Phonon-Frequency Distributions and Heat Capacities of Aluminum and Lead

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The phonon-frequency distributions of aluminum and lead have been determined from individual frequencies measured by neutron spectrometry. The measurements were mainly for wave vectors in the symmetry directions, but were sufficient elsewhere to permit interpolation throughout a cell of the wave-vector space solely with the help of symmetry conditions. Since there is little latitude for subjectivity in this process, the resulting distributions may be regarded as experimentally determined. They differ appreciably from distributions obtained by Born–von Kármán analysis of dispersion curves. The distributions have been used to calculate heat capacities at temperatures up to 800° (Al) and 500°K (Pb), with corrections for anharmonicity based on shifts of phonon frequencies with temperature. Formulas for the anharmonic corrections are derived on the assumption of effectively independent modes, with small relative frequency shifts that vary with temperature in the same way as the vibrational energy of the lattice. One correction affects both C_p and C_v, but is actually very small. Another, which is more important, is approximately of the form aC^2T, where a is closely related to an average value of the rate at which phonon frequencies vary with temperature at the temperature concerned. When a corresponds to frequency shifts at constant pressure (observed), this gives the anharmonic contribution to C_p; the anharmonic contribution to C_v requires shifts at constant volume, which cannot be observed directly. Calculated and calorimetric values of C_p agree well in the range of temperature where the expression aC^2T is a fair approximation. The corresponding expression with the parameter appropriate to constant-volume changes is expected to be a good approximation over a wider range of temperature, and it has been evaluated by comparison of calculations and calorimetric results. For both aluminum and lead, the anharmonic contribution to C_v thus arrived at is some 10 times smaller than the theoretical estimates of Keller and Wallace, which were based on a Lennard-Jones interatomic potential. The quasiharmonic approximation used here gives a very good account of the heat capacity up to at least 500°K in Al and 400°K in Pb. No conclusion can be drawn about the variation of the electronic heat capacity with temperature, mainly because of uncertainty in the calorimetric data. It seems that the lattice heat capacity of aluminum should vary in an anomalous manner below 20°K, first falling below a T^3 curve and then rising above it in the usual way; unfortunately, precise measurements that might reveal such behavior do not extend beyond 4°K.

1. INTRODUCTION

OUR neutron spectrometric measurements on the dispersion relations for phonons in aluminium and lead have been reported elsewhere.[1,2] For both metals they include frequencies in the principal symmetry directions of wave-vector space and at many other points, at 80°K. The data were comprehensive enough and accurate enough to permit reliable interpolation over a cell of reciprocal space, solely on the basis of measured values and symmetry conditions. This interpolation was carried out graphically for the three branches in each metal to obtain tables of phonon frequencies at intervals of 0.1 in three directions of reciprocal space (145 points for each branch). A computer then calculated frequencies at 1000 points in a cube around each point of the table network, using a Taylor expansion, and counted the number of frequency values falling in each of a series of small intervals. This sample of frequencies at points uniformly distributed in q space gave the frequency distribution at 80°K, after a little rounding off to remove statistical fluctuations. As no theory of interatomic forces is involved in this procedure and as the interpolation procedure is quite objective, the distributions thus obtained for

aluminium and lead may be regarded as experimentally determined.

Values of the lattice heat capacity at a series of temperatures are easily calculated from the frequency distribution by means of the formula for a harmonic solid, but it is of course desirable to improve on this result by calculating the anharmonic contribution as well. Theoretical work on anharmonicity is to a great extent formal; where estimates of the anharmonic contribution have been made they have been based on some model of the interatomic potential, i.e., not in any simple way on observable quantities, and in fact the estimates are intended as tests of the theory, not for practical use. The effects of anharmonicity are observable in neutron measurements as frequency widths and frequency shifts of phonons, and it would presumably be possible to calculate the anharmonic contribution to the heat capacity to any desired degree of accuracy in terms of these quantities if a good enough data sample were available. Our measurements at 80 and 300°K suffice for a calculation which gives the anharmonic contribution to c_p below 300°K within roughly 20%, which corresponds to about 1% of the total heat capacity at 300°K. The result may be further improved upon by adjusting a parameter so that calculated and calorimetric values of c_v agree over a wide range of temperatures (according to a formula derived in Sec. 3.2, the anharmonic contribution to c_v

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[1] R. Stedman and G. Nilsson, Phys. Rev. **145**, 492 (1966).

[2] R. Stedman, L. Almqvist, G. Nilsson, and G. Raunio, preceding paper, Phys. Rev. **162**, 545 (1967).

depends on a single parameter which is related to a mean value of phonon frequency shifts at constant volume).

It may seem that there is little point in performing the approximate calculation of c_p just mentioned if parameter fitting gives a better result, but the former calculation does provide a test of the formula concerned in terms of observed frequency shifts, and is therefore included here. The parameter fitting, in its turn, is more than a restatement of the experimental data on which it is based: It serves to eliminate the experimental fluctuations in these data, it reveals the temperature at which processes not included in a simple treatment of the nonharmonic contribution to the heat capacity (e.g., vacancy formation and complex anharmonic interactions between phonons) begin to be significant, and it provides a definite measure of the anharmonic heat capacity that is easily compared with estimates based on a proper theory of anharmonicity.

2. FREQUENCY DISTRIBUTIONS

2.1 Graphical Interpolation

The first step towards a frequency distribution, a table of phonon frequencies at regular intervals in reciprocal space, was made by carrying out a graphical interpolation of measured data, because this seemed quicker and easier to check than a computer program including all the same considerations.

The method was briefly as follows. For each branch, six diagrams were drawn, the diagrams being for successive "floors" of reciprocal space, i.e., the 0th diagram for points with $q_3 = 0$, the 1st for points with $q_3 = 0.1$, and so on up to $q_3 = 0.5$. [(q_1, q_2, q_3) is the phonon wave vector; the diagram for $q_3 = 0.6$ would be a reflection of that for $q_3 = 0.4$, and so on.] Each diagram consisted of 11 curves or profiles for $q_2 = 0, 0.1, 0.2, \cdots$, 1.0, each profile showing the variation of frequency along the line in question. Permutation of components gives points equivalent to (q_1, q_2, q_3). A point and its equivalents in general occur in two profiles in each of three diagrams. The three different profiles among these six represent the variation of frequency in three directions through the point in question, while the occurrence of each profile in two diagrams allows it to be compared with its neighbors in two directions. The information put into a set of diagrams was all the measured frequencies for the branch in question which fell on the profiles, each frequency being inserted at all possible positions in accordance with symmetry conditions, as well as the slope of the profile at places where the slope was known from more detailed measurements [e.g., at points in the (2,2,0) direction]. Then, having regard for the zero slope at the end of each profile, the similarity of adjacent profiles, and the six different positions at which each interpolated frequency must fit, the various profiles were constructed. The con-

struction proceeded from regions of greater density of information to regions of lesser density. Because of the several conditions to be observed, the procedure permitted remarkably little latitude of choice.

The result is three tables of phonon frequencies for each metal; Table I gives the figures for lead, while a similar table for aluminium is available on request. Measured values are italicized in the tables. The general level of accuracy is probably about 2%; the three or four significant figures of the tables merely serve to keep irregularities in the variation of frequency from point to point small.

It will be seen that the boundary of the region covered by the tables is a tetrahedron with vertices (0,0,0), (1,0,0), (1,1,0), and (0.5,0.5,0.5). The boundary opposite the origin thus differs from that of the first Brillouin zone. For phonons, Bragg reflection is of no consequence, and the Brillouin-zone construction, involving perpendicular-bisector planes, appears unnecessarily complicated; the present construction exhibits the symmetry of the lattice in a more obvious way, and tetrahedral elements may be easily put together to form the rhombohedral unit cell of the bcc lattice or a cube.

2.2 The Frequency Distribution Program

Since phonons are uniformly distributed in **q** space, the obvious way to compute their frequency distribution is to work out frequencies for a uniform network of **q** points and count frequencies in a sequence of frequency intervals. To obtain a more finely meshed sampling of frequencies than the tables of the last section provide, frequency values were computed for 1000 points in a cube of side 0.1 around each of the **q** points of the tables, i.e., in a cube extending halfway to each neighboring point. The frequencies were generated by a Taylor expansion, for which the six nearest neighbors of each point in the table network gave the gradient vector and the diagonal terms of the curvature tensor, while six pairs of next-nearest neighbors gave the other terms of the curvature tensor. No attempt was made to achieve continuity between frequency values in adjacent small cubes. Discontinuities between **q** intervals give rise to fluctuations in the frequency distribution, but these are small and almost random, like the fluctuations arising from the limited number of frequencies and frequency intervals involved in the computation, and are smoothed out when the final distribution curve is drawn.

The Taylor expansion must be a poor approximation for frequencies near crossover singularities, curves in reciprocal space where two branches are in sharp contact, and where the slope of each branch is discontinuous. However, the rounding off which the Taylor expansion leads to in the neighborhood of such singularities (the discontinuity in the gradient disappears) is not noticeable in the final frequency distribution, evidently because the regions concerned are

TABLE I. Phonons in Pb at 80°K. ω values (10^{10} rad sec^{-1}) for a complete set of q vectors (q_1,q_2,q_3). Italicized figures are measured, others interpolated.

10 q			ω_1	ω_2	ω_3	10 q			ω_1	ω_2	ω_3	10 q			ω_1	ω_2	ω_3
0	0	1	274	157	157	0	5	10	1089	1089	926	1	6	8	1247	1133	793
0	0	2	554	309	309	0	6	6	1354	1143	674	1	7	7	1291	1165	737
0	0	3	796	447	447	0	6	7	1300	1190	743	1	7	8	1303	1070	778
0	0	4	1001	567	567	0	6	8	1218	1184	831	1	8	8	1322	957	749
0	0	5	1155	655	655	0	6	9	1218	1007	881	2	2	2	985	359	359
0	0	6	1272	696	696	0	7	7	1234	1212	743	2	2	3	1089	428	419
0	0	7	1366	702	702	0	7	8	1281	1064	787	2	2	4	1162	504	482
0	0	8	1391	680	680	0	7	9	1303	944	796	2	2	5	1209	604	541
0	0	9	1316	633	633	0	8	8	1297	963	756	2	2	6	1237	774	614
0	0	10	1184	576	576	0	8	9	1316	850	718	2	2	7	1265	881	671
0	1	1	434	230	125	0	9	9	1278	749	617	2	2	8	1297	944	730
0	1	2	642	346	246	1	1	1	523	186	186	2	3	3	1159	478	444
0	1	3	850	469	409	1	1	2	708	290	283	2	3	4	1206	548	485
0	1	4	1026	586	529	1	1	3	913	428	422	2	3	5	1234	636	523
0	1	5	1165	674	623	1	1	4	1061	560	541	2	3	6	1256	793	592
0	1	6	1253	711	682	1	1	5	1171	674	630	2	3	7	1278	935	677
0	1	7	1341	711	699	1	1	6	1247	711	661	2	3	8	1297	1033	740
0	1	8	1366	686	686	1	1	7	1328	711	680	2	4	4	1253	630	497
0	1	9	1322	671	642	1	1	8	1354	727	667	2	4	5	1278	711	523
0	1	10	1240	667	623	1	1	9	1322	724	623	2	4	6	1310	825	592
0	2	2	818	441	233	1	2	2	863	365	277	2	4	7	1322	951	655
0	2	3	963	541	337	1	2	3	1001	491	371	2	4	8	1297	1051	718
0	2	4	1089	642	453	1	2	4	1108	592	460	2	5	5	1335	787	545
0	2	5	1162	730	541	1	2	5	1174	693	545	2	5	6	1360	869	595
0	2	6	1228	771	636	1	2	6	1231	756	630	2	5	7	1360	963	652
0	2	7	1278	768	689	1	2	7	1284	781	680	2	5	8	1322	1039	705
0	2	8	1303	743	735	1	2	8	1309	800	727	2	6	6	1360	951	630
0	2	9	1322	787	718	1	2	9	1322	837	724	2	6	7	1316	1007	667
0	2	10	1322	806	711	1	3	3	1089	573	375	2	7	7	1288	1064	705
0	3	3	1064	623	337	1	3	4	1146	674	447	3	3	3	1221	472	472
0	3	4	1118	724	428	1	3	5	1187	768	526	3	3	4	1253	501	491
0	3	5	1171	825	519	1	3	6	1240	863	611	3	3	5	1265	586	510
0	3	6	1221	907	617	1	3	7	1291	932	708	3	3	6	1269	724	567
0	3	7	1272	910	705	1	3	8	1291	932	784	3	3	7	1275	916	636
0	3	8	1291	856	793	1	3	9	1303	938	803	3	4	4	1294	519	510
0	3	9	1303	863	815	1	4	4	1203	768	478	3	4	5	1306	592	529
0	3	10	1310	894	806	1	4	5	1240	863	532	3	4	6	1328	702	573
0	4	4	1168	818	482	1	4	6	1297	944	617	3	4	7	1347	869	617
0	4	5	1228	910	560	1	4	7	1316	1014	715	3	5	5	1335	630	545
0	4	6	1297	991	645	1	4	8	1284	1020	803	3	5	6	1360	724	573
0	4	7	1316	1026	743	1	4	9	1234	1014	856	3	5	7	1366	850	614
0	4	8	1284	1014	837	1	5	5	1306	944	554	3	6	6	1373	793	595
0	4	9	1234	951	891	1	5	6	1344	1014	620	4	4	4	1325	513	513
0	4	10	1215	926	919	1	5	7	1350	1077	705	4	4	5	1322	563	545
0	5	5	1303	988	589	1	5	8	1284	1108	803	4	4	6	1366	661	573
0	5	6	1341	1077	655	1	5	9	1202	1108	866	4	5	5	1354	586	548
0	5	7	1354	1133	756	1	6	6	1354	1064	648	4	5	6	1379	636	563
0	5	8	1265	1152	847	1	6	7	1306	1127	711	5	5	5	1385	554	554
0	5	9	1149	1102	894												

small and the small spurious frequency shifts that arise for two branches in contact tend to neutralize each other in the later averaging process. This was checked by carrying out a graphical integration of a crossover region in aluminium, with the correct frequency variation, and comparing the result with that obtained by the computer using the Taylor expansion. The expansion is also inadequate at Kohn anomalies, but for reasons similar to those just mentioned it has been assumed that this does not noticeably affect the frequency distribution. Near the origin the method breaks down altogether, because the curvature of $\omega(q)$ perpendicular to q varies so rapidly. There it is a much better approximation to assume that the frequency varies

almost linearly out from the origin in all directions,[3] as far as a limiting frequency which is chosen by inspection of the dispersion curves in the symmetry directions, (for aluminum this frequency was taken to be 2, and for lead 0.4—the unit 10^{13} rad sec^{-1} to be understood here and elsewhere). If we further assume that the deviation from linearity is about the same for the different directions within this frequency interval, we may describe the frequency distribution there by

[3] This is so even though in the case of aluminum the slopes of the dispersion curves for transverse phonons in the region where our measurements commence is somewhat larger than the velocity of sound (see Ref. 1) and this may be expected to give a slight enhancement of $g(\omega)$ at very low frequencies. No similar effect was observed for lead.
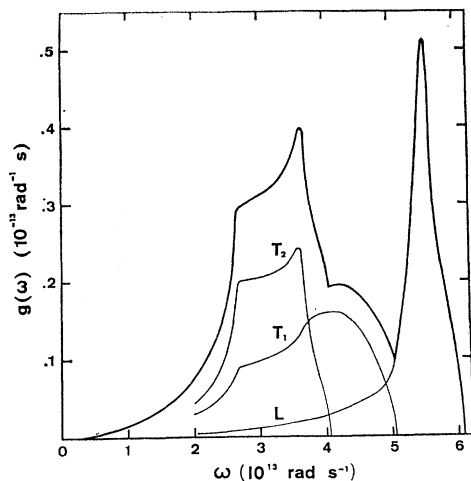
FIG. 1. The phonon-frequency distribution of aluminum.

$(a\omega^2+b\omega^n)$, and determine a, b, and n to fit the rest of the computed distribution, utilizing the integral of $g(\omega)$ out to the limit chosen, together with the value of $g(\omega)$ and the slope of $g(\omega)$ at the limit chosen. A good approximate description of the first part of the distribution in aluminium is $(0.0151\omega^2+0.000106\omega^7)$ and in lead $(1.33\omega^2+39.6\omega^7)$. For units, see Figs. 1 and 2. The power 7 in the small term is in good qualitative agreement with the observed shapes of dispersion curves near the origin—notably straight for some distance before falling off.

The frequency distributions for phonons in aluminum and lead at 80°K are shown in Figs. 1 and 2. The integral for the total curve in each case is 1. The contributions from the L, T_1, and T_2 branches are shown separately. In rounding off the curves, phonon widths have been taken into account, which means that each phonon frequency is replaced by a distribution of frequencies about the same mean and with a small but appreciable width: The only effect worth mentioning is a broadening and lowering of the high longitudinal peak in both metals.

2.3 Comments on the Frequency Distribution for Aluminum

The three peaks of the aluminum distribution are easily referred to stationary points on dispersion curves. The maxima at $(0.5,0.5,0.5)$ T, $(1,0,0)$ T, and $(0.6,0.6,0)$ L, for which the respective frequencies are 2.64, 3.66, and 5.45, turn out to be saddle points when examined in three dimensions, and correspond closely to the peaks in the frequency distribution.

Gilat and Nicklow[4] have calculated a frequency distribution at 80°K from our dispersion curves for aluminum, using Born–von Kármán formulas with suitable parameters to interpolate over a network

similar to ours in Table I, though with an interval of $\frac{1}{16}$ in each $\mathbf{q}$ component, followed by a linear Taylor expansion of frequencies locally in this network. Their results differ from ours mainly in the relative intensities of the peaks near 2.6 and 3.6, but in other details as well. (In comparing the two distributions it should be noted that theirs is not normalized as ours is.) The source of the differences between the two distributions must be in the frequencies for points off the main symmetry directions, since they have attained a remarkably close fit for frequencies in the symmetry directions. Dr. Gilat kindly sent us the data which are their equivalent of our tables for aluminum, and we have compared the two sets. The differences are apparent in the two frequencies for $\mathbf{q}=(1,0.5,0)$: They have $4.45(T_2)$ and $5.18(L,T_1)$, while the measured values are 4.06 and 5.00. The deviations from the correct values affect the shapes of the saddle points previously mentioned; in the frequency distribution the most marked effect is a displacement of intensity from the peak in the T_2 contribution at 3.6 towards higher frequencies.

The discrepancy between the calculated frequencies of Gilat *et al.* and the measured values is of interest outside the particular case of aluminum, since it illustrates the fallibility of the method which they and several others[5] have used to derive phonon frequency distributions for metals, via an analysis of dispersion curves for symmetry directions in terms of a Born–von Kármán model. A simple sketch will verify that it is easy to interpolate graphically between symmetry directions in aluminum with at least the accuracy of the complicated computer program involved in the
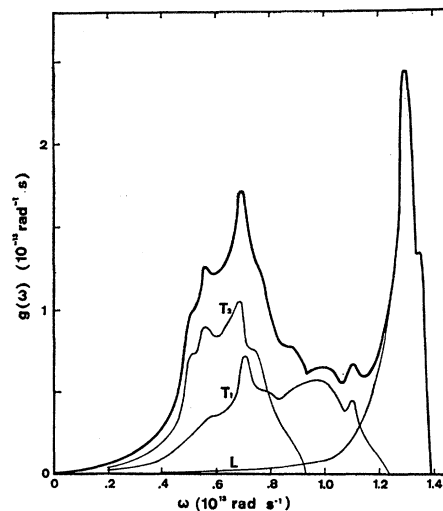

FIG. 2. The phonon-frequency distribution of lead.

[4] G. Gilat and R. M. Nicklow, Phys. Rev. **143**, 487 (1966).

[5] For example: C. B. Walker, Phys. Rev. **103**, 547 (1956) (aluminum); A. D. B. Woods, *ibid.* **136**, 781 (1964) (tantalum); R. A. Cowley, A. D. B. Woods, and G. Dolling, *ibid.* **150**, 487 (1966) (potassium).

latter method: Draw three "profiles" for the line from (1,0,0) to (1,1,0), the end values of the frequencies being 3.66 and 6.10, utilizing symmetry conditions and the circumstance that the three branches retain their order $(L > T_1 > T_2)$, while tending to be closer together in regions where the simple distinction between longitudinal and transverse modes of vibration is lost [the symmetry conditions are that each profile is symmetric, with zero slope at the ends, and that L and T_1 have a "cross-over" singularity at $(1,\frac{1}{2},0)$]. Yet aluminum might be expected to be particularly favorable for a Born–von Kármán model, since it is regarded as a relatively simple metal, with uncomplicated dispersion curves to which the model provides an exceptional fit. It seems that a few more experimental data and simple interpolation are to be preferred in generating dispersion relations for a complete cell of reciprocal space.

2.4 Comments on the Frequency Distribution for Lead

It will be seen that the frequency distribution for lead is less regular than that for aluminum, which is to be expected from the less regular dispersion relations. However, the three main peaks, at $\omega = 0.56$, 0.70, and 1.30, are exactly analogous to those in aluminum. Various small humps can all be identified: That at $\omega = 0.5(T_2)$ is due to irregularity near $(0.5,0.5,0.5)$, that at $\omega = 0.75(T_2)$ to the maximum at $(0.75,0.75,0)$, the dips at $\omega = 0.84$ and $1.08(T_1)$ to the two crossover singularities for this branch, and the hump at $\omega = 1.35$ (L) to the Kohn anomaly near $(0.5,0.5,0.5)$.

Gilat[6] has calculated the phonon frequency distribution for lead from the dispersion curves of Brockhouse et al. by the method mentioned in Sec. 2.3. His result is considerably different from ours, but in view of the complexity of the dispersion curves for lead the Born–von Kármán analysis cannot be expected to give a good account of the actual phonon frequencies, not even in symmetry directions.

3. THE LATTICE HEAT CAPACITY

3.1 Basic Formulas and Introductory Remarks

In the harmonic approximation we may define a heat capacity for phonons associated with a particular normal coordinate and polarization (or the ith of $3N$ modes) by

$$C_i = k \left[\frac{\hbar\omega_i/2kT}{\sinh(\hbar\omega_i/2kT)} \right]^2, \tag{1}$$

where ω_i is the characteristic frequency. Transforming the sum of the heat capacities for $3N$ modes to an integral, the lattice heat capacity per mole is

$$C = 3R \int_0^{\omega_{max}} d\omega\, g(\omega) \left[\frac{\hbar\omega/2kT}{\sinh(\hbar\omega/2kT)} \right]^2, \tag{2}$$

where $g(\omega)$ is the distribution of phonon frequencies.

Observed frequency widths of phonons and shifts of frequency with temperature indicate an appreciable departure from harmonic behavior, which becomes more pronounced as the temperature rises. But even in lead at 300°K—which, being more than three times the Debye temperature, is a relatively high temperature—the observed phonons are still quite well defined. So it is reasonable to apply formula (2) to the frequency distributions described in Secs. 2.3 and 2.4 in order to calculate a "harmonic" heat capacity at a series of temperatures up to 300°K, and tentatively even beyond that, subsequently applying anharmonic corrections. One obvious correction corresponds to a slight change of $g(\omega)$ with temperature, owing to shifts of individual phonon frequencies, and we may hope to derive this correction from our data on shifts. Another correction may be attributed to a small term in the temperature derivative of a function involving phonon frequencies, a term of type $(d\omega/dT)[\partial(\text{energy})/\partial\omega]$; in harmonic formulas frequencies are taken to be constant, and no such term occurs. This term involves the temperature derivatives of phonon frequencies, and in principle may also be evaluated from observations on frequency shifts.

3.2 Anharmonic Corrections

We use a quasiharmonic model of the thermal motion of the lattice, i.e., the vibrational energy is associated with $3N$ separate modes, the interactions between phonons in the different modes being included here in the shifts and widths of the phonon frequencies. It is assumed that only the mean frequencies of phonons are of significance for the heat capacity—i.e., that frequency widths may be disregarded—and that the right mean frequency in this connection is the mean frequency obtained from neutron measurements. A quasiharmonic approximation of this kind has been discussed by Cowley[7]; it is expected to be good in several applications as long as the temperature is not too high.

Our aim is to produce a formula for the anharmonic contribution to the heat capacity which, while not rigorously correct, is based on reasonable assumptions and approximations, and which contains quantities such as the thermal energy and heat capacity calculable from our phonon frequency distributions, together with a mean frequency shift. To begin with we consider how frequencies may be supposed to vary with temperature (since we have no more than values at 80 and 300°K), and how to determine appropriate mean values of the frequency shifts.

The variation of each ω_i with temperature is expressed in terms of a small relative shift δ_i, where

$$\omega_i(T) = \omega_i(0) \exp\delta_i(T). \tag{3}$$

Our observed shifts are shifts at constant pressure, and are related to shifts at constant volume and at constant

[6] G. Gilat, Solid State Commun. 3, 101 (1965).

[7] R. A. Cowley, Advan. Phys. 12, 421 (1963).

temperature by

$$(d\delta_i/dT)_p = (d\delta_i/dT)_v + V\gamma(d\delta_i/dV)_T, \qquad (4)$$

where γ is the coefficient of volume expansion. For shifts at constant volume we make the drastic though plausible assumption that they are proportional to the total vibrational energy of the lattice, not including the zero-point energy, i.e., that the constant-volume derivative in Eq. (4) is proportional to the heat capacity (at constant volume, though this is not important here). This agrees with the expected linear variation of shifts relative to T at high temperatures (see, for instance, Ref. 7, p. 435), and with the zero values of the temperature derivatives in Eq. (4) at 0°K, and it will be seen later that the corrections calculated on the basis of the shifts are in any case insensitive to detail in the uncertain region of intermediate temperatures, because of their smallness and the averaging processes involved in calculating them. Over a range of temperature which may be obtained by examining a table of expansion coefficients it is also a fair approximation to take γ (or, more strictly $V\gamma$) to be proportional to the heat capacity, and since we may assume the constant-temperature derivative in Eq. (4) to be independent of temperature, the constant-pressure derivative in Eq. (4) is then also proportional to the heat capacity in the range of temperature concerned. There are several approximations and assumptions involved here, but in practice the result is better than might be supposed, because we evaluate the shifts at constant pressure from frequencies observed at 80 and 300°K, and only need the general form of the variation with temperature to get good enough values elsewhere (actually we extend the range of validity of our result down to 0°K to obtain convenient formulas). We thus write

$$\delta_i = a_i E, \qquad (5)$$

where E is the thermal energy of the lattice, a quantity which can be calculated from $g(\omega)$ by appropriate integration, and a_i is a constant which may be derived from measurements at 80 and 300°K, or, where such measurements are lacking, by assuming shifts measured for other phonons to be typical of their polarization branch and frequency.

The correction to the heat capacity which arises because the values of ω_i in Eq. (1) must be appropriate to the particular temperature, i.e., because $g(\omega)$ in Eq. (2) varies slightly with temperature, is

$$-T[E(T)-E(80)]\sum_i (dC_i/dT)a_i, \qquad (6)$$

because for functions of (ω/T) such as that in (1), $\partial/\partial\omega = -T\partial/\partial T$, and because our calculation of C uses the frequency distribution for 80°K. The correction may be evaluated by dividing the phonons into frequency intervals, each interval with a known average shift, working out (dC/dT) for each phonon group, and then

determining the average parameter $\bar{a}(T)$, using the appropriate temperature-dependent weights for each group. The correction is then

$$-T[E(T)-E(80)](\partial C/\partial T)\bar{a}(T). \qquad (7)$$

Five or six frequency intervals should usually suffice: Where the interval is narrow [e.g., that including the main L peak in $g(\omega)$] the variation of C_i with T may be regarded as nearly the same for all modes and the shift is a simple average, while if the shifts are similar (e.g., for the low frequencies) the width of the interval need not be restricted. The correction is of course zero at 80°K in our case, and for both metals it is positive above that temperature and negative below. For temperatures greater than $\Theta/2$ (where Θ is the Debye temperature, about 380°K for aluminium and 90°K for lead), all dC_i/dT vary approximately as T^{-3} (and consequently dC/dT does too), and the thermal energy varies as T; so the correction varies as T^{-1} at higher temperatures. In the cases we are dealing with, it turns out that the correction is negligible at the upper end of the temperature range for which the approximation $\gamma = \text{const} \times C$ is fairly good. Below $\Theta/2$, $\bar{a}(T)$ increases in size to a maximum value at 0°K which is determined by the shifts in the velocities of transverse sound waves between 80 and 0°K, and relative to the specific heat the correction is largest near 0°K. However, the correction is nowhere large enough for even a 20% inaccuracy to be of significance.

When the original "harmonic" specific heat is corrected in the manner described above, the result is something intermediate between C_v and C_p. With the correct formula for the anharmonic contribution and our observed shifts, we can proceed to C_p, but as already pointed out, the temperature range in which the approximation expressed by Eq. (5) is fairly good is limited, and therefore we cannot expect our calculated C_p to be a fair approximation at higher temperatures. However, Eq. (5) should be a better approximation in the case of the frequency shifts at constant volume involved in the anharmonic contribution to C_v, and in this case the formula arrived at should be a good approximation over a wider range of temperature. We first consider changes at constant volume, and then extend the results to conditions of constant pressure.

There are three alternative points of departure for the heat capacity,

$$C_v = T\left(\frac{dS}{dT}\right)_v = -T\left(\frac{d^2F}{dT^2}\right)_v = \left(\frac{dE}{dT}\right)_v, \qquad (8)$$

where S is the entropy, F the free energy, and E the vibrational energy of the lattice (we neglect the ground state, which we take to be independent of temperature). S, F, and E are all approximately equal to the harmonic expressions involving summation with respect to i of known functions of ω_i and T, but there is no immediate way of knowing the deviation from the harmonic form

for any of them. If we use a harmonic expression for S, allow frequencies to vary with temperature, and carry out total differentiation with respect to T, we obtain an anharmonic correction which is $\sum_i [-C_i T(d\delta_i/dT)]$. Starting from a harmonic expression for F, we arrive at a correction $\sum_i [-2C_i T(d\delta_i/dT) - E_i T(d^2\delta_i/dT^2)]$, and starting from a harmonic expression for E we arrive at a correction $\sum_i (E_i - C_i T)(d\delta_i/dT)$. Of these three alternatives, that based on the entropy is best, because (1) Barron[8] found that the entropy is the appropriate quantity in the present connection, (2) Cowley[7] found that when the quasiharmonic temperature shifts (those observed with neutrons) are inserted into the harmonic expression for the free energy, the change in the temperature-dependent part of the free energy is twice the amount obtained by a more proper consideration of phonon-phonon interactions, and (3) the correction derived from a harmonic expression for E approaches a constant value at high temperatures, whereas according to anharmonicity theory it should vary as T. The following general argument confirms the "entropy" correction, though with a modification which may be significant at fairly low temperatures.

If the average number of phonons in the ith mode at temperature T is n_i', the associated entropy is (see, for instance, Landau and Lifshitz[9])

$$S_i' = (n_i'+1)\ln(n_i'+1) - n_i'\ln n_i', \qquad (9)$$

where the prime indicates a value which includes anharmonicity. Putting $n_i' = n_i(1+\epsilon_i)$, where n_i is the number of phonons in the harmonic approximation $\{[\exp(\hbar\omega_i/kT) - 1]^{-1}$, ω_i being the frequency at some standard temperature$\}$ we have

$$S_i' = S_i + \epsilon_i E_i/T \qquad (10)$$

to the first order of small quantities. The anharmonic contribution to the heat capacity is

$$d(\epsilon_i E_i)/dT - \epsilon_i E_i/T. \qquad (11)$$

Starting from the energy, $n_i\omega_i(1+\epsilon_i+\delta_i)$, the anharmonic contribution is

$$d(\epsilon_i E_i)/dT + E_i(d\delta_i/dT). \qquad (12)$$

Equating (11) and (12), $\epsilon_i = -T(d\delta_i/dT)$, and the anharmonic contribution to the heat capacity is

$$-T[C_i(d\delta_i/dT) + E_i(d^2\delta_i/dT^2)]. \qquad (13)$$

Straight differentiation of the energy would give an additional term $C_i\delta_i$ in (12), which would make the first term in (13) twice as large; this term is omitted because it corresponds to a change of energy where the number of phonons in the ith mode and the frequency change simultaneously, i.e., to interaction between phonons

belonging to the same mode, an effect which is included in the changes of energy registered by neutrons. The factor 2 appearing in the anharmonic correction if this term is included presumably corresponds to the factor 2 previously mentioned in comparing results derived from harmonic expressions for S and F, and to that mentioned by Cowley.[7]

In order to achieve a practical summation of (13) over $3N$ modes, we adopt a procedure similar to that used previously—divide phonons up into groups with given average shifts, and determine average values of the parameters a_i by appropriate weighting. The weights here are C_i and E_i, so the average parameter will not be the same as before. Above $\Theta/2$ it will be almost constant and about the same for both terms in (13), and since in this case the shift of emphasis towards low frequencies at low temperatures is not as great as in the previous case and anyway occurs in a region where the correction is almost negligible, we assume that the average value of a_i is independent of temperature, and call it a. The correction is then

$$-aT[C^2 + E(dC/dT)]. \qquad (14)$$

The second term is negligible or almost so: At Θ it is about one-tenth of the first term, and above that temperature falls off approximately as T^{-2} while the first term increases approximately as T. In order to be able to assess the second term below Θ, approximate factors of proportionality relative to the first term may be derived from the Debye specific heat: They are 0.5, 0.3, 0.2, 0.15, and 0.1 at $T/\Theta = 0.2$, 0.4, 0.6, 0.8, and 1.0.

If the second term in (13) is neglected, it will be seen that (13) is of the form $T(\partial S/\partial\omega_i)(d\omega_i/dT)_v$, and the corresponding term for changes at constant pressure is evidently $T(\partial S/\partial\omega_i)(d\omega_i/dT)_p$. That is, the anharmonic contribution to C_p is approximately $-a'C^2T$, where a' is the average parameter derived from observed shifts at constant pressure in the manner described above.

3.3 The Heat Capacity of Aluminum

In Table II, C denotes the heat capacity per mole calculated from the phonon-frequency distribution of Sec. 2.3, with the correction (7) included. The correction is everywhere almost negligible. The next column, $(C_p - C_e)$ (calculated value), is obtained from the first by adding the correction (14), with the parameter a determined from experimental frequency shifts ($a = 5.4 \times 10^{-6}$ J^{-1} mole). Experimental values of C_p have been taken from Giauque and Meads[10] up to 300°K, and above that from the *American Institute of Physics Handbook*; of these latter values, only that at 800°K is measured, the others being obtained by an interpolation formula. The values of the electronic heat capacity C_e

[8] T. H. K. Barron, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 247.

[9] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), especially Chap. 5.

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

TABLE II. The heat capacity of aluminum. T and Θ are in °K, other quantities in J deg^{-1} mole^{-1}.

T	C (calc)	C_p-C_e (calc)	C_p-C_e (expt)	C_e	C_v-C_e (expt)	Θ (calc)
0						446
10						442
20	0.19	0.19	0.20	0.03	0.20	432
30	0.78	0.78	0.81	0.04	0.81	405
40	1.99	1.99	2.04	0.05	2.04	392
50	3.68	3.69	3.75	0.07	3.74	389
60	5.61	5.63	5.67	0.09	5.65	390
80	9.45	9.51	9.53	0.12	9.48	393
100	12.71	12.83	12.91	0.13	12.78	395
120	15.24	15.44	15.51	0.14	15.32	396
140	17.17	17.46	17.51	0.15	17.22	396
160	18.63	19.01	19.13	0.16	18.73	396
200	20.62	21.16	21.39	0.19	20.81	396
250	22.06	22.84	23.02	0.23	22.16	395
300	22.91	23.92	24.09	0.28	22.95	394
400	23.81		25.24	0.37	23.61	
500	24.23		26.39	0.47	24.28	
600	24.44		27.56	0.56	24.86	
700	24.55		28.68	0.65	25.29	
800	24.63		29.85	0.74	25.48	

have been taken from the low-temperature data of Phillips[11] and the free-electron value: According to Buckingham[12] and Buckingham and Schafroth[13] the low-temperature value is enhanced by electron-phonon interaction,[14] so that there is a hump in the curve of C_e versus T at temperatures well below the Debye frequency, and C_e may be supposed to approach the free-electron value at higher temperatures. Krebs[15] has calculated some of the integrals involved, and on the basis of his curves we have supposed the electronic specific heat to attain the free-electron value at $\Theta/2$, after starting from 0°K as found by Phillips.[11] The experimental values of (C_v-C_e) have been obtained from (C_p-C_e) with (C_p-C_v) calculated from expansion data of Nix and Macnair[16] and compressibility data of Kamm and Alers,[17] using the formula $(C_p-C_v)=V\gamma^2/\kappa_T$ Θ indicates effective Debye temperatures obtained by referring the C values to a table of the Debye specific heat function. That at 0°K corresponds to the polynomial fitted to the low-frequency part of $g(\omega)$ in Sec. 2.2, taking into account shifts of frequency between 80 and 0°K in agreement with the ultrasound data of Kamm and Alers.[17] (The shifts of low transverse phonon frequencies between 80 and 300°K are the same as the shifts of the corresponding sound velocities between these temperatures, so we have assumed agreement between 0 and 80°K as well.)

[11] E. Phillips, Phys. Rev. 114, 676 (1959).
[12] M. J. Buckingham, Nature 168, 281 (1951).
[13] M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) 67, 828 (1954).
[14] N. W. Ashcroft and J. W. Wilkins [Phys. Letters 14, 285 (1965)] find that the enhancement of the low-temperature electronic specific heat in aluminum and lead is wholly due to electron-phonon interaction.
[15] K. Krebs. Phys. Letters 6, 31 (1963).
[16] F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).
[17] G. N. Kamm and G. A. Alers, J. Appl. Phys. 35, 327 (1964).

Comparison of the calculated and experimental values of (C_p-C_e) indicates that the correction calculated on the basis of our observed frequency shifts is correct to within 10%, which is as good as could be expected [the approximation adopted in Sec. 3.2, $\gamma \sim C$, makes our value of (C_p-C_e) at 300°K too low, and the average shift must be assigned an error of at least 10%]. Since C and the experimental values of (C_v-C_e) agree within estimated margins of error up to 500°K, we may conclude that any correction of form (14) to be applied in this case is very small, which means that a quasiharmonic approximation with frequency shifts entirely determined by changes of volume is excellent up to 500°K. On the bases of a Lennard-Jones interatomic potential, Keller and Wallace[18] estimated the anharmonic contribution to C_v as $-6.7\times10^{-3}T$ J deg^{-1} mole^{-1} above the Debye temperature; a glance at Table II shows that this is at least a factor of 10 too large, and not necessarily of the right sign. From 600°K to the melting point (933°K) processes other than the type of anharmonicity considered here evidently become important.

The low-temperature values of the heat capacity, stated in Table II as effective Debye temperatures, are of some interest. Kamm and Alers[17] obtained a value of 430.3°K at 0°K on the basis of their ultrasound data, Phillips[11] 427.7°K from measurements of the heat capacity below 4°K. Our value at 0°K is extrapolated, and so of little weight. If we instead accept a value near 430°K, we conclude that there should be an anomaly in the lattice heat capacity somewhere below 20°K, at which temperature our value should be near the true value. The reason that our values of Θ at 0, 10, and 20°K are higher than that derived from ultrasound data has already been given[3]: The phonon frequency distribution determined by us must contain fewer phonons in the range below 10^{13} rad sec^{-1} than the Debye distribution based on the ultrasound data, so that even if we allow the two distributions to coincide at the origin the heat capacity must fall below the corresponding T^3 value before 20°K is reached (the specific heat at 20°K is predominantly due to frequencies in the range of our measurements). Unfortunately, the particularly accurate measurements of the heat capacity by Phillips[11] do not extend beyond 4°K, at which temperature the lattice heat capacity is only about 0.2 of the whole, and a downward shift of even a few percent might be difficult to see—particularly in view of the effect of alternative temperature scales (see his Fig. 6). The effective Debye temperature derived from the data of Giauque and Meads[10] at 15°K is 450±5°K and at 20°K, 428±2°K (our corresponding figures are 438 and 432°K). However, irregularities in a curve of effective Debye temperatures from their data plotted against temperature (see Gilat and Nicklow,[4] Fig. 5) indicate that the errors are probably larger than estimated by

[18] J. M. Keller and D. C. Wallace, Phys. Rev. 126, 1275 (1962).

them, and it is not possible to draw any conclusion from the notably high value at 15°K. It may in any case be difficult to observe an anomaly in the low-temperature lattice heat capacity, because an anomaly of the opposite kind and of a similar order of magnitude is expected in the electronic heat capacity in the same temperature region (see Buckingham[12] and Krebs[16]).

3.4 The Heat Capacity of Lead

Table III for lead is analogous to Table II for aluminum. The experimental values of C_p are from various sources: At 4°K from van der Hoeven and Keesom,[19] at 10°K from National Bureau of Standards tables, at 15–300°K from Meads et al.,[20] and at 400 and 500°K from Douglas and Dever.[21] Meads et al. do not give a direct estimate of errors, but comparisons of their results with later results at three temperatures where this is possible indicate an uncertainty of roughly 1% (C_p at 60°K is 23.0, at 80°K, 23.0 J deg^{-1} mole^{-1}, according to Horowitz et al.,[22] while at 300°K Douglas and Dever[21] have $C_p = 26.49$ J deg^{-1} mole^{-1} and make the comment that the results of Meads et al. appear to be systematically too high near this temperature]. The electronic heat capacity in Table III is mainly the free-electron value, except at temperatures below 50°K, where there is a slight "hump" as earlier described, with a transition to the value given by van der Hoeven and

TABLE III. The heat capacity of lead. T and Θ are in °K, other quantities in J deg^{-1} mole^{-1}.

T	C calc	$C_p - C_e$ calc	$C_p - C_e$ expt	C_e	$C_v - C_e$ expt	$C_v - C_e$ calc	Θ calc
0							103.5
4	0.13	0.13	0.13	0.01	0.13	0.13	98.0
10	2.92	2.93	2.78	0.03	2.78	2.93	85.2
15	7.06	7.07	7.18	0.05	7.18	7.06	87.2
20	10.93	10.95	10.94	0.07	10.92	10.92	89.2
25	14.05	14.08	13.99	0.07	13.95	14.03	90.5
30	16.38	16.43	16.43	0.07	16.36	16.36	91.2
35	18.11	18.18	18.21	0.07	18.12	18.08	92.1
40	19.41	19.50	19.50	0.07	19.38	19.37	92.8
50	21.14	21.28	21.26	0.08	21.07	21.09	94
60	22.20	22.39	22.34	0.09	22.09	22.13	95
80	23.33	23.60	23.56	0.12	23.18	23.24	97
100	23.89	24.25	24.27	0.15	23.78	23.78	98
150	24.46	25.02	25.04	0.22	24.28	24.28	
200	24.66	25.42	25.57	0.30	24.50	24.42	
250	24.76	25.72	25.99	0.37	24.62	24.45	
300	24.81	25.97	26.40	0.45	24.69	24.45	
400	24.86		26.85	0.60	24.56	24.37	
500	24.89		27.67	0.75	24.61	24.27	

[19] J. C. Van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. 137, 103 (1965).
[20] P. F. Meads, W. R. Forsythe, and W. F. Giauque, J. Am. Chem. Soc. 63, 1902 (1941).
[21] T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954).
[22] M. Horowitz, A. A. Silvidi, S. F. Malaker, and J. G. Daunt, Phys. Rev. 88, 1182 (1952).

Keesom[19] for the region 0 to 4°K (it will be seen that this latter feature is not important here). In calculating $(C_p - C_v)$, data on compressibility were taken from Waldorf and Alers,[23] on expansion from Channing and Weintroub[24] and, above 300°K, from the American Institute of Physics Handbook.

The constant a in correction (14), determined from observed shifts of phonon frequency, was 4.8×10^{-6} J^{-1} mole. The calculated and experimental values of $(C_p - C_e)$ agree within about 10%, having regard to the fact that our correction is somewhat too low at 300°K and the experimental value quoted probably too high. This indicates that the correction formula is satisfactory for lead, as it was for aluminum. Irregularities in the experimental data make it difficult to estimate the constant for a calculation of the anharmonic contribution to C_v in accordance with formula (14), and there is of course always the uncertainty about C_e, but we have nevertheless derived a rough estimate of the parameter concerned in order to have a definite estimate of the effect of anharmonicity on C_v. With $a = 2.10^{-6}$ J^{-1} mole, we obtain the calculated values of $(C_v - C_e)$ shown in Table III. The general close agreement between the calculated and experimental values of $(C_v - C_e)$ seems to hold up to about 400°K (at 300°K two alternative experimental values[20,21] lie on either side of the calculated value), while beyond that temperature more complicated anharmonic effects and/or vacancy formation begin to make an appreciable contribution. Keller and Wallace[18] estimated the anharmonic contribution to C_v above the Debye temperature as $-1.14 \times 10^{-2} T$ J deg^{-1} mole^{-1}; this is nine times the present result, and obviously at variance with the experimental data.

The effective Debye temperatures in the last column of Table III are derived from the calculated values of $(C_v - C_e)$. At 0°K ultrasound measurements[23] yield a value 105.4°K, and calorimetry[19] 105.3±0.8°K, and our value, 103.5±2°K, is in satisfactory agreement here, which also applies to the values at 4°K–98.0±1°K here and 99.1°K from calorimetry.[19] Above 4°K our results rapidly increase in accuracy as a larger part of the frequency distribution comes into play and errors in individual phonon frequencies become of little significance [between 10 and 30°K the estimated error in the calculated value of $(C_v - C_e)$ is 0.01 J deg^{-1} mole^{-1}] but unfortunately the calorimetric results in this region are very uncertain (see Figs. 3 and 5 of Ref. 22).

ACKNOWLEDGMENTS

[23] D. L. Waldorf and G. A. Alers, J. Appl. Phys. 33, 3266 (1962).
[24] D. A. Channing and S. Weintroub, Can. J. Phys. 43, 955 (1965).