SPECIFIC HEAT OF DILUTE Cu(Fe) ALLOYS FAR BELOW THE KONDO TEMPERATURE*

M. D. Daybell, W. P. Pratt, Jr., and W. A. Steyert
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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Specific-heat data on the well-studied copper-iron Kondo alloy have been taken at temperatures down to $2\times10^{-3}T_K$, where the Kondo temperature $T_K\approx 20$°K. Results suggest a choice among current theoretical models of the quasibound state, and indicate the apparent existence of a significant amount of entropy at still lower temperatures.

Two unresolved questions concerning the simpler properties of the quasibound state arising from the Kondo effect in dilute alloys of transition metals in normal metal hosts are directly related to the specific heat $C_v(\simeq C_p)$ of these alloys in the $T=0$ limit. One of these questions is simply what is the form of C_v vs T—recent theoretical expectations range from C_v linear[1,2] in T through[3] $T\ln(T/T_K)$ to[4,5] $T^{1/2}$. The other question is how much entropy ΔS comes out of the system during the formation of the quasibound state as the alloy is cooled from far above the Kondo temperature to absolute zero. Measurements reported here on two dilute Cu(Fe) alloys should serve to resolve these two questions, while at the same time complicating efforts to describe in detail the ground state of real Kondo systems within the framework of existing models. Evidence is given for the apparent persistence of large amounts of entropy to extremely low temperatures. Some information about the specific heat of pure copper down to 40 mdeg K is also presented.

The three 200-g samples were prepared as described earlier,[6] cut into 3.1-cm-diam by 3.5-cm-long cylinders, and placed in an ultrahigh-purity graphite (type CCH) holder rigidly attached to the bottom of a He^3-He^4 dilution refrigerator. A tin heat switch (area/length ratio $\approx10^{-4}$ cm) was connected between a cadmium-bismuth[7] solder joint on the refrigerator and a spot weld on the sample by two lengths of copper-coil foil, indium soldered to the tin switch proper. Heat was provided to the sample by one of two means. Above 200 mdeg K, a 200-Ω Manganin resistance heater was wound directly on the sample and secured with a small quantity of General Electric 7031 varnish. An electronically timed mercury relay controlled the current pulses into this heater, which were chosen to increase the sample temperature in increments of 10 to 20%. Heater power was monitored by a four-lead arrangement terminating at bath temperature. Measurements were also made in the absence of this heater, which had a finite specific heat arising from its magnetic properties. In this case, heating was accomplished by a removable Co^{60} γ-ray source (nominally 20 mCi) located about 17 cm from the center of the sample. Doses (monitored by a sodium-iodide counter) of from 5 to 180 sec were used to produce temperature increments in the sample of approximately 10%. The energy deposited in the sample by a given γ-ray dose was established by requiring the specific heats of the pure copper plus addenda measured using the two heating methods to agree over the 200- to 350-mdeg K range. Small geometrical corrections to the γ-ray calibration from sample to sample contributed about 1% to the uncertainty of the final results.

The sample thermometer was a 100-Ω Speer resistor mounted in a closely fitting hole in the sample using Apiezon-N grease, and thermally lagged to the sample using two 3-cm lengths of 0.1-mm-diam insulated copper wire soldered to its terminals and varnished to the sample. A total of 7 cm of 64-μm-diam Manganin wire connected the resistor to a pair of terminals on the cold end of the graphite sample holder. Niobium leads 64 μm in diameter passed from these terminals up along the graphite and the refrigerator and on up to bath temperature, where connection was made to other leads leading out of the Dewar. Similar leads were used for the heater, when needed. The use of a phase-locked ac bridge enabled the power dissipated in the measuring resistors to be kept below 10^{-13} W; quadrupling this power had no effect on the resistance reading. The output of this bridge was displayed on a recorder, and the temperature readings were extrapolated to the center of each heat pulse. The sample resistor and another resistor attached to the refrigerator were initially calibrated against a 10% cerium-90% lanthanum-magnesium-nitrate crystal, and were recalibrated near the end of the experiment against a 100% cerium-magnesium-nitrate crystal. No observable change was noticed between the two calibrations, and the two resistors continued to agree until the end of the experiment. Absolute resistance-thermometer calibrations were accurate to ±5 mdeg K, while temperature increments were measured to ±4%.

The entire apparatus was enclosed in a lead-shrouded Pyrex vacuum bulb immersed in a 1.2°K helium bath. Initial cooldown was accomplished using about 0.1 Torr of neon exchange gas, which was pumped out at nitrogen temperature before the Dewar bath space was filled with liquid helium. Below 77°K, cooldown was facilitated by a pair of judiciously chosen graphite heat shunts, whose thermal conductivity became negligible in the helium range. This technique avoided the use of helium exchange gas.

The raw specific-heat data, divided by the number of moles of sample material, are shown in Fig. 1. In each case, the addenda, consisting of the sample holder, the thermometer and its leads, the heater, when used, and its leads, and a small quantity of grease and varnish, was the same to within the precision of the specific-heat measurements themselves. The pure-copper-plus-addenda runs served as "empty" calorimeter measurements for the alloy runs. The absence of true empty calorimeter data, inconvenient to obtain with our arrangement, makes it impossible to quote values for the specific heat of pure copper; but the agreement of the present data in the 0.4-1.0°K range with existing measurements (see Fig. 1), along with their approximately linear T dependence over much of the range covered, confirms that the specific heat of the addenda was in fact small, and that the calibration of the resistance thermometer used was more than adequate to the present purposes. In the 40-mdeg K temperature region the heat leak into the sample was about $\frac{1}{2}$ erg/min. It is seen that the dilution refrigerator is useful for measuring very small specific heats (of the order of 10^{-4} J/°K) in the tens of mdeg K temperature range.

The specific heat of the impurity state in the alloy samples was obtained by subtracting from the specific heat of the alloy itself the background specific heat taken from a smoothed curve through the copper-plus-addenda data of Fig. 1, and dividing by the number of moles of iron impurity in the alloy. The impurity specific heat, divided by the temperature to emphasize the relationship of the data to various theoretical predictions, is plotted in Fig. 2, together with the 500-ppm iron-in-copper data of Franck, Manchester, and Martin[8] above 0.4°K. Despite the large scatter in the 112-ppm data, it can be seen that the impurity

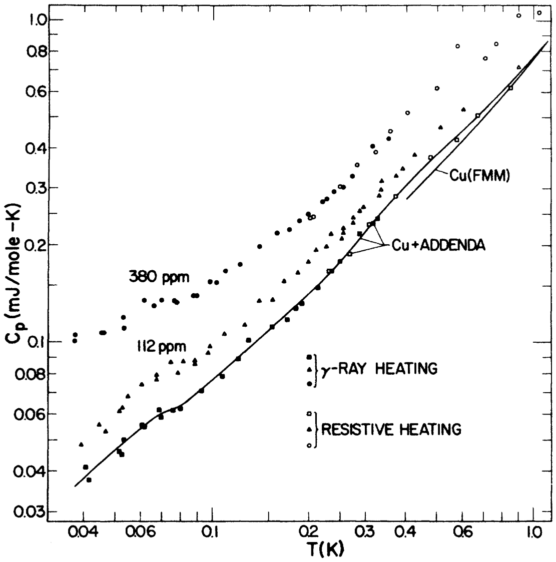

FIG. 1. Specific-heat data for two dilute alloys of iron in copper (iron concentrations in atomic ppm) and for pure copper. In each case, data are for a 200-g sample, and include the specific heat of the thermometer, calorimeter, and heater (when used). The smoothed curve through the pure copper-plus-addenda data was used to obtain the impurity specific-heat results presented in Figs. 2 and 3. The pure-copper specific-heat data of Franck, Manchester, and Martin (Ref. 8) are represented by the curve at the upper right.

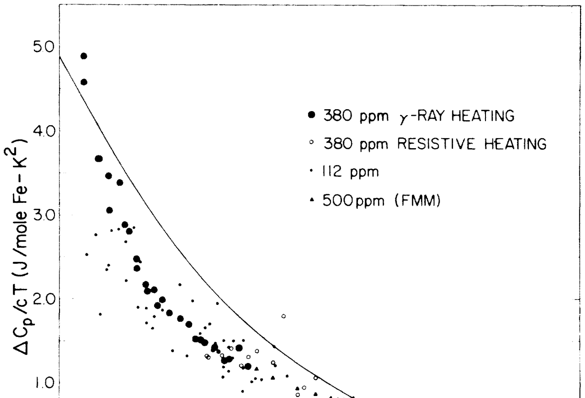

FIG. 2. Impurity specific heat divided by absolute temperature, per mole of impurity, for several dilute concentrations c of iron in copper. The 500-ppm data are from Ref. 8. The theoretical curve (from Ref 4) is well represented by C_p proportional to $T^{0.577}$ below 1°K.

specific-heat data scale with concentration, except possibly at the very lowest temperatures attained. Although, as noticed earlier by Heeger, et al.,[9] C_p/T is proportional to $-\ln T$ down to about 0.4°K, below this temperature it increases more rapidly with decreasing $\ln T$.[10] Clearly C_p/T is not independent of T, in contradiction to several theoretical calculations.[1,2] One perennial problem in discussing the Kondo effect in the region where many-body effects become important is that there is no theory on hand which treats systems of bare local spin $S \neq \frac{1}{2}$ with much confidence, nor is the effect of the ordinary potential scattering on the specific heat available in current theories. Keeping this in mind, it is still instructive to compare the present data with some existing $S = \frac{1}{2}$ (s-wave) theories.

It has been suggested[4,5] that, as $T \rightarrow 0$°K, $C_v \rightarrow T^m$ with m about $\frac{1}{2}$. A detailed calculation of this type,[4] based on Nagaoka's equations of motion technique, yields the theoretical curve shown in Fig. 2. Here we have followed a suggestion of the authors and allowed for the fact that Cu(Fe) apparently has $S = \frac{3}{2}$ by multiplying their $S = \frac{1}{2}$ result by a factor of 2 to allow for the increased entropy expected in the higher spin system, although this is by no means the only reasonable choice for this factor. While this curve, which becomes $C_v/T = 1.12/T^{0.423}$ (i.e., $m = 0.577$) below about 1°K, is seen to be in good qualitative agreement with the (more accurate) high-concentration data, an even better fit to the sub 1°K results can be obtained by choosing m slightly less than $\frac{1}{2}$. The fact that $C_v/T \rightarrow T^{-1/2}$ as $T \rightarrow 0$ lends support to the low-field susceptibility behavior observed in similar alloys earlier,[6] where it was found that the susceptibility $\chi \rightarrow T^{-1/2}$ for fields below about 1000 Oe as $T \rightarrow 0$.

An overall picture of the well known Cu(Fe) specific-heat anomaly[8,11] is presented in Fig. 3. A peak occurs at about $\frac{1}{3}T_K$ as calculated by Bloomfield and Hamann,[4] and C_p is falling slowly at very low temperatures. The scatter in these results at high temperatures is associated with taking differences in the presence of very large lattice specific heats, while below about 1°K impurity interaction may influence the higher concentration measurements. The area under this curve represents the entropy change associated with the breakup of the quasibound state [$\Delta S = \int C_p d(\ln T)$ for zero pressure] or more precisely, an upper limit to this entropy change.[10] The entropy change from 0.035 to 35°K is $R \ln 2 \pm 5\%$ according to our high-temperature extrapolation and those of previous authors,[8,11] with only 10% of the area in the region under the extrapolation (R is the gas constant per mole). It is not possible to account experimentally for the $R \ln 4 = 2R \times \ln 2$ of entropy that is generally expected to be present for $T \gg T_K$, based on the high-temperature spin of $\frac{3}{2}$. Thus below 0.04°K half the entropy is still available (in zero magnetic field).

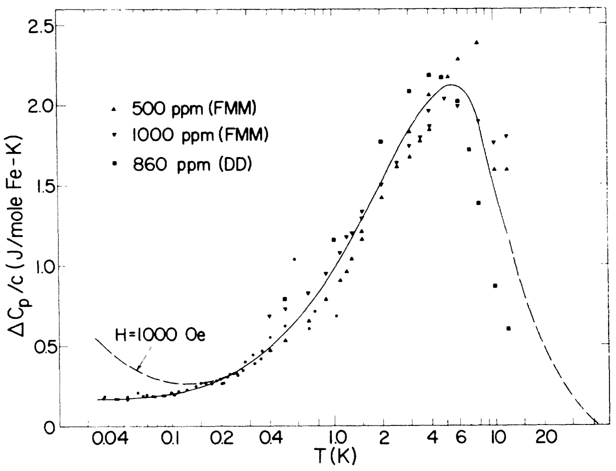

FIG. 3. Impurity specific heat per mole of impurity for several alloys of iron in copper, showing the relation of older data (Refs. 8 and 10) at the specific-heat peak just below the Kondo temperature to the present low-temperature limit results for 380 ppm (solid circles). The specific heat in a magnetic field can be calculated thermodynamically from the susceptibility data of Ref. 6, and is shown in the figure. It is seen that a significant amount of entropy (represented by the area under the curve) remains in the quasibound state even below the range of the present measurements.

This entropy is exhibited in a magnetic field. From susceptibility measurements made on similar samples,[6] it is possible to calculate the specific heat in a magnetic field using the thermodynamic relation $\partial C_p(H,T)/\partial H = T[\partial^2 M(H,T)/\partial T^2]_H$. The ac susceptibility $\chi(H,T)$ can be well represented by[6,12]

$$\chi(H,T) = (aT^{-\frac{1}{2}} - b)e^{-H/d} + b, \quad T < 200 \text{ mdeg K}, \tag{1}$$

leading to a relation

$$C_p(H,T) \approx C_p(0,T) + 3ad(H-d)/4T^{3/2}, \quad T < 200 \text{ mdeg K}, \; H \gtrsim 3d. \tag{2}$$

This behavior is shown in Fig. 3, with $a = 0.23 \times 10^{-8}$ emu °K$^{1/2}$/g ppm Fe and $d = 300$ Oe, both from Ref. 6. This relation fails at very high fields where Eq. (1) is expected to break down.[13]

The present measurements of the low-temperature limit of the specific heat of a typical Kondo system thus not only suggest a choice between various theoretical models, but also yield important conclusions concerning the entropy of the very low-temperature state of the system.

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[10] Contributions to the impurity specific heat arising from mechanisms other than the Kondo effect can be estimated to be smaller than the precision in the present data. For example, at 37 mdeg K the inverse T^2 specific heat of 20 copper nuclear quadrupole moments Q in the effective electric field gradient eq produced by Fridel oscillations around the iron impurity contributes only about 0.13×10^{-3} J/mole Fe K, taking $q=5\times10^{23}$ cm^{-3}, the largest value estimated for this quantity by Kohn and Vosko [Phys. Rev. 119, 912 (1960)] for nonmagnetic impurities in copper. This contribution increases by less than an order of magnitude even if the Friedel screening is provided entirely by resonant d-wave scattering. The limited Au^{197} Mössbauer line broadening seen in the related $\mathrm{Au}_{95}\mathrm{Fe}_5$ alloy system also indicates that the nuclear quadrupole effect is quite small. [U. Gonser, R. W. Grant, C. J. Meechan, A. H. Muir, Jr., and H. Wiedersich, J. Appl. Phys. 36, 2124 (1965), and A. H. Muir, Jr., private communication.] Other unanticipated contributions to the measured impurity specific heat cannot be completely ruled out.

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CONDUCTION-BAND STRUCTURE IN ANTHRACENE DETERMINED BY PHOTOEMISSION

J. Dresner
RCA Laboratories, Princeton, New Jersey 08540

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The structure of the conduction-band system of crystalline anthracene has been investigated by means of electron photoemission from negative anthracene ions formed by reaction with K and Na. A sharp emission threshold is found at 0.79 ± 0.01 eV. The lowest conduction band is less than 0.03 eV wide in agreement with the calculated value. A second conduction band, 0.3 eV wide, is also found, separated from the lower one by less than 0.05 eV.

The detailed structure of the conduction and valence bands in anthracene is of considerable interest. Both bands have been calculated to be from 0.01 to 0.02 eV wide[1,2]; charge transport in such narrow bands has been shown to result in an anomalous Hall effect, where the sign is reversed and the measured mobility much larger than the microscopic mobility.[3-5] It has also been predicted that a broader conducting state must lie above the lowest conduction band.[6,7] From the photoemission of holes from metals into anthracene, Williams and Dresner[8] established that the valence band was less than 0.1 eV wide, as predicted, and broadened by vibrational overlap. Recently, two papers have appeared describing the use of photoemission of electrons to study the conduction-band structure.[9,10] Baessler and Vaubel[9] obtained photoemission from alkali metals, yielding photoemission thresholds of 0.8 eV for Cs and 1.0 eV for Na. These were interpreted as photoemission from the Fermi level of the metal (yielding a width for the lowest conduction band approximately 0.2 eV) followed by emission into a higher band beginning 0.45 eV