

angular range of observation of the limiting-point resonance on the lens and of the resonance from the diagonal arms of the monster were extended beyond that reported by previous workers. Four mass branches previously reported by SSE were not observed when **H** was parallel to the sample surface. Three of these resonances were reproduced in tip studies, and we are convinced that all four resonances are the result of tip effects.

Seven new cyclotron-resonance orbits in zinc have been observed. The orbits from the needles and from the horizontal arms of the monster were observed and their effective masses compared to the effective masses measured in the dHvA effect. Three orbits were observed which suffered from magnetic breakdown. The orbits were assigned to the Fermi surface, and the breakdown was interpreted as being between the first- and second-band hole surfaces. Based on the breakdown

field, the energy gap between the first-band caps and the diagonal arms of the second-band monster was estimated to be 0.03 eV. This value is in agreement with the spin-orbit gap previously calculated by Cohen and Falicov.

The topologies and dimensions of the Fermi surface deduced from the mass anisotropies presented here are consistent with the results of other experimental techniques. The effective mass measurements reported in this paper support the current model of the Fermi surface of zinc.

#### ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor A. F. Kip, under whose direction this work was performed, and to Dr. J. J. LePage for many valuable suggestions concerning experimental techniques.

PHYSICAL REVIEW B

VOLUME 1, NUMBER 4

15 FEBRUARY 1970

### Enhancement of the Lattice Heat Capacity Due to Low-Frequency Resonance Modes in Dilute Aluminum-Silver Alloys\*

W. M. HARTMANN

*Argonne National Laboratory, Argonne, Illinois 60439  
and  
Michigan State University, East Lansing, Michigan 48823*

AND

H. V. CULBERT AND R. P. HUEBENER

*Argonne National Laboratory, Argonne, Illinois 60439  
(Received 8 August 1969)*

The lattice component of the specific heat of high-purity aluminum and of two aluminum alloys containing 0.5 and 0.95 at. % Ag, respectively, has been measured between 1.3 and 25°K. In the aluminum alloys, an enhancement of the lattice specific heat has been observed which can be explained in terms of low-frequency resonance modes associated with the heavy silver ions. A lattice-dynamical treatment of the heavy-mass defect in a light-host lattice is presented. The calculation is based on the aluminum density of states as obtained from neutron-scattering data, and the silver impurities are treated as mass defects only. The mass-defect calculation accounts for about 80% of the observed specific-heat enhancement. The values of the electronic specific-heat coefficient  $\gamma_0$  and the Debye temperature  $\Theta_D$  for pure aluminum are in agreement with previous data.

#### I. INTRODUCTION

THE phonon properties of a solid are affected appreciably by the presence of small concentrations of impurities which differ from the atoms of the host lattice in mass or in the interatomic force constants.<sup>1</sup> The introduction of isolated *heavy* impurities into a relatively light-host lattice causes a change in the phonon spectrum which is characterized by the

existence of low-frequency resonance modes localized at the impurity site. Recently, the enhancement in the lattice-heat capacity at low temperatures caused by low-frequency resonance modes has been reported in a series of papers.<sup>2-4</sup> Changes in the phonon spectrum due to small concentrations of very heavy or very light

\* Based in part on work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.

<sup>2</sup> G. Kh. Panova and B. N. Samoilov, *Zh. Eksperim. i Teor. Fiz.* **49**, 456 (1965) [English transl.: *Soviet Phys.—JETP* **22**, 32D (1966)].

<sup>3</sup> J. A. Cape, G. W. Lehman, W. V. Johnston, and R. E. DeWames, *Phys. Rev. Letters* **16**, 892 (1966).

<sup>4</sup> N. A. Chernoplekov, G. Kh. Panova, M. G. Zemlyanov, B. N. Samoilov, and V. I. Kutaitsev, *Phys. Status Solidi* **20**, 767 (1967).

impurities have been studied more extensively using inelastic neutron scattering.<sup>5-9</sup>

In this paper, we report measurements of the enhancement of the lattice-heat capacity at low temperatures due to low-frequency resonance modes in dilute Al-Ag alloys. The experimental results are compared with a lattice-dynamical treatment which is based on the Al density of states as obtained from neutron-scattering data and in which the Ag impurities are treated as mass defects only. Our mass-defect calculation accounts for roughly 80% of the observed specific-heat enhancement. A preliminary account of the experimental results has been given earlier.<sup>10,11</sup>

## II. EXPERIMENTAL

The specific heats of the pure Al and Al-Ag alloy samples were measured in a calorimeter and He<sup>3</sup> cryostat described elsewhere.<sup>12,13</sup> In brief, the calorimeter is a pair of copper caps which screw into the ends of the cylindrical samples. The upper cap has attached to it a Ge resistance thermometer and three supporting threads for the assembled calorimeter and sample. The sample heater is bifilarly wound on the bottom cap of the calorimeter. The leads from the thermometer and heater are thermally anchored to the copper caps before leading out of the calorimeter vacuum space. The measurement technique is the usual drift-heat-drift method and is described in detail elsewhere.<sup>12</sup> The Ge resistance thermometer was calibrated against the vapor pressure of He<sup>3</sup> below 2.2°K and He<sup>4</sup> between 2.2 and 4°K. Below 4°K, the calibration is consistent with the 1958 He<sup>4</sup> and 1962 He<sup>3</sup> temperature scales to better than 1 m°K. The calibration above 4°K is traceable to the gas-thermometer calibration of Osborne, Flotow, and Schreiner.<sup>14</sup>

The samples were cast from 99.9999% pure Al and Ag in the form of cylinders 2 in. long and 1 in. in diameter. They were annealed at 600°C in a He atmosphere for one week. In addition to pure Al, two Al alloy samples containing 0.95 and 0.5 at.% Ag were investi-

gated. The alloy composition was determined from chemical analysis.

Specific-heat data were taken for pure Al and the alloy containing 0.95 at.% Ag between 1.3 and 25°K. For the alloy containing 0.5 at.% Ag, data were taken in the region between 10 and 20°K.

## III. ANALYSIS AND RESULTS

The specific heat of a simple metal at low temperatures can be separated into an electronic contribution  $C_e$  and a lattice contribution  $C_L$  where

$$C_e = \gamma_0 T, \quad \text{and} \quad C_L = (12/5)\pi^4 [R/\Theta_D^3(0)] T^3. \quad (1)$$

$R$  is the gas constant,  $T$  the absolute temperature, and  $\Theta_D(0)$  is the Debye temperature at 0°K. We were able to fit our data with this low-temperature approximation up to 5°K for Al. The parameters obtained from a least-squares fit of the pure Al data are

$$\gamma_0 = 1.351 \pm 0.004 \frac{mJ}{\text{mole } ^\circ K^2}$$

and

$$\Theta_D(0) = (432.6 \pm 1.8) ^\circ K. \quad (2)$$

The error estimates correspond to 95% confidence limits. Both  $\gamma_0$  and  $\Theta_D(0)$  are in fair agreement with previous measurements<sup>15-17</sup> although our value for  $\gamma_0$  does fall slightly lower than the value obtained by Dixon, Hoare, Holden, and Moody<sup>16</sup> with error estimates taken into account. The reason for the discrepancy may be due to the different temperature ranges over which the low-temperature approximation according to Eq. (1) was used, i.e., below 4.2°K by Dixon *et al.* and below 5°K by us. Dixon *et al.* have also used a different weighting scheme in fitting their data. Our fitting procedure weighs each data point equally.

Above 5°K, we have calculated  $\Theta_D$  for Al using standard tables.<sup>18</sup> We find good quantitative agreement with the  $\Theta_D(T)$  obtained by Berg<sup>19</sup> for aluminum above 6°K, including the maximum in  $\Theta_D(T)$  at about 13°K. The systematic disagreement of our  $\Theta_D$  values with Berg below 6°K is within assigned errors.

The increased density of states for phonons due to the low-frequency resonant modes of the heavy-mass impurities increases the lattice specific heat of the dilute alloy over that of the pure metal. This increase has been obtained by fitting the data for pure Al and for the alloy containing 0.95 at.% Ag with polynomials in odd powers of temperature up to  $T^7$ . The difference of the coefficients of the polynomials than yielded the

<sup>5</sup> H. B. Møller and A. R. Mackintosh, Phys. Rev. Letters **15**, 623 (1965).

<sup>6</sup> N. A. Chernoplekov and M. G. Zemlyanov, Zh. Eksperim. i Teor. Fiz. **49**, 449 (1965) [English transl.: Soviet Phys.—JETP **22**, 320 (1966)].

<sup>7</sup> I. Natcaniec, K. Parlinski, A. Bajorek, and M. Sudnik-Hryniewicz, Phys. Letters **24A**, 517 (1967).

<sup>8</sup> E. C. Svensson and B. N. Brockhouse, Phys. Rev. Letters **18**, 858 (1967); E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Solid State Commun. **3**, 245 (1965).

<sup>9</sup> M. G. Zemlyanov, V. A. Somenkov, and N. A. Chernoplekov, Zh. Eksperim. i Teor. Fiz. **52**, 665 (1967) [English transl.: Soviet Phys.—JETP **25**, 436 (1967)].

<sup>10</sup> H. V. Culbert and R. P. Huebener, Phys. Letters **24A**, 530 (1967).

<sup>11</sup> H. V. Culbert and R. P. Huebener, *Localized Excitations in Solids* (Plenum Publishing Corp., New York, 1968), p. 469.

<sup>12</sup> O. V. Lounasmaa, Phys. Rev. **126**, 1357 (1962).

<sup>13</sup> H. V. Culbert, D. E. Farrell, and B. S. Chandrasekhar (unpublished).

<sup>14</sup> D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. **38**, 159 (1967).

<sup>15</sup> N. E. Phillips, Phys. Rev. **114**, 676 (1959).

<sup>16</sup> M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) **A285**, 561 (1965).

<sup>17</sup> G. N. Kamm and G. A. Alers, J. Appl. Phys. **35**, 327 (1964).

<sup>18</sup> Six place tables of the Debye functions  $(\bar{E} - E_0)/3RT$ ,  $C_v/3R$ , and  $S/3R$ , J. E. Kilpatrick and R. H. Sherman, Los Alamos Scientific Laboratory of the University of California Report No. LA-3114, 1964 (unpublished).

<sup>19</sup> W. T. Berg, Phys. Rev. **167**, 583 (1968).

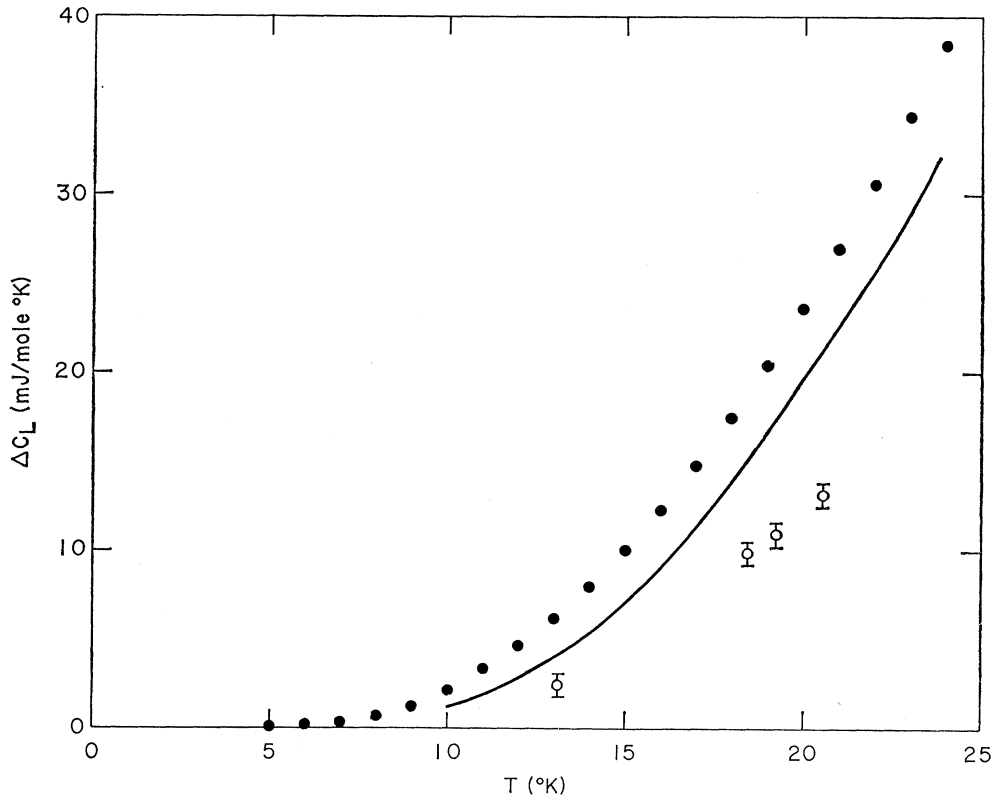


FIG. 1. Experimental values of the enhanced lattice specific heat in  $\text{Al}_{99.05}\text{Ag}_{0.95}$  alloy  $\bullet$ , and  $\text{Al}_{99.5}\text{Ag}_{0.5}$  alloy  $\circ$ ; the solid line represents the calculated values from the exact low-concentration harmonic mass-defect theory for the 0.95 at.% alloy.

specific-heat enhancement  $\Delta C_L$ . The results for the Al alloy containing 0.95 at.% Ag are shown in Fig. 1 as the solid circles. We also show data for alloy containing 0.5 at.% Ag as the open circles. We took these few data for the alloy containing 0.5 at.% Ag to check the variation of  $\Delta C_L$  with impurity concentration. The linearity of  $\Delta C_L$  versus concentration expected for small-defect concentrations is shown in Fig. 2 at three different temperatures.

#### IV. THEORETICAL DISCUSSION

In this section, we use thermal Green's functions to review and apply the low-concentration harmonic theory of the specific-heat enhancement previously developed by classical Green's function techniques.<sup>3,20,21</sup>

The enhancement of the low-temperature vibrational specific heat by heavy impurity atoms is due to a low-frequency resonant mode of vibration which absorbs energy at low temperatures. The increase in specific heat per mole ( $N$  atoms),

$$\Delta C_L(T) = \frac{3N\hbar^2}{4k_B T^2} \int_0^\infty \omega^2 \Delta g(\omega) \text{csch}^2(\hbar\omega/2k_B T) d\omega, \quad (3)$$

<sup>20</sup> Yu. Kagan and Y. A. Iosilevskii, Zh. Eksperim. i Teor. Fiz. 45, 819 (1963) [English transl.: Soviet Phys.—JETP 18, 562 (1964)].

is found from the change in the phonon spectrum  $\Delta g(\omega) \equiv g'(\omega) - g(\omega)$ , where primes refer to the imperfect crystal properties.

The spectral function perturbed by a single mass defect at the origin ( $m_l = m$  for  $l \neq 0$ ,  $m_0 = m'$ ) may be written in terms of the Green's function for this perturbed system  $G_{ll\alpha\beta}(\omega)$ ,

$$g_s'(\omega) = \frac{-2\omega}{3N\pi} \sum_{l\alpha} \text{Im} G_{ll\alpha\alpha}(\omega) m_l. \quad (4)$$

In the notation of Elliott and Taylor,<sup>22</sup> the imperfect-crystal retarded Green's function is given by the matrix equation

$$\mathbf{G} = \mathbf{P} + \mathbf{P} \mathbf{C} \mathbf{G}, \quad (5)$$

where the analogous perfect-crystal Green's function is

$$P_{ll'\alpha\beta}(\omega) = \frac{1}{mN} \sum_{jk} \frac{\sigma_\alpha^{*j}(\mathbf{k}) \sigma_\beta^j(\mathbf{k})}{\omega^2 - \omega_j^2(\mathbf{k})} e^{-ik \cdot (\mathbf{R}_l - \mathbf{R}_{l'})}, \quad (6)$$

$$P_{00\alpha\beta}(\omega) = \frac{\delta_{\alpha\beta}}{m} \int_0^\infty \frac{g(\omega') d\omega'}{\omega^2 - \omega'^2}. \quad (7)$$

<sup>21</sup> G. W. Lehman and R. E. DeWames, Phys. Rev. 131, 1008 (1963).

<sup>22</sup> R. J. Elliott and D. W. Taylor, Proc. Phys. Soc. (London) 83, 189 (1964); Proc. Roy. Soc. (London) 296, 161 (1967).

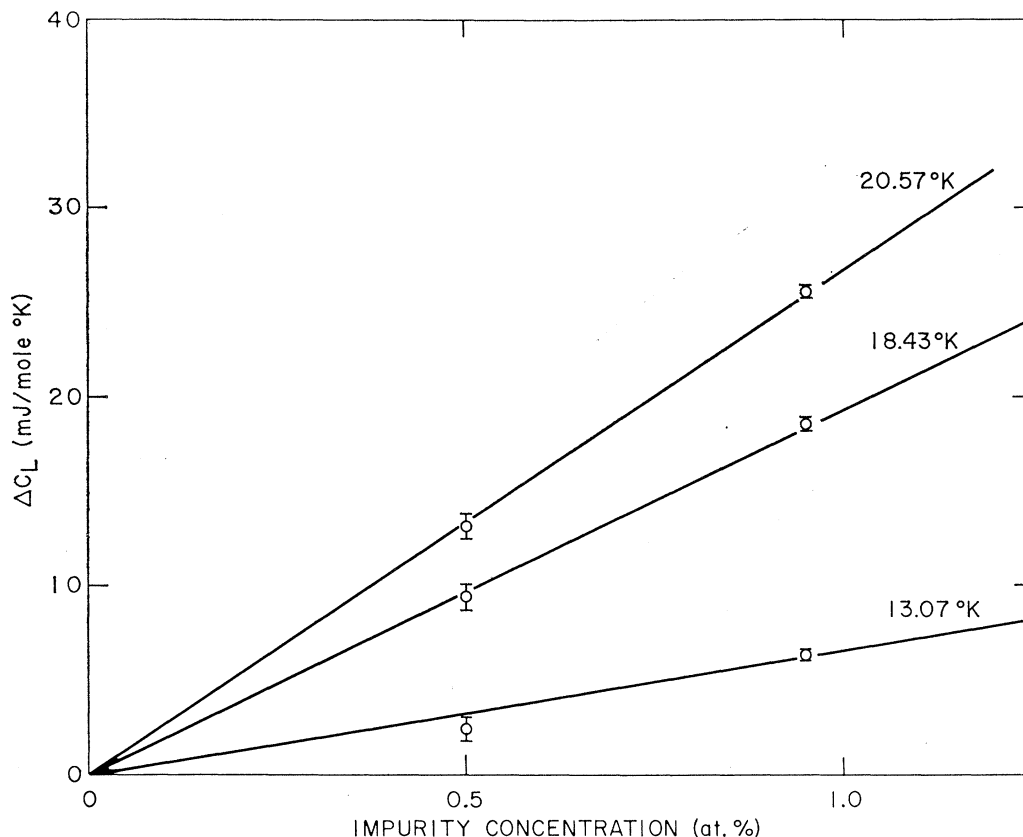


FIG. 2. The enhanced lattice specific heat  $\Delta C_L$  versus impurity concentration for three different temperatures.

The eigenfunctions  $\sigma_{\alpha}^j(\mathbf{k})$  for the displacements in the  $\alpha$ th direction for the mode of wave vector  $\mathbf{k}$  and branch  $j$  are particularly convenient for a crystal of cubic symmetry and lead to Eq. (7). The perturbing matrix  $\mathbf{C}$  is diagonal,

$$C_{ll'\alpha\beta} = m\epsilon\omega^2\delta_{ll'}\delta_{\alpha\beta}, \quad (8)$$

where  $\epsilon$  is the mass-change parameter,  $\epsilon \equiv 1 - m'/m$ . In the low-concentration limit  $\Delta g(\omega)$  for a finite concentration,  $c$  of defects is simply  $c$  times the  $\Delta g(\omega)$  calculated for a single defect.

Equation (5) may be solved for  $\mathbf{G}$  and the result substituted into Eq. (4). Then, because

$$\sum_{l\gamma} P_{0l\alpha\gamma} P_{l0\gamma\alpha} = \frac{-1}{m} \frac{d}{d\omega^2} P_{00\alpha\alpha}, \quad (9)$$

$$\Delta g(\omega) = \frac{-2\omega c}{3\pi} \text{Im} m\epsilon \sum_{\alpha} \frac{P_{00\alpha\alpha} + \omega^2 (d/d\omega^2) P_{00\alpha\alpha}}{1 - m\epsilon\omega^2 P_{00\alpha\alpha}}. \quad (10)$$

The change in density of states may be written in terms of the phase shift  $\theta$  for phonon scattering,<sup>23-25</sup>

$$\Delta g(\omega) = (2\omega c/3\pi) (d/d\omega^2) \theta(\omega), \quad (11)$$

where

$$\theta(\omega) = 3 \text{Im} \ln(1 - m\epsilon\omega^2 P_{00xx}). \quad (12)$$

After substituting into Eq. (3) and integrating once by parts, we have

$$\Delta C_L(T) = \frac{-2k_B c N}{\pi} \gamma \int_0^{\infty} d\omega \theta(\omega) \gamma \omega \times \text{csch}^2(\gamma\omega) [1 - \gamma\omega \coth(\gamma\omega)], \quad (13)$$

where  $\gamma \equiv \hbar/2k_B T$ . The relevant lattice dynamics of the imperfect crystal is then contained in the function  $\theta(\omega)$ . The appropriate generalization of Eq. (13) to noncubic crystals is given in Ref. 3.

We may apply this formalism to the calculation of the specific heat of Al with Ag defects ( $\epsilon = -3.0$ ) if we assume that the vibrations are essentially harmonic in the temperature range 0–25°K, and that there is no significant clustering among the Ag atoms. To calculate  $P_{00xx}(\omega)$ , we use an Al density of states derived from neutron scattering data at 80°K.<sup>26</sup> To check the suit-

*Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963).

<sup>23</sup> G. F. Nardelli and N. Terzi, *J. Phys. Chem. Solids* **25**, 815 (1964).

<sup>24</sup> A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in

<sup>25</sup> G. Toulouse and J. Friedel, *Natl. Bur. Std. (U. S.) Misc. Publ.* **287**, 141 (1967).

<sup>26</sup> G. Gilat and R. M. Nicklow, *Phys. Rev.* **143**, 487 (1966); G. Gilat and L. J. Raubenheimer, *ibid.* **144**, 390 (1966).

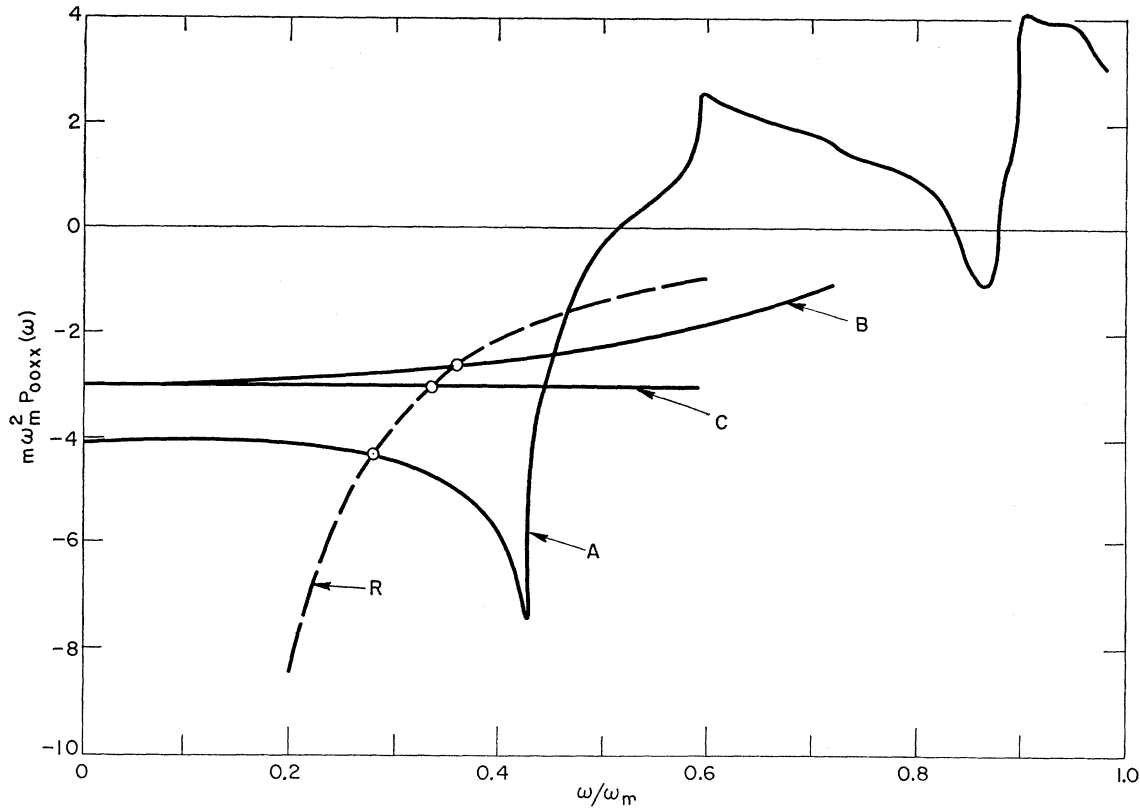


FIG. 3. The resonance condition. Curve R is  $\omega_m^2/\epsilon\omega^2$  and resonant frequencies are given by its intersections (circled) with the real part of the perfect-crystal Green's functions; curve A calculated exactly from the density of states determined from neutron scattering data (Ref. 8); curve B calculated from the Debye model; curve C calculated from the low-frequency limit of the Debye model.

ability of this density of states, we have used it to calculate the Debye  $\Theta_D(T)$  function for pure Al and found a maximum deviation of  $\frac{3}{4}\%$  from our experimental data and the experimental plot of Berg<sup>19</sup> over the temperature range of interest.

The real part of the pure Al Green's function is shown in Fig. 3. It predicts a resonance for the Ag ion at  $\omega/\omega_m = 0.28$ . The phase shift for this system is shown in Fig. 4, and the prediction for the enhanced specific heat is shown in Fig. 1 as the solid line along with the experimental results. The mass-defect calculation, which we expect to be accurate to within 2%, accounts for roughly 80% of the observed specific-heat enhancement. Calculations of the effect of force-constant changes on the specific heat can account for the remaining 20% and will be presented in a later paper.

In Fig. 5, the calculation of the enhanced specific heat is extended to higher temperature, beyond the limit of validity of the harmonic approximation. At high temperatures, the enhancement is given by the change in the first quantum mechanical term in the Thiring expansion,<sup>24</sup> proportional to  $T^{-2}$ ,

$$\Delta C_v(T) = Nk_B \{-\gamma^2 \Delta \mu_2 + \dots\}. \quad (14)$$

The change in the second moment of the frequency distribution can be expressed in terms of the second

moment of the unperturbed frequency distribution by a contour integration, as discussed by Montroll and Potts,<sup>27</sup>

$$\Delta \mu_2 = c\epsilon(1-\epsilon)^{-1}\mu_2, \quad (15)$$

which for our case gives  $\Delta \mu_2 = -1.217 \times 10^{21} \text{ (rad/sec)}^2$ . The area under the specific-heat curve, extrapolated to infinity, is 18.4 J/mole per at.% of Ag impurity. These considerations lead to the following interpretation of the excess specific heat. At high temperatures, the average energy per atom is simply the Dulong and Petit value independent of atomic mass. At  $T=0$ , the average zero-point energy per atom is lower for the crystal with heavy-mass defects than for the perfect crystal by an amount

$$\Delta U = \frac{-3\hbar}{2} \int_0^\infty \Delta g(\omega) \omega d\omega = \frac{c\hbar}{2\pi} \int_0^\infty \theta(\omega) d\omega. \quad (16)$$

The enhanced specific heat arises from adding enough extra energy to the imperfect crystal to reach the classical limit from a zero-point state of less than the perfect crystal energy.

It is interesting to compare the exact results with those obtained from the heuristic treatment of this

<sup>27</sup> E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

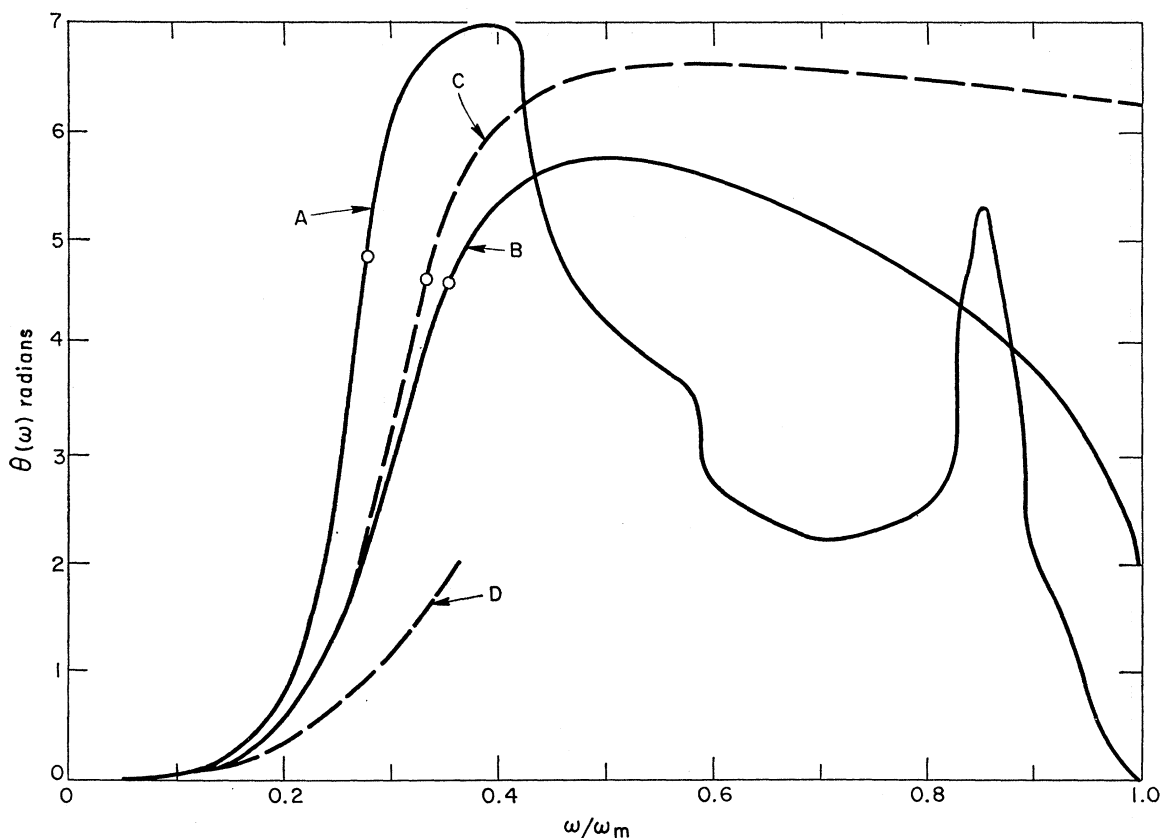


FIG. 4. The phase shift. Curve A plotted from the exact calculations for Al:Ag ( $\epsilon = -3.0$ ); curve B from the Debye model; curve C from the approximate Debye model of Kagan and Iosilevskii with a Lorentzian resonance; curve D from the extremely low-frequency limit. The frequencies of resonances are circled.

problem by Kagan and Iosilevskii<sup>20</sup> who have taken a simplified Debye model for the perfect crystal. An important aspect of the calculation is the determination of a resonance frequency for the heavy ion, at which the real part of the argument of the logarithm in (12) vanishes. Because the imaginary part of the argument increases with frequency, the maximum slope of  $\theta(\omega)$  occurs at somewhat lower frequency. In Fig. 3, the resonance condition for the actual Al crystal is compared with that for the Debye model and its low- $\omega$  limit. The Debye model seriously overestimates the resonance frequency because the  $\omega=0$  limit of  $P_{00}(\omega)$  is too high in the Debye model and because the curvature at low  $\omega$  is of the wrong sign.

The zero-frequency limit of  $-mP_{00}(\omega)$  is the inverse second moment of the vibrational spectrum, which is underestimated by neglecting the transverse modes. Indeed, if the spectrum is considered to be the sum of longitudinal and transverse spectra with  $\frac{2}{3}$  of the modes in the transverse branches with cutoff frequency  $\omega_T$ ,<sup>28</sup>

$$\omega_m^2 \langle \omega^{-2} \rangle = 3 + 2[(\omega_m/\omega_T)^2 - 1], \quad \geq 3. \quad (17)$$

<sup>28</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 128.

The negative curvature of  $P_{00}(\omega)$  for Al at low frequency arises from the square-root singularity in  $g(\omega)$  at  $\omega/\omega_m \approx 0.43$  (see Fig. 6). Such features of the transformation in (7) can be seen by integrating this equation once by parts,

$$P_{00\alpha\beta}(\omega) = -\frac{\delta_{\alpha\beta}}{m} \int_0^\infty W(\omega, \omega') g^{(1)}(\omega') d\omega'. \quad (18)$$

The function  $W$  is a logarithmic window through which the derivative  $g^{(1)}(\omega') \equiv dg(\omega')/d\omega'$  enters the Green's function,

$$W(\omega, \omega') = \frac{1}{2\omega} \ln \left| \frac{\omega + \omega'}{\omega - \omega'} \right|. \quad (19)$$

The strongly positive  $g^{(1)}(\omega)$  at the lowest singularity forces the Green's function to decrease. This singularity continues to be important as the Green's function rises slowly until the second singularity at  $\omega/\omega_m \approx 0.59$ , where  $g^{(1)}(\omega)$  is strongly negative. In the Debye model, however,

$$\begin{aligned} g^{(1)}(\omega) &= 6\omega/\omega_m^3 - 3\delta(\omega - \omega_m)/\omega_m, & \omega \leq \omega_m \\ &= 0, & \omega > \omega_m. \end{aligned} \quad (20)$$

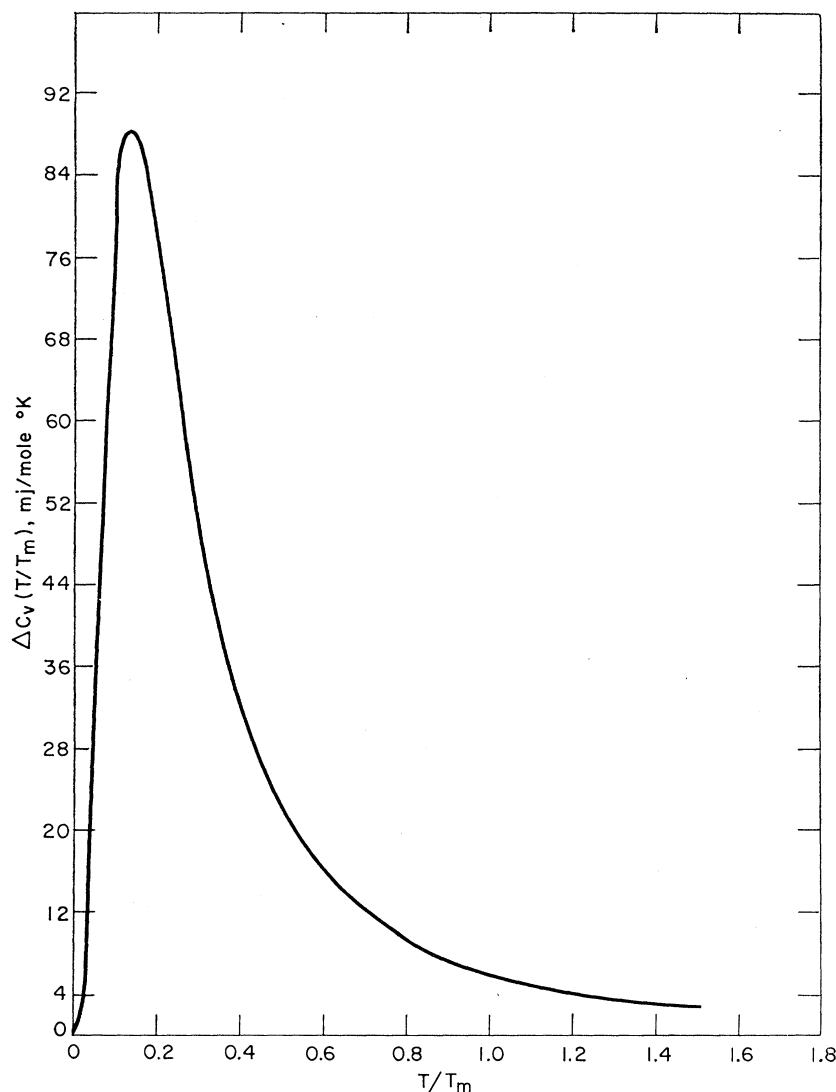


FIG. 5. Extended calculation of the enhanced specific heat in the harmonic approximation.  $T_m = 472.7^\circ\text{K}$ , for  $\text{Al}_{99.05}\text{Ag}_{0.95}$ .

The sharp negative contribution due to the cutoff at  $\omega_m$  produces the positive curvature over the whole frequency range which must be considered as unrealistic.

In Fig. 4, the phase shifts calculated from several models are compared. The phase shift in the Debye model is

$$\theta(\omega) = 3 \tan^{-1} \left\{ \frac{-1.5\pi\epsilon y^3}{1 - 1.5\epsilon y^2 [y \ln |(1+y)/(1-y)| - 2]} \right\}, \quad (21)$$

where  $y = \omega/\omega_m$  and where the principal value of the arctangent is taken to be  $0 \rightarrow \pi$ . Kagan and Iosilevskii have approximated the denominator above with the low-frequency term  $1 + 3\epsilon y^2$ , a Lorentzian form for the resonance, equivalent to setting the resonance frequency equal to  $(-\epsilon\langle\omega^{-2}\rangle)^{-1/2}$  as in curve C of Fig. 3. For

extremely low temperatures, lower than those of our experiments, the resonance nature of the defect vibrations might be neglected altogether by calculating the specific heat of a crystal with atoms of the average mass  $(1-c)m + cm'$ . This low-frequency limit corresponds to a phase shift which is the first term (in  $y^3$ ) in the expansion of the arctangent in (21) [Fig. 4, curve D] and gives a specific-heat enhancement proportional to the specific heat of the perfect crystal  $\Delta C_L = -1.5c\epsilon C_L$ , as noted in Ref. 20 and by Lehman *et al.*<sup>29</sup> Note that curves B, C, and D based on a Debye model with  $\omega_D = \omega_m$  would agree somewhat better at low frequency with curve A if an experimental Debye frequency ( $\approx 430^\circ\text{K}$ ) were used for a cutoff. Since the phase shift is multiplied by an exponentially decreasing function, which decreases faster with lower temperature, the

<sup>29</sup> G. W. Lehman, J. A. Cape, R. E. DeWames, and D. H. Leslie, *Bull. Am. Phys. Soc.* 9, 251 (1964).

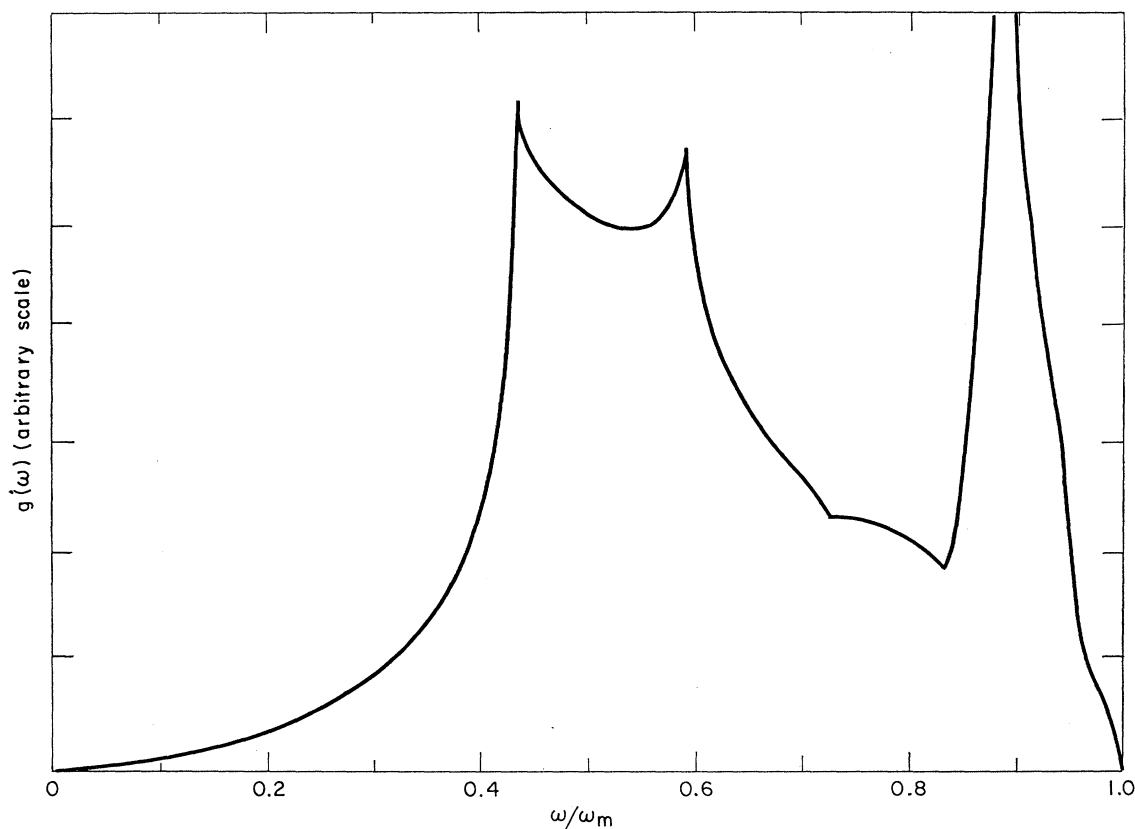


FIG. 6. The density of vibrational states from Ref. 26.

low-frequency part of  $\theta$  is most important. Nevertheless, the Debye-model expressions overestimate the specific heat for a given resonance frequency because of the large value of the phase shift at large  $\omega$ . For  $T \sim \Theta_D/20$ , the error is significant. However, since the Debye-model overestimates the resonance frequency as well, there is some tendency for the errors to cancel. In the case of Al:Ag alloy, the latter effect dominates, and the Debye model ultimately underestimates the specific-heat enhancement. Although the Debye model might well represent the low-temperature specific heat of a pure crystal, the resonance character of the lattice spectrum in the impure case depends upon the

whole of the perfect-crystal spectrum, for which the Debye model is quantitatively unreliable.

#### ACKNOWLEDGMENTS

We wish to thank Dr. R. M. Nicklow for providing a numerical density of states for Al and Dr. G. W. Lehman for a helpful discussion. We are indebted to Z. Sungaila for technical aid and to R. Bane and P. Peterson for the chemical analyses of the samples. Part of this work was done while W. M. Hartmann was partially supported by Michigan State University National Science Foundation Science Development Grant No. GU-2648.