Y in sample Bi II indicated a small shift of B_m from ~120 to ~145 G for a change of T from 10 to 1.2 °K.

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Low-Temperature Specific Heats in α-Phase CuSn Alloys

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Low-temperature specific-heat measurements have been made between 1.5 and 4.2 °K on a series of α-phase solid-solution alloys of Sn in Cu. The dependence of γ with $\mathfrak{z}$ (number of electrons per atom) is rather complex, the value of the initial derivative being much higher than that reported some years ago. The results are discussed in the light of recent band-structure calculations, charge-shielding effects, and Mössbauer spectra in α-phase CuSn alloys, as well as related experimental work on low-temperature specific heats in a number of systems based on the noble metals. A rapid decrease of Debye temperature with increasing solute concentration is attributed to the exceptionally large $d\ln V/d\mathfrak{z}$ value.

I. INTRODUCTION

The direct relationship between the electronic-specific-heat coefficient γ and the density of states at the Fermi level $N(E_F)$ has been established many years ago.[1] However, the experimental values of γ for pure simple metals are considerably larger than values computed from the expression $\gamma = \frac{1}{3}\pi^2 k_B^2 N(E_F)$, where k_B is Boltzmann's constant. The situation is even worse in the case of alloys where not only the measured values of γ but also the changes of γ on alloying disagree with simple models. For instance, the rigid-band models[2,3] predict that the electronic specfic heat of noble metals, whose Fermi surfaces are well known and topographically simple, should decrease upon alloying with polyvalent metals. The experimental results show in most cases the opposite behavior. The modified-rigid-band models[4,5] somewhat improve the situation but still cannot account satisfactorily for many experimentally observed features.

In an attempt to explain these discrepancies, different theories incorporate the effects of the valence and size of the solute atoms as well as many-body effects, such as electron-phonon, electron-electron, and electron-impurity interactions. Stern[6] interpreted the changes in the electron density of states with dilute alloying as related directly to the shielding of the added impurities, the attracted charge being proportional to the valence difference between the impurity and the solvent metal. Recently, the band-structure calculations for the α-brass-type alloys[7,8] showed that on alloying, the conduction bands are displaced to lower energies, a modification on the rigid-band approach which assumes only a change in the Fermi energy. In summary, the electronic behavior of alloys depends on interplay of several different factors. The electron density of states, and thus the electronic-specific-heat coefficient, must therefore be expected to be a rather complex function of empirical-alloying parameters, e. g., the number of electrons per atom $\mathfrak{z}$, or the size difference.

Most of the published experimental results in the case of alloys based on the noble metals, Cu, Ag, and Au, provide relatively limited support for the existing theoretical predictions. Since the electronic-specific-heat coefficient varies very little on alloying, the error of the measurement often exceeds the change of γ in the low-solute-content region. On the other hand, most theories give results only for the initial derivatives, or for values of γ in very dilute alloys, where the mean free path of electrons is long enough to neglect the imaginary part of the energy of the Bloch states. Clearly, there is a need at this time for more accurate data through which information can be gained on the behavior of the density states at the Fermi level, and other related parameters in alloys.

For the present work, a semidifferential type of calorimeter design was used to measure accurately values of γ in a succession of α-phase solid-solution alloys of Sn in Cu. The composition of low-concentration alloys varied in steps of 0.25 at.%. Both the individual values of γ, and the over-all behavior of γ with $\mathfrak{z}$, differ substantially from the results published some years ago.[9]

II. EXPERIMENTAL DETAILS

Heat-capacity measurements were made in a semiautomated differential calorimeter (Fig. 1), the details of which are in the process of being published.[10] Two samples (C) suspended on thin nylon threads (K) are measured at the same time. A mechanical-heat switch (A) is used to cool them down to 1.4 °K. The heaters (H) are made of manganin wire (0.05 mm in diam. and ~ 200 cm in length) and are directly wound around the cylindrically shaped samples. A carbon resistor (G) embedded in the body of the sample is used as a thermometer. The heaters are connected in series, so that the current through both heaters is the same. The resistors are connected in series for the same reason. The maximum possible error due to a contribution from these addenda to the coefficient γ and to the Debye temperature Θ_D is estimated to be less than ± 0.0005 mJ/mole °K and ± 0.5 °K, respectively. However, this error is the same for both samples and therefore does not affect the accuracy of measuring small differences in electronic specific heat or Debye temperature. The electrical connections are of niobium wires (0.04 mm in diam and ~ 60 cm in length), helically wound into a coil.

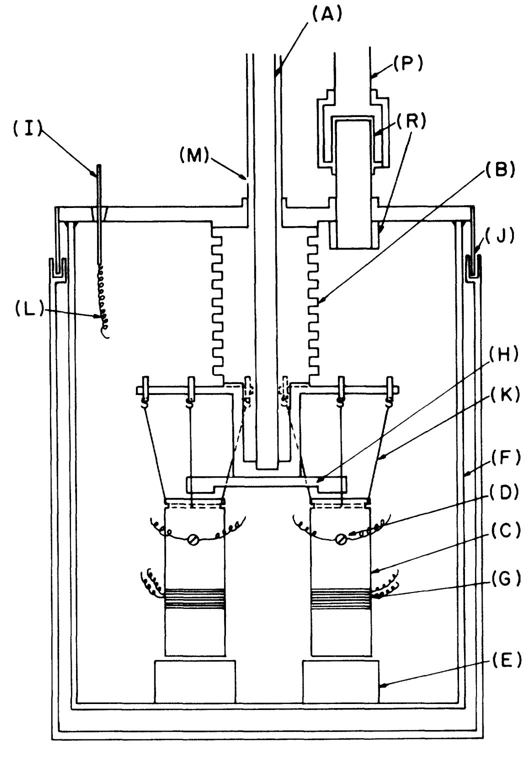

FIG. 1. Schematic cross section of the calorimeter assembly: (A) cupro-nickel shaft, (B) bellows, (C) samples, (D) carbon thermometer, (E) copper pillow, (F) copper frame, (G) manganin heater, (H) heat-switch assembly, (I) vacuum seal, (J) Wood's-metal seal, (K) supporting nylon string, (L) niobium-wire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

The "brain" of the equipment is a mechanical stepper which programs the measurements of temperature and energy input during heating and of pressure during calibration. The readings are taken every 3 sec and recorded automatically on punch tape. All tapes are then directly processed by computer, thus eliminating any possible human errors.

Allen-Bradley carbon resistors (47 Ω, 0.1 W) were used as thermometers and were recalibrated after each experiment against the 1958 He^4 vapor-pressure scale. A Hewlett-Packard digital voltmeter was used for measuring the resistance of the carbon resistors and the energy input during the heating. The accuracy of this instrument is ± 1 μV. The samples were heated for 20 sec, the heating time being determined by a Beckman electronic clock with accuracy of 10^{-5} ± sec. During the calibration the pressure was measured by a Texas Instrument Bourdon-tube-type pressure gauge. The calibration was represented by the polynominal of the type

$$\log_{10} R = \sum_{i=0}^{N} C_i (\log_{10} T)^i , \qquad (1)$$

with N equal to 5. The deviation of the individual calibration points from the fitted curve was less than 5×10^{-4} °K.

It is well known that the temperature calibration represents the major source of the error. Since two samples are measured at the same time, the systematic errors will be the same for both of them. Therefore, the errors in temperature calibration and in measurements of heat input will affect the derived values of the γ coefficient of both samples but will not affect the difference in γ between the two samples. As a test, two different temperature calibrations were used on the same two samples; even though the difference in absolute values was substantial, the relative difference remained practically the same. The errors listed in Table I are a sum of statistical errors from a least-squares fit (typically less than 0.001 mJ/mole $°K^2$) and estimated systematic errors. Figure 2 shows the

TABLE I. Values for γ, Θ_D, and δ coefficients for pure copper and α-phase copper-tin alloys. The errors indicated are the sum of statistical errors and estimated systematic errors. The values for γ are given to the fourth decimal place since the difference between the individual values are measured more accurately than the values themselves. See text for explanation.

No.	At. % Sn	$\mathfrak{z}$	γ (mJ/mole °K^2)	Θ_D(°K)	$10^5\delta$ (mJ/mole °K^6)
1	Pure	1.0000	0.6976 ± 0.003	343.3 ± 0.8	−0.2 ± 2.0
2	0.22	1.0066	0.7005 ± 0.003	342.1 ± 0.8	2.6 ± 2.0
3	0.48	1.0144	0.7068 ± 0.003	340.5 ± 0.8	7.0 ± 2.0
4	0.765	1.0230	0.7117 ± 0.003	339.8 ± 0.8	7.2 ± 2.0
5	1.00	1.0300	0.7151 ± 0.003	339.6 ± 0.8	12.7 ± 2.0
6	1.93	1.0579	0.7236 ± 0.003	332.1 ± 0.8	11.8 ± 2.0
7	3.93	1.1179	0.7256 ± 0.003	323.0 ± 0.8	13.5 ± 2.0
8	5.90	1.1770	0.7291 ± 0.003	311.3 ± 0.8	18.0 ± 2.0
9	8.71	1.2613	0.7596 ± 0.003	301.5 ± 0.8	42.0 ± 2.0

usual percentage-deviation plot for one of the samples (1.00 at.% Sn).

The samples were prepared from 99.999%-pure Cu and 99.9999%-pure Sn supplied by United Mineral and Chemical Corp. They were cast in quartz tubes under reduced He atmosphere and subsequently annealed in vacuum. Wet chemical analysis of the top and bottom of each sample was performed to confirm the exact composition, and metallographic examination was done to check for possible solute segregation. Spectroscopic analysis of each sample showed either no traces or less than 1–2 ppm of ferromagnetic impurities.

III. RESULTS

The values of the coefficients γ, Θ_D, and δ have been calculated using least-squares fitting of the specific-heat and temperature data to the usual expression: $C/T = \gamma + AT^2 + \delta T^4$, where A is related to the limiting Debye temperature by the expression $A = 12\pi^4 R / 5\Theta_D{}^3$, and δ represents the deviation from Debye approximation. In order to obtain the trends of the electronic specific heat and the Debye temperature on alloying as accurately as possible, each sample was measured twice, once with a sample of lower and once with a sample of higher Sn content. The difference between each two samples obtained in each measurement is considered to be substantially more accurate than the individual absolute values. Therefore, the final values for γ and Θ_D of each sample were derived by adding the differences between the values of successive samples to the values of γ and Θ_D for the pure Cu sample (Table I). In Fig. 3 the γ and Θ_D are plotted as a function of $\mathfrak{z}$, together with earlier results of Clune and Green.[9] The present data for the dilute alloys up to 1.0 at.% Sn in Cu give for the initial logarithmic derivative of γ with respect to $\mathfrak{z}$ the value: $d\ln\gamma/d\mathfrak{z} = 0.62 \pm 0.08$ which is some three times higher than the value 0.24 ± 0.06, suggested by the straight-line plot through the data of Clune and Green, or the value ≈ 0.25 suggested by similar linear plots through the data obtained for a number of primary solid solutions based on Cu or Ag.[11]

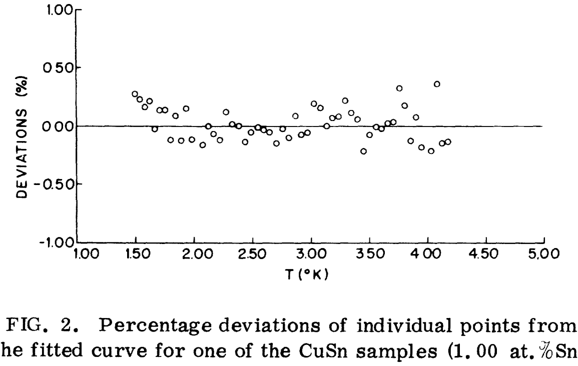

FIG. 2. Percentage deviations of individual points from the fitted curve for one of the CuSn samples (1.00 at.%Sn).

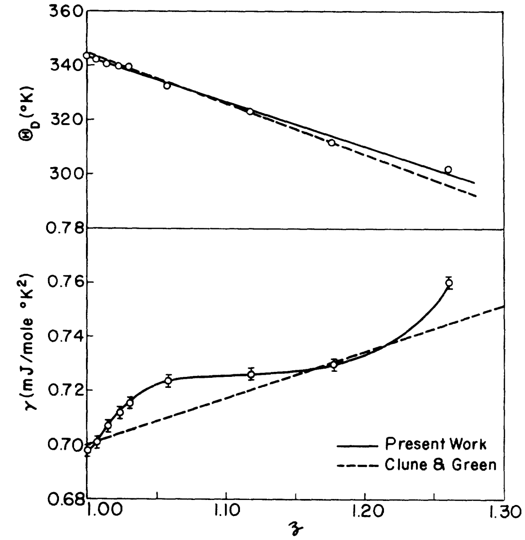

FIG. 3. Electronic-specific-heat coefficient and Debye temperature as a function of electron concentration; solid curves—present work, dashed lines—results from work of Clune and Green (1966).

The values of the Debye temperature lie fairly close on a straight line, a linear least-squares fit yielding: $\Theta_D = (343.1 \pm 0.7)$ °K $- (166 \pm 6)(\mathfrak{z} - 1)$ °K, as compared with the Clune and Green[9] relationship $\Theta_D = (344.7 \pm 0.8)$ °K $- (188 \pm 9)(\mathfrak{z} - 1)$ °K. The important conclusion from the present work is that the relationship between the γ and $\mathfrak{z}$ in the system CuSn is not linear, and that the greatest change occurs in the low-concentration region. Substantial differences are evident between the initial derivative and those based on the more concentrated alloys.

IV. DISCUSSION

The differences in the γ values between the present and the earlier reported data, as evident in Fig. 3, seem to arise from two possible reasons. Firstly, the lowest temperature at which Clune and Green measured the electronic specific heat was 2 °K, compared to our 1.5 °K. Secondly, in their analysis of results, the δ terms were neglected as insignificant. Our measurements, however, show that δ, although small, has appreciable values at higher Sn concentrations and changes most rapidly in the low-concentration range (Fig. 4). The net effect of the differences in the measurement and in the evaluation tends to make the values of Clune and Green to be lower than our values. Similarly, the Debye temperatures of Clune and Green tend to decrease faster, the differences becoming larger with increasing Sn concentration, that is with increasing values of the δ coefficient.

Furthermore, one particular sample of Clune and Green, with approximately 6-at.% Sn was reported to contain about 26 ppm of Fe. The contribution of such impurities to the derived values of γ can be corrected for [12] and, had the authors made the necessary correction, the γ value for this sample would change drastically downward and the shape of the general γ vs $\mathfrak{z}$ curve, at least in the middle range, would be somewhat similar to ours. It is of interest that the trend of γ vs $\mathfrak{z}$ obtained by Will and Green[13] in the α- phase of the AuSn system does resemble strongly our present results in the CuSn system. There is an initially steep slope, followed by a relatively flat portion in the middle range, and followed again by an increase of γ with further increase of $\mathfrak{z}$. To derive the initial slope, Will and Green still used a linear fit but it is clear that the deviation of the plotted values from the straight line is beyond the experimental error. Of course, their values for γ, Θ_D, and δ derived from alloys in the two-phase region cannot be used as an extension of the α-phase since they represent approximately an arithmetic mean of the corresponding tie-line alloys representing two different structures.

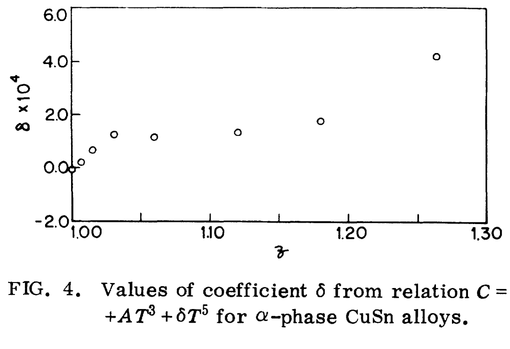

FIG. 4. Values of coefficient δ from relation $C = \gamma T + AT^3 + \delta T^5$ for α-phase CuSn alloys.

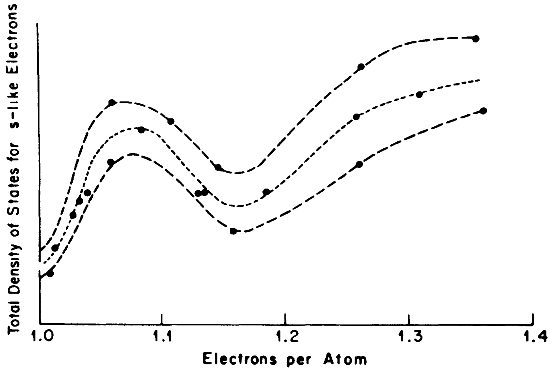

FIG. 5. Mössbauer results for Cu-based alloys (Ref. 14).

Recently, Lees and Flinn[14] reported on measurements of the Mössbauer effect of Sn in α-phase CuSn and related alloy systems. By measuring the isomer shift in the quadrupole moment of Sn in a number of alloys of copper, they were able to observe changes in the s character of the band wave functions which are related to the electronic configuration of the tin atoms. Their data is shown in Fig. 5 and the comparison with our results is most interesting. Again one can infer a sharp initial increase of the density of states up to $\mathfrak{z}$ of about 1.1. Density of states then decreases to a minimum but increases again near the phase boundary. This general behavior in an fcc α-phase solid solution, showing a complicated nonlinear trend, is also consistent with a study of the x-ray absorption edges of CuZn alloys by Yeh and Azaroff,[15] and with the positron annihilation measurements in CuAl reported by Fujiwara *et al.*[16] In both cases the indicated trend in the density of states at the Fermi level is far from linear.

The above experimental details are consistent with energy-band calculations for α-brass made by Soven,[7] and independently by Amar, Johnson, and Sommers.[8] Both theories, the latter one using Kohn-Rostoker method in combination with "pseudoperiodic potential" and the former using Beeby's averaged-t-matrix formulation, show that in addition to an increase in the Fermi energy, the shape of the density-of-states curve as a function of energy also changes. As a result, the conduction bands are displaced to lower energies. The two primary energy bands whose changes effect the over-all density of states are the Γ_1(which is primarily s like) and L_2 (primarily p like). The level of the Γ_1 band decreases rapidly for $\mathfrak{z}$ between 1 and about 1.1, then it continues to decrease but at a slower rate up to the phase boundary. The level of the L_2

band, on the other hand, decreases slowly up to a $\mathfrak{z}$ value of 1.1; it then decreases more rapidly up to a $\mathfrak{z}$ value of 1.2. From this point to the phase boundary it again decreases more slowly. Considered together the calculated changes in these two bands suggest an initial sharp increase in the total density of states followed by a leveling off in the region between 1.1 and 1.2 and then again an increase to the phase boundary but not as rapid as in the low-solute-content region. This seems to be exactly the behavior that we have observed by accurately measuring the electronic specific heat, which therefore must primarily reflect the behavior of the s and p electrons on alloying.

Our present results viewed in the light of other measurements, such as isomer shift and positron annihilation, as well as the band calculations, strongly suggest that despite the rather small relative changes of γ on alloying wrong conclusions may be reached if these changes are considered as being essentially linear with electron concentration $\mathfrak{z}$. This assumption was used as a basis for a recent study by Mizutani *et al.*[11] of which one of us is a co-author. Assuming that both the vol/atom (V) and electronic specific heat (γ) trends with $\mathfrak{z}$ are linear in each binary system studied, a general expression could be established for Cu and Ag alloys, based on the logarithmic derivatives:

$$\frac{d\ln\gamma}{d\mathfrak{z}} = A + B\frac{d\ln V}{d\mathfrak{z}}\ , \tag{2}$$

where $A = (\partial\ln\gamma/\partial\mathfrak{z})_V$ and $B = (\partial\ln\gamma/\partial V)_{\mathfrak{z}}$. A plot of the data for a number of alloy systems suggested a lack of dependence on volume with $B = (\partial\ln\gamma/\partial\ln V)_{\mathfrak{z}} \approx 0$, a rather surprising result in view of the fact that a calculation of this coefficient, based on a simple band model, suggested a positive value of about 0.68. Attempts to reconcile the discrepancy in terms of possible contributions from electron-phonon interactions and level-broadening effects were not successful. It seems likely that an explanation may lie in the treatment of the experimental data: The initial logarithmic derivatives from each system must be considered very carefully because the trends in the low-concentration alloys and the high-concentration alloys of the same system may be different. The present results certainly indicate this behavior, but more measurements are needed in the low-concentration region in a number of related systems.

It is also of interest to compare our results with predictions of Stern's recent model.[6] He proposes a general expression:

$$\rho(E) \approx \rho^{\circ}(E)(1 + n\,\delta\sigma_E), \tag{3}$$

where $\rho(E)$ and $\rho^{\circ}(E)$ are the densities of states at energy E for the alloy and the pure solvent, respectively, n is the number of impurities per unit volume, and $\delta\sigma_E$ is a quantity proportional to the average excess charge at energy E attracted by each impurity.

Following Stern's calculations, our value 0.62 for $d\ln\gamma/d\mathfrak{z}$ based on the low-concentration region, yields for the ratio of the total charge attracted around impurities to the charge contributed by states at the Fermi level $\sigma_{\text{imp}}/\sigma_{\text{host}} \approx 3.3$. In other words, the electrons at Fermi energy deposit 3.3 times as much charge on Sn atoms as on the Cu atoms. The same ratio for CuZn is only 1.5.[6] Both values satisfactorily correlate with the valence difference between Sn and Zn with respect to Cu.

The fact that Debye temperature of CuSn decreases much faster than in other alloys measured so far can be attributed to the exceptionally large $d\ln V/d\mathfrak{z}$ values observed in this system, where V is the atomic volume. Mizutani *et al.*[11] analyzed the behavior of the Debye temperature for several Cu-based systems.

Using the expression,

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

they plotted experimentally-obtained values of $d\ln\Theta_D/d\mathfrak{z}$ vs $d\ln V/d\mathfrak{z}$ (Fig. 6). The value of the

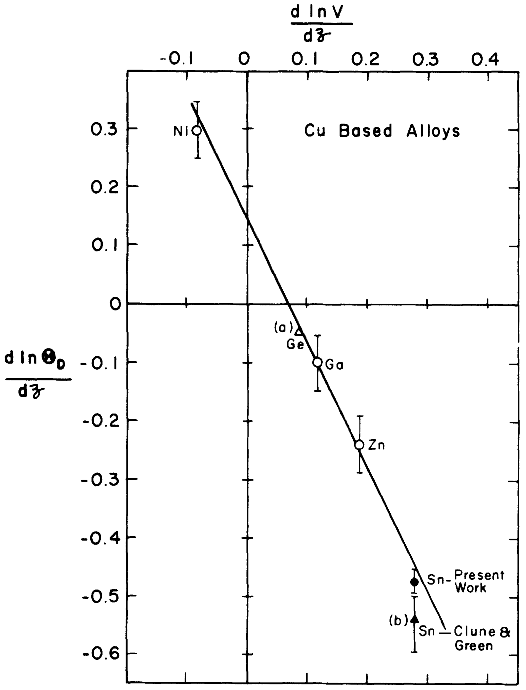

FIG. 6. Relation between the initial derivatives $d\ln\Theta/d\mathfrak{z}$ and $d\ln V/d\mathfrak{z}$ from Mizutani *et al.*, including the value of $d\ln\Theta_D/d\mathfrak{z} = -0.48 \pm 0.02$ from present work on CuSn alloys.

slope of the resulting straight line is 2.0, remarkably close to the value of the Grüneisen constant Γ for Cu (1.96). This value can be calculated directly from the expression $-\partial \ln \Theta_D/\partial \ln V = 3V\delta/kc_V \equiv \Gamma$, where δ is the linear expansion coefficient, k is the compressibility, c_v is the specific heat, and V is the volume. While the above expression is only an approximation, it describes surprisingly accurately the behvaior of experimental results. Our measurements of the Debye-temperature trend on alloying with Sn yields $d\ln\Theta_D/d\mathfrak{z} = -0.48 \pm 0.02$. This value lies closer to the straight line on Fig. 6, thus further improving the agreement between the value of the Grüneisen constant Γ and the slope of the line as determined from other experimental results. We conclude that in Cu-based alloys the rate of change of the Debye temperature when normalized in terms of $\mathfrak{z}$, depends mostly on size effects. Other contributions, such as, for example, electron-phonon interaction, appear to be less dependent on the particular solute and its valence, and more on the value of the electron concentration.

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Fermi Surface of Lead at Normal and High Pressure*

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The pressure dependence of the Fermi surface of lead has been studied by means of NMR-calibrated de Haas–van Alphen–effect measurements. In order to carry out these investigations, the values of Fermi-surface areas, obtained from pulsed-magnetic-field measurements, have been redetermined to correct for a calibration error. Attempts to fit the measurements with a local model potential were not completely successful, but a nonlocal calculation based on the Heine-Abarenkov model potential gave satisfactory agreement with the experimental results.

I. INTRODUCTION

There has been considerable interest recently in the Fermi surface of lead and in pseudopotential models used to describe this surface. This is partly due to the fact that lead is a strong-coupling superconductor whose density of states has been determined from electronic-tunneling[1] and specific-heat[2] measurements. In addition there is a great wealth of experimental information about the electronic structure of lead, e.g., de Haas–van Alphen (dHvA) effect,[3] cyclotron resonance,[4,5] magnetoacoustic[6] effect, optical properties,[7,8] and Kohn effect.[9]

A calibration error was discovered in previous pulsed-field experiments[3] (hereafter referred to as I) making it desirable to remeasure the dHvA frequencies for magnetic field H along symmetry di-