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Heat Capacity of Beryllium below 30°K

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The heat capacity of high-purity beryllium ($R_{300}/R_{4.2}=1100$) was measured from 1.4°K to 30°K. The results can be expressed by the sum of contributions proportional to T, T^3, and T^5 with the coefficients (0.1714 ± 0.0008) mJ/M(°K)^2, $(0.598\pm0.020)\times10^{-3}$ mJ/M(°K)^4, and $(0.18\pm0.04)\times10^{-6}$ mJ/M(°K)^6, respectively. The Debye theta at 0°K (Θ_0) is (1481 ± 16)°K. The results are in good agreement with some of the recent lattice-dynamical and band-structure calculations and with Θ_0 derived from elastic constants. Phonon enhancement of the density of states does not appear important in beryllium. The heat capacity is smaller than the work of previous investigators indicated.

I. INTRODUCTION

THE low-temperature heat capacity of beryllium was first measured by Christescu and Simon[1] on a sample of 99% purity at temperatures above 10°K. They observed an anomaly at 11°K, which to them appeared similar to the anomalies which had been found in the heat capacities of superconductors. These observations motivated Hill and Smith[2] to repeat the measurements on a sample of 99.5% purity. Hill and Smith started their measurements at 5°K. They did not observe the anomaly reported by Cristescu and Simon. They analyzed their results in terms of an electronic and a lattice contribution and found 0.226 mJ/M(°K)^2 for the electronic term and a low-temperature Debye theta of 1160°K. The electronic term is in excellent agreement with the value 0.23, which was obtained from the band-structure calculations of Herring and Hill[3] by Seitz[4]. However, more recent calculations[5] show that this theoretical result is only very approximate, and that the agreement is fortuitous. This will be discussed in detail later. The Debye theta is considerably lower than 1462°K, the value derived from recent measurements of the elastic constants.[6]

Reich *et al.*[7] deduced a value of 1240°K for the Debye theta of beryllium samples somewhat purer than those used in the previous work from electrical-resistance measurements. The trend towards smaller heat capacities with higher purities caused Gmelin[8] to measure the heat capacity of a very pure sample between 1.2 and 4.4°K. Gmelin's sample had been zone-refined and contained less than 100 ppm impurities. It had a residual resistance ratio of 200. Gmelin obtained an electronic contribution to the heat capacity of 0.184 ±0.002 mJ/M(°K)^2, and a Debye theta of 1390°K. The trend towards lower heat capacity with increasing purity is thus continued. Gmelin's electronic term is clearly lower than that indicated by the band-structure calculations of Herring and Hill. The value of the Debye theta is still slightly lower than the value obtained from the elastic constants.[6]

Recently there has been considerable interest both in the electronic properties[5,9,10] and in the lattice dynamics[11–16] of beryllium. Also, very high-purity beryllium has become more readily available. The heat capacities of two samples, one of them a single crystal with a resistance ratio of 1100, were therefore measured between 1.4 and 30°K.

II. EXPERIMENTAL

A. Apparatus, Method, and Errors

The apparatus, measuring techniques, and the temperature scale are identical to those described elsewhere.[17]

Measurements of the heat capacity of beryllium present some special problems. The heat capacity is extremely small, and large high-purity samples are difficult to obtain. Thus, the heater, thermometer, and varnish which must be attached to the sample contribute appreciably to the total heat capacity. Often this contribution is estimated and subtracted. A correction of this type would lead to serious errors when the sample heat capacity is small. It was therefore considered preferable to mount the heater and thermometer on a sample holder and to measure the holder separately. The holder was described elsewhere.[17] The necessary material in the holder does, of course, further increase the correction. But the correction could be

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Table I. Relative contribution of the sample heat capacity to the total heat capacity and estimated errors in the sample heat capacity.

T (°K)	Contribution (%) of sample 1	2	Estimated error P (%)
2	65	73	0.5
4	49	56	0.5
10	22	26	0.5
20	13	18	1
30	···	18	2

measured with errors of less than 0.2%. In order to determine the reliability of this method, two samples were measured, each in a different holder. Within the experimental errors these experiments yielded identical results. The ratio of the sample heat capacity to the total heat capacity is given in Table I.

B. The Samples

The samples were spark cut from a 1-in-diam rod manufactured by Nuclear Metals, Incorporated[18] for W. A. Reed. The rod had been obtained by seven zone-refining passes from vacuum-distilled starting material. Sample 1 weighed 58.13 g and included the polycrystalline trailing end of the zone refining. The portion of sample 1 which was a single crystal had a resistance ratio of 380. Sample 2 weighed 37.98 g and was spark cut from the center section of the rod. It was a single crystal and had a resistance ratio of 1100.

III. RESULTS

The heat capacities of samples 1 and 2 were measured from 1.4 to 20°K and 1.4 to 30°K, respectively. The smoothed heat capacities of the sample holders were subtracted. For beryllium, 30°K corresponds to $T/\Theta \sim 0.02$; and therefore it should be possible to express the results in the form

$$C=\sum_{j=1}^{N} A_j T^{2j-1}\,, \tag{1}$$

where $A_1=\gamma$, $A_2=\alpha$, and $A_3=\beta$ in customary notation.

Table II. Parameters for Eq. (1) and sample 2 based on least-squares fits using two to four parameters, and root-mean-square deviations Q. The unit of energy is the millijoule.

	No. of Parameters 2	3	4
A_1	0.1698	0.1712	0.1713
$A_2 \times 10^3$	0.6561	0.6008	0.5971
$A_3 \times 10^6$	···	0.178	0.205
$A_4 \times 10^9$	···	···	−0.04
Q(%)	2.6	0.6	0.6

Inspection of the data for sample 1 revealed that above 10°K appreciable systematic deviations from a two-parameter fit were present. However, the maximum temperature of the measurements (20°K) was too low to assign a reliable value to the third parameter. The results for sample 1 were therefore used only in the determination of γ. In order to determine γ the data for the two samples were separately fitted to Eq. (1) by the least-squares method. A weight of $(PC_i)^{-2}$ was used, where P is the estimated error given in Table I, and C_i is the heat capacity. The coefficients A_j obtained for sample 2 with $N=2$ to $N=4$ (see Eq. 1) are given in Table II. It is clear that three parameters must be used and that more parameters would be superfluous. The values obtained for γ with three parameters are 0.1716 and 0.1712 mJ/M(°K)^2 for samples 1 and 2, respectively. The value 0.1714 was therefore adopted as the best estimate.

Estimates of α and β are based entirely on sample 2. The lattice heat capacity C_L was obtained by subtracting $0.1714T$ from the total heat capacity and a two-parameter least-squares fit to C_L with an additional weight of $(C_L/C_i)^2$ was obtained. The results are collected in Table III.

Table III. γ, α, β, and Θ_0 for beryllium. The unit of energy is the millijoule.

Parameter	Value
γ	0.1714±0.0008
$\alpha \times 10^3$	0.598±0.020
$\beta \times 10^6$	0.185±0.040
Θ_0(°K)	1481±16

Figure 1 shows the relative difference $(C_i-\gamma T-\alpha T^3-\beta T^5)/C_i$ between the measured heat capacity and the heat capacity calculated from the parameters in Table III for the two samples. There are no appreciable systematic differences between the heat capacities of the two samples.

The Debye theta was calculated from each point after the term γT was subtracted. The values obtained for sample 2 are shown in Fig. 2. The Debye theta values for sample 1 are essentially identical to those for sample 2. The solid line through the data is the one derived from α and β in Table III. The effect of a 0.2% error in the total measured heat capacity on Θ is shown at the top of the figure. Also shown in Fig. 2 are the theoretical results of DeWames *et al.*[11,19] and of Gupta and Dayal.[16] These calculations will be discussed later. The value obtained from elastic constants,[6] and the measurements of Gmelin[8] are likewise indicated.

The Debye theta at 0°K, Θ_0, is best determined from α. If it were determined graphically from Fig. 2, then the large effect of small systematic errors in C at low temperatures could be misleading and might result in

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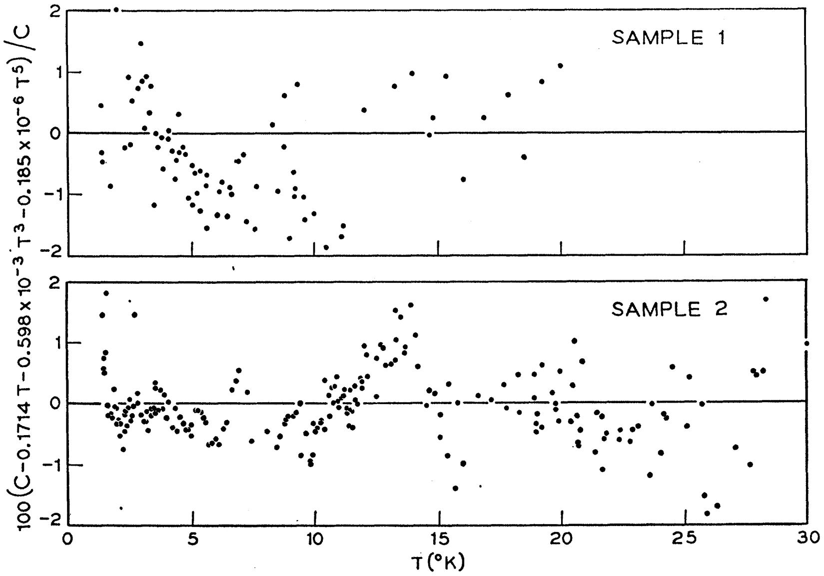

FIG. 1. The difference, in percent, between the measured heat capacity and the heat capacity calculated from the three parameters in Table III.

a poor extrapolation. The value of Θ_0 as determined from α is (1481±16)°K.

IV. DISCUSSION

A. General

Although both samples are purer than any previously studied, they differ considerably in resistance ratio. However, both samples have the same heat capacity within experimental error. It is thus very likely that impurities do not contribute to the heat capacity in either sample and that the observed heat capacity is that of pure beryllium. Both the lattice heat capacity and the electronic heat capacity are smaller than those observed by Gmelin,[8] and much smaller than those reported by Hill and Smith.[2] It is somewhat surprising that the results of Gmelin differ from the present results, since the resistance ratio of his sample was only a little smaller than that for one of the present samples. It must be remembered, however, that various heat-capacity contributions and the resistance ratio are all affected differently by different impurities, and that the resistance ratio is only a qualitative measure of purity. The possibility of systematic errors in Gmelin's results, due for instance to incorrect estimates of his addenda, cannot be ruled out.

B. The Lattice Heat Capacity

The experimental value of 1481°K for the Debye theta at 0°(Θ_0) is in good agreement with the value 1462°K obtained from elastic constants.[6] Theta is strongly temperature-dependent. At 30°K($T/\Theta_0=0.02$) it has dropped to 1365°K or (92.2±2.5)% of Θ_0. This strong temperature dependence of Θ appears to be characteristic of some other hexagonal metals.[20–23]

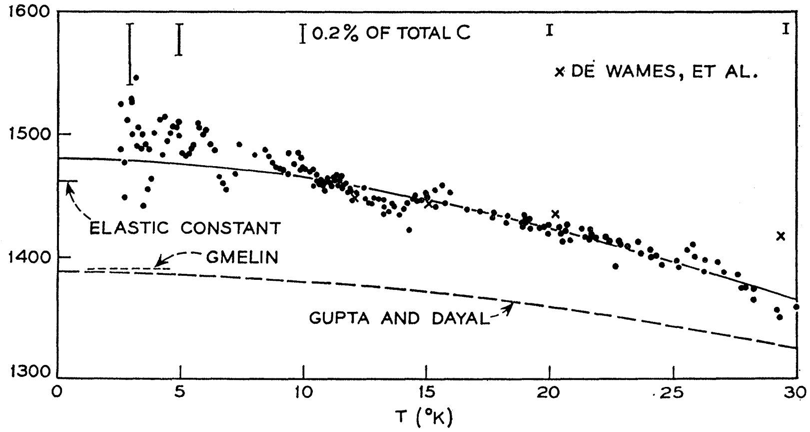

FIG. 2. The Debye theta as a function of the temperature. The vertical bars at the top of the figure show the effect of a 0.2% error in the total heat capacity on the Debye theta. The line through the data points is based on the three-parameter fit to the total heat capacity.

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However, the strong temperature dependence of Θ is not a general property of the hexagonal lattice, for it is not found in solid helium[24] and solid hydrogen.[25] These latter solids have a temperature dependence of Θ very similar to that observed in the cubic inert gas solids[26,27] and at $T/\Theta_0 \sim 0.02$ the value of Θ has dropped below Θ_0 by only about 1%. From a purely phenomenological viewpoint one is thus led to suspect that the electrons have a strong effect on the lattice dynamics of hexagonal metals. This idea was recently supported also by lattice dynamical calculations. The results of some of these calculations will be compared with the experimental lattice heat capacity below 30°K. Generally, in such a comparison not much significance can be attached to agreement between the experimental and theoretical value of Θ_0, because most of the theoretical models utilize the experimental elastic constants as parameters. Thus, unless the model is internally inconsistent, the correct value of Θ_0 should be predicted if Θ_0 as derived directly from the elastic constants agrees with the calorimetric Θ_0. At low temperatures the only meaningful comparison must thus be made between experimental and theoretical values of $\beta[A_3$ in Eq. (1)].

Slutsky and Garland[12] presented a lattice dynamical model (SG model) in which the nonshear experimental elastic constants were corrected for the bulk modulus of the free-electron gas before the elastic constants were used to calculate the frequency spectrum. The bulk modulus of the electron gas was determined from the deviation from the Cauchy relation. However, this model yielded a much weaker temperature dependence of Θ than is found experimentally for beryllium.[13] An extended version of the SG model as developed by Schmunk *et al.*[14] was not satisfactory for the quantitative interpretation of the dispersion relations determined by neutron scattering.

Recently Gupta and Dayal[15] questioned the validity of the SG Model and introduced the electron effect directly into the matrix elements of the dynamical matrix. This could not be done rigorously, and the model of Sharma and Joshi[28] was used to calculate the electronic contributions to the matrix elements. The calculated dispersion curves were in fair but not exact agreement with the experimental data.[14] A calculation of the lattice heat capacity based on the Gupta-Dayal modification of the SG Model[16] yielded good agreement with the experimental data of Hill and Smith[2] at high temperatures; but below 80°K the calculated Debye theta rose much more rapidly with decreasing temperature. The mesh of points in the Brillouin zone was too coarse to permit calculations of Θ below 60°K. But at 0°K the model should yield 1388°K for Θ_0, the value obtained from the elastic constants used to determine the force constants. If this value of Θ_0 is used to determine the coefficient of the T^3 term in the heat capacity expansion, then the theoretical heat capacity at 60°K yields a value of 0.12×10^{-6} mJ/M(°K)^6 for the coefficient of the T^5 terms, if higher order terms are assumed to be negligible. This is in reasonable agreement with the experimental value found in this work and at 30°K yields a drop of Θ to 95% of Θ_0. This deduction of the T^5 coefficient yields only an approximate value because at 60°K or $T/\Theta_0=0.04$ higher order terms are probably already important. It is regrettable that Gupta and Dayal changed the elastic constants of Smith and Arbogast[29] since this change shifted their calculated values and caused the difference between the present calorimetric and the theoretical Debye theta at 0°K. However, this change should have had little effect on the temperature dependence of theta. The extrapolation of Gupta and Dayal's calculations is shown in Fig. 2.

Another approach to the lattice dynamics of beryllium was taken by DeWames *et al.*[11] They used their previously developed axially symmetric (AS) model,[30] of which the SG model is a restricted form. The AS model takes into consideration nonzero-bond bending force constants, and the total energy of the system includes a volume-dependent term for the electron-gas self-energy. In general, good but not exact agreement with the available experimental dispersion curves is obtained. The Debye theta at low temperatures[19] agrees very well with the experimental data from this work. However, Θ dropped below Θ_0 by only about 2% at 30°K. At higher temperatures the theoretical theta drops more rapidly than that derived from the SG model[13] for hexagonal metals and agrees with the experimental data of Hill and Smith[2] and the calculations of Gupta and Dayal[16] above 100°K.

It appears that for beryllium the theoretically deduced temperature dependence of Θ at low temperatures agrees at least semiquantitatively with the experimentally determined dependence when the model used takes the effect of the electrons on the elements of the dynamical matrix into consideration, as was done by Gupta and Dayal.[15]

C. The Electronic Heat Capacity

As mentioned earlier, band-structure calculations yield a value of 0.23 mJ/M(°K)^2 for γ.[3,4] However, it must be realized that these calculations are for a finite number of points in the Brillouin zone (BZ) and that therefore the density-of-states curve is defined with limited accuracy from a purely statistical viewpoint.

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The calculations are particularly poor in a region where the density of states changes rapidly. In beryllium the Fermi energy lies near a sharp minimum in the density-of-states curve. Calculations for the vicinity of the Fermi surface, therefore, are not likely to be very accurate unless very many points near the Fermi surface are used. The only calculation in which a sufficient number of points were calculated is the recent one by Loucks.[5] Loucks calculated conduction-electron eigenvalues at the equivalent of 80 000 points in the first BZ in the immediate vicinity of the Fermi surface. However, he did not derive a density-of-states curve from his calculations; but he does give the virtual Fermi energy as a function of volume in 1/24th of the BZ. The density of states in the immediate vicinity of the Fermi surface can be derived from the slope of this function.[31] It yields an electronic heat-capacity coefficient of 0.166 mJ/M(°K)^2, in excellent agreement with the present experimental value. This agreement is indicative of the fact that phonon enhancement[32] does not play a major role in beryllium.

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Point-Defect Calculations for an fcc Lattice*

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Formation and migration energies and atomic configurations have been calculated for interstitials and vacancies in an fcc lattice, and the interaction of close Frenkel pairs has been studied. A mathematical model was used in which the atoms in a spherical crystallite of about 530 atoms are treated as individual particles, each with three degrees of freedom, while the remainder of the crystal is treated an an elastic continuum with atoms imbedded in it. A two-body central force previously used in calculations for α-iron (a bcc metal), was used to simulate the interaction of atoms in the fcc lattice. Configurations were found using a digital computer by choosing a starting configuration roughly approximating the situation under consideration and successively adjusting the value of each variable occurring in the energy equation so that the magnitude of the generalized force associated with it was zero until equilibrium was reached. The object of this calculation was to investigate the consequences of using an interatomic interaction for an fcc metal with a form similar to that used for previous bcc calculations. The interaction used should be reasonably appropriate for both γ-iron and nickel and the results are compared with experimental values for both metals. The stable interstitial was a "split" configuration in which two atoms were symmetrically split in a $\langle 100\rangle$ direction about a vacant normal lattice site. The formation energy was 4.08 eV and the activation energy for motion was 0.15 eV. A number of metastable configurations were found, the most important of which was the $\langle 111\rangle$ "split" interstitial, which was metastable by 0.16 eV and had a migration energy of 0.13 eV. The vacancy formation energy and activation energy for migration were 1.49 and 1.32 eV, respectively. The interaction between a vacancy and an interstitial was very complex and short in range. Configurations were found which were bound, repulsive, and trapped, and there were 32 unstable lattice sites.

INTRODUCTION

EXTENSIVE lattice calculations pertaining to the nature of point defects in metals have been carried out since the introduction of the high speed digital computer as a research device available to physicists. In such calculations a model is devised which matches various known physical properties of a metal and which, one hopes, can be extrapolated to yield results about unknown properties of the metal, e.g., configurations and energies associated with lattice defects. These models normally represent the solid by a crystallite in which the atoms interact, one with another, by two-body central forces and are given full freedom of motion, surrounded by a boundary region which is meant to simulate the remainder of the lattice. An energy equation is written which includes the interatomic forces and the boundary forces, and parameters in this equation are adjusted to yield a reasonable approximation of the perfect lattice. Then the energy equation is investigated in a region of configuration space where it represents the defect lattice, i.e., the whole process may be thought of as very complicated and sophisticated curve fitting to one section of configuration space and extrapolation to another section. There is, of course, no unique way of fitting the perfect lattice: Any number of quite different

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