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Electronic Specific Heat of α-Phase Alloys Based on Copper and Silver

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Electronic-specific-heat measurements have been made, in the liquid-helium temperature range, in the α-phase fcc solid solutions of the following systems based on Cu or Ag: Cu-Ni, Cu-Zn, Cu-Ga, Cu-Ge, Ag-Ga, Ag-Ge, and Ag-In. An initial increase in the electronic-specific-heat coefficient γ has been observed in all systems on alloying, and the initial electron-concentration derivatives of the density of states at the Fermi level, as indicated by the value of the coefficient $[\partial \ln N(E)_F/\partial \mathfrak{z}]_V$ are about 0.25 for all systems. The influence of atomic volume, as indicated by the coefficient $[\partial \ln N(E_F)/\partial \ln V]_{\mathfrak{z}}$, appears to be negligible. At higher solute concentrations, the trend of γ and the limiting Debye temperature Θ_D do not superimpose when scaled to the same electron concentration. The above results are discussed in terms of the electronic band structure and the theories that take into account electron-impurity interactions, electron-phonon interactions, and volume effects.

I. INTRODUCTION

The measurement of the electronic specific heat provides one of the very useful methods for studying the electronic structure of metals. Its application to the study of the alloy phases based on the noble metals has become of particular interest following the determination, by means of a number of new techniques, of the topography of the Fermi surface in copper, silver, and gold.[1] In all three cases, the existence of contact between the Fermi surface and the centers of the $\{111\}$ faces of the Brillouin zone has been well established. In terms of simple models of the band structure,[2] this suggests that the density of states at the Fermi level should decrease initially when the noble metals are alloyed with elements whose addition increases the electron concentration $\mathfrak{z}$. The magnitude of the electronic-specific-heat coefficient γ may be considered to give a measure of the density of states of the conduction electrons at the Fermi level. Therefore, measurements of the dependence of γ on alloying additions have been of special interest in testing the validity of the rigid-band model, and other factors such as the possible enhancement of the γ values by many-body effects, and the effect of changes in the atomic volume.

Recently, a number of low-temperature specific-heat investigations have been reported, with the specific goal of studying the band structure of the α phases, i.e., the terminal solid solutions based on the noble metals. The published results for a number of systems based on copper and silver[3] indicate that only very small changes occur in the density of states on alloying. The available data show, in addition, a considerable scatter of data points, chiefly owing to experimental difficulties. For example, opposite trends with solute concentration have been reported for the initial derivative of γ with respect to $\mathfrak{z}$ in Cu-Zn α-phase alloys; both a positive value[4] and a negative value[5] have been suggested. The present authors have repeated very carefully the measurements for this alloy system and also made similar measurements for several other systems, using a newly designed calorimeter. In this paper, in addition to the Cu-Zn data, we report the low-temperature specific-heat data for alloys within the face-centered-cubic α phase of the following alloy systems: Cu-Ni, Cu-Ga, Cu-Ge, Ag-Ga, Ag-In, and Ag-Ge.

II. EXPERIMENTAL DETAILS AND RESULTS

The details of the calorimeter arrangement are shown in Fig. 1. A mechanical heat switch was employed to cool the sample. A carbon resistor, used as a thermometer, was buried in a small screw made of pure copper (G) screwed into each sample. The heater (H) was made of manganin wire (0.05 mm in diameter and 200 cm in length), which was directly wound around the sample and was bonded with the GE-7031 varnish (using less than 0.01 g in weight). The resistance of the heater was about 460 Ω at liquid-helium temperatures. The combined mass of (G) and (H) was only 0.5 g, which is about $\frac{1}{200}$ of the mass of the sample to be measured. We estimate that the maximum possible error due to a contribution from these addenda to the coefficient γ and to the Debye temperature Θ_D is not greater than ± 0.0005 mJ/mole deg^2 and $\pm 0.5\,^{\circ}$K, respectively. In any case, the same

TABLE I. Electronic-specific-heat coefficient (γ) and Debye temperature (Θ_D) of pure copper.

Source	γ (mJ/mole deg^2)	Θ_D (°K)
Mitsubishi Metal Co.	0.690 ± 0.002	342.2 ± 0.8
Argonne Cu[a]	0.688 ± 0.002	344.9 ± 0.6
Mellon Cu[b]	0.687 ± 0.002	341.5 ± 0.6

[a] This was used as a standard reference sample for checking the low-temperature calorimeter, and was kindly supplied to us by Dr. D. W. Osborne and Dr. H. E. Flotow of Argonne National Laboratory. A similar sample measured by D. L. Martin (Ref. 6), yielded $\gamma = 0.6915 \pm 0.0034$ mJ/mole deg^2, $\Theta_D = (345.8 \pm 1.2)$ °K.

[b] This sample was prepared at the Mellon Institute of Science. The data on this sample are by Isaacs and Massalski (Ref. 5) ($\gamma = 0.698 \pm 0.002$ mJ/mole deg^2, $\Theta_D = 342.3$ °K). The origin of the copper used in this sample is American Smelting and Refining Company.

screw and identical heater wires were used with all samples, thus further minimizing the difference of the contribution of each addendum to the total specific heat. Niobium wires (0.04 mm in diameter, 600 mm in length) were used as lead wires from (G) and (H) to the vacuum seal (I) to attain a good thermal insulation. The samples were fixed tightly with thin nylon threads in order to prevent vibration. The samples were about 120 g in weight, 22 mm in diameter, and 44 mm in length. They were cast from very pure materials (99.999% or more pure), and special attention was paid during casting, handling, and processing to prevent possible ferromagnetic impurities. Casting was done in quartz tubes under vacuum. All samples were annealed after casting. Chemical analysis was performed in each case to confirm the exact composition, and metallographic examination was done to check for possible solute segregation. In addition, spectroscopic analysis was carried out to confirm the absence of ferromagnetic impurities. This analysis showed that the ferromagnetic impurities of Fe, Co, and Ni were of the order of ~1–2 ppm, or less.

An Allen-Bradley carbon resistor (47 Ω, 0.1 W) was used as a thermometer. Such a resistor has been known to lose the reproducibility of the relation between its resistance and temperature, especially after cycling between liquid-helium temperature and room temperature. Therefore, the carbon resistor was recalibrated following each measurement, using the vapour pressure of helium gas and the 1958 liquid-helium temperature scale. The initial test of the calorimeter performance was done by measuring three samples of pure copper. The results of these measurements are given in Table I. They show good agreement with data published in the literature.[6]

In the temperature range employed in the present experiments, the specific heat of a normal metal or alloy may be expressed in the usual form:

$$C/T = \gamma + \alpha T^2 , \tag{1}$$

where α and γ are lattice- and electronic-specific-heat coefficients, respectively. As is well known, γ is proportional to $N(E_F)$, the density of states of the conduction electrons at the Fermi level, by the expression $\gamma = \frac{1}{3}[\pi^2 k^2 N(E_F)]$, where k is the Boltzmann constant, and α is related to Debye temperature Θ_D by the expression $\Theta_D = (12\pi^4 R/5\alpha)^{1/3}$, where R is the gas constant.

The plotting of the calorimeter data and the evaluation of the γ and Θ_D values were done in the usual manner, employing the least-squares procedure. All the data for the alloy systems reported in the present investigation have shown linear behavior when expressed in the form given by Eq. (1). The values of γ and Θ_D are given in Table II. A typical deviation curve obtained with two measurements of a copper sample is shown in Fig. 2. The trends of γ and Θ_D with $\mathfrak{z}$ in Cu- and Ag-based systems are shown in Figs. 3–6. The initial derivatives of γ with respect to $\mathfrak{z}$ are plotted in Fig. 7 as a function of the initial volume-per-atom change with respect to $\mathfrak{z}$. Similar plots are also shown in Figs. 8 and 9 for the initial derivatives of Θ_D. The data for the Cu-Ge alloys and pure Cu were obtained with the use of a semiautomated calorimeter in which two samples are measured at the same time. The details of this technique will be published shortly.[12]

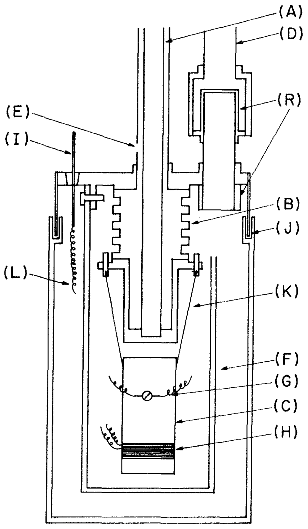

FIG. 1. Schematic cross section of the calorimeter assembly: (A) cupro-nickel shaft, (B) bellows, (C) sample, (D) cupro-nickel evacuation tube, (E) liquid-helium inlet into bellows, (F) copper frame (part of the heat-switch assembly), (G) carbon thermometer, (H) heater, (I) vacuum seal, (J) Wood's metal seal, (K) supporting nylon string, (L) niobium wire, (R) radiation shields.

TABLE II. Electronic-specific-heat coefficient γ and Debye temperature Θ_D.

Alloys	Concentration (at.% solute)	γ (mJ/mole °K^2)	Θ_D (°K)
pure Cu		0.690 ± 0.002	342.2 ± 0.8
Cu-Ni	1.0	0.697 ± 0.003	341.1 ± 1.0
	2.4	0.732 ± 0.002	344.9 ± 0.8
	4.4	0.808 ± 0.002	346.3 ± 0.8
Cu-Zn	2.6	0.694 ± 0.002	339.7 ± 0.6
	5.5	0.698 ± 0.002	337.7 ± 0.6
	8.2	0.709 ± 0.002	337.0 ± 0.6
	12.2	0.714 ± 0.002	334.7 ± 0.6
	20.0	0.711 ± 0.003	328.4 ± 0.7
	30.0	0.710 ± 0.003	317.9 ± 0.6
Cu-Ga	1.0	0.702 ± 0.002	342.2 ± 0.8
	3.0	0.706 ± 0.002	340.0 ± 0.8
	5.0	0.709 ± 0.002	338.0 ± 0.8
	7.5	0.721 ± 0.002	335.1 ± 0.8
	10.0	0.736 ± 0.002	332.8 ± 0.8
	15.0	0.741 ± 0.003	319.0 ± 1.0
	19.9	0.765 ± 0.002	300.2 ± 0.8
Cu-Ge	4.0	0.717 ± 0.005	330.9 ± 1.8
	10.0	0.746 ± 0.003	314.5 ± 1.0
pure Ag		0.641 ± 0.002	223.4 ± 0.5
Ag-Ga	2.1	0.648 ± 0.002	225.1 ± 0.5
	4.3	0.659 ± 0.004	222.9 ± 1.0
	8.0	0.687 ± 0.002	219.7 ± 0.5
	11.8	0.714 ± 0.002	215.2 ± 0.5
Ag-In	3.7	0.653 ± 0.002	224.7 ± 0.5
	6.2	0.665 ± 0.002	223.1 ± 0.5
	9.6	0.672 ± 0.002	219.7 ± 0.5
Ag-Ge	4.0	0.665 ± 0.004	221.3 ± 1.0
	8.2	0.724 ± 0.004	213.9 ± 1.0

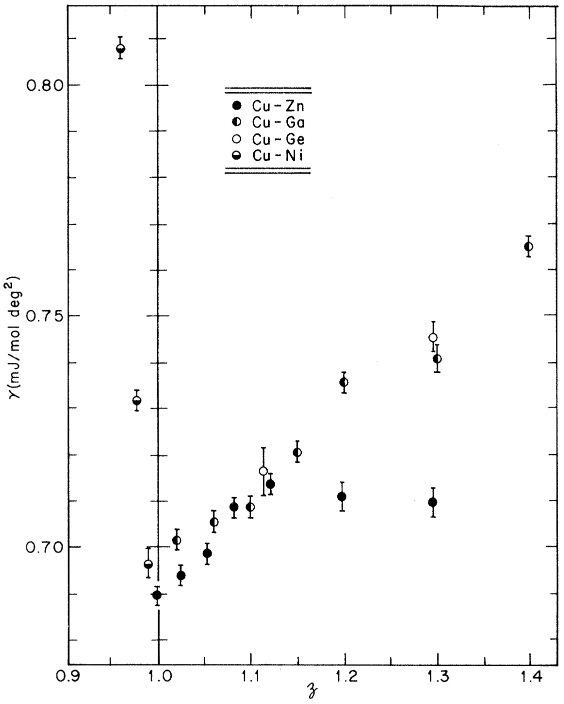

FIG. 3. Plot of the electronic-specific-heat coefficient γ as a function of the electron concentration for Cu-based systems. In the case of Ni the valence contribution is assumed to be zero.

III. DISCUSSION

A. Band-Structure Contributions

Following the recent theoretical discussions in the literature, the most likely alloying contributions to the coefficient γ arise from the changes in the band structure, from the many-body interactions, and from possible size effects. As shown in Fig. 4, the variation of the γ values with $\mathfrak{z}$ is quite similar from system to system for the three silver-based systems measured in the present experiment. In the case of Cu-Zn and Cu-Ga alloys, however, the γ trends are initially similar but diverge at higher values of $\mathfrak{z}$ (Fig. 3). The present results indicate also that the initial derivative of γ with $\mathfrak{z}$ for Cu-Zn alloys is positive, as obtained by Veal and Rayne,[4] and not negative as reported previously.[5] In fact, the initial derivatives of γ with respect to $\mathfrak{z}$ are positive for all alloy systems reported here. This suggests that the density of states at the Fermi level for α-phase alloys of the noble metals must increase with increasing $\mathfrak{z}$. Thus, as has already been pointed out by a number of authors,

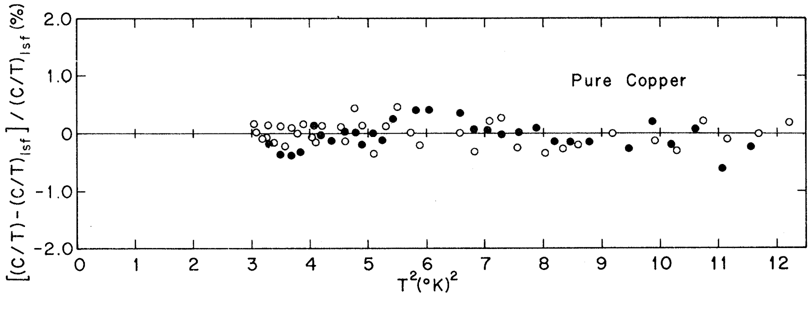

FIG. 2. Deviation from least-square-fit (lsf) curve for pure Cu.

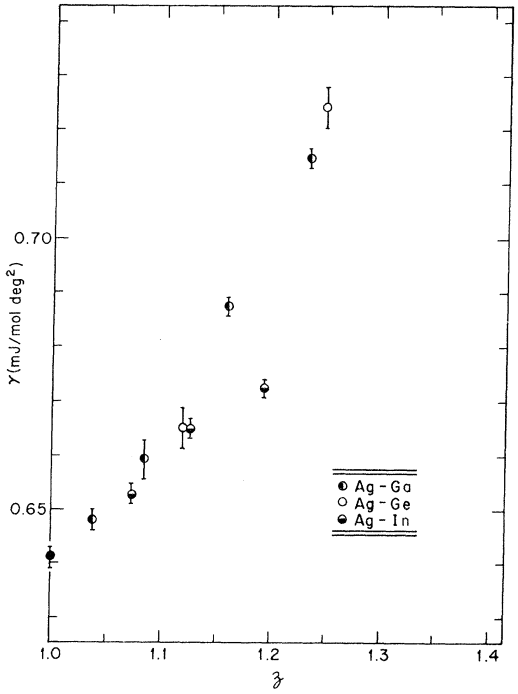

FIG. 4. Plot of the electronic-specific-heat coefficient γ as a function of the electron concentration for Ag-based systems.

a simple model, based on the rigid-band concept, is clearly not applicable to these alloys.

Ziman[13] has calculated the density of states for a noble metal and its alloys as a function of $\mathfrak{z}$, using the eight-cone model for the Brillouin zone and making the energy gap across the $\{111\}$ plane a variable parameter. Each density-of-states curve in this model corresponds to a rigid-band calculation for a fixed energy gap. The use of the value of the band gap for Cu, as deduced from the de Haas–van Alphen data, yields a trend in the density of states which correctly indicates the Brillouin-zone contact just below the Fermi level, but which shows a decrease of $N(E_F)$ with increasing $\mathfrak{z}$ [see Eq. (4) and below]. An increasing trend in γ with $\mathfrak{z}$ would result from a model with increasing band gaps on alloying, but this seems unlikely in view of some alloying features[14] which suggest that the band gaps most likely decrease. On the other hand, it seems desirable to take into account the contributions to γ resulting from the many-body effects, which would apply both to pure metals and to alloys, the contribution from level-broadening effects, resulting from the disturbance of the periodic potential by the solute atoms, and finally the contribution from size effects.

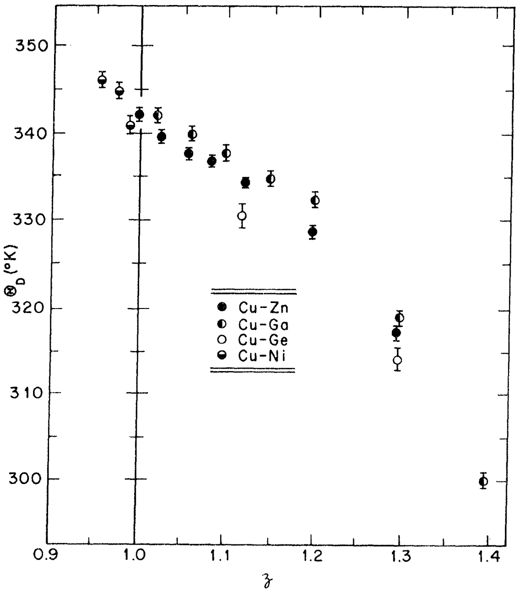

FIG. 5. Plot of the Debye temperature Θ_D as a function of the electron concentration for Cu-based systems.

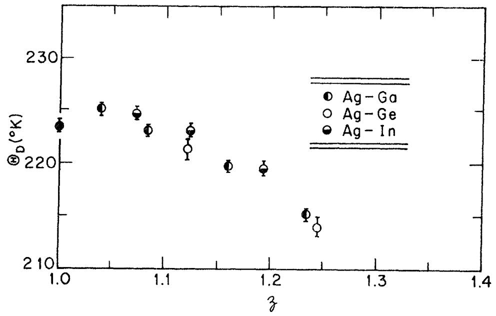

FIG. 6. Plot of the Debye temperature Θ_D as a function of electron concentration for Ag-based systems.

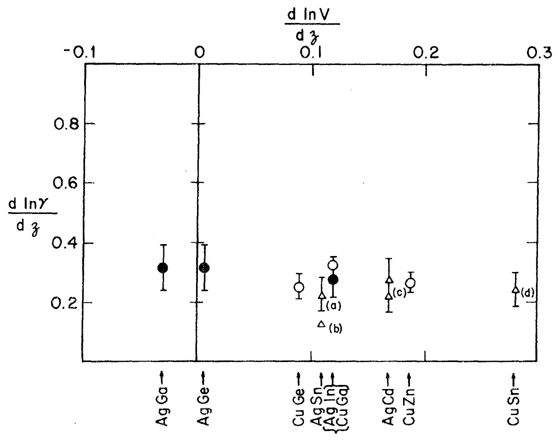

FIG. 7. Relation between the initial derivatives of $\gamma/\mathfrak{z}$ vs $V/\mathfrak{z}$. For (a), (b), (c), and (d), see Refs. 7–10, respectively.

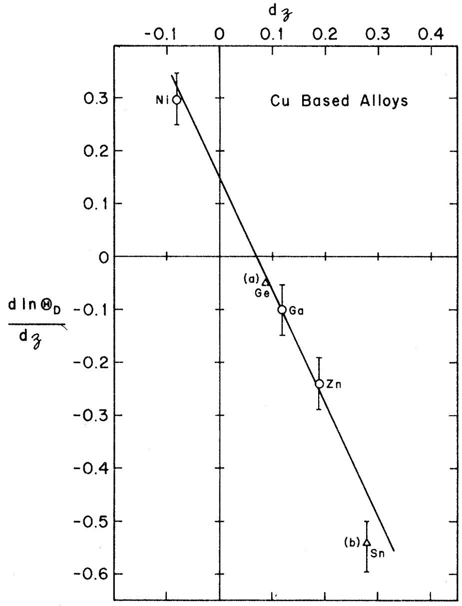

FIG. 8. Relation between the initial derivatives of $\Theta_D/\mathfrak{z}$ vs $V/\mathfrak{z}$ in Cu alloys. For (a) and (b), see Refs. 11 and 10, respectively.

B. Electron-Electron, Electron-Phonon, and Electron-Impurity Interactions

In discussing the electronic specific heat, it is convenient to define the thermal effective mass m_t^* as the ratio of the density of states at the Fermi level E_F of a real metal, $N(E_F)$, to the corresponding value for free electrons, $N_0(E_F)$:

$$m_t^* = N(E_F)/N_0(E_F) = \gamma/\gamma_0 . \qquad (2)$$

The thermal mass m_t^* deviates from unity when the density of states at the Fermi level is altered by the existence of the Brillouin-zone boundaries and when many-body effects, such as electron-phonon interactions, are present. The m_t^* obtained in the present experiment is equal to $(1.37 \pm 0.01)m_e$ for copper, which may be partly explained by the distortion of the Fermi surface. Recent calculations of energy bands for Cu,[15,16] using the Korringa-Kohn-Rostoker method, yielded a nonspherical Fermi surface touching the $\{111\}$ planes of the Brillouin zone, and the calculated density of states at the Fermi level[16] corresponded to an effective mass (thermal band mass) of $(1.25 \pm 0.01)m_e$. To explain the difference between the theoretical value dictated by the band structure above and the experimental mass of $(1.37 \pm 0.01)m_e$, many-body effects, which include electron-electron and electron-phonon interactions, must be considered. These effects cannot as yet be treated rigorously for actual metals but may be considered for metals with a spherical Fermi surface. Recent theoretical work[17,18] on such metals suggests that contributions from the electron-electron interactions are negligible when compared with the electron-phonon interactions. At the same time, evidence obtained from the measurement of cyclotron masses suggests that there is little anisotropy in the electron-phonon interactions in different directions and that the cyclotron masses of electrons corresponding to the belly and the neck orbits of copper are equally enhanced by about the same amount, i.e., about 10–15%, when compared with calculated values.[15,16] If the lack of anisotropy in the cyclotron mass is accepted to mean that this enhancement will also be similar (and isotropic) for the thermal-mass enhancement, then the experimental thermal-mass value of $(1.37 \pm 0.01)m_e$ for copper may be explained by assuming that the electron-phonon-interaction enhancement is responsible for the ~ 10% difference between the calculated $[\sim(1.22\text{–}1.28)m_e]$ and experimental $[(1.37 \pm 0.01)m_e]$ values. For Ag, on the other hand, the presently derived value of m_t^* is $(0.99 \pm 0.01)m_e$, and the m_b^* determined by a band calculation[19] is $(0.98 \pm 0.01) \times m_e$. Thus, the difference between the m_t^* and m_b^* is only ~ 1%, which is much smaller than the difference for Cu. We conclude that the enhancement factors, defined as

$$\lambda = m_t^*/m_b^* - 1 , \qquad (3)$$

are 0.10 and 0.01 for Cu and Ag, respectively.

The situation is less clear in the case of alloys. Electron-impurity interactions cause energy-level broadening because the electrons perturbed by the less periodic scattering potential cannot be described in terms of Bloch states.[20,21] According to Haga,[22,23] as a result of level broadening all states

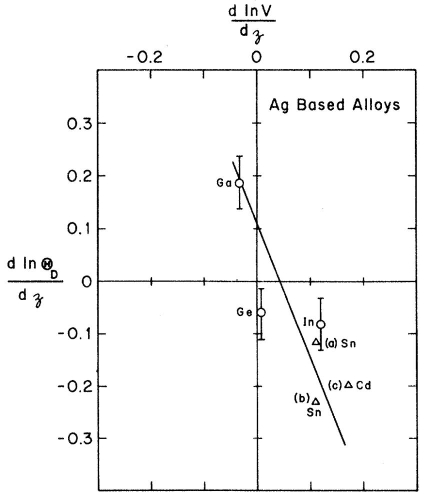

FIG. 9. Relation between the initial derivatives of $\Theta_D/\mathfrak{z}$ vs $V/\mathfrak{z}$ in Ag alloys. For (a), (b), and (c), see Refs. 7–9, respectively.

in the neighborhood of the Fermi level contribute to $N(E_F)$, including the d band with a large density of states. At the same time the enhancement of the specific heats due to the electron-phonon interaction tends to decrease on alloying as the concentration of impurity atoms is increased. Thus, the decrease of the γ values in the system Ag-Au, in which the size effect is small and the nominal electron concentration does not change, has been explained by assuming that the contribution to γ from the band structure is more or less linear between the two noble metals, but the electron-phonon enhancement is greatest in the pure metals and diminishes substantially on alloying.[22]

The increasing trends in the electronic specific heats of copper-based alloys have been interpreted recently in terms of a contribution from the d band through the energy-level broadening caused by the impurity potentials. Haga[23] has shown that the trend of the γ values in the Cu-Zn system may be explained by postulating a certain level-broadening value for the level breadth of the d states caused by the introduction of the Zn atoms. This broadening appears to be sufficient to cause a positive contribution to γ on alloying, which outweighs any possible decrease due to the decreasing band gaps, the broadening and decreasing contribution from the s band caused by a shift in the Fermi level, and the diminishing of the electron-phonon enhancement. Since level broadening of the d states is characteristic of each individual alloying element, it is certainly surprising that the initial slopes of the γ trends on alloying, when normalized in terms of $\mathfrak{z}$ and atomic volume, are found to be more or less the same for the different alloy systems reported in this paper (see Fig. 7). Furthermore, the d-level broadening effect can hardly explain the present results that indicate a very similar value of the $d(\ln\gamma)/d\mathfrak{z}$ parameter for both silver- and copper-based alloys, despite the fact that the energy difference between the top of d band and the Fermi level in silver is approximately twice as large as that in copper. In addition, the model for the Cu-Zn alloys appears to be inadequate to account for the differences observed in other related systems, for example, between the data for the dilute and concentrated alloys in the Cu-Zn and Cu-Ga systems. Initially, Zn, Ga, and Ge in copper have the same effect on γ when scaled according to the relative valence, but at higher solute concentrations this no longer holds true.

On the other hand, the electron-phonon interaction has been considered recently to play the main role in the enhancement of γ values of the lead-based alloys,[24] in the system Pb-Tl and Pb-Bi, and also in the α phase of In-Sn alloys.[25] Comparison of the measured γ values with the tunneling-effect measurements in the lead-based alloy systems has provided a relation between γ and the electron-phonon enhancement factor λ. According to the tunneling measurements, the enhancement factor λ increases with the increasing electron concentration $\mathfrak{z}$ for compositions near pure Pb. If the same situation holds for the noble-metal alloys, the increasing trend of γ values can be interpreted.

Another approach to the enhancement of γ values is suggested by Stern,[26] who interprets the observed increases with increasing $\mathfrak{z}$ in copper- or silver-based alloys in terms of the enhancement of the density of states by the screening electrons around impurity atoms.

The observed rapid increase of γ with respect to nickel contents in Cu-Ni alloys is most likely the result of the presence of virtual bound states at the Fermi level in such alloys. Until the exact trends of the γ and Θ_D coefficients are determined near the termination of the α phase in copper and silver alloys, and in the intermediate phases that follow them, detailed speculation about the influence of the d band seems premature.

C. Volume-Per-Atom and Electron-Concentration Dependence

The dependence of γ on volume effects was first taken into account by Green,[27] who used two indefinite parameters to describe the behavior of γ as a function of the atomic volume. We consider the electron concentration and the volume dependence of γ for the case of the noble-metal alloys. The result based on Ziman's eight-cone model[13] is shown to be in disagreement with the experimental data.

Assuming that the density of states at the Fermi level E_F may be expressed as a function of electron-per-atom ratio $\mathfrak{z}$ and volume per atom V, we write

$$\frac{d\ln N(E_F)}{d\mathfrak{z}} = \left(\frac{\partial \ln N(E_F)}{\partial \mathfrak{z}}\right)_V + \left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} \left(\frac{d\ln V}{d\mathfrak{z}}\right) . \tag{4}$$

The experimental values given in Table II are plotted in Fig. 7 in terms of the derivatives $(\partial \ln \gamma / \partial \mathfrak{z})_V$ against $(\partial \ln V / \partial \mathfrak{z})$, where V represents volume per atom as obtained from the literature.[4] The resulting plot is fairly well represented by a straight line of the form

$$\left(\frac{d\ln\gamma}{d\mathfrak{z}}\right)_{\mathfrak{z}=1} = A + B\left(\frac{d\ln V}{d\mathfrak{z}}\right)_{\mathfrak{z}=1} ,$$

provided that we assume that in each alloy system the behavior of γ vs $\mathfrak{z}$ is linear, and is correctly represented by points from both dilute and concentrated alloys. From Fig. 7 we conclude that for the presently examined alloys

$$A = \left(\frac{\partial \ln N(E_F)}{\partial \mathfrak{z}}\right)_V \approx 0.25, \quad B = \left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} \approx 0 .$$

On the other hand, the parameter $[\partial \ln N(E_F)/\partial \mathfrak{z}]_V$ has been estimated from the eight-cone model with a fixed energy gap [$0.17 < u < 0.20$, where $u = E_G/(\hbar^2G^2/m)$] to be -0.5, and from the band calculation by Faulkner *et al.*[16] to be -0.33. Both these theoretical values disagree with the above experimental value in sign and magnitude.

In order to evaluate the volume dependence of γ, we write for the density of states at the Fermi level E_F

$$N(E_F) = (V/4\pi^3)\, S_F(V, E_G)\, \langle (1/v)(V, E_G)\rangle_{\mathrm{FS}}\,, \tag{5}$$

where E_G is the energy gap across the $\{111\}$ faces of the Brillouin zone. V is the volume, S_F is the Fermi-surface area, and v is the group velocity of the electrons on the Fermi surface. Differentiation with respect to volume yields

$$\left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} = \frac{\partial \ln V}{\partial \ln V} + \left(\frac{\partial \ln S_F}{\partial \ln V}\right)_{E_G} + \left(\frac{\partial \ln\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln V}\right)_{E_G} + \left(\frac{\partial \ln S_F}{\partial \ln E_G}\right)_V \frac{d \ln E_G}{d \ln V} + \left(\frac{\partial \ln\langle 1/v\rangle_{\mathrm{SF}}}{\partial \ln E_G}\right)_V \frac{d \ln E_G}{d \ln V}\;. \tag{6}$$

The first three terms are easily estimated as

$$\frac{\partial \ln V}{\partial \ln V} = 1\,,$$

$$\left|\frac{\partial \ln S_F}{\partial \ln V}\right|_{E_G} = -\frac{2}{3} \quad (\text{since } S_F \propto \langle K^2\rangle \propto V^{-2/3})\,,$$

$$\left|\frac{\partial \ln\langle 1/v\rangle_{\mathrm{SF}}}{\partial \ln V}\right|_{E_G} = \frac{1}{3} \quad (\text{since } \langle 1/v\rangle \propto \langle m^*/k\rangle \propto V^{1/3})\,,$$

provided that the Fermi surface is treated as an undistorted sphere. Even if the belly and neck portions of the Fermi surface are considered in the eight-cone model, the departure from the values of $-\frac{2}{3}$ and $\frac{1}{3}$, given above, is negligibly small. The remaining two terms in Eq. (6) are combined into

$$\left(\frac{\partial \ln S_F}{\partial \ln E_G}\right)_V \frac{d \ln E_G}{d \ln V} + \left(\frac{\partial \ln\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln E_G}\right)_V \frac{d \ln E_G}{d \ln V} = \frac{d \ln E_G}{d \ln V}\left(\frac{\partial \ln S_F\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln E_G}\right)_V .$$

We estimate the value of the partial derivative on the right-hand side of the above equation from Ziman's model, where $u = E_G/(\hbar^2G^2/m)$, i.e., $u \propto E_G V^{2/3}$ and $S_F\langle 1/v\rangle_{\mathrm{FS}}$ is proportional to γ/γ_0 in Ziman's notation. This yields for $0.17 \lesssim u \lesssim 0.20$

$$\left(\frac{\partial \ln S_F\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln u}\right)_V \equiv \beta \cong \tfrac{1}{8}$$

and

$$\left(\frac{\partial \ln S_F\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln E_G}\right)_V \frac{d \ln E_G}{d \ln V} = \beta\left(\frac{d \ln E_G}{d \ln V} + \frac{2}{3}\right). \tag{7}$$

Summing up all terms in Eq. (5), we get

$$\left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} = \frac{2}{3} + \beta\left(\frac{d \ln E_G}{d \ln V} + \frac{2}{3}\right)\;. \tag{8}$$

Now the dependence of E_G on volume will be estimated. The energy gap E_G is proportional to the Fourier component of the lattice potential $U(\vec{r})$. The Fourier component is calculated for the case of the Thomas-Fermi potential, i.e.,

$$U(\vec{r}) = \sum_{\vec{l}} e\left(\frac{\exp(-q_s|\vec{r} - \vec{l}|)}{|\vec{r} - \vec{l}|}\right)\,,$$

where $\vec{l}$ denotes the lattice site and $q_s^2 = 4\pi e^2 N(E_F)/V$. Thus we obtain

$$\frac{d \ln E_G}{d \ln V} = -\frac{1}{3} - \frac{2(q_s/G)^2}{1 + (q_s/G)^2}\left[\frac{1}{2}\left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} - \frac{1}{6}\right], \tag{9}$$

where $\frac{1}{2}\vec{G}$ is the reciprocal vector to a $\{111\}$ face. Substituting Eq. (9) into Eq. (8), we finally have

$$\left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} = \frac{2}{3} + \frac{\beta}{3(\beta t^2 + t^2 + 1)}\,, \tag{10}$$

where $t = q_s/|\vec{G}|$. The calculated volume dependence in terms of t is shown in Fig. 10. The Thomas-Fermi potential turns to the Coulomb potential when $t = 0$. With this potential $[\partial \ln N(E_F)/\partial \ln V]_{\mathfrak{z}}$ becomes $\frac{1}{3}(\beta + 2) \cong 0.70$, since $\beta = \frac{1}{8}$. On the other hand, in the case of $t = \infty$, the potential $U(\vec{r})$ becomes zero and $[\partial \ln N(E_F)/\partial \ln V]_{\mathfrak{z}}$ tends to $\frac{2}{3} \approx 0.66$, independent of β, which is the same value as expected from the free-electron model.[27] In actual metals, the value of the screening radius t is estimated to be less than unity. If t is assumed to be unity, we obtain

$$\left(\frac{\partial \ln N(E_F)}{\partial \ln V}\right)_{\mathfrak{z}} \cong 0.68\,, \tag{11}$$

which is contrary to the experimental indication given in Fig. 7, that this derivative is nearly zero.

We return now to the dependence of γ on $\mathfrak{z}$ and volume. As shown above, Ziman's model suggests a negative derivative, again contrary to experiment. Two models, by Clune and Green[24] and by Stern,[26] have been proposed to explain the increasing trend of γ with increasing $\mathfrak{z}$ in the noble-metal alloys. We consider here the effect of the electron-phonon interaction including the effect of level broadening, proposed by Haga.[22] Equation (5) may be written in the form

$$N(E_F) = (V/4\pi^3)\, S_F(VE_G)\, \langle (1/v)\,(VE_G)\rangle_{\mathrm{FS}}\, [1 + \lambda G(y)]\,, \tag{12}$$

where λ is the enhancement factor due to electron-phonon interaction, and $G(y)$ is the function which represents the dependence of the density of states at the Fermi level upon the magnitude y of the electron-impurity interaction. Nakajima and Watabe[17] give the following expression for λ for free elec-

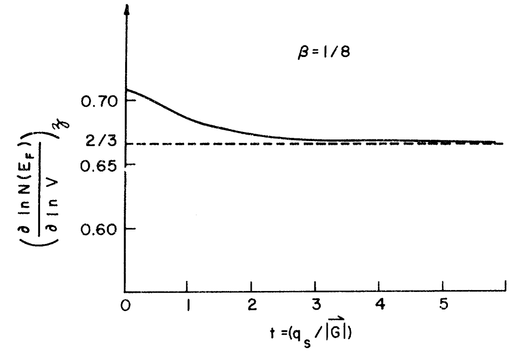

FIG. 10. Volume dependence of the density of states for noble-metal alloys expressed as a function of screening radius.

trons:

$$\lambda = \frac{E_F}{3\mathfrak{M}s^2}\,\frac{\rho}{\rho_i}\left(\frac{q_m}{2K_F}\right)^2 , \tag{13}$$

where ρ and ρ_i are electron and ion density per unit volume, respectively, s is velocity of sound for longitudinal phonons, and $\mathfrak{M}$ is the particle mass. The dependence of E_F and s on volume is easily obtained from the relationships

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\,(3\pi^2\rho)^{2/3} \propto V^{-2/3} ,$$

$$S^2 = \frac{k^2\Theta_D^2}{\hbar^2 q_m^2} = \left(\frac{k}{\hbar}\right)^2 (6\pi^2\rho_i)^{-2/3}\,\Theta_D^2 \propto V^{2/3}\,\Theta_D^2 .$$

It follows then that

$$\left(\frac{\partial \ln\lambda}{\partial \ln V}\right)_{\mathfrak{z}} = -\frac{4}{3} - 2\left(\frac{\partial \ln\Theta_D}{\partial \ln V}\right)_{\mathfrak{z}} . \tag{14}$$

We now make use of Figs. 8 and 9, from which the derivatives of the Debye temperature with respect to V and $\mathfrak{z}$ may be obtained. The values are as follows: for copper alloys $(\partial \ln\Theta_D/\partial \ln V)_{\mathfrak{z}} \approx -2.0$ and $(\partial \ln\Theta_D/\partial\mathfrak{z})_V \approx 0.1$, and for silver alloys $(\partial \ln\Theta_D/\partial \ln V)_{\mathfrak{z}} \approx -2.5$ and $(\partial \ln\Theta_D/\partial\mathfrak{z})_V \approx 0.2$. Using the value of $(\partial \ln\Theta_D/\partial \ln V)_{\mathfrak{z}}$ in Eq. (14), we obtain $(\partial \ln\lambda/\partial \ln V)_{\mathfrak{z}} \approx 2.66$ and 3.66 for Cu and Ag, respectively.

In order now to include the effect of level broadening on the density of states, we modify Eq. (14) to include Haga's $G(y)$ function:

$$\left(\frac{\partial \ln(1+\lambda G(y))}{\partial \ln V}\right)_{\mathfrak{z}} = \frac{\lambda G(y)}{1+\lambda G(y)}\left[\left(\frac{\partial \ln\lambda}{\partial \ln V}\right)_{\mathfrak{z}} + \left(\frac{\partial \ln G(y)}{\partial \ln V}\right)_{\mathfrak{z}}\right]. \tag{15}$$

The above additional contribution can now be added to Eq. (11). Following Haga, we take $G(y)$ to be nearly 1 for dilute alloys, which allows the value of $\lambda/(1+\lambda)$, estimated earlier for Cu as 0.1 and for Ag as 0.01, to be used in Eq. (15). We obtain for copper alloys

$$\left(\frac{\partial \ln N(E_F)}{\ln V}\right)_{\mathfrak{z}} = 0.68 + 0.1\left[2.66 + \left(\frac{\partial \ln G(y)}{\partial \ln V}\right)_{\mathfrak{z}}\right] . \tag{16}$$

The left-hand side of Eq. (16) is experimentally derived to be nearly zero. Therefore, the value of $[\partial \ln G(y)/\partial \ln V]_{\mathfrak{z}}$ should be large and negative if Haga's model is applicable. The value of $[\partial \ln G(y)/\partial \ln V]_{\mathfrak{z}}$ calculated directly using Haga's $G(y)$ function[22] turns out to be of negative sign, but the numerical value is too small to compensate the positive contribution of $(\partial \ln\lambda/\partial \ln V)_{\mathfrak{z}} \simeq 2.66$, established from Eq. (14). Therefore, the electron-phonon interaction, even corrected for level broadening, seems to be inadequate for explaining the experimentally obtained derivatives based on volume dependence.

D. Debye Temperature

The Debye temperature may also be expressed as a function of electron concentration and volume per atom:

$$\frac{d\ln\Theta_D}{d\mathfrak{z}} = \left(\frac{\partial \ln\Theta_D}{\partial\mathfrak{z}}\right)_V + \frac{\partial \ln\Theta_D}{\partial \ln V_{\mathfrak{z}}}\,\frac{d\ln V}{d\mathfrak{z}} . \tag{17}$$

The experimental results plotted in Figs. 8 and 9 for Cu- and Ag-based alloys, respectively, are presented as a relation between $d\ln\Theta_D/d\mathfrak{z}$ and $d\ln V/d\mathfrak{z}$. As shown in the figures, the data are well expressed as straight lines.

The quantity $\partial \ln\Theta_D/\partial \ln V$ can be expressed in terms of the linear expansion coefficient δ, compressibility κ, specific heat c_V, and volume V as follows:

$$-\frac{\partial \ln\Theta_D}{\partial \ln V} = -\frac{3V\delta}{\kappa c_V} \equiv \Gamma . \tag{18}$$

The Γ, the well-known Grüneisen constant, has been determined with Eq. (18) to be 1.96 and 2.4 for Cu and Ag alloys, respectively.[29] By comparison the values of $-\partial \ln\Theta_D/\partial \ln V$ determined from Figs. 8 and 9 are $+2.0$ and $+2.5$, for Cu and Ag alloys, respectively, showing a very good agreement with data based on the Grüneisen constant. Thus our measurements of Θ_D, and their volume dependence, show a remarkable self-consistency.

The Debye temperature is also coupled to the electronic structure through the electron-phonon interaction to the phonon field. We are currently exploring a possible interpretation of the $(\partial \ln\Theta_D/\partial\mathfrak{z})_V$ derivatives along these lines.

E. Conclusions

The electronic-specific-heat coefficients γ and the limiting Debye temperatures Θ_D have been determined by low-temperature specific-heat measurements for a number of α-phase alloys in the following systems: Cu-Ni, Cu-Zn, Cu-Ga, Cu-Ge, Ag-In, Ag-Ga, and Ag-Ge. The values of the initial slope of γ with respect to electron concentration, i.e., $(d\ln\gamma/d\mathfrak{z})_{\mathfrak{z}=1}$, can be expressed as a function of the initial slope of the volume-per-atom dependence on electron concentration, i.e., $(d\ln V/d\mathfrak{z})_{\mathfrak{z}=1}$, by the following relation for all the systems of Cu and Ag alloys measured in the present experiment:

$$\left(\frac{d\ln\gamma}{d\mathfrak{z}}\right)_{\mathfrak{z}=1}=A+B\left(\frac{d\ln V}{d\mathfrak{z}}\right)_{\mathfrak{z}=1}$$

where

$$A\equiv\left(\frac{\partial\ln\gamma}{\partial\mathfrak{z}}\right)_V\simeq 0.25\ ,\quad B\equiv\left(\frac{\partial\ln\gamma}{\ln V}\right)_{\mathfrak{z}}\simeq 0\ .$$

Quite unexpectedly, the experimental results for both Cu- and Ag-alloy systems are satisfied by the same values of A and B.

(ii) The value of $(\partial\ln\gamma/\partial\mathfrak{z})_V=0.25$ is substantially different from the value (-0.33) estimated from energy-band calculations and rigid-band assumption. We have not examined this discrepancy further in this paper. Other interpretations in the literature suggest that the answer lies in the contribution from electron-phonon interactions.

(iii) The volume dependence derivative of γ, $(\partial\ln\gamma/\partial\ln V)_{\mathfrak{z}}$, is determined in the present experiment to be nearly zero compared with the calculated value of $+0.68$, based only on the band effect. This value becomes of the general form $0.68+[\lambda/(1+\lambda)]$ $[2.67+(\partial\ln G/\partial\ln V)_{\mathfrak{z}}]$ for Cu alloys if the band effect, the electron-phonon interaction, and the level-broadening effect are combined. We were unable to improve the agreement between the experimental and the theoretical values by considering the level-broadening function of Haga, $G(y)$, because the term $2.67+(\partial\ln G/\partial\ln V)_{\mathfrak{z}}$ always remained positive.

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