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# Analysis of Alkali-Metal Specific-Heat Data

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Published data on the density, thermal-expansion coefficient, and compressibility of the alkali metals are reviewed, and best values for the density as a function of temperature and for the Grüneisen constant $\gamma(0)$ are selected. From published specific-heat data the entropy and its corresponding Debye temperature ($\Theta^S$) are computed as a function of temperature for the body-centered-cubic phase. The values of the first few even moments and some negative moments of the lattice-vibration spectrum are calculated for each alkali metal (bcc phase) on the basis of two different approximations as to the form of the anharmonic specific-heat contribution. The anharmonic contribution is found to be positive for all the alkali metals. There appears to be a systematic change in the shape of the vibration spectrum on going from sodium to cesium. The spectrum moments found for sodium are in good agreement with those obtained from neutron-scattering experiments on this metal.

## INTRODUCTION

FAIRLY accurate specific-heat data over a wide temperature range are now available for all the alkali metals, and the time seems ripe for a review of their thermal properties. Recent work by Tosi and Fumi[1] has shown that detailed analysis at higher temperatures is best made by use of the entropy rather than the specific heat. This is because the analysis is usually made from the equivalent Debye temperature and at high temperatures the Debye temperature obtained from the entropy ($\Theta^S$) is much less sensitive to small errors than is the corresponding Debye temperature ($\Theta^C$) obtained from the specific heat at constant volume ($C_v$). Also, the sometimes uncertain correction from the measured specific heat at constant pressure ($C_p$) to $C_v$ is avoided by use of the entropy.

In order to use Tosi and Fumi's method it is still necessary to convert $\Theta^S$ values from the volume at the temperature of measurement to the equivalent values at the absolute-zero volume. To do this a knowledge of the variation of density with temperature and of the Grüneisen constant $\gamma(0)$ is required. The paper commences with a discussion of the data required to compute these quantities.

The analysis of the specific-heat data yields values for the first few even moments and some negative moments of the lattice-vibration-frequency spectrum and for the anharmonic contribution to the specific heat. The paper concludes with a comparison of the results obtained for the various alkali metals. The moments obtained for sodium are also compared with moments deduced from neutron-scattering experiments on this metal.

The analysis given in this paper is similar to that made some years ago for the alkali halides by Barron, Berg, and Morrison.[2] However, more uncertainty attaches to the present work due to the complications of the martensitic transformation in lithium and sodium, and because the low Debye temperatures of the remaining metals make necessary accurate data down to rather low temperatures where the specific-heat measurements are less accurate than at higher temperatures.

## DENSITIES OF THE ALKALI METALS AS A FUNCTION OF TEMPERATURE

Early in the century macroscopic determinations were made in the room-temperature region, especially by Hackspill[3] who has listed the results of earlier work. More recent work has been mainly confined to x-ray determinations, the exceptions being work on lithium by Simon and Bergmann[4] and on sodium by Siegel and Quimby[5] and Sullivan and Weymouth.[6] Pearson[7] has summarized most of the results and it is clear that they are not very concordant. This may be due to the fact that the samples are often cast in glass tubes and strained on cooling because of adhesion to the walls. Impurities may also be responsible for significant discrepancies.

In order to smooth out the results and interpolate and extrapolate as necessary, the variation of density with temperature for each metal will be represented by the appropriate choice of constants in the following equation:

$$\rho_T/\rho_0=(1-BTD_W(\Theta^W/T)-CT^2-De^{-E/RT}),$$

where $\rho_T$ is the density at the temperature $T$; $\rho_0$ the density at the absolute zero; $B$, $C$, $D$, $\Theta^W$, and $E$ constants to be determined for each metal; $R$ the gas constant; and $D_W(\Theta^W/T)$ is the Debye function for (thermal energy/temperature), which has been tabulated by Simon.[8]

The term with coefficient $B$ represents the lattice

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[1] M. P. Tosi and F. G. Fumi, Phys. Rev. **131**, 1458 (1963).

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

[3] L. Hackspill, Compt. Rend. **152**, 259 (1911).

[4] F. E. Simon and R. Bergmann, Z. Physik. Chem. (Leipzig) **B8**, 255 (1930).

[5] S. Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938).

[6] G. A. Sullivan and J. W. Weymouth, Phys. Rev. **136**, A1141 (1964).

[7] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press Ltd., London, 1958).

[8] F. E. Simon, *Landolt-Börnstein Physikalisch-Chemische Tabellen* (Julius Springer, Berlin, 1927), 5 Auflage, Erster Ergänzungsband, p. 702.

TABLE I. Density of alkali metals.

$$\rho_T/\rho_0=(1-BTD_W(\Theta^W/T)-CT^2-De^{-E/RT})$$

| | Values of coefficients in density equation | | | | | Ratios computed from equation | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | $B$ | $C$ | $D$ | $\Theta^W$ | $E$ cal/ mole | $\rho_{80}/\rho_0$ | $\rho_{100}/\rho_0$ | $\rho_{200}/\rho_0$ | $\rho_{273.15}/\rho_0$ | $\rho_{293.15}/\rho_0$ | $\rho_{273.15}$ | $\rho_0$ |
| Li | $2.662\times10^{-5}$ | $3.727\times10^{-9}$ | 0.0 | 500.0 | 0.0 | 0.99908 | 0.99809 | 0.98862 | 0.97915 | 0.97638 | 0.5348[a] | $0.546_2$ |
| Na | $3.437\times10^{-5}$ | $3.200\times10^{-9}$ | $7.3\times10^2$ | 270.0 | $10.5\times10^3$ | 0.99605 | 0.99333 | 0.97599 | 0.96185 | 0.95790 | 0.9725[b] | 1.011 |
| K | $3.803\times10^{-5}$ | $5.030\times10^{-9}$ | $1.0\times10^3$ | 90.0 | $9.6\times10^3$ | 0.98836 | 0.98403 | 0.96167 | 0.94503 | 0.94042 | 0.859[b] | 0.909 |
| Rb | $3.824\times10^{-5}$ | $5.734\times10^{-9}$ | $1.2\times10^2$ | 56.0 | $7.2\times10^3$ | 0.98608 | 0.98159 | 0.95881 | 0.94178 | 0.93686 | 1.5248[b] | 1.619 |
| Cs | $3.925\times10^{-5}$ | $9.297\times10^{-9}$ | $7.2\times10^1$ | 38.5 | $6.5\times10^3$ | 0.98439 | 0.97972 | 0.95614 | 0.93831 | 0.93296 | 1.9029[b] | 2.028 |

[a] Mean of several x-ray determinations.
[b] Hackspill (Ref. 3).

thermal expansion and is of the form used by Tosi and Fumi.[1] The term with coefficient $C$ represents the electronic thermal expansion and has been discussed recently by White.[9] For a single-band free-electron model $C=\frac{1}{3}(\gamma\chi_T T/M)$ where $\gamma$ is the electronic specific-heat coefficient,[10] $\chi_T$ the isothermal compressibility, and $M$ the atomic weight. This term is quite small for the alkali metals and it has been assumed in the present work that the electronic thermal expansion may be represented adequately in this way. Electronic specific-heat coefficients have been taken from Martin[11,12] and Filby and Martin[13] and compressibilities from Mott and Jones.[14]

The last term represents the contribution of the thermally generated lattice vacancies to the thermal expansion. The constants used are based on those determined by Martin[15] from an analysis of specific-heat results. The constant $D$ has been adjusted to allow for relaxation round the vacancy which has arbitrarily been taken as 50%.

The data used in determining the remaining constants in the density equation will now be considered in detail for each metal.

*Lithium.* Several sets of data, in rather good agreement with one another, exist between about 80°K and room temperature. (Macroscopic expansion data are by Simon and Bergmann,[4] x-ray data by Lonsdale and Hume-Rothery,[16] Owen and Williams,[17] and Pearson.[18] All these values disagree with the unreferenced value of the expansion coefficient tabulated by Mott and Jones[14] which is clearly incorrect.) In order to represent this data a $\Theta^W$ of 500°K is necessary, as was pointed out by Simon and Bergmann. This value is considerably higher than the Debye temperature at the absolute zero obtained from specific-heat data[19] ($\Theta_0{}^C=344°$). The lattice-vacancy term is negligible up to 300°K and has been taken as zero.

The values of the coefficients obtained for lithium are shown in Table I. Barrett[20] gives a value for the lattice parameter at 78°K which leads to a density about 0.7% lower than the value obtained from the equation (which was based on the experimental data quoted above), suggesting that Barrett's lattice parameters might not be too reliable or that the discrepancy is due to the impurity (~0.5%) in Barrett's samples.

*Sodium.* A macroscopic determination of expansion coefficient between 80 and 290°K was made by Siegel and Quimby[5] and their results have been confirmed by the more recent, but less precise, work of Beecroft and Swenson.[21] These results overlap those of Hackspill[3] and Sullivan and Weymouth[6] in the room-temperature region, and agreement is quite good. It is again found that the $\Theta^W$ of 270°K required to represent these results is considerably higher than the $\Theta_0{}^C$ value[19] of 152.5°K.

Values of the coefficients for sodium, based on this data, are given in Table I. Densities obtained from this equation are 0.3% higher than a value obtained from Barrett's data[20] at 78°K and 0.15% lower than Barrett's value at 5°K. The disagreements are of the same order as Barrett's estimated uncertainties. Within these uncertainties Barrett found that varying the purity from "stock" to 99.998% had no effect on the lattice parameter.

*Potassium.* Comparatively few expansion-coefficient data are available on potassium, and the coefficients in the density equation have been obtained from Hackspill's data[3] at room temperature with the assumption that $\Theta^W\simeq\Theta_0{}^C$. These values are given in Table I. The densities obtained from the equation agree with Barrett's values[20] at 5 and 78°K, respectively. This

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[9] G. K. White, Phil. Mag. **6**, 815 (1961).

[10] Not to be confused with the Grüneisen $\gamma$ appearing later in this paper.

[11] D. L. Martin, Proc. Roy. Soc. (London) **A263**, 378 (1961).

[12] D. L. Martin, Phys. Rev. **124**, 438 (1961).

[13] J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A284**, 83 (1965).

[14] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

[15] D. L. Martin, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press Ltd., London, 1964), p. 255.

[16] K. Lonsdale and W. Hume-Rothery, Phil. Mag. **36**, 799 (1945).

[17] E. A. Owen and G. I. Williams, Proc. Phys. Soc. (London) **A67**, 895 (1954).

[18] W. B. Pearson, Can. J. Phys. **32**, 708 (1954).

[19] J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A276**, 187 (1963).

[20] C. S. Barrett, Acta Cryst. **9**, 671 (1956).

[21] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids **18**, 329 (1961).

TABLE II. Grüneisen constant for the alkali metals.

| Metal | $\beta$ | $M$ | $\chi_T$ cm$^2$/dyn | $\rho_T$ g/cm$^3$ | $C_v$ cal/°K g-atom | $\gamma$ |
|---|---|---|---|---|---|---|
| | | | Data at 293°K | | | |
| Li | 0.000140 | 6.94 | $0.089\times10^{-10}$ | 0.5333 | 5.70 | 0.86 |
| Na | 0.000205 | 22.997 | $0.158\times10^{-10}$ | 0.9684 | 6.21 | 1.19 |
| K | 0.000250 | 39.096 | $0.33\times10^{-10}$ | 0.8548 | 6.31 | 1.31 |
| Rb | 0.000270 | 85.48 | $0.40\times10^{-10}$ | 1.517 | 6.60 | 1.38 |
| Cs | 0.000290 | 132.91 | $0.61\times10^{-10}$ | 1.892 | 6.90 | 1.16 |
| | | | Data at 90°K | | | |
| Li | $0.000049_6$ | 6.94 | $0.088\times10^{-10}$ | 0.5454 | 2.73 | 0.63 |
| Na | $0.000136_7$ | 22.997 | $0.156\times10^{-10}$ | 1.006 | 5.10 | 0.94 |
| K | $0.000219_5$ | 39.096 | $0.293\times10^{-10}$ | 0.8965 | 5.67 | 1.38 |
| Rb | $0.000228_2$ | 85.48 | $0.389\times10^{-10}$ | 1.593 | 5.88 | 1.28 |
| Cs | $0.000237_8$ | 132.91 | $0.493\times10^{-10}$ | 1.992 | 5.99 | 1.28 |

might be fortuitous since Barrett's sample contained about 0.5% impurity. There seems to be no reason why $\Theta^W$ and $\Theta_0^C$ should be equal for potassium but not for lithium or sodium.

*Rubidium.* Macroscopic measurements by Hackspill[3] in the room-temperature region were in agreement with earlier work. X-ray measurements in the range 77 to 297°K are rather discordant and have been summarized by Pearson.[7] The coefficients in the density equation (Table I) have been based on the macroscopic measurements and the assumption that $\Theta^W \simeq \Theta_0^C$. The density calculated from the equation is 0.7% lower than the value obtained from Barrett's x-ray results[20] at 5°K and 1.0% lower than his value at 78°K. (Barrett's sample contained ~0.5% impurity.) Hume-Rothery and Lonsdale's density[22] at 90°K is 0.4% lower than the value given by the equation, and Kelly and Pearson's value[23] at this temperature is about 0.6% higher than the equation value.

*Cesium.* Few data are available. The equation coefficients have been based on Hackspill's macroscopic data[3] and the assumption that $\Theta^W \simeq \Theta_0^C$. The density obtained from the equation is 1.5% higher than Barrett's value[20] at 5°K and 1% higher than his value at 78°K. Barrett's sample contained 1.3% impurity.

It will be clear that the temperature variations of the densities of the alkali metals are not established with any great certainty. For lithium and sodium the values given by the equations may be accurate to ±0.2% but for rubidium and cesium the possible errors may be as high as ±1%. The only complete set of data at low temperatures is that of Barrett[20] but it appears not to be reliable due either to experimental errors or sample impurities. (The prime purpose of Barrett's work was an investigation of the possible martensitic transformations of the alkali metals and not the determination of lattice parameters.) Values derived from the equations for the various metals show a random scatter when compared with Barrett's work. It should be noted that the equations show that the expansion coefficient increases steadily on going from lithium to cesium, whereas Barrett's figures show that the expansion coefficient of rubidium exceeds that of cesium. The need for further accurate experimental work on the alkali-metal thermal expansions is evident.

## GRÜNEISEN CONSTANTS FOR THE ALKALI METALS

The Grüneisen constant required for the correction of the $\Theta^S$ values to the volume at the absolute zero is the $\gamma(0)$ of Barron's notation.[24,25] $\gamma(0)$ equals the high-temperature limit of $\gamma$ ($\gamma_\infty$) given by the following equation:

$$\gamma=\beta M/\chi_T\rho_T C_v,$$

where $\beta$ is the volume coefficient of thermal expansion, $M$ the atomic weight, $\chi_T$ the isothermal compressibility, $\rho_T$ the density at temperature $T$, and $C_v$ the specific heat at constant volume. In Table II are collected the data required for the calculation of $\gamma$ and the resulting values of $\gamma$. The density and thermal expansion are obtained from the tabulation in the previous section, room-temperature compressibility values are from Mott and Jones[14] and values at 90°K by a slight extrapolation of Swenson's data[26] at 4 and 77°K. The $C_v$ values are from Martin,[27,28] Krier, Craig, and Wallace,[29] and Filby and Martin.[13] Mott and Jones' compressibility data is probably that of Richards.[30] This data differs significantly from Bridgman[31,32] only for rubidium and cesium. Kleppa[33] has measured the compressibility of the liquid alkali metals by an ultrasonic technique and suggests that Bridgman's values for the compressibility of rubidium and of cesium may not be correct due to error in extrapolation to zero

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[22] W. Hume-Rothery and K. Lonsdale, Phil. Mag. **36**, 842 (1945).

[23] F. M. Kelly and W. B. Pearson, Can. J. Phys. **33**, 17 (1955).

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

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

[26] C. A. Swenson, Phys. Rev. **99**, 423 (1955).

[27] D. L. Martin, Proc. Roy. Soc. (London) **A254**, 433 (1960).

[28] D. L. Martin, Proc. Roy. Soc. (London) **A254**, 444 (1960).

[29] C. A. Krier, R. S. Craig, and W. E. Wallace, J. Phys. Chem. **61**, 522 (1957).

[30] T. W. Richards, J. Am. Chem. Soc. **37**, 1643 (1915).

[31] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **58**, 166 (1923).

[32] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 385 (1925).

[33] O. J. Kleppa, J. Chem. Phys. **18**, 1331 (1950).

TABLE III. Isothermal compressibility deduced from recent elastic-constant data. Resulting values for the Grüneisen constant.

| Metal | Temperature °K | $\chi_T$ cm$^2$/dyn | Author | $\gamma$ |
|---|---|---|---|---|
| Li | 78 | $0.0758\times10^{-10}$ | | 0.73 |
| | 155 | $0.0806\times10^{-10}$ | Nash and Smith[a] | ... |
| | 195 | $0.0851\times10^{-10}$ | | ... |
| | 298 | $0.0854\times10^{-10}$ | Trivissono and Smith[b] | 0.89 |
| Na | 300 | $0.164\times10^{-10}$ | Daniels[c] | 1.14 |
| K | 195 | $0.344\times10^{-10}$ | Marquardt, Trivissono, and Klucher[d] | ... |
| | 293 | $0.332\times10^{-10}$ | Smith and Smith[e] | 1.30 |

[a] H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).
[b] J. Trivissono and C. S. Smith, Acta Met. **9**, 1064 (1961).
[c] W. B. Daniels, Phys. Rev. **119**, 1246 (1960).
[d] W. Marquardt, J. Trivissono, and T. Klucher, Bull. Am. Phys. Soc. **7**, 546 (1962).
[e] P. A. Smith and C. S. Smith, Bull. Am. Phys. Soc. **9**, 238 (1964).

pressure. The data from Mott and Jones[14] are in reasonable agreement with values for the solid deduced from Kleppa's results. For sodium the recent compressibility work of Beecroft and Swenson[21] gives compressibilities of 1.57 and $1.40\times10^{-11}$ cm$^2$/dyn at 293 and 77°K, respectively. The room-temperature value confirms Mott and Jones' figure but the 77°K value supports the impression that the data of Swenson[26] might be systematically high.

Recently, elastic-constants measurements have been made on lithium, sodium, and potassium, and isothermal-compressibility data derived from these results are collected in Table III. $\gamma$ values in the 90°K and room-temperature regions have been calculated and are shown in the table.

Some of the variation of $\gamma$ for a given metal in Tables II and III is undoubtedly due to inaccurate data but there might be a real variation with temperature. The value of $\gamma$ at room temperature is probably known to within a few percent for lithium, sodium, and potassium but the uncertainty for rubidium and cesium might be as high as 20%. Remeasurement of the compressibilities of rubidium and cesium would be needed to reduce this uncertainty. Note the value of $C_v$ used in the calculation of $\gamma$ includes the electronic term. If the electronic term were subtracted the $\gamma$ values would be increased by 2 to 3%.

The following $\gamma(0)$ values are used later in the paper for the correction of $\Theta^S$ values and are representative of the values in Tables II and III—Li, 0.86; Na, 1.10; K, 1.30; Rb, 1.37; Cs, 1.20.

## ANALYSIS OF SPECIFIC-HEAT DATA

The following data have been selected for analysis. Other published data are reviewed in these papers.

"Natural" Lithium: Martin,[11] Filby and Martin,[19] and Martin.[28]

Sodium: Martin,[12] Filby and Martin,[19] and Martin.[27]

Potassium: Filby and Martin,[13] Krier, Craig, and Wallace.[29]

Rubidium: Filby and Martin.[13]

Cesium: Filby and Martin.[13]

Data on the low-temperature-limiting Debye temperature for the specific heat ($\Theta_0^C$) and the electronic specific-heat coefficient ($\gamma$) are collected in Table IV.

The entropy was obtained by Simpson's rule integration of the published data. An extrapolation to zero temperature assumed that the specific heat could be represented by the sum of terms linear and cubic in temperature. Entropy values (cal/°K g-atom) obtained at 298.15°K (25°C) are as follows:

| | |
|---|---|
| Lithium | 6.948±0.012, |
| Sodium | 12.23 ±0.04, |
| Potassium | 15.45 ±0.05, |
| Rubidium | 18.34 ±0.08, |
| Cesium | 20.37 ±0.09. |

The martensitic transformation in lithium and sodium is a complication. It was decided to restrict the analysis to the body-centered-cubic phase. For sodium an experimental separation of the specific heats of the two phases at low temperatures has been made (with some assumptions), and there is no problem in the calculation of the entropy of the bcc phase. For lithium no separation appears possible at the present time, and values for the bcc phase are only available above 90°K. In order to obtain a value for the entropy at 90°K it was assumed that the entropy of the bcc phase at 200°K was the same as that calculated for a sample of lithium measured through the two-phase and reversion

TABLE IV. Debye temperature and electronic specific-heat coefficient.

| Metal | $\Theta_0^C$ °K | $\gamma$ $\mu$cal/°K g-atom |
|---|---|---|
| Li | $344\ \pm2.5$[a] | $390\pm4$[a] |
| Na | $152.5\pm2.0$[b] | $330\pm5$[b] |
| K | $90.6^{+1.4}_{-0.3}$ | $497\pm20$ |
| Rb | $55.6\pm0.5$ | $576^{+70}_{-40}$ |
| Cs | $38.4\pm0.6$ | $764\pm250$ |

[a] These figures refer to a partially transformed sample probably containing about 80% faulted hcp phase.
[b] Body-centered-cubic phase.

Table V. Lattice entropy and $\Theta^S$ for the body-centered-cubic alkali metals.[a]

| | Lithium | | | Sodium | | | Potassium | | | Rubidium | | | Cesium | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. °K | Lattice entropy | $\Theta_{v(T)}{}^S$ | $\Theta_{v(0)}{}^S$ | Lattice entropy | $\Theta_{v(T)}{}^S$ | $\Theta_{v(0)}{}^S$ | Lattice entropy | $\Theta_{v(T)}{}^S$ | $\Theta_{v(0)}{}^S$ | Lattice entropy | $\Theta_{v(T)}{}^S$ | $\Theta_{v(0)}{}^S$ | Lattice entropy | $\Theta_{v(T)}{}^S$ | $\Theta_{v(0)}{}^S$ |
| 1 | ... | ... | ... | 0.0000436 | $152._5$ | $152._5$ | 0.000210 | $90._4$ | $90._4$ | 0.000903 | $55._6$ | $55._6$ | 0.00273 | $38._4$ | $38._4$ |
| 2 | ... | ... | ... | 0.000349 | $152._5$ | $152._5$ | 0.00174 | $89._4$ | $89._4$ | 0.00800 | $53._7$ | $53._7$ | 0.0341 | $33._1$ | $33._1$ |
| 3 | ... | ... | ... | 0.00118 | $152._5$ | $152._5$ | 0.00634 | $87._0$ | $87._0$ | 0.0289 | $52._5$ | $52._5$ | 0.0979 | $34._9$ | $34._9$ |
| 4 | ... | ... | ... | 0.00280 | $152._3$ | $152._3$ | 0.0154 | $86._3$ | $86._3$ | 0.0682 | $52._6$ | $52._6$ | 0.207 | $36._1$ | $36._1$ |
| 5 | ... | ... | ... | 0.00557 | $151._4$ | $151._4$ | 0.0316 | $85._0$ | $85._0$ | 0.131 | $52._7$ | $52._7$ | 0.354 | $37._4$ | $37._4$ |
| 6 | ... | ... | ... | 0.00977 | $150._7$ | $150._7$ | 0.0568 | $83._8$ | $83._8$ | 0.218 | $53._2$ | $53._2$ | 0.536 | $38._4$ | $38._4$ |
| 7 | ... | ... | ... | 0.0158 | $149._7$ | $149._7$ | 0.0911 | $83._5$ | $83._5$ | 0.325 | $53._9$ | $53._9$ | 0.747 | $39._2$ | $39._2$ |
| 8 | ... | ... | ... | 0.0242 | $148._6$ | $148._6$ | 0.135 | $83._6$ | $83._6$ | 0.453 | $54._6$ | $54._6$ | 0.979 | $39._9$ | $39._9$ |
| 9 | ... | ... | ... | 0.0351 | $147._6$ | $147._6$ | 0.188 | $84._0$ | $84._0$ | 0.599 | $55._2$ | $55._2$ | 1.23 | $40._5$ | $40._5$ |
| 10 | ... | ... | ... | 0.0488 | $146._9$ | $146._9$ | 0.250 | $84._5$ | $84._6$ | 0.756 | $55._8$ | $55._8$ | 1.49 | $40._9$ | $40._9$ |
| 12 | ... | ... | ... | 0.0856 | $146._1$ | $146._1$ | 0.397 | $85._9$ | $86._0$ | 1.10 | $56._7$ | $56._8$ | 2.02 | $41._6$ | $41._7$ |
| 14 | ... | ... | ... | 0.135 | $146._2$ | $146._2$ | 0.573 | $87._3$ | $87._3$ | 1.48 | $57._4$ | $57._5$ | 2.55 | $42._1$ | $42._1$ |
| 16 | ... | ... | ... | 0.198 | $146._8$ | $146._8$ | 0.771 | $88._5$ | $88._5$ | 1.87 | $57._9$ | $58._0$ | 3.07 | $42._4$ | $42._5$ |
| 18 | ... | ... | ... | 0.273 | $147._6$ | $147._6$ | 0.986 | $89._6$ | $89._6$ | 2.26 | $58._4$ | $58._4$ | 3.57 | $42._6$ | $42._7$ |
| 20 | ... | ... | ... | 0.360 | $148._5$ | $148._5$ | 1.21 | $90._4$ | $90._5$ | 2.65 | $58._6$ | $58._7$ | 4.05 | $42._8$ | $42._9$ |
| 40 | ... | ... | ... | 1.65 | $154._9$ | $155._0$ | 3.61 | $93._9$ | $94._3$ | 5.90 | $59._5$ | $59._9$ | 7.67 | $43._1$ | $43._5$ |
| 60 | ... | ... | ... | 3.11 | $157._5$ | $157._9$ | 5.60 | $94._4$ | $95._3$ | 8.15 | $59._4$ | $60._2$ | 10.01 | $43._0$ | $43._6$ |
| 80 | ... | ... | ... | 4.43 | $158._3$ | $158._9$ | 7.17 | $94._3$ | $95._7$ | 9.83 | $59._1$ | $60._3$ | 11.72 | $42._8$ | $43._6$ |
| 90 | 1.49 | 368 | 369 | 5.02 | $158._2$ | $159._1$ | 7.85 | $94._1$ | $95._8$ | 10.53 | $59._0$ | $60._3$ | 12.43 | $42._7$ | $43._6$ |
| 100 | 1.79 | 371 | 371 | 5.58 | $158._0$ | $159._2$ | 8.46 | $93._8$ | $95._8$ | 11.17 | $58._8$ | $60._3$ | 13.07 | $42._5$ | $43._6$ |
| 120 | 2.40 | 375 | 376 | 6.57 | $157._6$ | $159._3$ | 9.53 | $93._4$ | $95._9$ | 12.28 | $58._4$ | $60._3$ | 14.19 | $42._3$ | $43._6$ |
| 140 | 3.00 | 377 | 378 | 7.45 | $157._0$ | $159._3$ | 10.46 | $92._8$ | $95._9$ | 13.23 | $58._0$ | $60._3$ | 15.15 | $41._9$ | $43._5$ |
| 160 | 3.58 | 378 | 380 | 8.23 | $156._2$ | $159._1$ | 11.28 | $92._2$ | $95._8$ | 14.06 | $57._6$ | $60._2$ | 15.99 | $41._6$ | $43._4$ |
| 180 | 4.13 | 378 | 381 | 8.94 | $155._4$ | $158._9$ | 12.02 | $91._6$ | $95._8$ | 14.81 | $57._1$ | $60._1$ | 16.74 | $41._2$ | $43._3$ |
| 200 | 4.66 | 378 | 382 | 9.58 | $154._4$ | $158._6$ | 12.68 | $90._9$ | $95._7$ | 15.48 | $56._6$ | $60._0$ | 17.42 | $40._9$ | $43._1$ |
| 220 | 5.15 | 377 | 382 | 10.17 | $153._4$ | $158._3$ | 13.29 | $90._2$ | $95._5$ | 16.10 | $56._1$ | $59._9$ | 18.04 | $40._5$ | $43._0$ |
| 240 | 5.61 | 377 | 382 | 10.72 | $152._4$ | $157._9$ | 13.85 | $89._5$ | $95._3$ | 16.67 | $55._6$ | $59._7$ | 18.62 | $40._1$ | $42._8$ |
| 260 | 6.05 | 376 | 382 | 11.23 | $151._3$ | $157._4$ | 14.38 | $88._7$ | $95._1$ | 17.21 | $55._0$ | $59._5$ | 19.16 | $39._7$ | $42._6$ |
| 273.15 | 6.33 | 375 | 382 | 11.55 | $150._5$ | $157._1$ | 14.71 | $88._2$ | $94._9$ | 17.55 | $54._6$ | $59._3$ | 19.51 | $39._3$ | $42._5$ |
| 280 | 6.47 | 375 | 382 | 11.71 | $150._1$ | $156._9$ | 14.87 | $87._9$ | $94._8$ | 17.72 | $54._4$ | $59._2$ | 19.68 | $39._1$ | $42._4$ |
| 298.15 | 6.83 | 373 | 381 | 12.12 | $149._0$ | $156._4$ | 15.30 | $87._0$ | $94._4$ | 18.17 | $53._8$ | $58._9$ | 20.14 | $38._6$ | $42._0$ |
| 300 | 6.87 | 373 | 381 | 12.16 | $148._9$ | $156._3$ | 15.35 | $86._9$ | $94._4$ | 18.21 | $53._7$ | $58._9$ | 20.19 | $38._5$ | $42._0$ |

[a] Calorie units, $J = 4.186$.

regions. (Reversion to the bcc phase is complete at about 170°K.) A check on the validity of this assumption can be made by calculating the entropy of sodium at 90°K (where reversion is complete) from (i) the measured values for the two-phase and reversion regions, and (ii) the estimated values for the bcc phase. The results agree to about 0.5% which is within the accuracy of measurement.

The entropy of the crystal lattice is required for the present analysis and this was obtained from the measured total entropy by subtraction of the electronic contribution, using the values of $\gamma$ given in Table IV. A shortened list of lattice entropy values so obtained is given in Table V. Also shown are values of the Debye temperature ($\Theta^S$) obtained from the entropy values using Giguère and Boisvert's tables.[34] The equivalent values at the zero-temperature volume were obtained by use of the relation[25]

$$\Theta_{v(0)}{}^S/\Theta_{v(T)}{}^S=(\rho_0/\rho_T)^{\gamma(0)}.$$

The $\gamma(0)$ and $(\rho_0/\rho_T)$ values used are those given in the previous sections.

According to harmonic lattice theory (following Tosi and Fumi[1])

$$\Theta^S=\Theta(0)\{1+\sum_{n=1}^{\infty}a_nT^{-2n}\}.$$

This equation converges satisfactorily for temperatures down to $(\frac{1}{6}\Theta^S)$. It will be apparent from the equation that $\Theta^S$ is expected to reach a high-temperature limiting value $\Theta(0)$, otherwise written as $\Theta_\infty{}^S$. Inspection of the values of $\Theta^S$ as a function of temperature in Table V (see also Fig. 1) shows that the experimental results for $\Theta^S$ begin to decrease at high temperatures. This decrease is a result of the anharmonicity of the lattice vibrations. (At the highest temperatures effects due to the thermal generation of lattice vacancies become apparent. Data in this region are not used in the present analysis.)

The harmonic-lattice theory expansion, given above, was fitted to the appropriate data (see below) by a least-squares method. For each set of data analyzed the number of terms taken in the expansion was varied between one and twelve so that the dependence of results on number of terms taken could be studied. The results for the coefficients $a_n$ were converted to the characteristic temperatures $\Theta(n)$ using the relations given by Tosi and Fumi.[1] (Tosi and Fumi used the notation $\Theta_n$ for these characteristic temperatures, but it has been agreed that the notation used here, suggested by Barron, is preferable since it is less likely to be confused with other characteristic temperatures.) For a given metal and a given value of $n$ the value of $\Theta(n)$ is found to vary as the number of terms taken in the expansion is varied. The standard deviation of the experimental data from the fitted expansion is observed to pass through one or more minima as the number of terms in the expansion is varied from 1 to 12. The tabulated results are from the region of the first minimum. The value of $\Theta(0)$ shows little or no variation in the region of this minimum and hence seems well established. The results for the other characteristic temperatures are less well known. The results for lithium are relatively imprecise owing to the limited temperature range in which the expansion could be fitted to the results (no data below 90°K).

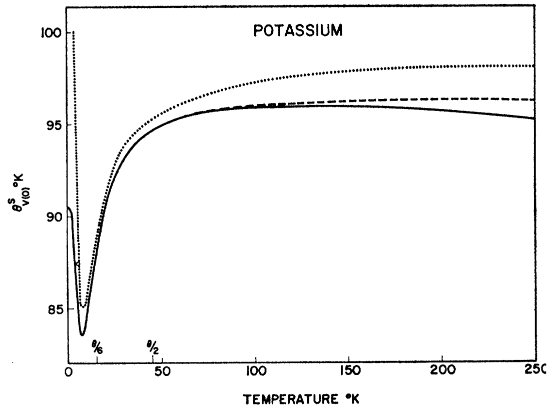

FIG. 1. The Debye temperature $\Theta^S$ derived from the entropy as a function of temperature for potassium. The solid line represents the experimental results. The dashed line is derived on the assumption that the results below a temperature of $\Theta^S/2$ are not affected by anharmonicity. The dotted line is derived on the assumption that the anharmonic contribution to specific heat is directly proportional to the temperature. This assumption obviously breaks down at low temperatures.

The alkali-metal data will be analyzed in two different ways. In the first method it will be *assumed* that anharmonic effects are negligible at temperatures

TABLE VI. Characteristic temperatures and anharmonic coefficients assuming that the specific heat below $(\frac{1}{2}\Theta^S)$°K is purely harmonic.[a]

| Metal | $10^4A$ | $T'$ | $\Theta(0)$ | $\Theta(2)$ | $\Theta(4)$ | $\Theta(6)$ |
|---|---|---|---|---|---|---|
| Li | 2.0±0.02 | 180 | 385.0±1.0 | ~400.0 | ~400.0 | ... |
| Na | 1.5±0.1 | 50 | 160.5±0.5 | 168.0±2.0 | 170.0±5.0 | 165.0±10.0 |
| K | 2.2±0.15 | 120 | 96.2±0.1 | 102.5±0.5 | 110.0±5.0 | 114.0± 5.0 |
| Rb | 1.8±0.1 | 90 | 60.4±0.1 | 64.5±0.5 | 67.0±1.0 | 69.0± 2.0 |
| Cs | 2.3±0.1 | 70 | 43.6±0.1 | 47.0±0.5 | 48.5±0.5 | ~50.0 |

[a] Note: The error limits for $A$ assume that the value of $T'$ is correct. As explained in the text there is considerable latitude in the choice of $T'$.

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[34] P. A. Giguère and M. Boisvert, *Table des Fonctions Thermodynamique de Debye* (Les Presses de l'Université Laval, Quebec, 1962).

TABLE VII. Characteristic temperatures and anharmonic coefficients assuming that an anharmonic contribution to specific heat, linear in temperature, persists down to a temperature of $(\frac{1}{6}\Theta^S)$°K.

| Metal | $A$ | $\Theta(0)$ | $\Theta(2)$ | $\Theta(4)$ | $\Theta(6)$ |
|---|---|---|---|---|---|
| Li | $0.60\times10^{-4}$ | $390.5\pm0.5$ | $\sim405$ | $\sim390$ | $\sim310$ |
| Na | $1.69\times10^{-4}$ | $165.4\pm0.2$ | $195.0\pm7.0$ | $250\pm30$ | $290\pm40$ |
| K | $1.21\times10^{-4}$ | $98.3\pm0.1$ | $120.0\pm4.0$ | $170\pm30$ | $190\pm40$ |
| Rb | $1.28\times10^{-4}$ | $61.5\pm0.1$ | $80.0\pm6.0$ | $110\pm20$ | $120\pm30$ |
| Cs | $1.73\times10^{-4}$ | $44.6\pm0.1$ | $60.0\pm6.0$ | $75\pm20$ | $90\pm30$ |

below $(\frac{1}{2}\Theta^S)$. (Similar assumptions have been made in some previous analyses[2,15] of specific-heat data.) The harmonic-lattice theory expansion, given above, is therefore fitted to the experimental results in the temperature range $(\frac{1}{6}\Theta^S)$ to $(\frac{1}{2}\Theta^S)$. Values of $\Theta(n)$ so obtained are given in Table VI. The 'harmonic' results may be extrapolated above $(\frac{1}{2}\Theta^S)$ using the harmonic expansion, and the experimental results are observed to diverge at some, rather indefinite, temperature $T'$ (see Fig. 1). Empirically, results above $T'$ are found[15] to fit the following relation rather well

$$C_v - C_{v\,\mathrm{har}} = 3NkA(T-T'),$$

(where har denotes harmonic and $A$ is a constant). In terms of entropy this corresponds to

$$S - S_{\mathrm{har}} = 3NkA\{(T-T') - T'\ln(T/T')\}.$$

Then it follows that

$$\Theta^S = \Theta_{\mathrm{har}}{}^S\left\{1 + \frac{A\{(T-T') - T'\ln(T/T')\}}{(\Theta_{\mathrm{har}}{}^S/T)(d(S_{\mathrm{har}}/3Nk)/d(\Theta_{\mathrm{har}}{}^S/T))}\right\}.$$

Values of the anharmonic coefficient $A$, found from this last equation, are given in Table VI. A least-squares analysis was used to select the best value of $T'$.

Recently, however, Tosi and Fumi[1] and Barron[35] have argued that the anharmonic effects must be present from the lowest temperatures. The good fit below a temperature of about $(\frac{1}{2}\Theta^S)$ between the experimental results and an expansion based on harmonic-lattice theory is because, to a first approximation, the anharmonic effects are equivalent to a displacement of the frequencies of the normal modes of vibration.[36]

In the second method of analyzing the alkali-metal data it will be *assumed*, following Tosi and Fumi,[1] that the leading anharmonic contribution to the specific heat is proportional to the absolute temperature. Then it follows that

$$C_v - C_{v\,\mathrm{har}} = S - S_{\mathrm{har}} = 3NkAT$$

and

$$\Theta^S = \Theta_{\mathrm{har}}{}^S\left\{1 + \frac{AT}{(\Theta_{\mathrm{har}}{}^S/T)(d(S_{\mathrm{har}}/3Nk)/d(\Theta_{\mathrm{har}}{}^S/T))}\right\}.$$

At high temperatures the denominator of this expression tends to the value minus one, also $\Theta_{\mathrm{har}}$ tends to constant value $(\Theta_{\infty\,\mathrm{har}}{}^S)$. Thus the value of $A$ can easily be estimated from the experimental data and values of $\Theta_{\mathrm{har}}{}^S$ can then be deduced from the measured $\Theta^S$ values at any temperature using the equation immediately above.[36a] The harmonic-lattice-theory expansion for $\Theta^S$, given earlier, may then be fitted to these $\Theta_{\mathrm{har}}{}^S$ values and results are given in Table VII.[36a] (The anharmonic coefficients in this table have not been given any error limits since the method is essentially a force fit to these values.)

The results obtained by both methods of analysis were checked by showing that the derived values of $\theta(n)$ and $A$, when substituted in the appropriate equations, gave back very nearly the original $\theta_{v(0)}{}^s$ values.

Tosi and Fumi's assumption may not be correct since the proportionality of the 'anharmonic' entropy to the temperature only holds in the classical limit and must alter at low temperatures.[37] (This will also be obvious from Fig. 1.) In order for the present analysis to be correct the assumption must hold reasonably well down to a temperature of $(\frac{1}{6}\Theta^S)$°K. If this is not so then, in the temperature region under discussion the 'anharmonic' specific heat might be approximately proportional to $(T-T'')$, where $T''$ is less than the $T'$ discussed above.

On this naive picture it is probable, therefore, that the correct values for the anharmonic coefficient and characteristic temperatures lie somewhere between the two sets of results given in Tables VI and VII. However, Barron (private communication) points out that the lattice-vibration spectrum obtained by the first method is an effective spectrum incorporating frequency shifts due to the zero-point energy. On the other hand, in the second method, Tosi and Fumi's approximation of a linear-anharmonic contribution at high temperatures is actually with respect to a vibration spectrum without zero-point energy shifts. Hence some difference is to be expected between the spectra involved in the two methods.

The effect of uncertainty in the value of $\gamma(0)$ was investigated by working through the results for potassium, on the Tosi and Fumi approximation, using $\gamma(0)$ values of 1.2 and 1.4 instead of the value 1.3 used in the above calculation. There was no significant change in the values of the characteristic temperature $\Theta(n)$ but the value of the anharmonic coefficient $A$ was increased and decreased by about twenty percent, respectively, in the two extremes considered. It is

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[35] T. H. K. Barron, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press Ltd., London, 1964), p. 247.

[36] T. H. K. Barron and M. L. Klein, Phys. Rev. **127**, 1997 (1962).

[36a] The method used in obtaining $A$ and $\Theta(0)$ is quite different from that used by Tosi and Fumi (Ref. 1). In the present method these quantities are determined directly from results at relatively high temperatures (but not so high that vacancy generation effects are significant) whereas Tosi and Fumi (Ref. 1) used a successive approximation procedure at lower temperatures. An objection to the present method is that higher order anharmonic contributions might influence the results. However, the linearity of the high-temperature specific heats (Ref. 15) suggests that these terms are not significant.

[37] D. C. Wallace, Phys. Rev. **133**, A153 (1964).

TABLE VIII. Geometric mean frequency and moments of the lattice-vibration spectrum assuming that the specific heat below $(\frac{1}{2}\Theta^S)$°K is purely harmonic.

| Metal | $\nu_g$ (sec$^{-1}$) | $\langle\nu^{-2}\rangle_{\text{av}}$ (sec$^{+2}$) | $\langle\nu^{-1}\rangle_{\text{av}}$ (sec$^{+1}$) | $\langle\nu^{2}\rangle_{\text{av}}$ (sec$^{-2}$) | $\langle\nu^{4}\rangle_{\text{av}}$ (sec$^{-4}$) | $\langle\nu^{6}\rangle_{\text{av}}$ (sec$^{-6}$) |
|---|---|---|---|---|---|---|
| Li | $2.028\pm0.007\times10^{13}$ | $5.08\pm0.05\times10^{-26}$ | $1.92\pm0.02\times10^{-13}$ | $\sim4.2\times10^{25}$ | $\sim2.1\times10^{51}$ | ... |
| Na | $8.45\pm0.03\times10^{12}$ | $2.96\pm0.03\times10^{-25}$ | $4.63\pm0.05\times10^{-13}$ | $7.35\pm0.20\times10^{24}$ | $6.7\pm1.1\times10^{49}$ | $5.5\pm2.0\times10^{74}$ |
| K | $5.066\pm0.006\times10^{12}$ | $8.68\pm0.09\times10^{-25}$ | $7.83\pm0.08\times10^{-13}$ | $2.74\pm0.03\times10^{24}$ | $1.2\pm0.2\times10^{49}$ | $6.0\pm1.5\times10^{73}$ |
| Rb | $3.181\pm0.005\times10^{12}$ | $2.18\pm0.02\times10^{-24}$ | $1.25\pm0.01\times10^{-12}$ | $1.084\pm0.02\times10^{24}$ | $1.6\pm0.1\times10^{48}$ | $2.9\pm0.6\times10^{72}$ |
| Cs | $2.296\pm0.005\times10^{12}$ | $4.72\pm0.05\times10^{-24}$ | $1.76\pm0.02\times10^{-12}$ | $5.75\pm0.1\times10^{23}$ | $4.5\pm0.2\times10^{47}$ | $\sim4.3\times10^{71}$ |

TABLE IX. Geometric mean frequency and moments of the lattice-vibration spectrum assuming that an anharmonic contribution to specific heat, linear in temperature, persists down to a temperature of $(\frac{1}{6}\Theta^S)$°K.

| Metal | $\nu_g$ (sec$^{-1}$) | $\langle\nu^{-2}\rangle_{\text{av}}$ (sec$^{+2}$) | $\langle\nu^{-1}\rangle_{\text{av}}$ (sec$^{+1}$) | $\langle\nu^{2}\rangle_{\text{av}}$ (sec$^{-2}$) | $\langle\nu^{4}\rangle_{\text{av}}$ (sec$^{-4}$) | $\langle\nu^{6}\rangle_{\text{av}}$ (sec$^{-6}$) |
|---|---|---|---|---|---|---|
| Li | $2.057\pm0.003\times10^{13}$ | $5.08\pm0.05\times10^{-26}$ | $1.92\pm0.02\times10^{-13}$ | $\sim4.3\times10^{25}$ | $\sim1.8\times10^{51}$ | $\sim2.2\times10^{76}$ |
| Na | $8.71\pm0.01\times10^{12}$ | $2.94\pm0.03\times10^{-25}$ | $4.58\pm0.05\times10^{-13}$ | $9.9\pm0.7\times10^{24}$ | $3.2\pm1.6\times10^{50}$ | $\sim1.6\times10^{76}$ |
| K | $5.18\pm0.005\times10^{12}$ | $8.66\pm0.09\times10^{-25}$ | $7.79\pm0.08\times10^{-13}$ | $3.8\pm0.2\times10^{24}$ | $6.7\pm4.5\times10^{49}$ | $\sim1.3\times10^{75}$ |
| Rb | $3.24\pm0.005\times10^{12}$ | $2.18\pm0.02\times10^{-24}$ | $1.24\pm0.01\times10^{-12}$ | $1.7\pm0.2\times10^{24}$ | $1.2\pm0.9\times10^{49}$ | $\sim8.1\times10^{73}$ |
| Cs | $2.35\pm0.005\times10^{12}$ | $4.71\pm0.05\times10^{-24}$ | $1.75\pm0.02\times10^{-12}$ | $0.94\pm0.2\times10^{24}$ | $2.6\pm2.6\times10^{48}$ | $\sim1.5\times10^{73}$ |

therefore concluded that uncertainties in the value of $\gamma(0)$ are not likely to affect the results very significantly.

The even moments of the lattice-vibration spectrum

$$\langle\nu^{2n}\rangle_{\text{av}}=\left(\textstyle\sum_j \nu_j^{2n}\right)/3N$$

are related to the characteristic temperatures as follows[1]:

$$\Theta(2n)=\left((2n+3)/3\right)^{1/2n}(h/k)\left(\langle\nu^{2n}\rangle_{\text{av}}\right)^{1/2n}.$$

The moments are given in Tables VIII and IX for the two extreme cases used in interpreting the data. Some negative moments are also given in the tables and have been obtained from integrals of $(C_{\text{har}}/T^n)$ using Eq. (5.5) of Barron *et al.*[2] (The results for lithium are rather uncertain due to the approximations necessary to circumvent the absence of data for the bcc phase below 90°K.) The geometric mean frequency $\nu_g$ $[=(\prod_j \nu_j)^{1/3N}]$ is obtained from $\Theta(0)$ using the relation

$$(k/h)\Theta(0)=e^{1/3}\nu_g.$$

For comparative purposes the results are also shown in Tables X and XI as the reduced values[2] $[\nu_D(n)/\nu_D(-3)]$, where

$$\nu_D(n)=\left\{\tfrac{1}{3}(n+3)\langle\nu^n\rangle_{\text{av}}\right\}^{1/n}\quad \begin{array}{l} n>-3 \\ n\neq0 \end{array}$$

and the limiting values

$$\nu_D(0)=(k/h)\Theta(0),$$
$$\nu_D(-3)=(k/h)\Theta_0{}^C.$$

[For lithium the $\Theta_0{}^C$ value given in Table IV has not been used for $\nu_D(-3)$. Instead the value of 336°K,

TABLE X. $\nu_D(n)/\nu_D(-3)$ assuming that the specific heat below $(\frac{1}{2}\Theta^S)$°K is purely harmonic.

| Metal | $n$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | −3 | −2 | −1 | 0 | 2 | 4 | 6 |
| Li | 1.00 | $1.10\pm0.02$ | $1.12\pm0.02$ | $1.15\pm0.01$ | $\sim1.19$ | $\sim1.19$ | ... |
| Na | 1.00 | $1.00\pm0.02$ | $1.02\pm0.02$ | $1.05\pm0.02$ | $1.10\pm0.03$ | $1.11\pm0.05$ | $1.08\pm0.08$ |
| K | 1.00 | $0.98_4\pm0.015$ | $1.02\pm0.02$ | $1.06\pm0.01$ | $1.13\pm0.015$ | $1.21\pm0.05$ | $1.26\pm0.05$ |
| Rb | 1.00 | $1.01\pm0.015$ | $1.03\pm0.02$ | $1.08\pm0.01$ | $1.16\pm0.02$ | $1.20\pm0.03$ | $1.24\pm0.06$ |
| Cs | 1.00 | $0.99_6\pm0.015$ | $1.07\pm0.02$ | $1.14\pm0.014$ | $1.22\pm0.02$ | $1.26\pm0.02$ | $\sim1.3$ |

TABLE XI. $\nu_D(n)/\nu_D(-3)$ assuming that an anharmonic contribution to specific heat, linear in temperature, persists down to a temperature of $(\frac{1}{6}\Theta^S)$°K.

| Metal | $n$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | −3 | −2 | −1 | 0 | 2 | 4 | 6 |
| Li | 1.00 | $1.10\pm0.02$ | $1.12\pm0.02$ | $1.16\pm0.01$ | $\sim1.2$ | $\sim1.2$ | $\sim0.9$ |
| Na | 1.00 | $1.00\pm0.02$ | $1.03\pm0.02$ | $1.08\pm0.02$ | $1.28\pm0.05$ | $1.6\pm0.1$ | $1.9\pm0.15$ |
| K | 1.00 | $0.99\pm0.015$ | $1.02\pm0.02$ | $1.08\pm0.01$ | $1.32\pm0.04$ | $1.9\pm0.2$ | $2.1\pm0.2$ |
| Rb | 1.00 | $1.01\pm0.015$ | $1.04\pm0.02$ | $1.10\pm0.01$ | $1.44\pm0.06$ | $2.0\pm0.2$ | $2.2\pm0.2$ |
| Cs | 1.00 | $1.00\pm0.02$ | $1.07\pm0.02$ | $1.16\pm0.01$ | $1.6\pm0.1$ | $2.0\pm0.3$ | $2.3\pm0.3$ |

TABLE XII. Comparison of calorimetric and other values for $\Theta_\infty^C$. $A=1.943\times10^{-3}$; $B=125.2$.

| Metal | $\Theta(2)$[a] | $\Theta^{\chi}$ | $\Theta^T$ |
|---|---|---|---|
| Li | ~400 | 380 | 431 |
| Na | 168.0±2.0 | 173 | 177 |
| K | 102.5±0.5 | 102.5 | 102.5 |
| Rb | 64.5±0.5 | 65.2 | 62.5 |
| Cs | 46.5±0.5 | 43.9 | 45.7 |

[a] $\Theta(2)$ values are taken from Table VI.

computed from extrapolated elastic-constant data,[38] has been taken as more appropriate to the bcc phase.]

## DISCUSSION

The positive anharmonic contribution to specific heat seems well established for all the alkali metals. The coefficient $A$ is of the order $10^{-4}$, irrespective of the exact form assumed for the anharmonic term. This value is of the same order as values obtained previously from an analysis of specific heat rather than entropy.[15] Agreement is also good with the theoretical estimates of Stern[39] and Liebfried and Ludwig[40] for sodium. The theoretical estimate of Keller and Wallace[41] for lithium is of the wrong sign due to the use of a Lennard-Jones potential which is more characteristic of a rare gas than a metal.[42] The analysis of the experimental results shows that the leading anharmonic term is sufficient to account for the anharmonic effects.

The previous specific-heat analysis,[15] mentioned above, also gave values for $\Theta_\infty^C$ [or $\Theta(2)$ in the present notation]. These values are in very good agreement with the present results except for rubidium where the disagreement is about 5%. Most of this disagreement may be due to uncertainties in the graphical extrapolation used in the previous work.

The values obtained for $\Theta(2)$ may also be compared with theta values obtained from the relations of Madelung and Lindemann (see Blackman[43]). These are

$$\Theta^{\chi}=A\chi^{-1/2}M^{-1/3}\rho^{-1/6}$$

$$\Theta^{T}=B(T_m/MV^{2/3})^{1/2},$$

where $A$ and $B$ are constants (which for the present purpose have been fixed by reference to the $\Theta(2)$ value for potassium), $\chi$ is the compressibility, $M$ the atomic weight, $V$ the atomic volume, $\rho$ the density, and $T_m$ the melting point. $\Theta^{\chi}$ and $\Theta^T$ are expected to correspond to the limiting value of $\Theta^C$ at high temperatures. Values of $\Theta(2)$, $\Theta^{\chi}$, and $\Theta^T$ are collected in Table XII, and it will be clear that the relations fit the alkali-metal data quite well.

The zero-point energy is given by

$$E_z=\tfrac{3}{2}Nh\langle\nu'\rangle_{\rm av}=(9/8)Nk\nu_D(1).$$

Values of $\nu_D(1)$ were estimated by interpolation, and values for $E_z$ cal/g-atom obtained from the data in Table VI are as follows:

| | |
|---|---|
| Lithium | 876, |
| Sodium | 367, |
| Potassium | 222, |
| Rubidium | 139, |
| Cesium | 101. |

Values obtained from Table VII would be about 10% higher.

The characteristic temperature $\Theta^M$ for the Debye-Waller effect is given[44] in the low-temperature limit by $(h/k)\nu_D(-1)$ and in the high-temperature limit by $(h/k)\nu_D(-2)$. It will be clear from Tables X and XI that the variation of $\Theta^M$ with temperature at constant volume is not likely to exceed a few percent. The effect of thermal expansion may be estimated[44] and will result in a lowering of $\Theta^M$ by a few percent at room temperature.

The results obtained for the moments of the vibration-frequency spectrum are best considered by reference to the reduced values of $\nu_D(n)$ in Tables X and XI. As explained above, the results for lithium are rather more uncertain than those for the other metals. Irrespective of the assumption made regarding the form of the anharmonic effects, it will be clear that on going from sodium to cesium the ratio of the higher to lower moments increases steadily. The actual magnitude of the higher moments is critically dependent on the form assumed for the anharmonic contribution.[44a]

The steady increase in the ratio of the higher to lower moments on going from sodium to cesium presumably indicates either (i) a gradual increase in the density of modes at the higher frequency end of the spectrum (at the expense of the density at the low-frequency end), or (ii) that the vibration spectrum extends to higher reduced frequencies.

This type of change is immediately apparent from an examination of the specific-heat results[13] since the ratio $(\Theta_\infty^C/\Theta_0^C)$ increases steadily on going from sodium to cesium. As shown above the value of $\Theta_\infty^C$ is approximately proportional to the reciprocal square root of the compressibility ($\chi$) which is related to the elastic constants as follows:

$$\chi=3/(C_{11}+2C_{12}).$$

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[38] G. A. Alers and J. R. Neighbours, Rev. Mod. Phys. **31**, 675 (1959).

[39] E. A. Stern, Phys. Rev. **111**, 786 (1958).

[40] G. Liebfried and W. Ludwig, Solid State Phys. **12**, 275 (1961).

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

[42] M. L. Klein (private communication).

[43] M. Blackman, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 325.

[44] T. H. K. Barron, M. L. Klein, A. J. Leadbetter, J. A. Morrison, and L. Salter, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1963), p. 415.

[44a] Fumi and Tosi (private communication) suggest that the rapid increase of $\Theta(n)$ with $n$ found by the second method of analysis might be caused simply by an overestimate of the anharmonic coefficient $A$.

The value of $\Theta_0^C$ is given by a much more complicated function of the elastic constants involving $C_{44}$ also.[43] An approximate relation, applying to anisotropic crystals such as the alkali metals, is as follows[45]

$$\Theta_0^C=\left[\frac{D(C_{11}-C_{12})^{1/2}(C_{11}+C_{12}+2C_{44})^{1/2}(C_{44})^{1/2}}{\rho^{3/2}\Delta}\right]^{1/3},$$

where $D$ is a constant, $\rho$ the density, and $\Delta$ the volume of a unit cell of the crystal. The lack of reliable low-temperature elastic-constant data on the alkali metals (see, for example, Huntington[46]) and the approximate nature of the above formulas make a direct comparison of the elastic and thermal data of little significance at the present time.

Clark[47] has calculated the vibration-frequency spectra for bcc lattices assuming central force nearest and next-nearest neighbor interactions. These calculations were made for a number of different values of the parameter $\beta$ defined as follows:

$$\beta=(C_{11}-C_{12})/3C_{44}.$$

Moments have been calculated from a few of these spectra, and ratios of some of the characteristic frequencies $\nu_D(n)$ are shown in Table XIII as a function of $\beta$. It will be seen that as $\beta$ increases the ratio of higher to lower characteristic frequencies decreases. Thus, if this simple model is to explain the alkali-metal spectra, obtained from experiment, it is necessary that $\beta$ decreases on going from sodium to cesium. Clark[47] gives elastic-constant values for lithium, sodium, and potassium suggesting a variation in the opposite direction but, as mentioned above (see also Huntington[46]), the alkali-metal elastic constants at low temperatures are not known accurately for these three metals and have never been measured for rubidium and cesium. Thus, lack of reliable elastic-constant data prevents any definite conclusions being drawn from Clark's work at the present time.

TABLE XIII. Characteristic frequency ratios from Clark's lattice-vibration spectra for bcc lattices.

| $\beta$ | $\frac{\nu_D(2)}{\nu_D(0)}$ | $\frac{\nu_D(4)}{\nu_D(0)}$ | $\frac{\nu_D(6)}{\nu_D(0)}$ |
|---|---|---|---|
| 0.05 | 1.066 | 1.099 | 1.117 |
| 0.2 | 1.025 | 1.045 | 1.059 |
| 0.4 | 1.003 | 1.015 | 1.026 |
| 0.7 | 0.993 | 0.998 | 1.006 |
| 1.0 | 0.991 | 0.995 | 1.003 |

Comparison of the present results for sodium can be made with experimental data of another type. A lattice-vibration spectrum has been derived[48] from neutron-scattering results[49] obtained at 90°K, and the characteristic frequencies $\nu_D(n)$ obtained from this spectrum are compared in Table XIV with those obtained from the specific-heat data. It will be clear that agreement between the neutron data and specific-heat data obtained in the assumption of harmonicity up to $\frac{1}{2}\Theta^S$ ($\sim$80°K for sodium) is rather good. The neutron measurements do not extend below frequencies of about $10^{12}$ cps, and the low-frequency end of the 'neutron spectrum' has been obtained[48] by fitting a Born–von Karman model to the neutron data and to the rather uncertain elastic-constants data (which are given low weight). Thus the disagreement between the $\nu_D(-3)$ values, obtained from the specific-heat and neutron data, respectively, is probably not significant. The agreement between the two spectra is even better than appears from Table XIV since the neutron results refer to the 90°K volume and should be increased by the factor $(\rho_0/\rho_{90})^{\gamma(n)}$ ($\sim\frac{1}{2}\%$ for sodium) to convert to the 0°K volume basis of the specific-heat data.[42]

The neutron scattering and specific heat are both due to an effective spectrum, incorporating frequency shifts due to zero-point energy and anharmonicity. Barron has shown[35] that the effective harmonic frequencies for the entropy are the same at all temperatures as those derived from neutron-scattering data.

The agreement between the specific-heat and neutron results substantiates the assumptions[19] regarding the amount of sodium transforming to the low-temperature phase which are implicit in the bcc sodium specific-heat results.[19]

TABLE XIV. Characteristic frequencies of sodium from neutron-scattering and specific-heat data.[a]

| | $\nu_D(-3)$ | $\nu_D(-2)$ | $\nu_D(-1)$ | $\nu_D(0)$ | $\nu_D(2)$ | $\nu_D(4)$ | $\nu_D(6)$ |
|---|---|---|---|---|---|---|---|
| Neutron scattering | 3.41 | 3.16 | 3.21 | 3.31 | 3.48 | 3.58 | 3.63 |
| Specific heat (Table VIII) | 3.18±0.05 | 3.183±0.015 | 3.24±0.03 | 3.34 ±0.01 | 3.50±0.04 | 3.5±0.1 | 3.4±0.2 |
| Specific heat (Table IX) | 3.18±0.05 | 3.194±0.015 | 3.28±0.03 | 3.446±0.004 | 4.06±0.14 | 5.2±0.6 | 6.0±0.8 |

[a] Units $10^{12}$ sec$^{-1}$.

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[45] M. Blackman, Phil. Mag. 42, 1441 (1951).

[46] H. B. Huntington, Solid State Phys. 7, 288 (1958).

[47] C. B. Clark, J. Grad. Res. Center (Southern Methodist University) 29, 10 (1961).

[48] A. E. Dixon, A. D. B. Woods, and B. N. Brockhouse, Proc. Phys. Soc. (London) 81, 973 (1963). The characteristic frequencies from neutron-scattering data shown in Table XIV were kindly supplied by Dr. G. Dolling and were obtained using the method of G. Gilat and G. Dolling, Phys. Letters 8, 304 (1964).

[49] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. 128, 1112 (1962).

## CONCLUSIONS

Analysis of specific-heat data on the alkali metals shows (i) that all these metals have a positive anharmonic contribution to the specific heat and (ii) that there is a systematic change in the shape of the vibration-frequency spectrum on going from sodium to cesium. While this qualitative interpretation of the results seems clear, some uncertainty arises in the quantitative results due to lack of knowledge of the form of the temperature variation of the anharmonic specific-heat contribution. There is also a need of accurate experimental data on the variation of density and elastic constants with temperature.

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# Study of the Cowley and the Christy-Hall Theories of Order Parameters*

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Relationships between autocorrelations of the Flinn function, certain joint probabilities, and the Warren-Cowley order parameters are established for a specific configuration of a disordered alloy, for a canonical ensemble (CE) of alloys with a given concentration, and for a grand canonical ensemble (GCE) of alloys with a given average concentration. The average internal energy for the CE and that for the GCE are of the same form as that previously reported by Christy and Hall (CH) for a specific configuration. We show that a certain approximation on order parameters (or an equivalent approximation on probabilities) is inherent in Cowley's energy expression. Although this approximation may seem a reasonable one by analogy with the Chapman-Kolmogorov equations for a Markov process, it is definitely inexact in general. For example, it is inexact for one-dimensional alloys with either first- and second-neighbor interactions or just a single interaction at other than the first-neighbor distance, although the approximation is exact for a one-dimensional alloy with first-neighbor interactions. We compute all the order parameters for these one-dimensional cases using the usual procedure of the chemical potential to fix the average concentration. For the case of a single interaction at an arbitrary distance, the CH equations give the order parameter for that distance exactly and all others inexactly; the Cowley equations give none of the parameters exactly and incorrectly give a finite transition temperature. The Cowley equations, which are probably the better of the two for three-dimensional cases because they yield a finite transition temperature and contain coupling, clearly do not contain the proper coupling between the order parameters for the one-dimensional case. We propose that the Cowley and the CH theories, which are both inadequate, are somewhat complementary and constitute steps in the right direction. We discuss preliminary results of an attempt to derive new equilibrium equations more general than those of Cowley and CH.

## 1. INTRODUCTION

THE Ising[1,2] problem with arbitrary temperature has been solved exactly only for a limited number of cases: (1) one dimension, first-neighbor interactions, and arbitrary external field; (2) one dimension, first- and second-neighbor interactions, and zero external field; and (3) two dimensions, first-neighbor interactions, and zero external field. Since the alloy problem with arbitrary concentration and given interactions is equivalent to an Ising problem with nonzero field (zero field corresponds to equal concentrations) and the same interactions, it is clear that the alloy problem with arbitrary concentration and temperature has been solved exactly only for the case of one dimension and first-neighbor interactions. In order to study metallic alloys, we need, of course, a theory for three dimensions and for interactions over a fairly large number of neighbors. In this paper, we report results of a study of the Cowley[3–5] and the Christy and Hall (CH)[6] theories of binary substitutional alloys, which have been developed for the three-dimensional case. The principal purpose of the study is

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[1] G. F. Newell and E. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

[2] C. Domb, Advan. Phys. **9**, 149, 245 (1960).

[3] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[4] J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

[5] J. M. Cowley, Phys. Rev. (to be published).

[6] D. O. Christy and G. L. Hall, Phys. Rev. **132**, 1959 (1963).