KONDO TRANSITION IN Cu(Cr): SUSCEPTIBILITY AND SPECIFIC HEAT*

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Specific-heat and magnetic-susceptibility measurements on very dilute Cu(Cr) alloys are reported. As in Cu(Fe), a zero-field susceptibility inversely proportional to the square root of temperature down to 14 mK is seen. A specific-heat peak at 0.35 K is observed. Thus it is now possible to make a detailed comparison between two simple dilute magnetic alloys differing primarily with respect to their Kondo temperatures.

Two puzzling features of the properties of dilute magnetic alloys have been exhibited in the extensive recent work on alloys of iron in copper. These alloys, which undergo their "Kondo" transition to a nonmagnetic low-temperature state below the Kondo temperature $T_K \simeq 18$ K, have a susceptibility in approximately zero field that does not approach a limiting value as $T \to 0$, but instead diverges approximately as $T^{-1/2}$.[1] At higher fields (above 1 kOe) the susceptibility behaves more nearly as expected, becoming temperature independent as $T \to 0$, with $\chi(T=0) = \mu_{\rm eff}^2/3kT_K$ ($H > 1$ kOe)[1] ($\mu_{\rm eff}$ is the high-temperature effective magnetic moment taken as $3.6\mu_B$). Another problem arises in the specific-heat results, which indicate that only $R\ln 2$ of entropy per mole of iron impurity comes out of the impurity system[2] as it is cooled from high temperatures to temperatures below $0.002T_K$,[3] even though this is apparently a spin-$\frac{3}{2}$ system,[4] and should, at least naively, have $R\ln 4$ of entropy if the ground state is a singlet. (See, however, the discussion of Müller-Hartman and Zittartz.[5])

These features are not included in s-d exchange models of localized moments[6] nor, as yet, in the more recent localized spin fluctuation model which is now being treated in sufficient detail to predict the behavior of localized magnetic moments.[7,8] For these reasons, data on the susceptibility and specific heat of a system differing in as few ways as possible from Cu(Fe) are enlightening.

Susceptibility measurements in a magnetic field were made on 33- and 15-ppm Cu(Cr) samples using a mutual-inductance bridge operating in the frequency range 1.7 to 3.5 Hz.[9] The susceptibility values reported are dM/dH (M and H are magnetic moment and field). The laminated samples were fabricated and mounted on the cryostat in the same fashion as reported earlier for the Cu(Fe) alloy.[1] However, rather than rely on pressure for thermal contact in the 15-mK region, the ends of two pieces of copper-coil foil were spot-welded to the samples (as far as possible from the bridge coils) and to the copper mount which screws onto the bottom of a He^3-He^4 dilution refrigerator. A 100-Ω Speer resistor mounted in a close-fitting hole in the above-mentioned copper mount provided thermometry down to 30 mK, using a phased-locked ac bridge with a power input to the resistor of 10^{-13} W. In the region below 30 mK, where the resistance-thermometer calibration was unreliable from run to run, a γ-ray anisotropy thermometer was employed. This consisted of a single crystal of lanthanum magnesium nitrate doped with 2 μCi of Mn^{54} and sandwiched between the two pieces of coil foil using Apiezon-N grease. Two 3-in. ×3-in. sodium iodide counters mounted at 0° and 90° relative to the axis of symmetry of the crystal were used to determine the anistropy of the γ radiation. The resistance and anisotropy thermometers were calibrated (with an accuracy of ±7% and ±10%, respectively) down to 13 mK against single crystals of cerium magnesium nitrate and of 10% cerium magnesium nitrate in 90% lanthanum magnesium nitrate.

The experimental procedure on any given run was to first measure the susceptibility of the sample in zero field over the full temperature range, while calibrating the resistance thermometer against the anisotropy thermometer below 30 mK. For subsequent temperature sweeps in a field, the now-calibrated resistance thermometer was used over the full temperature range.

Specific-heat measurements were made on two 200-g copper samples, one of pure copper and the other of a 32-ppm Cu(Cr) alloy, using the same apparatus and procedures as reported[2] for Cu(Fe) with the following exceptions: First, the Manganin heater was replaced by a 33-Ω Speer resistor mounted in a closely fitting hole in the sample using Apiezon-N grease. This resistor was driven by a constant-current source, and the time-average voltage across the resistor was measured using a voltage-to-frequency converter. Second, above 0.5 K a majority of the data were taken with the tin heat switch, which had connected the refrigerator to the sample, removed. The graphite sample holder provided sufficient thermal contact to the refrigerator to effect cooling of the sample to 0.4 K. As before, the impurity specific heat was obtained by taking the difference in specific heats between the alloy sample plus addenda and the pure copper sample plus addenda.

The zero-field susceptibility per impurity shown in Fig. 1 can be fitted by a power law $\Delta\chi_i|_{H=0} \propto T^{-0.55\pm0.15}$, and scales reasonably well with the concentration assigned to the two alloys (nearly perfect scaling would be obtained if the ratio of the concentrations were taken to be the same as the ratio of the impurity resistivities of the two samples, which differed somewhat from the ratio of the nominal concentrations). These same data, represented by the curves in the $1/T$ plot of Fig. 2, are reproduced there in order to help illustrate a surprising low-field effect first seen[1] in Cu(Fe) and now appearing again in Cu(Cr). The data of Fig. 2 show that in very small fields $\mu H \simeq kT \ll kT_K$ the susceptibility $\Delta\chi_i = (dM/dH)/c$ drops below its zero-field value to a smaller, temperature-independent value, which is expected[6] to be given by $\mu_{eff}^2/3kT_K$. For very low temperatures, this initial rapid drop in susceptibility as the field is increased is followed by a long region in which the susceptibility decreases very slowly toward zero as the field increases toward $\mu H = kT_K$, as is exhibited in the insets of Figs. 1 and 2.

The most interesting feature of the specific-heat results (Fig. 3) is the peak in C_p at $T_{max} \simeq 0.35$ K. The entropy under this peak is $R\ln 3 \pm 15\%$, per mole of impurity.

Several new results follow from the present work. We have two new estimates of the Kondo temperature of the important Cu(Cr) system; from $\Delta\chi_i = \mu_{eff}^2/3kT_K$, with $\mu_{eff} = 3.6\mu_B$ and H small but finite, $T_K = 1.3 \pm 0.1$ K, while[6] from $T_K \approx 3T_{max}$, $T_K = 1.1$ K. It has been clearly demonstrated that the peculiar small-field behavior seen earlier in Cu(Fe) is repeated in a second very similar alloy, and that, in fact, using our estimates for T_K in Cu(Cr) (which are consistent with those obtained elsewhere[10]), $\Delta\chi_i$ for both al-

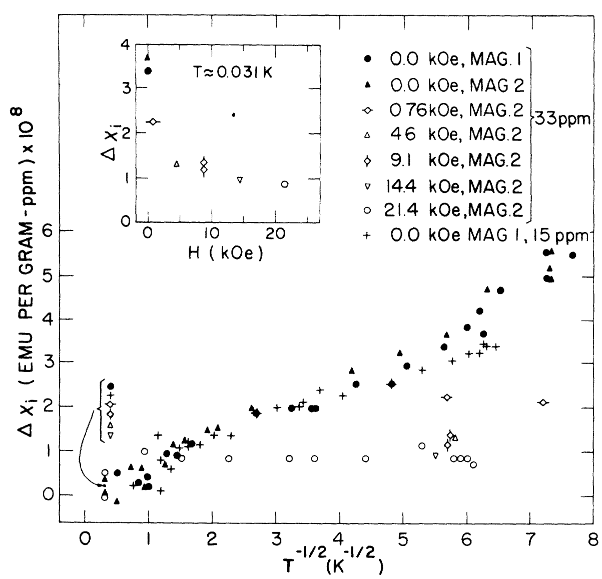

FIG. 1. Incremental susceptibility per gram of alloy per atomic ppm for two concentrations of Cr in Cu, vs $T^{-1/2}$, at zero and high fields. Mag. 1 was used below 0.6 kOe, Mag. 2 above 0.6 kOe. $\Delta\chi_i$ vs $T^{-1/2}$ is shown for one relatively high field value, while a field sweep of $\Delta\chi_i$ at $T \simeq 0.031$ K is presented in the inset. The uncertainty in the zero of $\Delta\chi_i$ at high fields may be as large as 0.5×10^{-8} emu/g ppm. In zero field, $\Delta\chi_i \approx 0.63\times10^{-8}\, T^{-1/2}$ emu/g ppm. Concentrations are known to within ±10% and represent the major uncertainty in $\Delta\chi_i$.

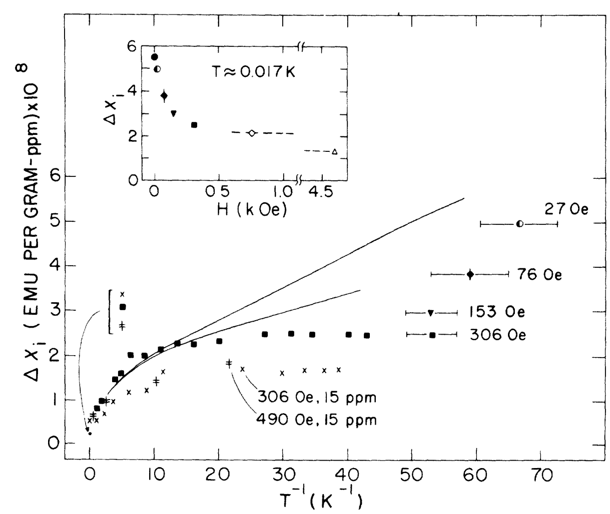

FIG. 2. Field dependence of the incremental susceptibility per gram of alloy per atomic ppm, versus reciprocal temperature, for two concentrations of Cr in Cu. Except where noted otherwise, data are for the 33-ppm chromium sample. The applied field (in Oe) is shown for each symbol. Thermometry in a field deteriorated at the lowest temperatures, as shown. Insert indicates the field dependence for $\Delta\chi_i$ at temperatures of 15 to 19 mK, including an interpolation between two data points shown in Fig. 1. Curves represent the zero-field data of Fig. 1. The shift from a Curie-Weiss-like behavior at moderate fields to a $T^{-1/2}$ law in zero applied field is clearly shown.

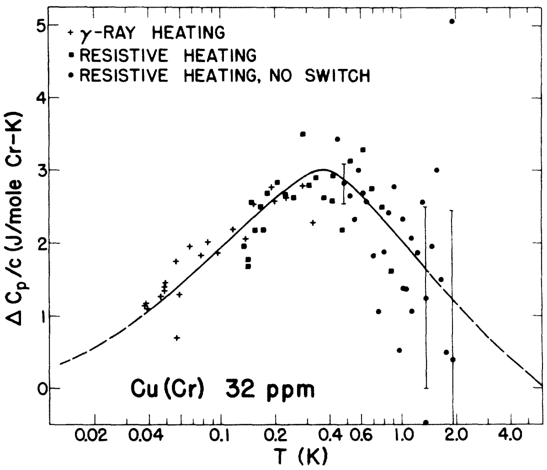

FIG. 3. The impurity specific heat, ΔC_p, of chromium in copper per mole of chromium. Resistivity [M. D. Daybell and W. A. Steyert, Phys. Rev. Letters 20, 195 (1968)] and susceptibility measurements reported here show that this concentration is low enough that impurity interaction effects are not important. Larger errors above 1 K reflect the small C_p difference between the alloy and pure copper at high temperatures.

loys can be represented in zero field by the single expression

$$\Delta\chi_i = a(T_K T)^{-1/2} \qquad (1)$$

as might be expected from dimensional arguments or by requiring that the mean-square moment be a universal function[11] of T/T_K (here $a = 0.7\times10^{-8}$ emu K/g ppm). It is found that the entropy under the C_p peak is, in a simple picture, too small in Cu(Cr), as was the case in Cu(Fe). The present susceptibility data taken together with earlier magnetoresistance[12] results are consistent, within rather large experimental uncertainties, with $\Delta\rho(H)/\Delta\rho(H=0) = bM^2$, where $\Delta\rho$ is the resistivity per impurity and $b = 3.7\times10^6$ (emu/g ppm)$^{-2}$. The results also show the magnetization beginning to approach saturation at the highest fields used (21.4 kOe).

With these measurements, added to those already available on resistivity,[12] high-temperature susceptibility, and NMR,[10] Cu(Cr) has become almost as thoroughly explored experimentally as Cu(Fe), the classic Kondo system. In fact, it is interesting to note that ESR has been done[10] on Cu(Cr) but not on Cu(Fe).

We can conclude with an intercomparison of the Cu(Cr) data and the older Cu(Fe) data with Suhl's localized spin fluctuation theory.[7] First, as predicted, in both systems $\Delta\chi_i$ in a small magnetic field becomes temperature independent (with a value $\mu_{eff}^2/3kT_K$) below the same temperature at which ρ becomes temperature independent. There are more decades of temperature between the high- and low-temperature limiting ρ values for the low-T_K system [Cu(Cr)], again in accordance with this theory, as is the fact that the lower T_K system also shows the greater fractional change in ρ and the lower resistivity at high temperature. These last results were not contained in the calculations done on the s-d model. No detailed specific-heat predictions have come out of the spin-fluctuation picture as yet.

It is apparent that however much the localized spin-fluctuation theory may differ from the s-d model in principle, it is going to be no easy matter to distinguish the two in practice, and we look forward to further attempts by the theorists to demonstrate a fundamental relation between them.

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[1]M. D. Daybell and W. A. Steyert, Phys. Rev. 167, 536 (1968).

[2]M. D. Daybell, W. P. Pratt, Jr., and W. A. Steyert, Phys. Rev. Letters 21, 353 (1968).

[3]C_p as $T\to 0$ in zero field is found to fall at least as fast as $T^{-1/2}$, which allows almost no entropy below $0.002T_K$. Only if C_p were to stop falling below $0.002T_K$ and become approximately temperature independent would appreciable entropy be available.

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[5]E. Müller-Hartman and J. Zittartz, Phys. Letters 26A, 284 (1968).

[6]For a bibliography on the s-d exchange model, see M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. 40, 380 (1968).

[7]H. Suhl, Phys. Rev. Letters 19, 442 (1967); M. J. Levine, T. V. Ramakrishnan, and R. A. Weiner, Phys. Rev. Letters 20, 1370 (1968); M. Levine and H. Suhl, Phys. Rev. 171, 567 (1968).

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[9]M. D. Daybell, Rev. Sci., Instr. 38, 1412 (1967).

[10]A. J. Heeger, L. B. Welsh, M. A. Jensen, and G. Gladstone, Phys. Rev. 172, 302 (1968); P. Monod and S. Schultz, Phys. Rev. 173, 645 (1968).

[11]For rotationally invariant isolated impurities, $\Delta\chi_i = \langle\mu^2\rangle/3kT$; compare Levine and Suhl, Ref. 7. For two systems like Cu(Fe) and Cu(Cr), which have very similar high-temperature moments, the simplest model is that $\langle\mu^2\rangle$ is a universal function of $T/T_K = \tau$, $\mu^2(\tau)$. Then $\Delta\chi_i = \mu^2(\tau)/3kT$; and since empirically $\Delta\chi_i \propto T^{-1/2}$, $\mu^2(\tau)$ must be proportional to $\tau^{1/2}$ in order that $\Delta\chi_i \propto (1/T)(T/T_K)^{1/2}$ which is the same form as Eq. (1).

[12]M. D. Daybell and W. A. Steyert, Phys. Rev. Letters 20, 195 (1968).