters. The Brillouin sums are carried out exactly. The atomic interactions are modelled according to a force constant potential: angular forces and long-range central forces are included in the harmonic part of the potential, while the anharmonic part is first-neighbours ranged. The model is shown to be successful in describing both the thermoelastic and the caloric properties.

1. Introduction

The thermodynamical properties of solids are of great importance in the study of the anharmonic interactions in metals.

A fully microscopic theory of the thermoelastic properties is not yet available because, in order to construct the free energy, one should know the volume dependence of the effective interatomic potential.

The approach which is commonly used (Born and Huang 1954), to include the volume dependence in the free energy, consists in straining the crystal by the method of homogeneous deformations and, then, expanding the nuclear displacements of the strained crystal in terms of the normal phonon coordinates. With this method, the lattice-dynamical problem is solved at a fixed volume and the explicit volume dependence of the potential is not required any more. The derivative of the free energy with respect to the strain parameters are directly related to the thermoelastic properties.

MacDonald and MacDonald (1981) have carried out computations of thermodynamics in FCC metals: a Morse-like potential is adopted by these authors and the unknown parameters are fitted to some thermodynamical properties.

Their approach was based on Shukla's previous calculations (1980) of the lattice sums needed to obtain the Helmholtz free energy as a function of temperature and volume, $F(V, T)$. However, this scheme is justified only in the high-temperature limit ($T \geq \theta_D$, the Debye temperature) and for a wholly nearest-neighbour central forces model potential.

In dealing with simple metals, pseudopotential theory has been used (Koehler *et al* 1970, Gillis and Koehler 1971) to determine the anharmonic interactions. In the case of noble metals the situation is more complex: the s–d electron interaction gives rise to many-body forces and the construction of a pseudopotential is not very accurate. To describe, at the same time, simple and noble metals we will use a force constant

scheme and consider the potential as a sum of a central part and of an angular part related to three-body forces.

The harmonic potential consists of long-range central forces and a nearest-neighbour angular force. The parameters are fitted to, within the experimental errors, the measured phonon frequencies (Nilsson and Rolandson 1974, Stedman and Nilsson 1966) and second-order elastic constants. The angular part avoids the fulfilment of the second-order Cauchy relations.

We will use the cubic force constants that we have derived in a previous paper (Zoli *et al* 1990) by expanding the internal energy both in terms of strain parameters and in terms of lattice waves. The two expansions give relations between the third-order elastic constants and the cubic force constants.

In the same paper we have shown that for those metals which almost fulfil the third-order Cauchy relations as Cu and Al (Hiki and Granato 1966, Thomas 1968) the nearest-neighbour cubic force constant gives the largest contribution to the anharmonic interaction responsible of the phonon linewidth.

In this paper we also want to show that the anharmonic interactions related to the thermal expansion, Grüneisen parameter, temperature dependence of the elastic constants and specific heat, are mainly determined by the nearest-neighbour cubic central force constant.

A very general scheme, allowing for an explicit dependence of $F(V, T)$ on the strain tensor, is adopted here (Barron and Klein 1974). The effects of deformations on atomic mean positions are introduced via a perturbative method, yielding a double power series in the interaction Hamiltonian: a purely anharmonic one (H_{anh}) plus a strain contribution (H_S).

From the first and second strain derivatives of $F(V, T)$, the temperature effects on the isothermal second-order elastic constants are deduced, while the mixed (both temperature and strain) derivatives of $F(V, T)$ are required in the evaluation of the coefficient of linear expansion.

We remark that no approximation affects the thermoelastic calculations, except for the truncation of the series in the perturbation H_S.

Moreover, the lowest-order (third and fourth) anharmonic terms in the constant volume specific heat (C_V) are calculated exactly, providing a good test for the fourth derivative of the interatomic potential.

Since the constant pressure specific heat (C_P) is the directly measured quantity, we compute it as a function of temperature, by adding C_V and the thermoelastic contribution (Huang 1963).

In section 2 we outline the theory we have used for the perturbation free energy; in section 3 the results are reported for both metals and comparisons with experimental data are discussed; in section 4 the conclusions are drawn.

2. Free energy

The Helmholtz free energy $F(V, T)$ of a crystal can be decomposed into the harmonic contribution $F_0(V, T)$ plus the perturbation term $F_1(V, T)$.

According to the linked-cluster theorem (Mahan 1981):

$$F_1 = -\beta^{-1} \sum_{l=1}^{\infty} U_l \tag{1}$$

where β is the inverse temperature and

$$U_l = \frac{(-1)^l}{l!} \int_0^\beta \mathrm{d}\tau_1 \dots \int_0^\beta \mathrm{d}\tau_l \langle T_\tau (\hat{U}(\tau_1) \dots \hat{U}(\tau_l)) \rangle_{0,\mathrm{conn}}. \tag{2}$$

In equation (2), the usual quantum theory symbols are adopted: T_τ is the time ordering operator; $\hat{U}(\tau_l)$ is the perturbation in the interaction representation; $\langle \dots \rangle_{0,\mathrm{conn}}$ denotes that quantum averages are made on the unperturbed eigenstates and only connected diagrams must be retained. Thermal averages are obviously implied by the formalism. In equation (1), terms are retained up to the second order ($l = 2$).

If an homogeneous deformation is applied to the crystal, the Cartesian component of the displacement field can be written in terms of the normal coordinates as (Barron and Klein 1974)

$$u_\alpha(L) = \sum_\beta (\delta_{\alpha\beta} + u_{\alpha\beta}) R_\beta(L) + \sum_{qj} T_\alpha(L; q\,j) A_{qj} \tag{3}$$

where $u_{\alpha\beta}$ is the strain-rotation tensor, $R(L)$ denotes the lattice site in the undeformed state, A_{qj} is the mode normal coordinate,

$$T_\alpha(L; q\,j) = \left(\frac{\hbar}{2MN} \right)^{1/2} \frac{e_\alpha(q\,j)}{\sqrt{\omega(q\,j)}} \exp(i q \cdot R(L)) \tag{4}$$

In equation (4), M and N are atomic mass and number of atoms of the crystal, respectively; the eigenstates $e(q\,j)$ and the eigenvalues $\omega(q\,j)$ are computed within the usual force constant harmonic model.

The effects of strain on the harmonic Hamiltonian yield the relations (which are reported in Appendix 1) between second-order elastic constants and harmonic force constants. Then, equation (3) is substituted into the third- and fourth-order anharmonic Hamiltonian, and the following expression is derived for the perturbation U:

$$U = H_{\mathrm{anh}} + H_S$$

$$H_{\mathrm{anh}} = \sum_{\lambda_1\lambda_2\lambda_3} V^{(3)}(\lambda_1; \lambda_2; \lambda_3) A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} + \sum_{\substack{\lambda_1\lambda_2\\\lambda_3\lambda_4}} V^{(4)}(\lambda_1; \lambda_2; \lambda_3; \lambda_4) A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} A_{\lambda_4} \tag{5}$$

$$H_S = \sum_{\alpha\beta} u_{\alpha\beta} H_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\alpha'\beta'} u_{\alpha\beta} u_{\alpha'\beta'} H_{\alpha\beta\alpha'\beta'} + \dots$$

where $\lambda_i \equiv (q_i j_i)$, $V^{(3)}$ and $V^{(4)}$ are the Fourier transform of the third and fourth-order atomic force constants, respectively; moreover:

$$H_{\alpha\beta} = \sum_{\lambda_1} V_{\alpha\beta}(\lambda_1) A_{\lambda_1} + \sum_{\lambda_1\lambda_2} V_{\alpha\beta}(\lambda_1; \lambda_2) A_{\lambda_1} A_{\lambda_2} + \dots$$

$$H_{\alpha\beta\alpha'\beta'} = \sum_{\lambda_1} V_{\alpha\beta\alpha'\beta'}(\lambda_1) A_{\lambda_1} + \sum_{\lambda_1\lambda_2} V_{\alpha\beta\alpha'\beta'}(\lambda_1; \lambda_2) A_{\lambda_1} A_{\lambda_2} + \dots \tag{6}$$

with

$$V_{\alpha\beta}(\lambda_1) = \frac{1}{2}\sum_{L,L'}\sum_{\gamma\delta}\phi_{\alpha\gamma\delta}(L,L')R_\beta(L,L')R_{\gamma}(L,L')T_\delta(L,L';\lambda_1)$$

$$+\frac{1}{4}\sum_{L,L'}\sum_{\gamma\delta\mu}\phi_{\alpha\gamma\delta\mu}(L,L')R_\beta(L,L')R_{\gamma}(L,L')R_\delta(L,L')T_\mu(L,L';\lambda_1)$$

$$V_{\alpha\beta}(\lambda_1;\lambda_2) = \frac{1}{4}\sum_{L,L'}\sum_{\gamma\delta}\phi_{\alpha\gamma\delta}(L,L')R_\beta(L,L')T_{\gamma}(L,L';\lambda_1)T_\delta(L,L';\lambda_2)$$

$$V_{\alpha\beta\alpha'\beta'}(\lambda_1) = \frac{1}{2}\sum_{L,L'}\sum_{\gamma}\phi_{\alpha\alpha'\gamma}(L,L')R_\beta(L,L')R_{\beta'}(L,L')T_{\gamma}(L,L';\lambda_1)+$$

$$\frac{1}{2}\sum_{L,L'}\sum_{\gamma\delta}\phi_{\alpha\alpha'\gamma\delta}(L,L')R_\beta(L,L')R_{\beta'}(L,L')R_{\gamma}(L,L')T_\delta(L,L';\lambda_1)$$

$$V_{\alpha\beta\alpha'\beta'}(\lambda_1;\lambda_2) = \frac{1}{4}\sum_{L,L'}\sum_{\gamma\delta}\phi_{\alpha\alpha'\gamma\delta}(L,L')R_\beta(L,L')R_{\beta'}(L,L')T_{\gamma}(L,L';\lambda_1)T_\delta(L,L';\lambda_2)$$

(7)

In equations (7), $R(L,L') \equiv R(L) - R(L')$ whereas $\phi_{\alpha\gamma\delta}(L,L')$ and $\phi_{\alpha\gamma\delta\mu}(L,L')$ are the third- and fourth-order force constant tensors, respectively. In equation (6), static lattice terms are omitted since they do not have any effect on thermal properties; moreover, the second-order truncation of the normal coordinate power series (consistent with equation (5)) allows a description of the main effects of deformation.

Once the perturbation given by equation (5) is inserted in equation (2), one gets from equation (1) to the second order:

$$F_1 = \beta^{-1}\left\langle T_\tau\left(\int_0^\beta d\tau_1\,H_S(\tau_1) - \frac{1}{2}\int_0^\beta d\tau_1\int_0^\beta d\tau_2\,H_S(\tau_1)H_S(\tau_2)\right)S(\beta)\right\rangle_{0,\text{conn}}$$

(8)

with

$$S(\beta) = 1 - \int_0^\beta d\tau_1'\,H_{\text{anh}}(\tau_1')$$

(9)

From equation (8), the temperature dependence of the thermoelastic quantities will be easily derived in the next section.

3. Results and discussion

We denote by $\eta_{\alpha\beta}$ the strain tensor that vanishes for pure rotations; the $u_{\alpha\beta}$ (strain–rotation) derivatives, as obtained from equation (8), have to be converted into $\eta_{\alpha\beta}$ strain derivatives in order to define physical quantities. The relations between the $\eta_{\alpha\beta}$ derivatives and the $u_{\alpha\beta}$ derivatives are

$$\frac{\partial F_1}{\partial\eta_{\alpha\beta}} = \frac{\partial F_1}{\partial u_{\alpha\beta}}$$

(10)

$$\frac{\partial^2 F_1}{\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta}} = \frac{\partial^2 F_1}{\partial u_{\alpha\beta}\partial u_{\gamma\delta}} - \delta_{\beta\delta}\frac{\partial F_1}{\partial\eta_{\alpha\gamma}}.$$

We have calculated the temperature dependence of the following quantities.

(1) The stress tensor $\sigma_{\alpha\beta}$

$$V \cdot \sigma_{\alpha\beta}(T) = \left(\frac{\partial F_1}{\partial \eta_{\alpha\beta}} \right)_0 \tag{11}$$

V is the crystal volume in the undeformed state.

(2) The isothermal second-order elastic constants $C^T_{\alpha\beta\alpha'\beta'}$

$$V \cdot C^T_{\alpha\beta\alpha'\beta'}(T) = \left(\frac{\partial^2 F_1}{\partial \eta_{\alpha\beta} \partial \eta_{\alpha'\beta'}} \right)_0 \tag{12}$$

(3) The linear coefficient of thermal expansion α

$$\alpha(T) = -(S^T_{11} + 2S^T_{12}) \left(\frac{\partial \sigma_{11}}{\partial T} \right)_0 \tag{13}$$

where the Voigt notation is used for the elastic compliances $S^T_{\alpha\beta\alpha'\beta'}$.

(4) The thermodynamic Grüneisen parameter γ_{td}, which is given in the quasiharmonic approximation by

$$\gamma_{td} = \frac{\sum_{qj} \gamma(qj) C^h_V(qj)}{\sum_{qj} C^h_V(qj)} \tag{14}$$

where $\gamma(qj)$ is the microscopic Grüneisen parameter and $C^h_V(qj)$ is the (qj)-mode contribution to the harmonic constant volume specific heat C^h_V.

(5) The constant pressure specific heat C_P

$$C_P = C^h_V(T) + C^{anh}_V(T) + 9TV\alpha^2 B_T \tag{15}$$

where C^{anh}_V is the constant volume anharmonic specific heat and B_T is the isothermal bulk modulus.

The lowest-order diagrams that contribute to the stress tensor and to the elastic constants are shown in figures 1 and 2, respectively. Their analytic expressions are reported in Appendix 2. Note that, according to equations (10)–(12), the stress tensor diagram has also to be considered in the evaluation of the second-order elastic constants. Higher-order diagrams, which involve H_{anh} in equation (9), have been taken into account but their contribution to the thermoelastic properties was found to be smaller by three orders of magnitude, at high temperatures; (moreover the computation of higher-order diagrams is time consuming since double Brillouin zone sums are implied by the fourth-order anharmonic term).
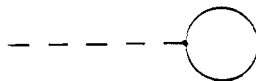

Figure 1. First-order diagram ($D1$) contributing to the stress tensor. The broken line is associated with the strain coefficient $V_{\alpha\beta}$; the full line denotes the phonon loop.
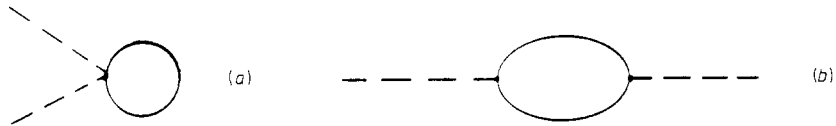
Figure 2. (a) First-order diagram (D2) contributing to the second-order elastic constants: the broken line is associated with the strain coefficient $V_{\alpha\beta\alpha'\beta'}$. (b) second-order diagram (D3) contributing to the second-order elastic constants: the broken lines denote the strain coefficients $V_{\alpha\beta}$ and $V_{\alpha'\beta'}$.

Therefore, our thermoelastic properties calculation is carried out within the quasi-harmonic approximation. To evaluate the diagram in figure 1 (D1) and the second-order diagram in figure 2 (D3) one has to know the third-order force constant. Since we use a first-neighbours central forces anharmonic model potential, the cubic force constant (Y_1) can be determined by knowledge of the experimental second and third-order elastic constants (along the path detailed by Zoli *et al* 1990). The equation we use to evaluate Y_1 is reported in Appendix 1.

In the evaluation of the first-order diagram in figure 2 (D2) one needs the fourth-order force constant (Q_1).

Fourth-order effects are important in the temperature derivatives of the bulk modulus and in the strain derivatives of the Grüneisen parameters $(\partial \ln \gamma / \partial \ln V)_T$ (Hiki *et al* 1967). We have derived an equation between Q_1 and $(\partial \ln \gamma / \partial \ln V)_T$, being this quantity known from the experiments (Hiki *et al* 1967, Wallace 1972).

Table 1. Experimental values for the strain logarithmic derivative of Grüneisen parameters. a: see Hiki *et al* (1967); b: see Wallace (1972). The first-neighbours fourth-order force constants are obtained by equation (A3.8). The units are $(10^{12} \text{ Dyn cm}^{-2})$.

	Cu	Al
$(\partial \ln \gamma / \partial \ln V)_T$	1.2[a]	1.3[b]
Q_1/a	93.8	61.0

The procedure is outlined in Appendix 3, whereas the experimental values of $(\partial \ln \gamma / \partial \ln V)_T$ and the corresponding values of Q_1 are given in table 1. In tables 2 and 3 the contributions to C_{11}^T from the three leading diagrams are listed, at some selected temperatures, for Cu and Al, respectively: D3 turns out to be predominant throughout the whole range of temperatures, its effect being only partly cancelled by D2 and D1 accounts for the linear decreasing of C_{11}^T with temperature observed. One might comment analogously about C_{12}^T and C_{44}^T.

In figures 3 and 4 the isothermal bulk modulus is reported as a function of temperature for Cu and Al, respectively; the coefficient of linear expansion as a function of temperature is shown in figures 5 and 6 for Cu and Al, respectively.

The overall agreement with experiment is quite satisfactory, in spite of some discrepancies that affect α for Al near the melting temperature.

γ_{td} has been calculated from equation (14), after relating the mode dependent Grüneisen parameter to the third-order force constant via equation (A2.3); table 4 shows that our results are quite close to the available experimental data (Hiki *et al* 1967, Gupta 1983).

Table 2. Copper: contributions to C_{11}^T from the leading diagrams, as a function of temperature. The units are $(10^{12}$ Dyn cm$^{-2})$.

Temp. (K)	$D1$	$D2$	$D3$
100	−0.011	0.028	−0.043
200	−0.016	0.041	−0.083
300	−0.023	0.058	−0.124
400	−0.029	0.075	−0.165
500	−0.036	0.092	−0.206
600	−0.043	0.109	−0.247
700	−0.050	0.127	−0.288
800	−0.057	0.145	−0.330
900	−0.065	0.163	−0.371
1000	−0.072	0.181	−0.412

Table 3. Aluminum: contributions to C_{11}^T from the leading diagrams, as a function of temperature. The units are $(10^{12}$ Dyn cm$^{-2})$.

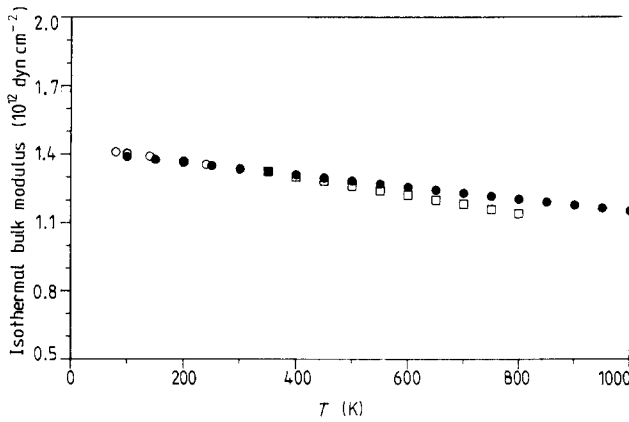| Temp. (K)	$D1$	$D2$	$D3$
100	−0.010	0.027	−0.043
200	−0.014	0.037	−0.079
300	−0.019	0.050	−0.117
400	−0.024	0.063	−0.156
500	−0.030	0.078	−0.196
600	−0.035	0.092	−0.235
700	−0.041	0.107	−0.274
800	−0.047	0.122	−0.313
900	−0.053	0.137	−0.352

Figure 3. Isothermal bulk modulus plotted against temperature in copper. ●, our calculation; ○, Overton and Gaffney (1955); □, Chang and Himmel (1966).

The complete relationships between microscopic Grüneisen parameters and the third-order force constants are reported elsewhere (Zoli 1989); here, we only point out that such equations provide an independent determination of Y_1, being the $\gamma(q\,j)$ that are experimentally known at some high symmetry points: the Y_1 obtained have been
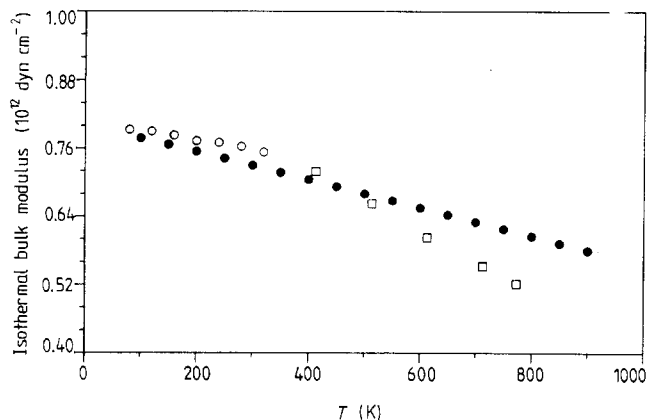
Figure 4. Isothermal bulk modulus against temperature in aluminium. ●, our calculation; ○, Kamm and Alers (1964); □, Sutton (1953).
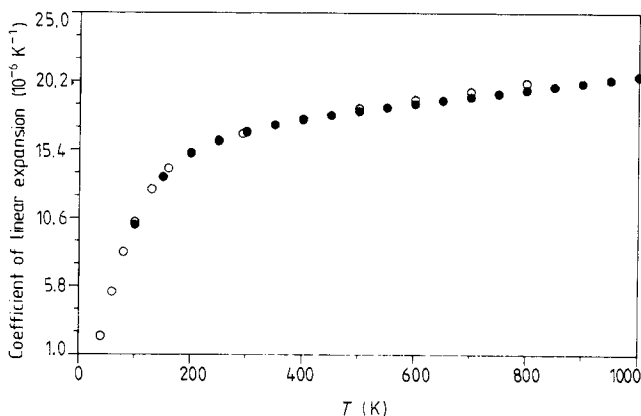

Figure 5. Coefficient of linear expansion plotted against temperature in copper. ●, our calculation; ○, Hahn (1970).

found to agree with the values given by equation (A1.3), both for Cu and Al.

In order to evaluate the constant-volume anharmonic specific heat C_V^{anh}, the perturbation U in equation (5) is identified with the anharmonic Hamiltonian H_{anh} and the strain Hamiltonian H_S is dropped. Once H_{anh} has been inserted in equation (2), the purely anharmonic free energy F_1^{anh} is obtained from equation (1). Since $C_V^{anh} = -T(\partial^2 F_1^{anh}/\partial T^2)$, the temperature dependence of C_V^{anh} can be easily established. The lowest-order diagrams which contribute to C_V^{anh} are shown in figure 7; their analytic expressions have been published frequently (see Leibfried and Ludwig 1961) and are not repeated here. The two anharmonic terms in the constant volume specific heat have been computed by using 2024 points over the entire Brillouin zone. The estimated error in the integration is on the order of 2%. Double Brillouin zone sums are necessary to evaluate the diagram in figure 7(a). The two anharmonic contributions essentially balance each other in the whole range of temperatures, so that explicit anharmonic effects in C_P are provided only by the dilation term (last addendum in equation (15)).

In figures 8 and 9, the theoretical results are seen to fit the experimental data, both
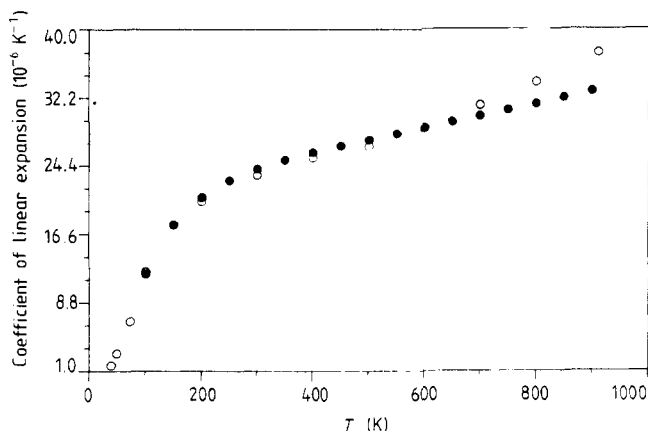
Figure 6. Coefficient of linear expansion plotted against temperature in aluminium. ●, our calculation; ○, Touloukian *et al* (1970).

Table 4. Thermodynamic Grüneisen parameters of Cu and Al, at some temperatures.

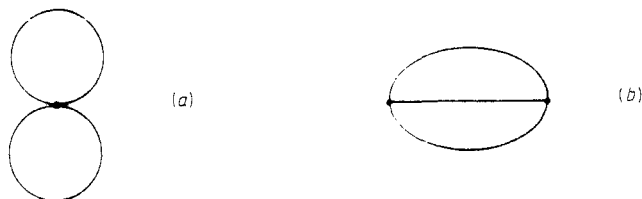|	Temp. (K)	γ_{td}^{th}	γ_{td}^{exp}
Copper	100	1.983	1.994
	300	2.019	2.0
	700	2.023	2.021
Aluminium	100	2.287	2.2
	300	2.312	2.2
	900	2.316	2.281

Figure 7. (*a*) First-order diagram contributing to C_V^{anh}; (*b*) second-order diagram contributing to C_V^{anh}.

for Cu and Al. We found that the C_P slopes, at high temperatures, is very sensitive to the fourth-order force constant. Therefore these calculations furnish an independent check on the reliability of the Q_1 values which we have derived through equation (A3.8).

We also remark that the two lower-order anharmonic terms in C_V^{anh} are opposite in sign. According to our calculations, C_V^{anh} turns out to be slightly negative up to 400 K in the case of aluminium and even further (up to 600 K) in the case of copper. At room temperature we have calculated:

$$C_V^{anh} = -0.46 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (aluminium)}$$

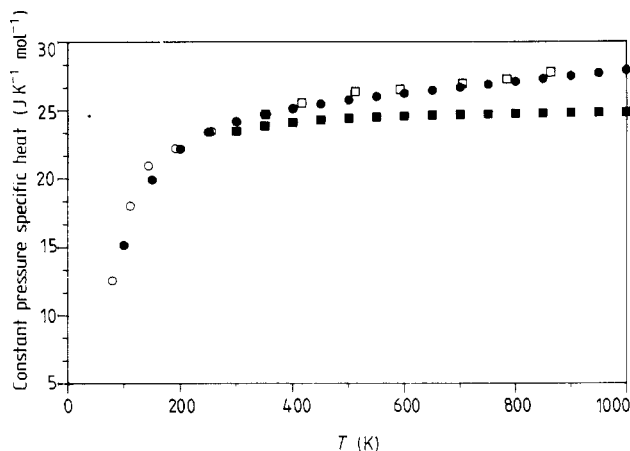$$C_V^{anh} = -0.44 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (copper).}$$

Figure 8. Constant pressure specific heat plotted against temperature in copper; ●, our calculation (C_p); ○, Martin (1960); □, Pawel and Stausburg (1965); ■, our calculation (C_v^h).
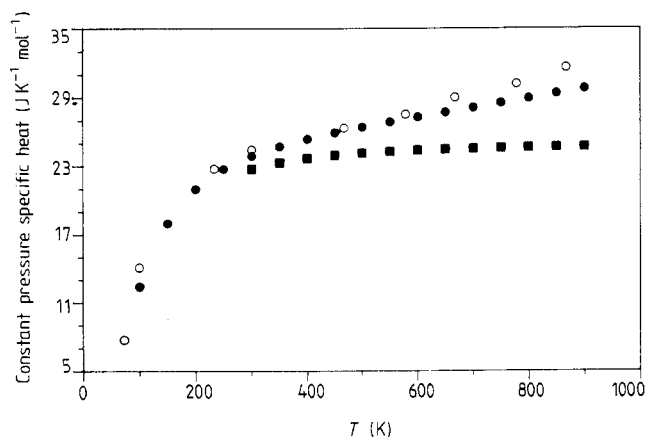

Figure 9. Constant pressure specific heat plotted against temperature in aluminium; ●, our calculation (C_p); ○, Touloukian *et al* (1970); ■, our calculation (C_v^h).

Experimental inquiries about the excess heat capacity due to anharmonic lattice vibrations are known to be very delicate. Recently, Martin (1987a, b) has carried out accurate specific heat measurements on noble metals, below room temperature; from the results obtainedthe Debye temperature was seen to be a slightly increasing function of temperature, suggesting that negative values of C_V^{anh} are to be expected; such a tendency, present in copper, should be even more evident on silver and gold. Similar speculations have been proposed by Rosèn and Grimvall (1983) and by Cordoba and Brooks (1971).

As for aluminium, our result is in good agreement with previous evaluation by Leadbetter (1968) at room temperature, although, unlike that which was found by Leadbetter (1968), our values of C_V^{anh} fast become positive above 400 K. Therefore, our calculation would better agree with the C_V^{anh} slope obtained by Brooks and Bingham (1968).

4. Conclusions

Thermoelastic and caloric properties of Cu and Al have been computed over a wide range of temperatures. Both the microscopic effects of deformations and the pure anharmonic interactions have been included in the Helmholtz free energy. By applying the second-order perturbative method, the temperature dependence of the physical quantities has been derived. In order to reproduce accurately the experimental phonon frequencies and polarisation vectors, the harmonic part of the interactions has been modelled with long-range central forces and nearest-neighbours angular forces. The sums, which appear in equations (A2.1), (A2.4), (A2.5) and in the analytic expressions of the diagrams in figure 7, have been carried out exactly over the first Brillouin zone; as already pointed out by Shukla (1980) this is a crucial point in the evaluation of the thermodynamical quantities. We remark that a correct handling of the $(q\,j)$-mode contributions enables a computation of thermodynamical properties even below the Debye temperature, which may be of particular interest in the case of the thermal expansion.

We have shown that the thermoelastic properties are mainly determined by the nearest-neighbours cubic central force constant: the use of a short-ranged central cubic potential suffices in fitting the experimental data over a wide range of temperatures.

The overall success of our calculations suggests that many body effects are scarcely relevant in the anharmonic tail of the potential in the case of both Cu and Al. It is interesting that the coefficient of linear expansion can be well reproduced by a cubic force constant derived through third-order elastic constant data; a further convincing check is furnished by the thermodynamic Grüneisen parameter.

In calculations of the constant volume specific heat, the quartic anharmonic Hamiltonian has to be taken into account, since it contributes to the first perturbative order in the S-matrix expansion. We have derived an equation (see equation (A3.8)) which relates the fourth-order force constant to the lower-order force constants and to the strain derivative of the Grüneisen parameter. The fourth-order anharmonic term turns out to be responsible for a slightly negative contribution to the specific heat which has been experimentally observed, both in Cu and Al, below room temperature. At high temperatures, anharmonic effects in the constant pressure specific heat are mainly provided by the dilation term (last addendum in equation (15)). However, we believe that the whole matter of anharmonic lattice vibrations contributions merits further investigation: we plan to carry out exact calculations for silver and gold, to investigate the effects of many-body forces. We stress that the input parameters δ_T and B'_T are crucial to our evaluation of C_V^{anh}, so that further experimental studies, mostly on the isothermal pressure derivative of the isothermal bulk modulus $(\partial B_T/\partial P)_T$, would be worthwhile for noble metals.

Appendix 1

The second-order elastic constants as functions of the harmonic force constants are here reported. We define:

$$\alpha_i = \frac{\phi'(r_i)}{r_i} \qquad \beta_i = \phi''(r_i) \qquad \delta_i = \frac{1}{3a^2}W''(\cos\theta^{J\hat{K}L}) \qquad (A1.1)$$

where a is the lattice constant; i indexes the neighbour shell; $\phi(r_i)$ is the pairwise potential; $W(\cos\theta^{J\hat{K}L})$ is the three-body potential, $(J\hat{K}L)$ labelling the tern of atoms.

Since we consider first-neighbours angular forces, it follows that (i) J and L are nearest-neighbours of K; (ii) J and L have to be nearest neighbours of each other.

Then, in a first through sixth central forces plus first-neighbours angular forces model potential, one gets:

$$a \cdot C_{11} = 2(\beta_1 - \alpha_1) + 4(\beta_2 - \alpha_2) + 12(\beta_3 - \alpha_3) + 8(\beta_4 - \alpha_4) + \tfrac{164}{5}(\beta_5 - \alpha_5) + \tfrac{16}{3}(\beta_6 - \alpha_6) + 12\delta_1$$

$$a \cdot C_{12} = (\beta_1 - \alpha_1) + 6(\beta_3 - \alpha_3) + 4(\beta_4 - \alpha_4) + \tfrac{18}{5}(\beta_5 - \alpha_5) + \tfrac{16}{3}(\beta_6 - \alpha_6) - 6\delta_1$$

$$a \cdot C_{44} = a \cdot C_{12} + 18\delta_1. \tag{A1.2}$$

The force constants are obtained by a least-squares fit of the experimental phonon frequencies and second-order elastic constants at 80 K.

From Zoli *et al* (1990), the cubic anharmonic force constant $(Y_1 \equiv r_1 \cdot \phi'''(r_1))$ as a function of second- and third-order elastic constants is

$$Y_1 = \tfrac{1}{2}a\left(\tfrac{1}{2}C_{111} + 3C_{112} + C_{123} + \tfrac{3}{2}C_{11} + 3C_{12}\right). \tag{A1.3}$$

The Voigt notation is adopted for the elastic constants.

Appendix 2

The diagram in figure 1 contributes to the stress tensor with

$$V \cdot \sigma_{\alpha\beta}(T) = \sum_{qj} V_{\alpha\beta}(q\,j; -q\,j)(2n_{qj} + 1). \tag{A2.1}$$

$V_{\alpha\beta}(q\,j; -q\,j)$ is given in equation (7); n_{qj} is the Bose–Einstein factor; V is the volume in the undeformed state. In a quasiharmonic approximation, the stress tensor is related to the mode Grüneisen tensor $\gamma_{\alpha\beta}(q\,j)$ as follows:

$$V \cdot \sigma_{\alpha\beta}(T) = -\sum_{qj} \gamma_{\alpha\beta}(q\,j)\hbar\omega(q\,j)\left(n_{qj} + \tfrac{1}{2}\right). \tag{A2.2}$$

Then, from equations (A2.1), (A2.2), one gets

$$\gamma_{\alpha\beta}(q\,j) = -\frac{2V_{\alpha\beta}(q\,j; -q\,j)}{\hbar\omega(q\,j)} \tag{A2.3}$$

which allows us to obtain the mode Grüneisen parameter $\gamma(q\,j)$ $\left(\gamma(q\,j) = \tfrac{1}{3}\sum_{\alpha=1}^{3}\gamma_{\alpha\alpha}(q\,j)\right)$ as a function of the third-order force constant.

Equations (8) and (9) yield two second-order contributions to the stress tensor: the first is associated with the $V^{(3)}$ coefficient and vanishes for monoatomic lattices; the second, which depends on the $V^{(4)}$ coefficient, is negligible. From equation (A2.1), the stress tensor temperature derivatives, which appears in equation (13), can be easily derived.

The first-order diagram in figure 2 gives:

$$V \cdot C^{(1)}_{\alpha\beta\alpha'\beta'}(T) = \sum_{qj} V_{\alpha\beta\alpha'\beta'}(q\,j; -q\,j)(2n_{qj} + 1) \tag{A2.4}$$

with $V_{\alpha\beta\alpha'\beta'}(q\,j\,;-q\,j)$ detailed in equation (7).

The second-order diagram in figure 2 contributes with

$$V \cdot C^{(2)}_{\alpha\beta\alpha'\beta'}(T) = -\frac{4}{\hbar} \sum_{\substack{q \\ j_1 \neq j_2}} V_{\alpha\beta}(q\,j_1\,;-q\,j_2)V_{\alpha'\beta'}(q\,j_1\,;-q\,j_2)\left(\frac{\omega_2(2n_1+1)-\omega_1(2n_2+1)}{\omega_2^2-\omega_1^2}\right)$$

$$-\frac{2}{\hbar}\sum_{qj}V_{\alpha\beta}(q\,j\,;-q\,j)V_{\alpha'\beta'}(q\,j\,;-q\,j)\left(\frac{(2n_{qj}+1)}{\omega(q\,j)}+2\beta\hbar n_{qj}(n_{qj}+1)\right)$$

(A2.5)

where $\omega_i \equiv \omega(q\,j_i)$ and $n_i \equiv n(\omega_i)$.

Appendix 3

The microscopic Grüneisen parameter can be written as (Leibfried and Ludwig 1961):

$$\gamma(q\,j,\eta) = -\frac{1}{6\omega^2(q\,j)} \sum_{\alpha=1}^{3} \frac{\partial\omega^2(q\,j)}{\partial\eta_{\alpha\alpha}}$$

(A3.1)

We assume the 'Grüneisen approximation' (Davies 1973), according to which the $(q\,j)$-mode dependence is dropped in $\gamma(q\,j,\eta)$, hence $\gamma(\eta)$ is identified with the thermodynamic Grüneisen parameter appearing in the Mie–Grüneisen equation of state.

Although such an approximation is generally quite crude (Cantrell 1980, Prasad and Srivastava 1978, Wallace 1970) it might hold better at high temperatures, where all modes are excited. Since fourth-order effects are important at high temperatures, we hope not to affect the value of the fourth-order force constant greatly by assuming the 'Grüneisen approximation'.

Then, from equation (A3.1) one gets

$$\gamma(\eta) = -\frac{1}{6\bar{\omega}^2} \sum_{\alpha=1}^{3} \frac{\partial\bar{\omega}^2}{\partial\eta_{\alpha\alpha}}$$

(A3.2)

where the spectral average $\bar{\omega}^2$ is given by

$$\bar{\omega}^2 = \frac{1}{3M} \sum_{\alpha=1}^{3} \phi_{\alpha\alpha}.$$

(A3.3)

In equation (A3.3), $\phi_{\alpha\alpha}$ is the second-order force constant tensor in the deformed state. For small strains $u_{\alpha\beta}$, $\phi_{\alpha\alpha}$ can be expanded about the minimum of the potential energy in the undeformed state, so that equation (A3.3) yields

$$\bar{\omega}^2 = \frac{1}{3M}\left(\sum_{\alpha} f_\alpha + \sum_{\alpha\beta} g_{\alpha\beta}u_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta\gamma} h_{\alpha\beta\gamma}u_{\alpha\beta}u_{\alpha\gamma}\right)$$

(A3.4)

with

$$f_\alpha = \sum_i \sum_J \left(\frac{(\beta_i - \alpha_i)}{r_i^2} R_\alpha^2(J) + \alpha_i \delta_{\alpha\alpha} \right)$$

$$g_{\alpha\beta} = \sum_J \phi_{\alpha\alpha\beta}(J) R_\beta(J) \tag{A3.5}$$

$$h_{\alpha\beta\gamma} = \sum_J \phi_{\alpha\alpha\beta\gamma}(J) R_\beta(J) R_\gamma(J)$$

In equation (A3.5), $\phi_{\alpha\alpha\beta}(J)$ and $\phi_{\alpha\alpha\beta\gamma}(J)$ are the third- and fourth-order force constants tensors; for symbols occurring in f_α, see Appendix 1.

Since $\partial\bar\omega^2/\partial\eta_{\alpha\alpha} \equiv \partial\bar\omega^2/\partial u_{\alpha\alpha}$, from equations (A3.2), (A3.4) one easily gets

$$\left(\frac{\partial \ln\gamma(\eta)}{\partial\eta} \right)_{\eta=0} = \frac{h}{g} - \frac{g}{f} \tag{A3.6}$$

where

$$f = \sum_i N_i(\beta_i + 2\alpha_i)$$

$$g = 12(Y_1 + 2(\beta_1 - \alpha_1)) \tag{A3.7}$$

$$h = 12(Q_1 + 2Y_1 - 4(\beta_1 - \alpha_1))$$

N_i is the number of atoms in the i-neighbour shell; $Q_1 \equiv r_1^2 \cdot \phi''''(r_1)$.

Converting the strain derivative to the volume derivative, from equations (A3.6) and (A3.7):

$$Q_1 = \left[3\left(\frac{\partial \ln\gamma}{\partial \ln V} \right)_{T,\eta=0} + \frac{g}{f} \right] \frac{g}{12} - 2Y_1 + 4(\beta_1 - \alpha_1). \tag{A3.8}$$

According to thermodynamics (Bassett *et al* 1968):

$$\left(\frac{\partial \ln\gamma}{\partial \ln V} \right)_T = 1 + \delta_T - B_T' - \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T \tag{A3.9}$$

with

$$\delta_T = -\frac{1}{3\alpha B_T}\left(\frac{\partial B_T}{\partial T} \right)_P \qquad \text{and} \qquad B_T' = \left(\frac{\partial B_T}{\partial P} \right)_T.$$

Constant volume specific heat is customarily assumed independent of volume at high temperatures (Christian 1981), so that the last term in equation (A3.9) can be dropped. Since δ_T and B_T' are measurable quantities, by insertion of equation (A3.9) in equation (A3.8) one is led to evaluate the fourth-order derivative of the interatomic potential.

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