in T_c and the electronic-specific-heat coefficient as reported by Wernick *et al.*[7]

IV. CONCLUSIONS

The results of pressure and Pd alloying on the Fermi surface of $AuGa_2$ are consistent with the band-structure picture given by Switendick when the calculation as a function of lattice parameter and the rigid-band model, respectively, is considered. An unusual change in the magnitude of the pressure derivative of the cross section associated with the neck of the third-zone hole surface near 6 kbar is interpreted as a consequence of the electron transition occurring when the second band passes through the Fermi energy from below. Two experiments are needed, pressure studies of the superconducting transition temperature and of the Ga Knight shift, to demonstrate the validity of this interpretation.

Note added in proof. A large and abrupt change in the superconducting transition temperature near 6 kbar has been demonstrated since submission of this paper. [See J. E. Schirber, Phys. Rev. Letters 28, 1127 (1972).]

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Low-Temperature Specific Heat of α-Phase Cu-Au Alloys[*]

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The specific heats of α-phase Cu-Au alloys with Au concentrations of 2.4, 4.8, and 10.0 at.% were measured in the temperature range 1–5 K. The electronic coefficient of specific heat showed no significant change, but the Debye temperature was found to decrease with increasing Au concentration. This decrease was consistent with high-Au-concentration results of other investigators and correlated with the predictions from elastic-constant data.

I. INTRODUCTION

Low-temperature specific-heat data for Cu-Au alloys have been reported by several investigators.[1–4] These papers, however, were mainly concerned with order-disorder effects where sample systems with high Au concentrations such as Cu_3Au, CuAu, or $CuAu_3$ were used. The present paper reports the results of specific-heat measurements in the temperature range 1–5 K for Cu-Au samples with Au concentrations of 2.4, 4.8, and 10.0 at.%. These samples allowed a study to be made of Cu-Au alloys in the primary solid-solution phase. Since this primary solid-solution phase of Au in Cu extends to about 18 at.% Au,[5] complications due to different metallurgical phases were not encountered with these alloys. Attention was focused on the effect that increasing amounts of Au had on the electronic coefficient of specific heat and the Debye temperature.

II. SAMPLE PREPARATION

The polycrystalline α-phase samples of the alloys were prepared by the Materials Research Corporation of Orangeburg, N. Y. The starting materials of 99.999% Cu and 99.999% Au were combined in spectrographically pure high-density graphite molds, induction melted in a vacuum, and held at the melting temperature for 8 h. The alloys were then allowed to solidify, encapsulated in argon-filled quartz tubes, held at 900 °C for 72 h, and quenched in ice water. The manufacturer stated that because of preferential evaporation during melting under vacuum, they could only guarantee a maximum uncertainty of ± 0.5 at.% Au for samples whose desired composition was 2.5 and 5.0 at.% Au and ± 1.0 at.% Au for a 10.0-at.% Au sample. The actual compositions of the alloys were determined in several different laboratories by the following methods: standard quantitative analysis, atomic-absorption analysis, precision back-reflection x-ray powder pictures, and from density measurements determined by hydrostatic weighing. All of these techniques produced concentration results which were in satisfactory agreement with each other except the atomic-absorption analysis. This method gave values which were well below the other results and below the assumed guaranteed concentrations. Since these alloys were extremely resistant to etches, it is believed these low results were unreliable and were possibly caused because of the difficulty in getting the Au from the test specimens to dissolve in the reagents used for the analysis. The samples used in the density method of determining Au concentrations were exactly the same samples as were used in the specific-heat measurements; these concentration results are considered by us to be the best values and are the ones quoted for the alloys. The absence of a detectable rise in the electrical resistivity at temperatures below 10 K for the alloys indicated they were free from transition-metal impurities.[6] Before mounting the samples in the calorimeter, they were etched in aqua regia and then in a mixture of 10% solution of potassium cyanide and ammonium persulphate to remove the black Au film. Final cleaning was in distilled water and then in methanol. The mass of each of the 2.58-cm-diam ×2.95-cm-long cylindrical samples was approximately 150 g.

III. EXPERIMENTAL TECHNIQUE AND RESULTS

The calorimeter[7] as described previously was used in a ^{4}He cryostat and employed a mechanical heat switch to cool the sample. Temperatures below 4.2 K were obtained by pumping on the helium bath in which the sample chamber was submerged. A continuous-heating method was used to determine the specific-heat values and temperatures were measured with a germanium resistance thermometer connected in an ac bridge circuit.

The specific-heat results were analyzed by the formula

$$C = \gamma T + \alpha T^3 ,$$

where C is the specific heat, T is the temperature, γ is the electronic coefficient of specific heat, and α is related to the characteristic limiting Debye temperature Θ_0 by the equation $\Theta_0 = (12\pi^4 R/5\alpha)^{1/3}$, where R is the gas constant. The values of γ and α were determined for each sample from approximately 150 measured C and T data points. The calculations were performed on an IBM 360/65 digital computer using a least-squares-fitting program. Weighting factors equal to the reciprocal of the measured specific-heat values were used in the program so the sum of squares of the fractional deviations of the observed C from the calculated C was minimized. Values of γ and Θ_0 determined in the present research along with the values of γ and Θ_0 given by Martin,[2,8] and Martin and Waterhouse[3] for Au and disordered Cu_3Au, CuAu, and $CuAu_3$ are listed in Table I.

The errors listed in Table I for γ and Θ_0 for the samples studied in this paper include both random errors determined from a least-squares analysis of the data and estimated errors due to other sources. Generally, in arriving at the total error for the parameters, it was necessary to significantly increase the standard deviation as determined by the least-squares results. It was particularly difficult to determine γ accurately and this is indicated by the errors quoted. This difficulty, however, seems to be a common problem as has been dramatically demonstrated recently by Boerstoel *et al.*[9] for Au. They have shown that, although the specific heat may be measured quite accurately at ^{4}He temperatures, an equally accurate value of γ

TABLE I. Values of the electronic coefficient γ and Debye temperature Θ_0 for Cu, Au, and disorded Cu-Au alloys as determined by low-temperature specific-heat measurements.

Element or alloy	γ (mJ/mole K^2)	Θ_0 (K)	Symbol Fig. 1
Cu[a]	0.696 ± 0.005	343.3 ± 1.5	▼
Cu–2.4-at.%-Au[b]	0.693 ± 0.010	331.7 ± 1.5	●
Cu–4.8-at.%-Au[b]	0.698 ± 0.010	321.7 ± 1.5	●
Cu–10.0-at.%-Au[b]	0.698 ± 0.010	301.4 ± 1.5	●
Cu_3Au[c]	0.677 ± 0.001[d]	269.1 ± 0.5	▲
CuAu[e]	0.677 ± 0.002[d]	219.8 ± 0.6	◆
$CuAu_3$[e]	0.684 ± 0.002[d]	186.2 ± 0.3	◆
Au[f]	0.691 ± 0.004[d]	162.3 ± 0.5	■

[a] Reference 7.

[b] This work.

[c] Reference 2.

[d] Units converted from μcal $mole^{-1}$ K^{-2}.

[e] Reference 3.

[f] Reference 8.

TABLE II. Debye temperatures Θ_D for Cu, Au, and disordered Cu-Au alloys calculated by numerical integration using low-temperature elastic-constant data from the literature.

Element or alloy	Θ_0 (K)	Source of elastic constants (Reference)
Cu	345.3	11
Cu-0.23-at.%-Au	345.2	14
Cu-2.8-at.%-Au	331.2	14
Cu-10.0-at.%-Au	309.7	14
Cu_3Au	281.7	13
Au	161.7	12

is not guaranteed. They made two independent measurements of specific heat of a Au sample and found the specific-heat values agreed to within ±0.2% at all temperatures. Separate analyses, however, yielded values for γ of 0.671 and 0.682 mJ $mole^{-1} K^{-2}$. For comparison, Table I shows Martin's[8] value of γ for Au is (0.691 ± 0.004) mJ $mole^{-1} K^{-2}$. Since we analyzed all our data in the same way and kept our experimental conditions the same and thus kept possible systematic errors the same for all our Cu-Au specific-heat measurements, it may be more appropriate to consider only random errors when determining changes in the values of γ for our alloys. These random errors are at least a factor of 2 less than the errors given in Table I.

At ^{4}He temperatures, the simple Debye continuum model for a solid should be applicable and the Debye temperature as derived from calorimetric measurements should agree with the Debye temperature as determined from elastic-constant measurements. Although there is some evidence to show the two Θ do not agree exactly even at 0 K, the difference, if real, is small. For example, a statistical analysis by Overton[10] of experimental data for Cu has shown that $\Theta_0(\text{elastic}) - \Theta_0(\text{calorimetric}) = (2.12 \pm 1.02)$ K.

To determine Θ_0 from elastic-constant data, one may use the equation

$$\Theta_0 = \frac{h}{k}\left(\frac{3}{4\pi}\,\frac{N\rho}{M}\right)^{1/3}\bar{v}\,,$$

where h is Planck's constant, k is Boltzmann's constant, N is Avogadro's number, ρ is the density, M is the atomic weight (average atomic weight for alloys), and $\bar{v}$ is a mean sound velocity defined by

$$\bar{v} = \left[\frac{1}{3}\int \sum_{i=1}^{3}\left(\frac{1}{v_i^3}\right)\frac{d\Omega}{4\pi}\right]^{-1/3}$$

Since low-temperature single-crystal elastic-constant data were available for Cu,[11] Au,[12] and Cu-Au alloys,[13,14] a computer program was written to determine the elastic Debye temperatures.[15] A numerical-integration method similar to the one described by Wanner[16] was used for the calculations. The cubic equation[17] for the three sound velocities v_1, v_2, v_3 was solved numerically for 200 directions in $\frac{1}{16}$ of the unit sphere to evaluate the integral. The results of the integration are given in Table II.

IV. DISCUSSION

Consider first the electronic coefficient of specific heat γ. Table I shows the values of γ for the Cu-Au alloys studied in this paper. One may also see from Table I that Martin [2] and Martin and Waterhouse[3] found small changes in γ for disordered Cu_3Au, CuAu, and $CuAu_3$ alloys, and their values lie on a smooth curve slightly below the linear interpolation line drawn between the value of γ for pure Cu and Au. Our values of γ do not show a significant change upon alloying for concentrations up to about 10 at.% Au. Very small changes in γ, however, could not be resolved because of our estimated experimental uncertainties.

According to Stern's[18] theoretical arguments, a change is expected in γ when Au is alloyed with Cu. He has shown the electron density of states $n(E)$ changes upon alloying because of shielding of the added solute atoms by states near the Fermi energy E_F. The electronic coefficient of specific heat is related to $n(E)$ through

$$\gamma = \tfrac{2}{3}\pi^2 k^2 n(E_F)\,,$$

where k is Boltzmann's constant. Thus γ should reflect the electronic shielding of the Au. Since Cu and Au have the same valence, shielding may be small for this alloy system. The effect, however, will still exist because there can be a net

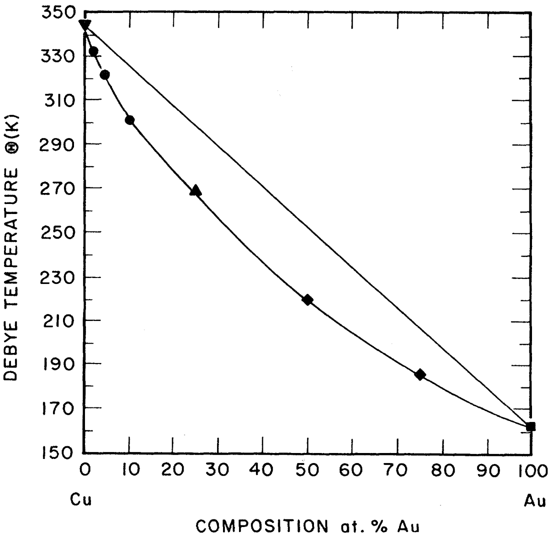

FIG. 1. Debye temperature as a function of composition for disordered Cu-Au alloys. The key to the symbols will be found in Table I.

charge transfer between Cu and Au atoms at E_F, although by charge neutrality, the net charge transfer integrated over all energies must be zero. For dilute Cu-Au alloys, Stern's[18] results predict that the ratio of the charge at E_F attracted around an Au atom to that around the Cu host atom is simply related to the change in γ with respect to Au concentration. In order to quantitatively estimate the shielding it is also necessary to correct for contributions to γ because of volume changes upon alloying. Since in the primary solid-solution phase the volume change per Au concentration for Cu-Au alloys[19] is about

$$\frac{1}{V}\frac{\Delta V}{\Delta x} = +0.48\%/\text{at.}\% ,$$

this correction is appreciable and it is difficult to make realistically.

In marked contrast to the relatively small changes in γ when Au is alloyed with Cu, the Debye temperature shows a definite decrease with increasing concentrations of Au. The values of Θ_0 obtained for the α-phase alloys lie on a smooth curve below the linearly interpolated values for the separate constituent elements and are consistent with the high-Au-concentration results of other investigators as is shown in Fig. 1. The decrease in Θ_0 with increasing Au also correlates with the decrease as predicted by elastic-constant data. Values of Θ_0 calculated by numerical integration using low-temperature single-crystal elastic constants determined by ultrasonic-pulse techniques are given in Table II for several Cu-Au alloys. The observed numerical difference between Θ_0 (calorimetric) and Θ_0 (elastic) for identical Au concentration may be partly attributed to the fact that the calorimetric samples were polycrystalline and the elastic-constant samples were single crystal.

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