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Specific Heats of α-Phase Cu-Al and Dilute Magnetic Cu-Al (Fe) Alloys*

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The specific heats of a series of α-phase Cu-Al and dilute magnetic Cu-Al (Fe) alloys with iron concentrations near 0.07 at.% have been measured over the temperature range 1–14 K. The alloys had aluminum concentrations of 0, 2.5, 5, and 10 at.%. The electronic specific-heat coefficient and the Debye temperature were determined for the iron-free samples. Both were found to increase with increasing aluminum concentration. The increase in the electronic coefficient can be related to shielding effects, and the change in the Debye temperature is consistent with the mass defect associated with an aluminum atom. The excess specific heat due to the iron impurities showed the broad peak characteristic of the Kondo effect. The temperature of the maximum was essentially independent of aluminum concentration, while the size of the peak decreased with aluminum additions. This behavior is contrasted with the behavior of similar dilute magnetic alloys.

I. INTRODUCTION

Dilute Cu(Fe) alloys have been extensively investigated for anomalous properties characteristic of the Kondo effect.[1] Various types of measurements indicate a Kondo temperature T_K for this system in the vicinity of 15 K. Measurements of the specific heat at temperatures of the order of T_K and below have been carried out by several investigators.[2–4] A broad excess specific-heat anomaly which peaks below T_K is observed. Because of the convenient value of T_K in the Cu(Fe) alloy, the excess specific-heat anomaly is not masked by the host specific heat at temperatures as high as T_K when the iron concentration is in the neighborhood of 0.05 at.%.

We report here specific-heat studies of dilute α-phase $Cu_{1-x}Al_x$(Fe) alloys in the temperature range 1–14 K. The purpose of this investigation was to determine the effect of the nonmagnetic aluminum additions on the previously observed behavior of dilute concentrations of iron in copper. Iron-bearing samples with aluminum concentrations of 0, 2.4, 5.0, and 10.2 at.% were measured. An attempt was made to have the iron concentrations of these samples the same and in the neighborhood of 0.07 at.%. Measurements were also made on four samples with similar aluminum concentrations but without iron impurities. This enabled the subtraction of the host specific heat in order to obtain the excess specific-heat anomaly. The excess specific heat was found to be suppressed with increasing aluminum concentration.[5]

The measurements of the specific heat of the host samples containing no iron impurities are of interest apart from the localized moment studies. We present results for the electronic specific-heat coefficient and the Debye temperature. Both the electronic specific-heat coefficient and the Debye temperature were found to increase with increasing aluminum additions.

The pure-copper sample measured was a portion of the 1965 Calorimetry Conference copper standard.[6] The measurements on this sample enabled us to establish our temperature scale and over-all uncertainties.

The samples, apparatus, measurement technique, and thermometry are described in Sec. II. Results of the measurements on the set of eight samples are presented in Sec. III. In Sec. IV, a discussion of these results is given.

II. EXPERIMENTAL

A. Samples

The pure-copper standard sample was kindly furnished by Argonne National Laboratory (ANL) from the collection of pieces of the same melt designated as the 1965 Calorimetry Conference copper standard.[6] The ANL copper sample (T7.5) was machined into a cylinder 3.19-cm diam × 2.95 cm long.

The copper-aluminum alloys studied in this work were made by the Materials Research Corp. of Orangeburg, N. Y. The starting pure materials were combined in 2.87-cm-diam molds made from spectrographically pure high-density graphite, induction melted for over 1 h under high-vacuum conditions, and slowly cooled in a vacuum. The samples were removed from their molds, annealed at 1000 °C in a protective argon atmosphere for 72 h, and quenched in cold water. The specific-heat samples were machined into cylinders 2.54-cm diam × 2.95 cm long. The compositions of the alloys investigated are given in Table I. The chemical compositions were supplied by the manufacturer in the form of a report of analysis conducted by standard quantitative analysis. Additional chemical analyses for iron were performed with atomic-

TABLE I. Results of chemical analysis of copper alloys investigated.

Sample no.	Al (at.%)	Fe (at.%)
1[a]	0	< 0.0001
2	0	0.077 ± 0.005
3	2.5 ± 0.1	< 0.003
4	2.4 ± 0.1	0.057 ± 0.005
5	5.6 ± 0.1	< 0.003
6	5.0 ± 0.1	0.066 ± 0.005
7	10.0 ± 0.1	< 0.003
8	10.2 ± 0.1	0.084 ± 0.005

[a] Sample T7.5 of the 1965 Calorimetry Conference copper standard.

absorption spectroscopy by two independent laboratories. An independent analysis for aluminum was also obtained. The absence of a detectable rise in electrical resistance at temperatures below 10 K for the iron-free alloys indicated they were free from transition-metal impurities.[7] The uncertainties in composition of the alloys represent the combination of the uncertainty in the chemical determinations and the variation in analysis of composition of pieces taken from portions of the original casting. The samples were etched in 50% nitric acid to remove damage caused by machining. This was followed by a brief etch in 50% hydrochloric acid and a final rinse in deionized water. Each sample had a mass of approximately 130 g.

B. Apparatus

The calorimeter used for these measurements is shown schematically in Fig. 1. The sample and addenda were suspended from silk threads and phosphor-bronze springs in a gold-plated brass vacuum chamber submerged in liquid helium. The chamber was sealed with an indium o-ring patterned after the design by Fraser.[8] A thin gold-plated copper radiation shield, supported from the guard platform, surrounded the sample assembly. The cryostat used nested glass Dewars for the liquid nitrogen and helium reservoirs. Helium loss was minimized by using low-thermal-conductivity materials for the electrical leads and mechanical supports and by using radiation baffles. The mechanical heat switch was a parallelogram type with indium-coated jaws as described by Cochran *et al.*[9] The weighted actuator proved to be a good method of loading the switch with enough force to provide thermal contact, yet it permitted the apparatus to go through the severe thermal contractions of cooling without sustaining damage.

The sample addenda, with a mass of approximately 40 g, was divided between two sections with the sample heater on the bottom section and the sample thermometer on the top section. General Electric 7031 varnish was used to attach the addenda parts to the sample. Very small quantities of varnish were also applied to the sample until the same amount (within ± 4 mg) was used for each new measurement.

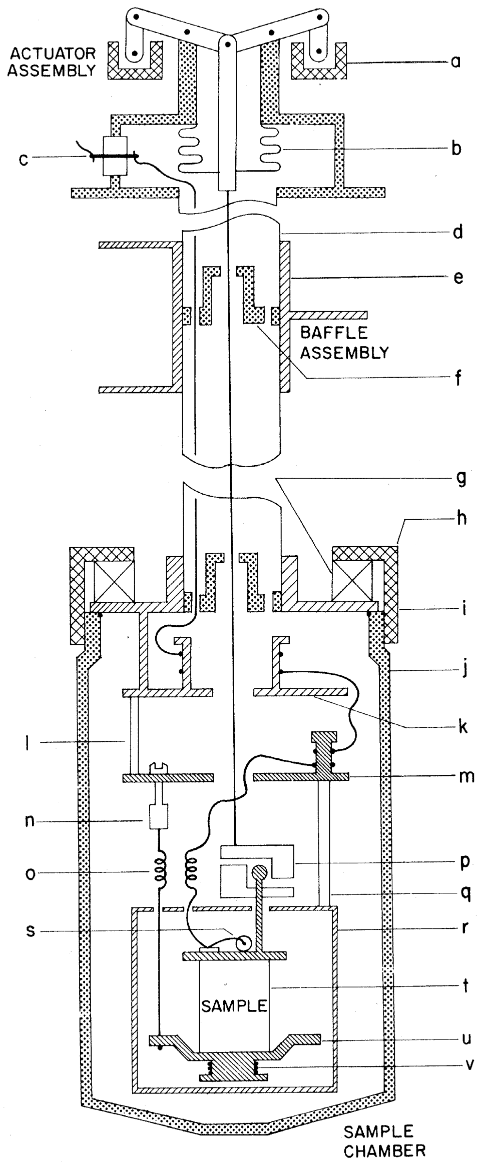

FIG. 1. Schematic drawing of the specific-heat cryostat: a, actuator weight and level assembly; b, bellows; c, electric leads; d, evacuation and support tube; e, external radiation baffle; f, internal radiation baffle; g, thrust bearing; h, nut; i, indium wire seal; j, calorimeter jacket; k, heat station; l, guard support; m, guard platform; n, leveling screw; o, one of three support springs and threads; p, heat switch; q, radiation shield support; r, radiation shield; s, germanium thermometer; t, sample; u, sample support; v, sample heater.

C. Measurement Technique

Specific-heat measurements were made using a continuous-heating technique. When data were taken, the guard-platform heater was adjusted to a temperature about 0.5 K higher than the sample. First, measurements were made to determine the stray heat. The sample was then heated through preset temperature intervals ranging from about 10 to 50 mK until the sample was about 0.5 K higher in temperature than the guard. Stray heat measurements were again made. The temperature of the thermal guard was then increased by about 1 K and the process repeated. Two sets of data were taken over the temperature range from 1 to 14 K with the sample-heater power differing by a factor of 3. Specific-heat measurements at the two power levels permitted thermal gradient corrections to be made. Such power-level corrections proved to be typically 0.1–0.5% of our measurements. Stray heat corrections were generally 0.1% or less. The specific heat of the addenda was determined by a separate measurement without the sample.

The sample-heater power and guard-thermometer currents and voltages were measured with a Leeds and Northrup K-3 potentiometer facility. Two digital clocks driven by a 150-Hz oscillator were automatically switched on and off as the sample temperature, as measured by a germanium resistance thermometer in thermal contact with the sample, passed through the preset temperature intervals. The gating circuit for the clocks was provided by the output of a commercial phase-lock amplifier[10] in conjunction with a bridge circuit. The three-terminal sample thermometer formed one arm of the ac bridge circuit.

D. Thermometry

Two germanium resistance thermometers were used in the present research. One thermometer was attached to the guard platform and served as a temperature monitor for the guard. The other thermometer, in thermal contact with the sample, was used to measure temperatures for the specific-heat determinations. The sample thermometer was calibrated by direct comparison with the guard thermometer. The calibration for the guard thermometer from 3.5 to 15 K was provided by Swenson at Iowa State University. The calibration was based on the temperature scale described by Rogers *et al.*[11] This temperature scale does not agree with the liquid-helium vapor-pressure scale T_{58} [12] but lies roughly 8 mK higher from 3 to 5 K.

A preliminary calibration based on T_{58} for temperatures from 1 to 4.2 K was made by us. Since a vapor bulb thermometer was not installed in our calorimeter, pressure measurements were made directly over the helium bath for the T_{58} data. For well-known technical reasons, this technique does not permit a calibration of adequate accuracy for our precision specific-heat measurements at the temperature extremes of the range 1–4.2 K. Therefore, the specific-heat measurements obtained on the ANL copper sample were used to refine the temperature scale below 4.2 K. Changes were made in the calibration temperatures below 4.2 K until a polynomial fit to the specific-heat values agreed with Osborne's reference equation[6] shifted by about +0.4%. This shift was the average systematic deviation for our specific-heat measurements for temperatures above 4.2 K as compared with the reference equation. This adjustment in temperature scale was further justified by the excellent agreement of our T_{58} based specific-heat values near the well-defined λ point with Osborne's reference equation[6] shifted by +0.4%. This procedure required changes in temperatures of a few mK with a maximum shift of 8 mk for the extreme low end of our scale. A final temperature scale was obtained by merging the improved T_{58} data and the calibration from the guard thermometer into a single smooth scale for the range 1–14 K. For the excess specific heat, which depended on differences in specific-heat values, possible systematic errors in our temperature scale were not a major source of error.

The calibration data for the guard and sample thermometers were fit, using the method of least squares, to a polynomial of the form

$$\ln R = \sum_{n=0}^{m} A_n (\ln T)^n ,$$

where R is the resistance and T is the temperature. The calculations were performed in double precision on an IBM 360/65 digital computer. A polynomial with $m = 12$ was chosen for the guard thermometer and $m = 9$ for the sample thermometer. These polynomials were chosen because they produced temperature deviations which were consistent with experimental uncertainties (± 5 mK), the coefficients were well defined (the ratio of the coefficient to its uncertainty was greater than 2), and the R-T relationship appeared smooth enough to give a valid interpolation between calibration points. The smoothness of the function was verified by examining a list of dT/dR and d^2T/dR^2 values obtained for successive 10-mK intervals.

III. RESULTS

Specific-heat values for each sample were obtained by subtracting a smooth polynomial fit to the measured specific-heat values of the addenda from the data. Molar units were used for the samples. The alloys were treated as stoichiometric compounds with the atomic weight of Cu = 63.54

TABLE II. Polynomial coefficients[a] for the iron-free copper alloys calculated from least-squares fitting of the expression $C=\sum_{n=0}^{4} B_n T^{2n+1}$ in the temperature range 1–14 K with C in units of mJ mole^{-1} K^{-1}.

Composition (at. % Al)	B_0 (10^{-1})	B_1 (10^{-2})	B_2 (10^{-5})	B_3 (10^{-7})	B_4 (10^{-10})
0[b]	6.9552 ± 0.0029	4.8354 ± 0.0053	−1.99 ± 0.18	3.33 ± 0.19	−8.87 ± 0.56
2.5	7.0967 ± 0.0055	4.7370 ± 0.0093	−1.21 ± 0.30	2.60 ± 0.30	−6.30 ± 0.88
5.6	7.3619 ± 0.0045	4.6223 ± 0.0075	1.36 ± 0.25	0.84 ± 0.25	−1.39 ± 0.77
10.0	7.4405 ± 0.0037	4.6376 ± 0.0063	−0.67 ± 0.21	3.10 ± 0.22	−8.15 ± 0.69

[a] The errors indicated are standard deviations determined from a least-squares analysis of the data.

[b] Sample T7.5 of the 1965 Calorimetry Conference copper standard.

and Al = 26.98.

For the temperature range 1–14 K, the specific-heat values for the four iron-free samples were fit using the method of least squares with a polynomial in odd powers of T,

$$C=\sum_{n=0}^{4} B_n T^{2n+1} ,$$

with each point weighted by the reciprocal of the measured specific heat. This weighting was used so the sum of squares of the fractional deviations of the observed C from the calculated C was minimized. Five-parameter fits were found adequate to represent the data for each sample with a standard percentage deviation of 0.5% or less. A fit to the data of higher order usually resulted in some poorly defined coefficients and no significant reduction in the standard deviation. The coefficients and uncertainties that were determined by a least-squares analysis of the data are listed in Table II.

The specific-heat values for the iron-free samples were also fit in the temperature range 1–5 K with the relation $C=\gamma T+\alpha T^3$. Here, C is the specific heat, γ is the electronic coefficient of the 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 evaluated for the four samples by a least-squares procedure. A weighting factor equal to the reciprocal of the measured specific heat was again used for the fits. The values of the parameters γ and Θ_0 are given in Table III. It should be emphasized that the values given in Tables II and III for the Calorimetry Conference copper standard do not represent independent results since the temperature scale below 4.2 K was refined on the basis of the measurements on this sample.

TABLE III. The values[a] of γ and Θ_0 for the iron-free copper alloys calculated from least-squares fitting of the expression $C=\gamma T+\alpha T^3$ in the temperature range 1–5 K with $\Theta_0=(12\pi^4 R/5\alpha)^{1/3}$, where R is the gas constant.

Composition (at. % Al)	γ (mJ/mole K^2)	Θ_0 (K)
0[b]	0.696 ± 0.005	343.3 ± 1.5
2.5	0.710 ± 0.005	345.2 ± 1.5
5.6	0.735 ± 0.005	346.8 ± 1.5
10.0	0.744 ± 0.005	347.5 ± 1.5

[a] The errors indicated include both random errors determined from a least-squares analysis of the data and estimated systematic errors.

[b] Sample T7.5 of the 1965 Calorimetry Conference copper standard.

Figure 2 shows the excess specific heat ΔC of our samples graphed as a function of temperature T. The values for ΔC were obtained by subtracting from the specific-heat values of the sample with iron a smoothed polynomial fit to the specific-heat, values of the corresponding sample without iron. The small differences in the aluminum concentrations between a given pair of samples were corrected on the basis of the dependence of the specific heat on aluminum concentration determined from the measurements of the samples without iron. A four-point Lagrangian interpolation was used for the concentration corrections.

The magnitude of the uncertainties in the measured values of specific heat varied over the temperature range of the experiment, with vibrational stray heat the dominant factor at the low-temperature end and a rapidly decreasing thermometer sensitivity causing electrical noise to dominate at the high-temperature end. For the specific-heat differences, the high-temperature noise and the cubic temperature dependence of the lattice specific heat both contributed to the increased scatter of ΔC with increasing temperature. Deviations of less than 0.3% between polynomial fits to specific-heat data for two completely independent measurements on the same sample indicate the high reproducibility in the specific-heat results by our method. This reproducibility within a laboratory is consistent with the experience of others. Our average deviation of + 0.4% from the copper reference equation for temperatures greater than 4.2 K is also consistent with deviations of approximately ± 0.5% for measurements on the Calorimetry Conference standard at other laboratories.

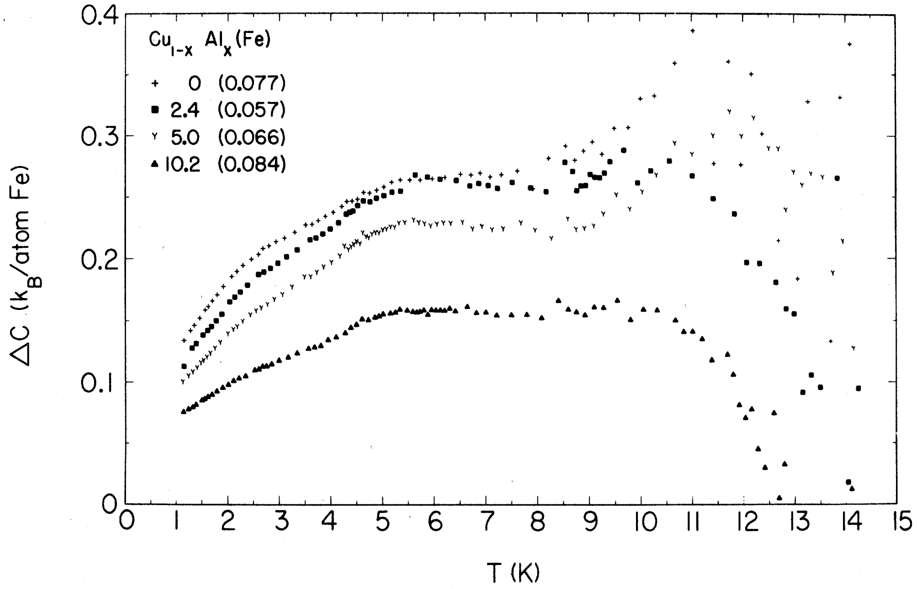

FIG. 2. Plot of the excess specific heat per iron impurity in units of Boltzmann's constant vs temperature. The concentrations of aluminum and iron listed are in atomic percent.

IV. DISCUSSION

First, let us consider the results for the copper-aluminum alloys without iron impurities. The results show an increase in the electronic[13] and a decrease in the lattice contributions to the specific heat with increasing aluminum concentration. This behavior is consistent with qualitative expectations for this alloy system for sufficiently low aluminum concentrations.

Stern[14] has demonstrated that the change in the electron density of states with dilute alloying is related to the shielding of the added impurities by states near the Fermi energy. The attraction of electronic charge to the vicinity of the impurities increases the density of states near the Fermi energy. In our case the aluminum impurities increase the electron-per-atom ratio and hence shielding requires that electronic charge be attracted to the impurities. Therefore, the electronic contribution to the specific heat, which is proportional to the density of states at the Fermi energy, should increase with increasing aluminum concentration. Our results are consistent with this picture.

The Stern theory is applicable when the alloy is sufficiently dilute that the average distance between impurities is large compared to the size of the shielding cloud. The change in the density of states is then linearly proportional to the impurity concentration. Our results indicate that this linear dependence may hold up to 5%. In order to quantitatively estimate the shielding charge from the change in the electronic specific heat one would have to correct for volume changes on alloying which also affect the density of states.

The decrease in the lattice contribution with increasing aluminum concentration can be qualitatively understood by describing the aluminum impurities by mass defects. It has been shown[15] that the change in the lattice specific heat relative to the pure host in the limit as the temperature goes to zero is given by

$$\Delta C_L/C_L = \tfrac{3}{2}(M_I/M_H - 1)c_I \, .$$

M_I and M_H are the masses of the impurity and host atoms, respectively, and c_I is the concentration of impurities. This result assumes that the concentration is sufficiently low that the contribution from all the impurities is simply c_I times that calculated for a single mass defect. For our alloy this predicts a decrease in the lattice specific heat. The relationship is quantitatively consistent with our results on the 2.5 and 5.6% alloys. Concentration effects are probably important in the 10.0% alloy. It should be noted that this theoretical estimate treats only mass defects while the specific heat can also change due to changes in the force constants. However, there is some evidence that the phonon spectrum is adequately described by a purely mass-defect theory in the Cu-Al alloy.[16]

Turning now to the results for the copper-aluminum alloys with dilute iron impurities, one sees clearly in Fig. 2 a systematic suppression of the anomalous excess specific heat per iron impurity with increasing aluminum concentration. Although the iron concentrations of the various samples differ by an appreciable amount, the observed suppression does not correlate with iron concentration. Furthermore, previous measurements of the excess specific heat of dilute Cu(Fe) alloys[2] indicate no appreciable concentration dependence up to concentrations of 0.1 at.% of iron for temperatures greater than 1 K. Therefore, this observed suppression must be attributed primarily to the changing host composition.

Quantitative changes in the anomalous properties associated with dilute transition-element impurities as a function of host material have often been observed.[1] This is expected in the picture of magnetic states as originally described by Friedel[17] and Anderson.[18] However, many-body effects involved in the theoretical description are sufficiently intractable that the structure of the impurity state is not fully understood even for simple host systems.[1] Furthermore, in the case of a disordered binary-host material, the structure of an individual impurity state may depend primarily on its local environment rather than on the average properties of the host alloy. Therefore, even if the structure of an impurity state were better understood, it would be most difficult to unequivocally attribute observed changes in macroscopic properties to a particular structural change. Therefore, without the aid of microscopic measurements, we can only speculate on the explanation for our observed suppression of the excess specific heat with aluminum concentration.

There is direct evidence that the magnetic state of the transition-element impurity depends on the local environment in certain binary-host alloys. Measurements of ^{59}Co NMR in $Rh_{1-x}Pd_x$ [19] and in $Mo_{1-x}Nb_x$ and $Mo_{1-x}Ti_x$ [20] show that the Co impurity has either a full moment or no moment depending on neighboring configurations of ions. In these systems a continuous change in some average property with host composition can be related to the continuous change in the probability of a given local environment with host composition. This concept of a discontinuous moment formation depending on local environment is due to Jaccarino and Walker.[21] However, the electronic states of these 4*d* alloys should be quite complicated compared with our $Cu_{1-x}Al_x$-host alloys. Therefore, one does not expect the local environments to differ as appreciably from the average in the $Cu_{1-x}Al_x$-host alloys.

In contrast to those systems where the magnetic state can only be understood in terms of its local environment, the $Cu_{1-x}Au_x$(Fe) dilute alloy seems to be an example where the impurity state can be described in terms of the average properties of the $Cu_{1-x}Au_x$-host alloys. The resistivity measurements of the $Cu_{1-x}Au_x$(Fe) dilute alloy system by Loram *et al.*[22] strongly indicate a continuous change in the Kondo scattering which depends on the average host properties. They are able to fit the temperature dependence of the excess resistivity per iron impurity to a universal function of T/T_K with the parameter T_K decreasing two orders of magnitude between Cu(Fe) and Au(Fe). If one adopts the viewpoint of the Kondo model where the magnetic impurity has a well-defined spin which is coupled to the conduction-electron system by a negative *s-d* exchange interaction, then the impurity-host system is described by a single parameter T_K, the Kondo temperature. The universal behavior of the resistivity indicates that each impurity is described by the same T_K which must then be a function of the average properties of the host. However, it should be noted that they obtain their fit to this universal function only after shifts in the excess resistivity are made which bring the experimental curves in coincidence at $T = T_K$. Therefore, there may be a systematic quantitative dependence on host composition which requires a more realistic model for its explanation. The shifts required cannot be determined from their published data. However, it would be most surprising if the simple Kondo model could completely describe the situation.

Since the electronic states of the $Cu_{1-x}Al_x$ alloys should be similar to the states of the $Cu_{1-x}Au_x$ alloys, one expects many similarities for the iron impurity state in these two host alloys. Now in the $Cu_{1-x}Au_x$(Fe) alloy system, the T_K parameter needed to scale the temperature in order to obtain the universal behavior of the excess resistivity decreases with gold concentration in a nearly exponential manner for concentrations of gold up to 10 at.%.[22] At 10-at.% gold, the T_K parameter is reduced by a factor of 3 from the T_K for the Cu(Fe) system. The T_K for Au(Fe) is two orders of magnitude less than for Cu(Fe). Now if one attributes the absence of magnetic behavior in Al(Fe) to a high T_K, a reasonable estimate for T_K for the Al(Fe) system would be a value two orders of magnitude greater than for Cu(Fe). This suggests that one could expect T_K to increase with increasing aluminum concentration at a rate comparable to the decrease with gold concentration implied by the resistivity measurements. This picture, however, is not consistent with our specific-heat results shown in Fig. 2. In the simple Kondo model the excess specific heat should also be a universal function of T/T_K. One expects a broad anomaly peaked at $\frac{1}{3}T_K$.[23,24] Our results would then indicate a value for T_K between 18 and 24 K independent of aluminum concentration. Furthermore, Fig. 2 shows a systematic suppression of the excess-specific-heat anomaly with increasing aluminum concentration.

Resistivity measurements[7] made on the same $Cu_{1-x}Al_x$(Fe) system also exhibit a systematic suppression of the Kondo scattering with increasing aluminum concentration. If one allows for the possibility of making arbitrarily large shifts in the excess resistivity, the excess resistivity can be made to fit reasonably well a universal function of T/T_K with T_K increasing to about 3 times its

Cu(Fe) value at an aluminum concentration of 10 at.%. However, the shifts required are larger than the estimated experimental uncertainties in the resistivity measurements. Therefore, it seems unjustifiable in our case to place any significance in the T_K values determined by this procedure. The measurements are not inconsistent with a Kondo parameter which is nearly independent of aluminum concentration.

Measurements of the excess resistivity and static susceptibility of dilute iron dissolved in the ϵ CuZn phase by Caplin *et al.*[25] establish an empirical relationship in this system between the susceptibility and the excess resistivity.[26] This relationship takes the form

$$\frac{\partial \Delta\rho}{\partial \ln T} \propto p_{\text{eff}}^2 ,$$

where $\Delta\rho$ is the impurity resistivity due to the iron impurities and p_{eff} is the effective moment on each iron impurity obtained from the susceptibility using the relation $cp_{\text{eff}}^2 \mu_B^2/3k_BT$ for the susceptibility where c is the iron concentration. The relationship holds in the temperature range where the excess resistivity depends logarithmically on temperature. The value of p_{eff} changes rapidly across the ϵ phase from $1.7\mu_B$ at 21-at.% Cu to $0.4\ \mu_B$ at 14-at.% Cu. Since the probabilities for given local environments cannot change appreciably over this very narrow concentration range, it is unlikely that local environmental effects contribute to the observed change in p_{eff} with host composition. This suggests a magnetic impurity state where the moment is not well defined. However, the characteristic time of the moment must be sufficiently long that the Kondo scattering is determined by p_{eff}.

High-temperature ($T > 115$ K) susceptibility measurements[27] on our $\text{Cu}_{1-x}\text{Al}_x$(Fe) alloys show a decreasing p_{eff} with increasing aluminum concentration. p_{eff} decreases by about 15% with the addition of 10-at.% aluminum. The observed suppression in the excess specific heat seen in Fig. 2 appears to correlate reasonably well with p_{eff}^2, although the large uncertainties in the measured values for p_{eff} do not permit a completely convincing demonstration of this correlation. It should be noted that the change in p_{eff} across the α Cu-Al phase is much less rapid than across the ϵ Cu-Zn phase. However, the results indicate a similar situation where the moment is not well defined, yet where the Kondo scattering is determined by p_{eff}.

Although the preceding discussion suggests a picture where local environmental effects are not required for the explanation of our specific-heat measurements, one cannot unambiguously rule out such effects. As already noted in discussing the electronic contribution to the specific heat of the iron-free copper-aluminum alloys, the valence difference of the aluminum requires appreciable shielding. This implies a locally varying density of states. Therefore, it is not unreasonable to picture a situation where a given impurity state behaves as a well-defined spin with a Kondo parameter T_K which may vary by an order of magnitude or more depending on the local environment. However, unpublished ^{63}Cu NMR measurements in α-phase Cu-Al(Fe) by Golibersuch[28] show no evidence for this type of behavior.

Since our specific-heat measurements did not go below 1 K, the data cannot clarify the uncertainties concerning the temperature dependence of the low-temperature ($T \ll T_K$) excess specific heat of dilute magnetic alloys.[1] Furthermore, the iron concentrations used were too high for interactions between impurities to be negligible for $T \ll T_K$. Nevertheless, it can be noted, as previously reported,[5] that our data for Fe in $\text{Cu}_{1-x}\text{Al}_x$ are consistent with a $T^{1/2}$ behavior as the temperature goes to zero for temperatures up to about 3 K. At present there seems to be very little theoretical or experimental evidence to suggest that the low-temperature excess specific heat of dilute magnetic alloys depends on temperature as $T^{1/2}$ if the interactions between the impurities are negligible. On the contrary, there now is good experimental evidence for a T dependence.[4,29] Our apparent $T^{1/2}$ behavior is based on data over a very limited temperature range. What is significant is that alloys with various aluminum concentrations show the same temperature dependence. This indicates that the observed suppression of the excess specific heat with increasing aluminum concentration is independent of temperature.

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Electronic Studies of KH_2PO_4[†]

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The results of electrocaloric studies of the electrical equation of state of KH_2PO_4 in the temperature region within 1 K of the ferroelectric transition are reported. Chief emphasis is given to determination of the spontaneous polarization. A discontinuous polarization jump of 1.87 ± 0.09 $\mu C/cm^2$ is found at T_c. Several tests of the validity of the phenomenological theory of ferroelectricity, including a noncalorimetric determination of the heat capacity, are made. It is shown that the phenomenological theory provides a good and consistent description of the thermodynamic behavior of KH_2PO_4. No major discrepancies which might be linked to behavior near a phase transition are found. Any possible discrepancies are minor and confined to the temperature region $T_c - T < 0.1$ K. It is shown that a term proportional to P^8 dominates the saturation behavior. Evidence is presented that a portion of the calorimetric anomaly near T_c is not directly related to the temperature dependence of the polarization.

INTRODUCTION

The most widely quoted measurements of the spontaneous polarization of the ferroelectric KH_2PO_4 (KDP) were obtained using the hysteresis-loop method nearly thirty years ago.[1] These measurements, and subsequent ones using the same method,[2,3] indicate that the polarization decreases abruptly, but smoothly, to zero at the transition temperature T_c. This implies that the transition is of second order. Recent dielectric[4,5] and calorimetric[6] data imply that the transition in KDP is of first order.

In addition to providing information concerning the order of the transition, precise polarization measurements, coupled with recent calorimetric data, allow a check of the temperature region of validity of the phenomenological theory (PT) of ferroelectricity. Such a test was the objective of the most recent hysteresis-loop investigation of the polarization in KDP.[3] This study claimed to support the application of the PT, but the results were completely at variance with the calorimetric data.[6,7] Thus, to provide a new test of the applicability of the PT and to reinvestigate the order of the transition, a new investigation of the spontane-