

# Lattice Dynamical Calculation of Some Thermodynamic Properties for Aluminum†

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A local-pseudopotential model is used to calculate the heat-capacity Debye temperature, the phonon Grüneisen parameters and lattice thermal-expansion coefficient, and the elastic constants and their pressure derivatives. The only serious discrepancy between theory and experiment is in the long-wavelength-phonon velocities. This discrepancy is most likely associated with the neglect of higher-order pseudopotential terms in the long-wavelength dynamical matrix.

IN a recent calculation, we adjusted the two parameters of a simple local pseudopotential to obtain a good over-all fit to the phonon spectrum, and to the Fermi-surface form factor, for aluminum.<sup>1</sup> Here we compare with experiment several additional properties, calculated for aluminum from the same pseudopotential, namely, the heat-capacity Debye temperature, the thermal-expansion coefficient, and the elastic constants and their pressure derivatives. This comparison provides two useful results. First, the pseudopotential model is found to give a reasonably good over-all description of the harmonic and anharmonic properties studied, but a rather poor description of properties associated with the sound velocities becomes apparent. Secondly, it is seen that comparison of calculations with accurate specific-heat and thermal-expansion measurements will provide sensitive tests of a detailed lattice-dynamics model.

The temperature dependence of thermodynamic quantities is generally measured at zero pressure  $P$ ; in this case both the dependence on the volume  $V$  and on the temperature  $T$  contribute to the observed temperature dependence. In comparison with theory, it is useful to correct thermodynamically the experimental data at each  $T$ , from the volume  $V$  corresponding to  $P=0$  to the fixed volume  $V_0$  corresponding to  $P=0$  and  $T=0$ . This is because it is much simpler to carry out accurate calculations for a fixed volume, say  $V_0$ , and the resulting comparison of theory and experiment then allows one to draw more definite conclusions about the theoretical model. Such thermodynamic corrections of experimental data have been discussed previously.<sup>2</sup>

Consider first the heat capacity as a function of temperature; a sensitive representation of this quantity is the equivalent Debye temperature  $\Theta$ . From the 4.2°K elastic constants of Kamm and Alers,<sup>3</sup> and a value of  $110.6a_0^3$  for the volume per atom at  $T=0$ ,<sup>1</sup> we calculated  $\Theta=430.5^\circ\text{K}$  at  $T=0$ . Note that Kamm and Alers obtained  $430.3^\circ\text{K}$ ; this difference is presumably due to the use of a slightly different atomic volume, and is completely negligible in the present work. Berg<sup>4</sup>

measured the heat capacity and tabulated  $\Theta$  for  $T=2.7\text{--}20^\circ\text{K}$ ; here it was not necessary to make  $C_P-C_V$  or volume corrections, but the electronic heat capacity was subtracted to obtain the lattice contribution. At higher temperatures we took tabulated values of  $C_P$  from two standard references<sup>5,6</sup> and found these to be in good agreement; these data were then corrected to  $C_V(V,T)$ , then to  $C_V(V_0,T)$ , and finally the measured electronic contribution<sup>7</sup> was subtracted to obtain the lattice heat capacity and then the equivalent  $\Theta$ . The experimental results are shown in Fig. 1.

Figure 1 also shows the theoretical  $\Theta$  as a function of  $T$ , based on a harmonic calculation of the lattice specific heat at fixed volume  $V_0$ . At nonzero temperatures, the calculation counted 915  $\mathbf{k}$  vectors in  $1/48$  of the Brillouin zone, equivalent to 32 059 points in the entire zone; this gives  $\Theta(T)$  accurately down to about  $8^\circ\text{K}$ . At  $T=0$  the calculation was based on the theoretical long-wavelength-phonon velocities, just as in the calculation based on the measured elastic constants; the  $\Theta(T)$  curve was then interpolated from  $0\text{--}8^\circ\text{K}$ . At  $T=0$  the value is  $\Theta=406^\circ\text{K}$ ; this large discrepancy (5.6%) from the experimental result shows the theoretical sound velocities (long-wavelength acoustic-phonon velocities) must be significantly different from experimental results. The initial increase of  $\Theta$  with  $T$  at low  $T$  reflects the phonon dispersion in the following way: The frequency  $\omega_{\mathbf{k}s}$  of a phonon with wave vector  $\mathbf{k}$  and polarization  $s$  may be written, in the long-wavelength limit for a fixed direction of  $\mathbf{k}$ ,

$$\omega_{\mathbf{k}s} = c_s |\mathbf{k}| + d_s \mathbf{k}^2 + \dots$$

The value of  $\Theta$  at  $T=0$  is determined by the velocities  $c_s$ . Since  $\Theta$  increases as  $T$  increases from  $T=0$ , the quantities  $d_s$  must be positive for a significant number of the low-lying (transverse) branches. The theory is seen to agree with experiment in this respect, showing an increase in  $\Theta$  of about the right magnitude and at about the right temperature. Above  $50^\circ\text{K}$ , the calculated and measured  $\Theta$  are in excellent agreement. In

<sup>5</sup> R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. (U. S.) Monograph 21, (1960).

<sup>6</sup> R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (Wiley, New York, 1963).

<sup>7</sup> M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) **A285**, 561 (1965).

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<sup>1</sup> D. C. Wallace, Phys. Rev. **187**, 991 (1969).

<sup>2</sup> D. C. Wallace, Phys. Rev. **176**, 827 (1968).

<sup>3</sup> G. N. Kamm and G. A. Alers, J. Appl. Phys. **35**, 327 (1964).

<sup>4</sup> W. T. Berg, Phys. Rev. **167**, 583 (1968).

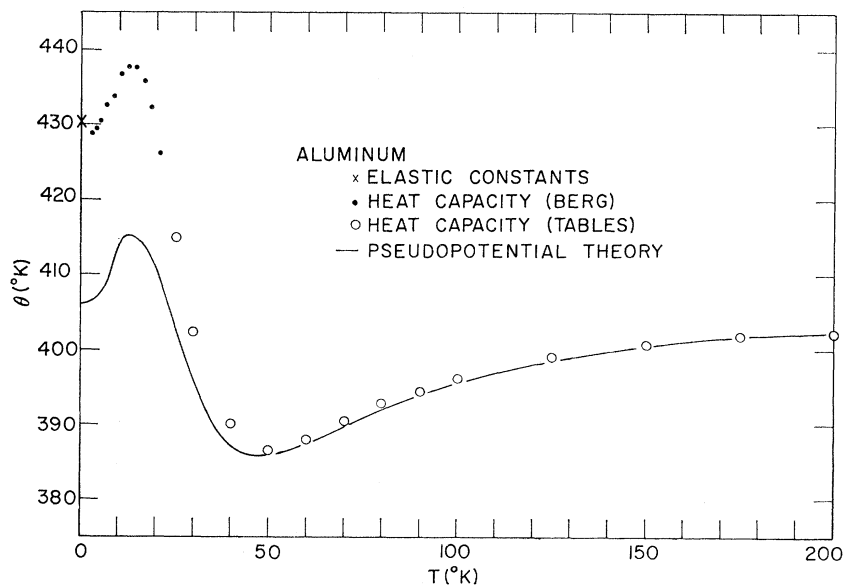


FIG. 1. Experimental and theoretical Debye temperatures for aluminum.

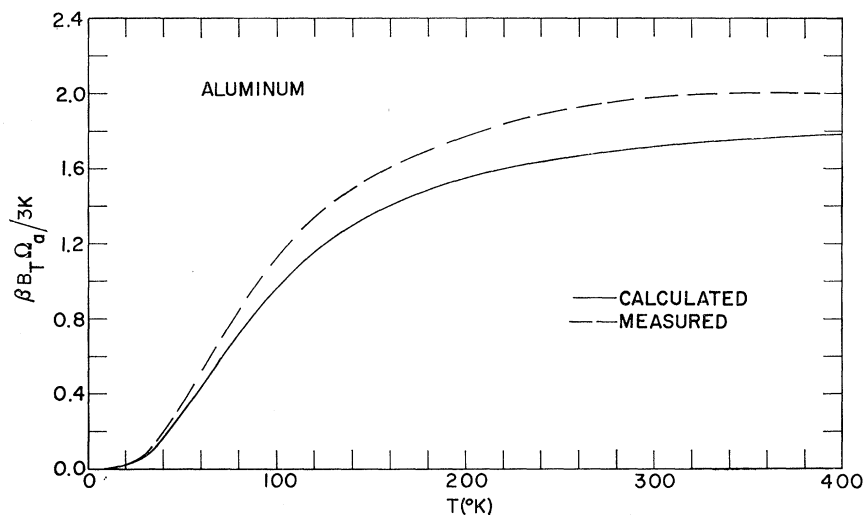


FIG. 2. Experimental and theoretical thermal expansion coefficients, in the form  $\beta B_T \Omega_a / 3K$ , for aluminum.

this region the variation of  $\Theta$  with  $T$  is determined by the even moments of the frequency distribution.

Now consider the thermal-expansion coefficient  $\beta$ . As we previously pointed out,<sup>8</sup> the quantity which is simple to calculate and which provides the most direct interpretation is the dimensionless combination  $\beta B_T \Omega_a / 3K$ , where  $B_T$  is the isothermal bulk modulus,  $\Omega_a$  is the  $T=0$  volume per atom, and  $K$  is the Boltzmann constant. This quantity is simply a weighted average of the phonon Grüneisen parameters  $\gamma_{ks}$ , which are defined by

$$\gamma_{ks} = -(d \ln \omega_{ks}) / d \ln V.$$

For the measured  $\beta$  at  $P=0$  we used Kirby's tabulation<sup>9</sup>; this table is in good agreement with published

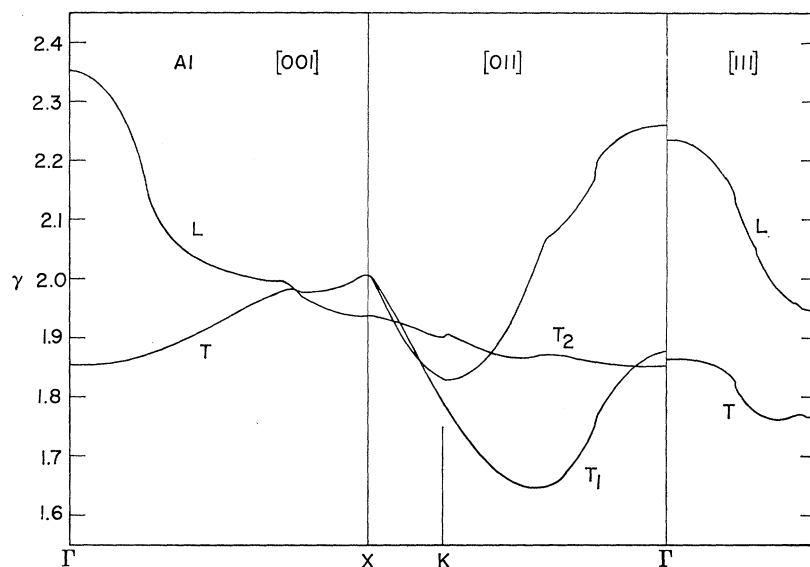
measurements for aluminum.<sup>10</sup> The adiabatic bulk modulus was taken from the measurements of Kamm and Alers,<sup>3</sup> the isothermal bulk modulus was then calculated, and the thermodynamic correction to fixed volume  $V_0$  was carried out for the quantity  $\beta B_T$ . This volume correction was negligibly small, being less than 1% up to 300°K, because of the near cancellation of the corrections for  $\beta$  and  $B_T$ . The experimental curve is shown in Fig. 2; above 300°K the value is questionable,

<sup>9</sup> R. K. Kirby, in *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1963), 2nd ed., p. 4-64.

<sup>10</sup> C. P. Abbiss, E. Huzar, and G. O. Jones, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961), p. 688; D. B. Fraser and A. C. Hollis Hallett, *ibid.*, p. 689.

<sup>8</sup> D. C. Wallace, *Phys. Rev.* **176**, 832 (1968).

FIG. 3. Theoretical Grüneisen parameters at  $P=0$ ,  $T=0$  for aluminum.



since there we relied on an interpolation of the bulk modulus toward the high-temperature data of Sutton.<sup>11</sup>

To calculate the thermal expansion, we first calculated the Grüneisen parameters  $\gamma_{ks}$ . Our computational errors are at most 1% for the  $\gamma_{ks}$ ; the result for  $\mathbf{k}$  along symmetry directions is shown in Fig. 3. Just as in the calculations for lithium, an abundant number of Kohn anomalies are apparent in the  $\gamma_{ks}$  curves.<sup>12</sup> Although there have not yet been any direct measurements of  $\gamma_{ks}$ , we are in hopes these will soon be carried out by neutron-scattering experiments on crystals under pressure. The calculated quasi-harmonic curve of  $\beta B_T \Omega_a / 3K$  as a function of  $T$  is shown in Fig. 2; the calculation is lower than the experimental result by about 12% at all temperatures. From this comparison, and since the calculated and measured  $\Theta$  are in agreement for  $T \geq 50^\circ\text{K}$ , we can conclude approximately that the calculated  $\gamma_{ks}$  are more or less uniformly too small by about 12%.

TABLE I. Measured elastic constants at zero temperature, and pressure derivatives at room temperature, compared with values calculated by the method of long waves at zero temperature, for aluminum.  $\Omega_a C_{\alpha\beta}$  and  $\Omega_a B$  are in Ry, and the pressure derivatives are dimensionless.

Quantity	Experiment	Theory
$\Omega_a C_{11}$	0.859	0.60
$\Omega_a C_{12}$	0.466	0.32
$\Omega_a C_{44}$	0.238	0.26
$\Omega_a B$	0.597	0.41
$dB_{11}/dP$	6.35	5.1
$dB_{12}/dP$	3.45	3.0
$dB_{44}/dP$	2.10	2.0
$dB/dP$	4.42	3.7

<sup>11</sup> P. M. Sutton, Phys. Rev. **91**, 816 (1953).

<sup>12</sup> D. C. Wallace, Phys. Rev. **178**, 900 (1969).

Finally, in Table I we compare the calculated and measured elastic constants and their pressure derivatives. The experimental values for the elastic constants  $C_{\alpha\beta}$  and the bulk modulus  $B$  are the  $4.2^\circ\text{K}$  results of Kamm and Alers.<sup>3</sup> When pressure is applied to the sample, the quantities directly measured are pressure derivatives of the Birch coefficients  $B_{\alpha\beta}$ <sup>13</sup>; the experimental pressure derivatives are the room-temperature results of Thomas.<sup>14</sup> The calculated values were obtained by the method of long waves. Since at  $P=0$  the  $C_{\alpha\beta}$  are proportional to  $\omega_{ks}^2$  for the long-wavelength phonons, the percentage difference between experiment and theory will be roughly twice as much for the  $C_{\alpha\beta}$  as for the corresponding  $\omega_{ks}$ . Indeed the measured  $C_{\alpha\beta}$  are much larger overall than the calculated values. The measured pressure derivatives are also larger than the calculated values; this comparison is more approximate since the measurements are at room temperature, while the calculations correspond to  $T=0$ .

We might conclude by considering what steps could be taken to bring the theory into better agreement with experiment; we recall, however, the well-taken remarks of Harrison,<sup>15</sup> that the pseudopotential perturbation theory is by nature approximate and should not be expected to reproduce all the experimental results. Nevertheless, the theory as presently developed is inconsistent in that the methods of long waves and homogeneous deformation do not give the same results for the longitudinal elastic constants.<sup>16</sup> This inconsistency, which relates directly to the discrepancies between theory and experiment we have noted here, can be removed by including higher-order pseudo-

<sup>13</sup> D. C. Wallace, Phys. Rev. **162**, 776 (1967).

<sup>14</sup> J. F. Thomas, Jr., Phys. Rev. **175**, 955 (1968).

<sup>15</sup> W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

<sup>16</sup> D. C. Wallace, Phys. Rev. **182**, 778 (1969).

potential terms in the dynamical matrix, especially in the long-wavelength limit. The required terms may be obtained by calculating the dielectric function to second order in the local pseudopotential, then keeping all terms in the dynamical matrix which are of second order in umklapp scatterings. We have not yet evaluated these terms numerically, but it appears they may give a significant contribution to the theoretical phonon

spectrum for aluminum. In addition the effect on the screening of the electronic exchange and correlation has been included by the Hubbard-Sham approximation in our formulation<sup>8</sup>; the accuracy of this approximation is quite unknown at present. We have neglected the explicit anharmonic free energy in our calculations; it is unlikely that this neglect significantly affects the discrepancies found here.

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## Quantum Theory of Diffusion with Application to Light Interstitials in Metals†

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A quantum theory of diffusion is presented and applied to the particular problem of light interstitial diffusion. The theory focuses attention on transitions among approximate localized eigenstates of the system. The diffusion rate of a light interstitial in bcc metals is shown to be determined principally by the self-trapping distortion which stabilizes the impurity at a particular interstice. A quantitative explanation of both the motion energy and the motion entropy follows from the theory. The differences between interstitial motion in bcc and fcc hosts, and also the dependence of the diffusion rate on isotopic mass, are discussed.

### 1. INTRODUCTION

SEVERAL efforts have been made to develop a quantum theory of diffusion since the early work of Wigner.<sup>1</sup> The classical theory, as developed for solid-state processes by Wert and Zener<sup>2</sup> and by Vineyard,<sup>3</sup> specifies the jump rate  $W$  in terms of Gibbs functions for different configurations of the system:

$$W = (kT/\hbar)e^{-g/kT}.$$

Here  $g \equiv G_s - G_0$ , with  $G_0$  the Gibbs function of the crystal vibrating with all atoms vibrating about points of stable equilibrium near regular lattice sites;  $G_s$  is the Gibbs function when the diffusive jump process is arrested in the saddlepoint plane between the points of stable equilibrium. Both Gibbs functions, of course, are essentially entropies of the crystal together with its enclosing constant temperature and pressure bath.

The classical formulation encounters a fundamental difficulty in that there exists no operationally satisfactory way of defining  $G_s$ . Despite this difficulty, attempts have been made to obtain quantum results

in the spirit of rate theory by an explicit treatment of the motion of a representative point through a model potential barrier in configuration space. The most recent and successful of these treatments are due to Weiner<sup>4</sup> and to Weiner and Partom<sup>5</sup>; references to related work will be found in these papers. It is widely believed that the classical theory must provide a correct description of diffusion for temperatures in excess of the Debye temperature  $\Theta_D$  at which the lattice vibrational energy becomes sensibly classical, and this has motivated quasiclassical discussions.

In this paper we derive an alternative and more satisfactory quantum theory of diffusion by focusing attention first on the question of the exact eigenstates of a system in which diffusion occurs. Diffusive jumps then appear as transitions which are induced by the crystal Hamiltonian among the approximate eigenstates, each of which is localized near some equilibrium point in configuration space. Detailed balance is assured by the Hermitian properties of the crystal Hamiltonian. From a formal point of view the theory is closely related to well-known treatments of the polaron problem<sup>6</sup> and of radiationless transitions.<sup>7</sup> After presenting the general theory in Sec. 2, we turn in Sec. 3 to a detailed treat-

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<sup>1</sup> E. Wigner, *Z. Phys. Chem.* **B19**, 203 (1963).

<sup>2</sup> C. A. Wert and C. Zener, *Phys. Rev.* **76**, 1169 (1949).

<sup>3</sup> G. H. Vineyard, *J. Phys. Chem. Solids* **3**, 121 (1957).

<sup>4</sup> J. H. Weiner, *Phys. Rev.* **169**, 570 (1968).

<sup>5</sup> J. H. Weiner and Y. Partom, *Phys. Rev.* (to be published).

<sup>6</sup> T. Holstein, *Ann. Phys. (N. Y.)* **8**, 325 (1959); **8**, 343 (1959).

<sup>7</sup> K. Huang and A. Rhys, *Proc. Roy. Soc. (London)* **A204**, 406 (1951).