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Normal Vibrations in Aluminum and Derived Thermodynamic Properties*

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The experimental phonon-dispersion curves of aluminum at 80°K and at 300°K have been analyzed in terms of axially symmetric Born–von Kármán force-constant models, including 8 nearest neighbors. The resulting models have been used to compute a frequency distribution function $g(\omega)$ at each temperature from which various thermodynamic properties have been derived. The specific-heat curve predicted by the $g(\omega)$ appropriate to 80°K fits excellently the experimental results in the temperature range 20 to 80°K. At higher temperatures the experimental results deviate from this calculated curve and approach the curve appropriate to $g(\omega)$ at 300°K. Similar behavior is found for the experimental Debye-Waller coefficient in the range above 100°K. It is concluded that inelastic-neutron-scattering data and thermodynamic data are compatible in the range of sufficiently low temperatures where deviations from the quasiharmonic approximation are small, provided a good force-constant model as well as a statistically adequate $g(\omega)$ are available. There is evidence that the quasiharmonic approximation in aluminum is invalid at room temperature at least for the extreme low-frequency part of $g(\omega)$.

I. INTRODUCTION

THE coherent inelastic scattering of slow neutrons is a powerful experimental technique for the study of the lattice dynamics of crystals. In principle, detailed phonon-dispersion curves can be determined and then analyzed to yield information about the interatomic forces. In practice, such analyses are made in terms of the Born–von Kármán theory which employs the harmonic approximation and yields a set of interatomic force constants of as many nearest neighbors as required to fit the data. One might expect that such a force-constant model which reproduces the experimental dispersion curves even approximately will also yield, via a frequency distribution $g(\omega)$, an accurate reproduction of thermodynamic properties, e.g., the specific heat, which are not believed to depend sensitively on these forces. In reality, however, such good agreement generally has not been experineced, especially if the phonon-dispersion curves were measured at high (room) temperature. Probably, this lack of agreement occurs because the interatomic forces are not harmonic; i.e., the measured phonon frequencies are temperature-dependent. Barron[1] has pointed out that owing to anharmonicity, the "effective" frequency distributions $g(\omega)$ required to reproduce two different thermodynamic properties, are not necessarily the same. The frequency distribution function can be uniquely defined only in the quasiharmonic approximation in which the frequencies are assumed to vary with respect to volume changes only. It is quite feasible then, that the Born–von Kármán model will be a good representation only if the quasiharmonic approximation is applicable. It is expected, however, that at low temperatures, "effective" frequency distributions will not differ appreciably from one another. The zero-point vibrational energy, although a contributor to anharmonic effects, causes shifts in frequencies which are independent of temperature,[1] and thus does not impair the quasiharmonic approximation at low temperatures. It might be possible that the quasiharmonic approximation is already invalid for many materials at temperatures (~300°K) where most neutron-scattering experiments have been performed.

A second reason for the inability to reproduce satisfactorily specific-heat data from neutron-scattering experiments might be of more technical nature. The specific-heat data, especially when expressed in terms of the characteristic Debye temperature $\Theta_c(T)$, are more sensitive to the details of the force-constant model as well as to the derived frequency-distribution function than is generally believed. (This fact has been experienced in our computations.) Because of this sensitivity one should make use of the most accurate experimental data, try to obtain the best fitting force-constant model, and then derive the best possible frequency-distribution function. All of these are required in order not to sacrifice precision in the process of analyzing the data.

In view of the preceding remarks, it was desirable to analyze inelastic neutron-scattering data obtained at two different temperatures in order to observe any temperature dependence of the frequency distribution. Such data are now available for aluminum. Phonon-dispersion curves in aluminum have been measured by inelastic coherent scattering of slow neutrons at room temperature in numerous experiments.[2–6] In one experiment[7]

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[1] T. H. K. Barron, *Lattice Dynamics, Proceedings of the International Conference Held at Copenhagen*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1963), p. 247.

[2] B. N. Brockhouse and A. T. Stewart, Rev. Mod. Phys. **30**, 236 (1958).

[3] R. S. Carter, H. Palevsky and D. J. Hughes, Phys. Rev. **106**, 1168 (1957).

[4] K. E. Larsson, V. Dahlborg, and S. Holmryd, Arkiv. Fysik. **17**, 369 (1960).

[5] J. L. Yarnell, J. L. Warren, and S. H. Koenig, Ref. 1, p. 57. (We are indebted to these authors for providing us with their detailed experimental data.)

[6] R. Stedman and G. Nilsson, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 211. The data utilized throughout this article were read from graphs. More accurate data were recently available to us (for which we are grateful to these authors), and were subjected to the same analysis, showing that only negligibly small corrections to the original analysis were required.

[7] C. B. Walker, Phys. Rev. **103**, 547 (1956).

they have been measured by the less accurate technique of diffuse x-ray scattering. The data chosen for the purpose of the present calculations are those of Yarnell *et al.*,[5] at 300°K, and of Stedman and Nilsson[6] at 80°K. These two experiments have been performed with a triple-axis spectrometer and thus have provided the most accurate data available for aluminum.

There have been some earlier attempts to analyze the experimental data for aluminum in terms of Born–von Kármán models. Walker[7] analyzed his own data derived from diffuse x-ray scattering and the same data have also been analyzed by Squires.[8] More recently, Squires[9] analyzed the data of Larsson, Dohlborg, and Holmryd.[4] Flinn and McManus[10] used a first-nearest-neighbor model derived from elastic constants at low temperature to calculate $g(\omega)$ as well as a specific heat curve. Although all the above models agree qualitatively with the experimental $\Theta_c(T)$, we believe that the calculations to be described improve this agreement.

II. BORN–VON KÁRMÁN MODELS

The validity of an analysis of measured phonon dispersion curves for metals in terms of Born–von Kármán models may be questioned, because of the presence of electron phonon interactions. At the present stage, theories including electron-phonon interactions imply the existence of a possible long-range oscillatory interatomic potential. Yarnell *et al.*[5] have pointed out that their data indicate interactions in aluminum out to 15 neighbors. Harrison[11] and, very recently, Vosko *et al.*[12] have attempted calculations of the phonon dispersion curves in aluminum from first principles. Since the motivation of the present work was to attempt to reproduce from measured dispersion curves the thermodymanic properties of aluminum, it was necessary to rely on a model which could best fit these curves. This could be achieved at present only by a force-constant model based on the Born–von Kármán theory. Such a model may not provide the best physically sound interpretation of the lattice dynamics of aluminum, but rather, we believe that it will provide the best available interpolation formula both for fitting the observed phonon frequencies and for use in the derivation of a frequency distribution, $g(\omega)$.

A model for 300°K was based on the data of Yarnlel *et al.*,[5] along the $[\zeta 00]$ and $[\zeta\zeta 0]$ directions together with the data of Stedman and Nilsson[6] along the $[\zeta\zeta\zeta]$ direction. (The only data of Stedman and Nilsson[6] reported for the $[\zeta 00]$ direction is for 80°K. We obtained a 300°K $[\zeta\zeta\zeta]$ dispersion curve by adjusting their reported frequencies according to the average shift measured between 80° and 300° for the $[\zeta 00]$ direction. The 300°K data of Yarnell *et al.*,[5] and of Stedman and Nilsson[6] along the $[\zeta 00]$ direction are in excellent agreement.) The model for 80°K was based on the data of Stedman and Nilsson. The elastic constants measured[13,14] at 300°K and at[13] 80°K are in excellent agreement with the measured dispersion curves and were used as independent data.

A linear least-squares fitting analysis was performed on the squares of the observed frequencies subject to the condition that appropriate linear combinations of the force constants agree with measured elastic constants. The experimental errors for the neutron scattering data were assumed to be 2% of the measured phonon frequencies. The uncertainty in the elastic constants was assumed to be 0.3%. In order to obtain a good fit to the measured frequencies, one should include in the fitting model interactions out to as many neighbors as the uncertainty in the available data will allow. In the present case the number of independent symmetry directions experimentally studied does not permit the use of a general force model which includes interactions beyond four neighbors. In order to extend the range of interaction, it is required to put some restrictions on

TABLE I. Best-fit 8-nearest-neighbor axially symmetric models. (Notation of force constants is explained in the text.)

Neighbor and location		Best-fit value of force constants (dyn/cm)		Restrictions for the axially symmetric model
		$T=80°K$	$T=300°K$	
1 (110)	α_1^1	10107	9808	
	α_3^1	−1337	−1616	
	β_3^1	11444	11424	$\beta_3^1=\alpha_1^1-\alpha_3^1$
2 (200)	α_1^2	2452	2494	
	α_2^2	−529	−515	
3 (211)	α_1^3	−625	−439	
	α_2^3	−182	−167	
	β_1^3	−148	−91	$\beta_1^3=\frac{1}{3}(\alpha_1^3-\alpha_2^3)$
	β_2^3	−296	−182	$\beta_2^3=\frac{2}{3}(\alpha_1^3-\alpha_2^3)$
4 (220)	α_1^4	271	27	
	α_3^4	321	465	
	β_3^4	−50	−438	$\beta_3^4=\alpha_1^4-\alpha_3^4$
5 (310)	α_1^5	461	518	
	α_2^5	227	141	
	α_3^5	198	94	$\alpha_3^5=\frac{1}{8}(9\alpha_2^5-\alpha_1^5)$
	β_3^5	88	141	$\beta_3^5=\frac{3}{8}(\alpha_1^5-\alpha_2^5)$
6 (222)	α_1^6	142	76	
	β_1^6	−109	−61	
7 (321)	α_1^7	−64	−49	
	α_2^7	−94	−65	
	α_3^7	−111	−74	$\alpha_3^7=\frac{1}{5}(8\alpha_2^7-3\alpha_1^7)$
	β_1^7	12	6	$\beta_1^7=\frac{2}{5}(\alpha_1^7-\alpha_2^7)$
	β_2^7	18	9	$\beta_2^7=\frac{3}{5}(\alpha_1^7-\alpha_2^7)$
	β_3^7	36	19	$\beta_3^7=(6/5)(\alpha_1^7-\alpha_2^7)$
8 (400)	α_1^8	−534	−756	
	α_2^8	−116	−63	

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[8] G. L. Squires, Phys. Rev. **103**, 304 (1956).

[9] G. L. Squires, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 55.

[10] P. A. Flinn and G. M. McManus, Phys. Rev. **132**, 2458 (1963).

[11] W. A. Harrison, Phys. Rev. **136**, A1107 (1964).

[12] S. H. Vosko, R. Taylor, and G. H. Keech, Can. J. Phys. **43**, 1187 (1965).

[13] G. N. Kamm and G. A. Alers, J. Appl. Phys. **35**, 327 (1964).

[14] R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids **9**, 100 (1959).

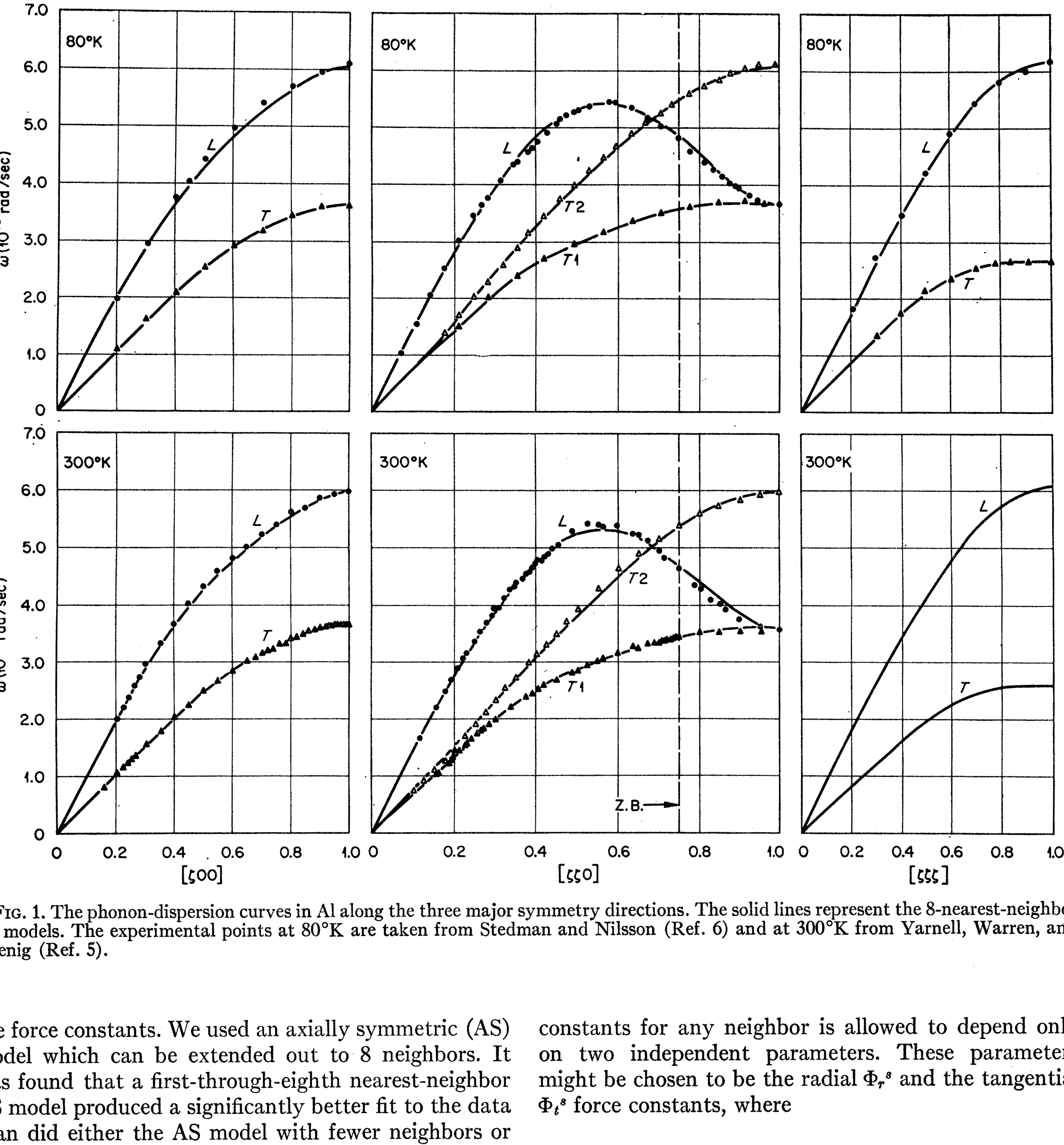

FIG. 1. The phonon-dispersion curves in Al along the three major symmetry directions. The solid lines represent the 8-nearest-neighbor AS models. The experimental points at 80°K are taken from Stedman and Nilsson (Ref. 6) and at 300°K from Yarnell, Warren, and Koenig (Ref. 5).

the force constants. We used an axially symmetric (AS) model which can be extended out to 8 neighbors. It was found that a first-through-eighth nearest-neighbor AS model produced a significantly better fit to the data than did either the AS model with fewer neighbors or the general 4-neighbor model.

The notation of Squires[15] for the force constants is adopted throughout this work. If Φ_{ij}^s is the force acting on an atom at the origin along the ith direction while the sth nearest-neighbor atom moves a unit displacement along the jth direction ($i,j=x,y,z$) then the force constant array representing Φ_{ij}^s is given by

$$\begin{matrix} \alpha_1^s & \beta_3^s & \beta_2^s \\ \beta_3^s & \alpha_2^s & \beta_1^s \\ \beta_2^s & \beta_1^s & \alpha_3^s \end{matrix} \qquad (1)$$

In the case of axially symmetric forces, the set of force constants for any neighbor is allowed to depend only on two independent parameters. These parameters might be chosen to be the radial Φ_r^s and the tangential Φ_t^s force constants, where

$$\Phi_r^s=(\partial^2V/\partial r^2)_{r=r^s} \qquad (2)$$

and

$$\Phi_t^s=\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)_{r=r^s}. \qquad (3)$$

Here V is the interaction potential function and $\mathbf{r}^s$ denotes the equilibrium position of the sth neighbor relative to the origin, i.e.,

$$\mathbf{r}^s=\tfrac{1}{2}a(h_1^s\mathbf{i}+h_2^s\mathbf{j}+h_3^s\mathbf{k}), \qquad (4)$$

where a is the lattice parameter and h_1^s, h_2^s, h_3^s are

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[15] G. L. Squires, Ref. 9, p. 71.

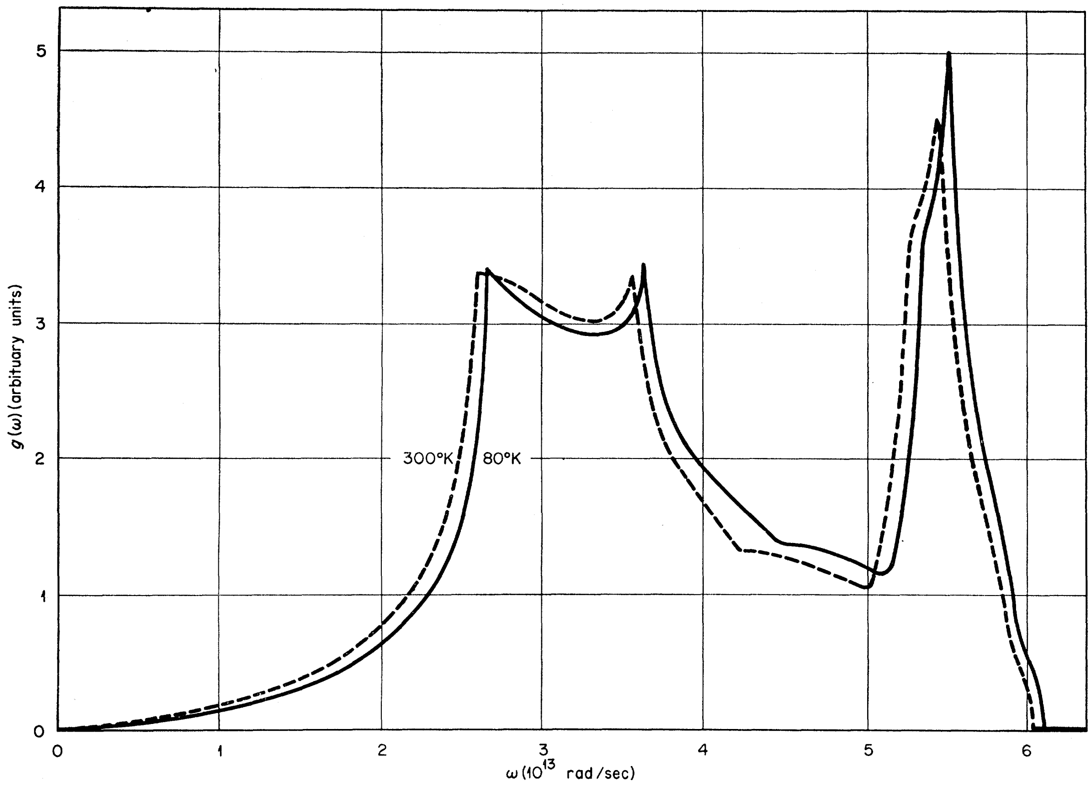

FIG. 2. Frequency-distribution functions for Al at 80 and 300°K obtained from the AS models by the extrapolation method (Ref. 16).

integers. The $\Phi_{ij}{}^{s}$ can then be constructed from

$$\Phi_{ij}{}^{s}=\frac{a^2h_i{}^{s}h_j{}^{s}}{4(r^{s})^2}(\Phi_r{}^{s}-\Phi_t{}^{s})+\delta_{ij}\Phi_t{}^{s}\,, \tag{5}$$

where δ_{ij} is the Kronecker delta.

The best-fit values we obtained for the force constants of the AS model for both 80 and 300°K are listed in Table I. The number of independent parameters in each case is 16. The dispersion curves given by these best-fit force constants are compared to the experimental data in Fig. 1. The lower part represents the 300° data, primarily that of Yarnell *et al.*,[5] and the upper part represents the 80°K data of Stedman and Nilsson.[6] The average fluctuation of the experimental frequencies around the calculated values is about 1.5% for both temperatures.

III. CALCULATIONS OF $g(\omega)$ AND THERMODYNAMIC PROPERTIES

From the 8-neighbor AS models just described, we have used the extrapolation method[16] to compute a frequency-distribution function $g(\omega)$, for both 80 and 300° K. The basic idea behind the extrapolation method, which is an improvement of the usual sampling method, is the following. In the usual sampling method, given a force-constant model, one proceeds to solve the secular equation of the dynamical matrix for as many as possible different wave vectors which uniformly fill the irreducible section of the first Brillouin zone of the reciprocal lattice. Then, by sorting all the different eigenfrequencies one obtains a sample of $g(\omega)$. In the extrapolation method[16] one makes use of the eigenvectors for every wave vector in the sample, in order to derive the frequency gradient. This is achieved by imposing artificial small changes on the wave vectors (along the three orthogonal axes) and then applying a first-order perturbation technique to calculate the corresponding changes in frequencies. After the frequency gradients are obtained, it is easy to apply a linear extrapolation by means of a Taylor expansion to obtain the eigenfrequencies corresponding to any of the neighboring wave vectors and thus extract as many additional frequencies as desired. This procedure will result in a very substantial improvement of the sampling for the same computing time. The technical details of our computations are identical to those described by Birgeneau *et al.*,[17] except that the statistical fluctuations in the relatively unpopulated small-wave-vector regions have been improved. The curves shown in Fig. 2 are histogram plots of the computed frequency distributions but the statistical fluctuations of each point (about 1%)

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[16] G. Gilat and G. Dolling, Phys. Letters 8, 304 (1964).

[17] R. J. Birgeneau, J. Cordes, G. Dolling, and A. D. B. Woods, Phys. Rev. 136, A1359 (1964). See Appendix A, in particular.

are too small to be seen. Each curve, representing 35 831 808 frequencies sorted into approximately 200 intervals, required 615 matrix diagonalizations (compared to 254 040 diagonalizations which would have been required if the usual sampling method had been used). A comparison of the spectrum $g(\omega)$ at the two temperatures reveals a rather uniform shift in frequencies ($\sim 3\%$) accompained by a slight change ($\sim 10\%$) in the relative heights of the peaks in $g(\omega)$ due to the longitudinal and transverse modes. The over-all shape of the distribution does not change appreciably.

A more quantitative comparison of the two spectra can be made through the various moments μ_n defined by

$$\mu_n = \int_0^\infty \omega^n g(\omega) d\omega \Big/ \int_0^\infty g(\omega) d\omega . \qquad (6)$$

Since the μ_n span a very wide range, it is convenient to define a Debye distribution of "cutoff" frequency ω_n,[18] where

$$\omega_n = \left[\frac{n+3}{3} \int_0^\infty \omega^n g(\omega) d\omega \Big/ \int_0^\infty g(\omega) d\omega \right]^{1/n} \qquad (7)$$

for $n \neq 0$, $n > -3$.

For $n=0$ and -3 we have

$$\omega_0 = \exp\left[\tfrac{1}{3} + \int_0^\infty g(\omega) \ln\omega \, d\omega \Big/ \int_0^\infty g(\omega) \, d\omega \right], \qquad (8)$$

$$\omega_{-3} = (k/h)\Theta_c(0^\circ) , \qquad (9)$$

where h is Planck's constant, k is the Boltzman constant and $\Theta_c(0^\circ)$ is the specific-heat Debye temperature at 0°K. The ω_n are shown in Fig. 3 as a function of n for the two temperatures. Other values for several of the μ_n (corrected to the crystal volume at 0°K) were derived by Salter,[19] who analyzed the specific-heat data of Phillips[20] and of Giauque and Meads.[21] These are compared to the calculated moments in Fig. 3 and Table II.

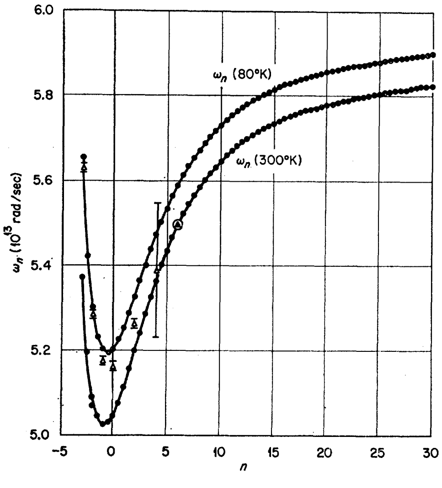

FIG. 3. Debye "cutoff" frequencies ω_n [defined in Eqs. (7), (8), and (9)] obtained from $g(\omega)$ at 80 and 300°K. The experimental points were obtained by Salter (Ref. 19) from analysis of specific-heat data. (The error corresponding to ω_6—marked by a circle—is too large to show on the graph.)

TABLE II. Comparison of various moments ω_n derived from heat-capacity analysis to those computed from spectra at 80 and 300°K.

Moment	Heat-capacity analysis[a]	Computed from $g(\omega)$ $T=80$°K	$T=300$°K
ω_{-3}	5.633±0.010	5.657	5.373
ω_{-2}	5.287±0.010	5.303	5.094
ω_{-1}	5.178±0.009	5.206	5.029
ω_0	5.165±0.008	5.207	5.051
ω_2	5.265±0.010	5.335	5.201
ω_4	5.39 ±0.16	5.473	5.367
ω_6	5.5 ±0.9	5.591	5.497

[a] See Ref. 19.

It is interesting to try to draw some conclusions from the observed shifts in ω_n as one raises the temperature from 80° to 300°K. As long as these shifts are small, one can apply the following expression[22] to describe the real part of these shifts:

$$\omega_n(T) = \omega_n(0)(1 + \gamma_n\delta + \tau_n\langle\epsilon\rangle) , \qquad (10)$$

where δ is the volume dilation $[\delta = (V_0 - V)/V_0]$ at temperature T, γ_n is an appropriate Grüneisen parameter, and $\langle\epsilon\rangle$ is the average energy per mode at T, and τ_n some anharmonic parameters. In the quasiharmonic approximation, one neglects $\tau_n\langle\epsilon\rangle$ in comparison to $\gamma_n\delta$,

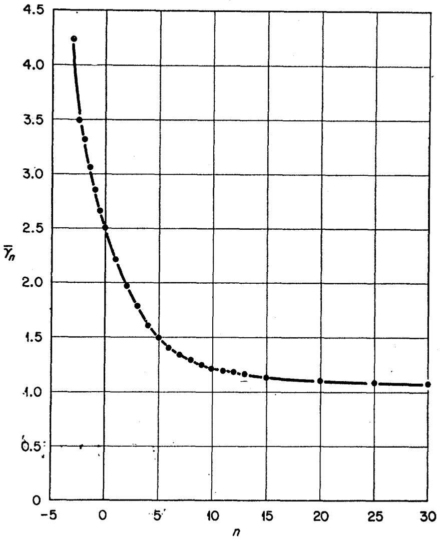

FIG. 4. $\bar{\gamma}_n$ obtained from the variation of ω_n with temperature using Eq. (11). Uncertainties of $\bar{\gamma}_n$ are of the order of 5–10%.

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[18] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).

[19] L. S. Salter (private communication).

[20] N. E. Phillips, Phys. Rev. **114**, 676 (1959).

[21] W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

[22] L. S. Salter, Advan. Phys. **14**, 1 (1965).

but it should be noted that $\langle\epsilon\rangle$ does not vanish even at 0°K owing to the zero-point energy. In the present case, we compare $\omega_n(300°)$ to $\omega_n(80°)$ and this involves slight modifications of Eq. (10).

We proceed now to define another set of parameters $\bar{\gamma}_n$ as following:

$$\bar{\gamma}_n = -\frac{d\ln\omega_n(T)}{d\ln V}. \tag{11}$$

If the quasiharmonic approximation were good, we should get $\bar{\gamma}_n=\gamma_n$ for this range. In the actual calculation we get

$$\bar{\gamma}_n \approx \gamma_n + r_n \frac{\langle\epsilon(300°)\rangle - \langle\epsilon(80°)\rangle}{\delta(300°)-\delta(80°)}. \tag{12}$$

The values of $\bar{\gamma}_n$ are calculated from the data of Fig. 3 and shown graphically in Fig. 4.

Unfortunately, the individual $\bar{\gamma}_n$ are not subject to direct measurement. Use can be made, however, of the macroscopic Grüneisen parameter given by [23]

$$\gamma_g = \beta V/\kappa C_v\,, \tag{13}$$

where β is the volume coefficient of thermal expansion and κ is the isothermal compressibility. If one assumes quasiharmonicity one obtains[23]

$$\gamma_g(T=0)=\gamma_{-3}$$

and

$$\gamma_g(T\to\infty)=\gamma_0\,. \tag{14}$$

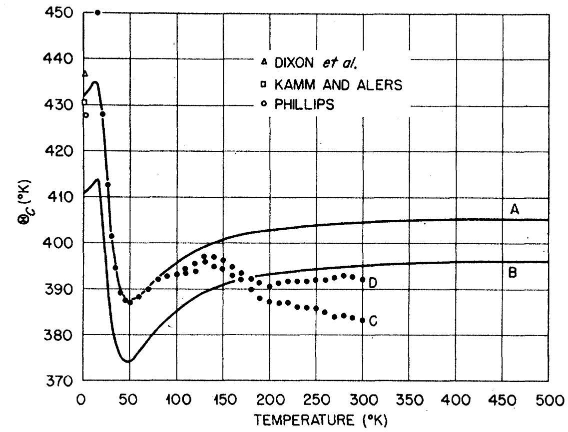

FIG. 5. Comparison of calculated $\Theta_c(T)$ with experiment. Curves (A) and (B) are calculated from $g(\omega)$ at 80 and 300°K, respectively. Curves (C) and (D) represent the experimental results of Giauque and Meads. (See text.) Experimental results at 0°K were obtained from Refs. 13, 20, and 31.

Of these two parameters, $\gamma_g(0°)$ can provide the only evidence to the validity of the quasiharmonic approximation at room temperature, since in principle if it were valid, one would obtain the same $\gamma_g(0°)$ from thermodynamic data near $T=0$°K and from pressure derivatives of the elastic constants. Values derived from thermodynamic data[24–27] are apparently subject to large experimental error as temperature is lowered, but most measurements seem to show a rising trend in γ_g as T is reduced, γ_g being near 4. The value obtained from pressure derivatives of elastic constants at room temperature[28] is $\gamma_{-3}=2.61$. The value that we obtain for $\bar{\gamma}_{-3}$ in the present analysis is 4.2 ± 0.6 and it probably should be compatible with $\gamma_g(0°)$. This leads to the conclusion that at least the long-wave part of the spectrum in aluminum is not quasiharmonic at room temperature.[29] By applying Eq. (12) for $n=-3$, we obtain

$$r_{-3}(\langle\epsilon(300°)\rangle - \langle\epsilon(80°)\rangle) = 0.02\pm0.003. \tag{15}$$

The comparison of the high-temperature γ_g to the present $\bar{\gamma}_n$ is less clear if the quasiharmonic approximation is invalid. However, if we assume the validity of this approximation for the rest of the spectrum we get a value of $\bar{\gamma}_0=2.50$ which, when corrected to 300°K according to Barron,[30] yields a calculated value of $\bar{\gamma}_g(300°) = 2.55$ in comparison to the measured[25] value of 2.34. We estimate the statistical errors involved in calculating $\bar{\gamma}_n$ to be of the order of 5–10%.

The results obtained for the specific heat calculated from the 80 and 300°K spectra are expressed in terms of the conventional Debye temperature Θ_c versus temperature plot in Fig. 5, curves (A) and (B), respectively. The experimental $\Theta_c(0°)$ are quoted from Refs. 13, 20, and 31. The experimental points on curve (C) are derived from the smoothed C_v values reported by Giauque and Meads[21] corrected for the appropriate electronic contributions. The points of curve (D) were derived from the smoothed C_p data of Giauque and Meads[21] after application of the same electronic correction but with C_p-C_v determined according to

$$C_p-C_v=\beta^2VT/\kappa\,, \tag{16}$$

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[23] T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, Proc. Roy. Soc. (London) **A279**, 62 (1964).

[24] C. P. Abbiss, Eva Huzam, and G. O. Jones, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (Toronto University Press, Toronto, 1960), p. 689.

[25] D. B. Fraser and A. C. Hollis-Hallett, Ref. 24, p. 688.

[26] R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. Monograph 29 (1961).

[27] D. B. Fraser and A. C. Hollis-Hallett, Can. J. Phys. **43**, 193 (1965).

[28] J. G. Collins, Phil. Mag. **8**, 323 (1963).

[29] Additional analysis has been done by the present authors. The mode-dependent Grüneisen parameters taken from a paper by W. B. Daniels, Ref. 1, p. 273, and calculated from pressure derivatives of elastic constant were compared for four different metals, namely, Al, Ag, and Cu with the Grüneisen parameters calculated from the temperature dependence of the elastic constants taken from the papers of W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955) and J. R. Neighbours and G. A. Alers, *ibid.* **111**, 707 (1958). The common feature of these comparisons is a disagreement of about a factor of 2 for transverse modes (the latter parameter being larger), and a crude agreement for longitudinal modes. This pattern of behavior persists at least down to 50°K and casts doubts about the validity of the quasiharmonic model even for low temperatures.

[30] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[31] M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) **A285**, 561 (1965).

where β is the volume coefficient of thermal expansion, V the molar volume, and κ is the isothermal compressibility. Giauque and Meads used a different formula for $C_p - C_v$, apparently due to a lack of good data for either β or κ in the 15°–300°K temperature range. Now, however, there are reliable data for both β[25,26] and κ [obtainable from the variation of the elastic constants $(C_{11}+2C_{12})/3$ with temperature].[13] The difference between these corrections for $C_p - C_v$, being negligible for $T<100$°K, becomes appreciable at higher temperatures and tends to shift the experimental points [curve D] more closely to curve (B) obtained from $g(\omega)$ at 300°K. It should be pointed out, however, that for $T>\Theta_c/2$ ($T>200$°K) the experimental Θ_c are quite sensitive to experimental error and thus are probably not too reliable.

Several observations are worthy of note. The agreement between the experimental Θ_c and those calculated from the $g(\omega)$ for 80°K is very good in the 20–80°K temperature range. Such agreement is considered significant because temperature dependent anharmonic effects, in the quasiharmonic approximation, probably contribute negligibly in this temperature range to both the specific-heat and the neutron-dispersion-curve data. Thus a good model based on accurate neutron data is here shown to be capable of precisely reproducing specific-heat data in a temperature range where anharmonic effects have not hampered a comparison. Also the agreement obtained here in the 20–80°K range is substantially better than that obtained by Flinn and McManus[10] from a first-neighbor model based on 0°K elastic constants. We believe the first-neighbor model must be considered inadequate. As a matter of fact, during the course of the present investigation several other force-constant models have been attempted (e.g., general third-nearest-neighbor models). A common feature of these attempts was the high sensitivity of $g(\omega)$ to the model chosen and resultantly the sensitive dependence of $\Theta_c(T)$ on the model. We found that the better the model fitted the dispersion curves, the better was the fit of the calculated $\Theta_c(T)$ to the experimental points in the range 20–80°K.

Below 20°K the data of Giauque and Meads seem to be less reliable. Here the effects of smoothing the data are quite large, and in fact, the unsmoothed data are in somewhat better agreement with the calculations below 20°K. More specific-heat measurements are highly desirable, especially in view of the slight increase in Θ_c around 15°K predicted by the present calculation. Above 80°K, the experimental Θ_c deviates from the curve obtained from the 80° $g(\omega)$ and tends toward the curve obtained from the 300° $g(\omega)$. It is of interest to note that the experimental data below 80°K cannot be accounted for by the 300°K $g(\omega)$ when a correction for the volume dependence of the calculated Θ_c is based on the Grüneisen parameter obtained from high-temperature thermodynamic data, i.e., $\gamma \approx 2.3$.

In view of the explicit temperature dependence of ω_{-3}, and, hence, possibly of other moments, the apparent agreement found between the measured "high"-temperature C_v and the calculations based on $g(\omega)$ at 300°K, possibly should not be taken too seriously. Barron[1] has pointed out that in the absence of quasiharmonicity the frequency distribution obtained from inelastic neutron scattering data is appropriate for the calculation of the entropy S. In principle the correct way to calculate C_v from our $g(\omega)$ would be first to calculate S and then to differentiate S with respect to temperature, taking into account the explicit temperature dependence of the frequencies. In practice this calculation of C_v is impossible because it requires a separation of the shifts of all the frequencies into volume contributions and explicit temperature contributions. We have not attempted to compare in detail the measured lattice entropy for aluminum[21] with calculations based on $g(\omega)$. The $g(\omega)$ appropriate to 80°K must reproduce the experimental entropy below 80°K because of the excellent agreement obtained for C_v in this temperature range. According to Barron one expects the entropy at 300°K to be reproduced by calculations based on the present $g(\omega)$ at 300°K. The experimental entropy at 300°K,[21] corrected for electronic contributions, yields a Debye temperature $\Theta_s = 386 \pm 2$°K. Calculations of the high-temperature limit of Θ_s with the ω_0 computed from the $g(\omega)$ at 300°K (see Table II and page 13 of Ref. 22) yield a value of 386°K which is in excellent agreement with the measured value.

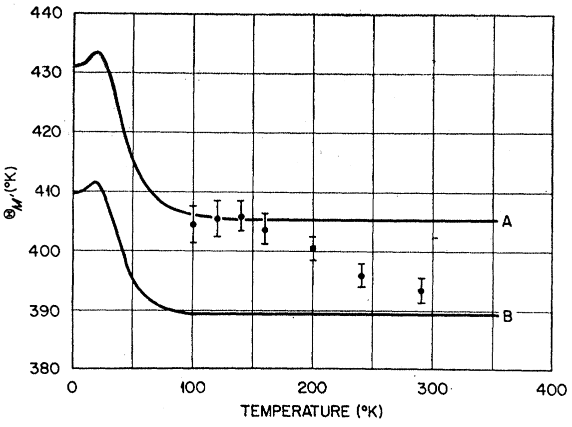

FIG. 6. Comparison of calculated $\Theta_{M'}(T)$ with experiment (Ref. 32). Curves (A) and (B) are calculated from $g(\omega)$ at 80 and at 300°K, respectively.

In Fig. 6 the Debye temperatures appropriate to recent measurements[32] of the temperature dependence of x-ray Bragg intensities in aluminum are shown. Although the analysis of these measurements are described fully elsewhere,[32] it is necessary to point out here that the experimental and calculated Debye temperatures were obtained from expressions for the tem-

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[32] R. M. Nicklow and R. A. Young, Technical Report No. 3, Project A-389, Georgia Institute of Technology, Atlanta, Georgia, 1964 (unpublished).

perature derivative dM/dT, of the Debye Waller factor M. The Debye temperature obtained in this manner is labeled $\Theta_{M'}$. Curve (A) was obtained from the 80°K $g(\omega)$ and curve (B) was obtained from the 300°K $g(\omega)$. At low temperatures ($\sim$100°K) the measurements agree well with curve (A) and tend toward curve (B) as the temperature increases.

All the calculations described in this section have been performed on the CDC–1604 at the Oak Ridge National Laboratory.

IV. CONCLUSIONS

The computations presented in this article show that the phonon-dispersion curves in aluminum as obtained from the one-phonon coherent inelastic scattering of neutrons can be correlated to detailed thermodynamic data (e.g., specific heat as a function of temperature) to quite a high degree of precision. In order to achieve this consistency at low temperatures, the neutron-scattering data must be taken at a sufficiently low temperature. An estimate of the required low temperature can be provided by the thermal expansion coefficient and an estimate of the Grüneisen parameter γ_g. If $\bar{\beta}(T)$ is an average volume coeffient of expansion between 0° and T°K, then the average shift in frequencies relative to 0°K is approximately

$$\Delta\omega/\omega \cong \bar{\beta}\gamma_g T\,. \tag{17}$$

Thus $\Delta\omega$ tends to zero quite strongly as a function of temperature, so that in many cases 80°K may be a sufficiently low temperature to calculate a $g(\omega)$ which will reproduce thermodynamic data satisfactorily.

Having observed the dispersion relations, it is important to obtain the best force-constant model possible. By best model we do not imply that it is the best physical description of the normal vibration, but rather, that it presents the best interpolation formula which is able to represent the observed frequencies as closely as possible. Furthermore, having computed a satisfactory model, one should derive the best possible frequency-distribution function $g(\omega)$, which can be obtained by the extrapolation method.[16] Special care must be taken for low ω (since the ω_n for $n<0$ depend strongly on them) by increasing substantially the sampling size near the origin of the Brillouin zone. It has been found that the *calculated* functions $\Theta_c(T)$ and $\Theta_{M'}(T)$ as well as ω_n depend quite sensitively upon the model chosen. For example, $\Theta_c(T)$ can be computed to 1°K, whereas differences in Θ_c using different models can reach 20°K. Although it is difficult to estimate the experimental uncertainty in the data of Giauque and Meads,[21] present day techniques allow a determination of Θ_c to much better than 20°K.

The question of the validity of the quasiharmonic approximation at high (room) temperature in aluminum cannot be satisfactorily answered by the present kind of analysis alone. A direct answer to this problem should be sought in the pressure behavior of phonon-dispersion curves obtained from inelastic neutron scattering (a very difficult experiment itself) as well as by the pressure behavior of the elastic constants. However, the latter source of data is available and can be compared to the temperature behavior of the elastic constants. In the present work we find that the value of γ_{-3} (2.61) calculated from the pressure dependence of the elastic constants does not agree with the value of $\bar{\gamma}_{-3}$ (4.2) derived from the temperature dependence of the elastic constants. This disagreement implies that at least for the extremely low-frequency part of the spectrum, the quasiharmonic approximation is invalid at room temperature.[29] In light of this, care must be taken to distinguish between γ_n calculated from volume changes at constant temperature and those calculated when the temperature is allowed to vary. The $\bar{\gamma}_n$ in the present work belong, of course, to the second category.

Observation of phonon-dispersion curves at two temperatures can lead to conclusions about the size and nature of the anharmonic contribution, which can be interpreted in terms of the parameter $\bar{\gamma}_n$ sensitive to the over-all changes in $g(\omega)$ as a function of temperature. In the present calculation $\bar{\gamma}_n$ is a decreasing function of n, which indicates that for aluminum the high-frequency part of the spectrum (i.e., longitudinal modes) is less temperature-dependent than the low-frequency part (transverse modes).

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