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# Calorimetric Evidence for a Singlet Ground State in CuCr and CuFe†

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## Abstract

Heat capacity measurements show that the entropy reduction associated with the formation of the spin compensated state in CuCr is R ln (2S + 1). The magnetic field dependence of the heat capacity of CuFe suggests that at $T \ll T_K$ the susceptibility has the form $\chi = \chi_o[1 - 15(T/T_K)^2]$, which is consistent with the third law of thermodynamics.

The ground state of a single magnetic impurity in a metal continues to be an unsolved problem in spite of the attention it has received. Different theories give different physical pictures for the ground state and make different predictions for the 0 K entropy and the temperature dependences of physical properties at $T \ll T_K$, where $T_K$ is the Kondo temperature.[1] Heat capacity measurements on both CuFe and CuCr have been interpreted as showing that $\Delta S$, the entropy reduction associated with the formation of the spin-compensated state, is less than $R \ln(2S + 1)$.[2,3] In the same systems, the temperature dependence of the magnetic susceptibility[2-5] $\chi$, if extrapolated to $T = 0$, does not satisfy the third law of thermodynamics requirement $[\partial\chi/\partial T]_{T=0} = 0$. This also implies that the spin degeneracy is not completely removed at $T = 0$. We report here new heat capacity measurements on CuCr and an extension of earlier measurements[6] on CuFe to higher temperatures. In the single-impurity limit the new data show that the heat capacity anomalies are broader than had been indicated by earlier measurements. The CuCr data are well represented by the Bloomfield-Hamann theory for $T/T_K > 0.07$ and gives $\Delta S = R \ln(2S + 1)$. The CuFe data are consistent with $\Delta S = R \ln(2S + 1)$. Their field dependence shows that the low-temperature single-impurity $\chi$ deviates from an extrapolation of the above 1 K data[4,5] in the direction required by the third law, and suggests that $\chi = \chi_0[1 - 15(T/T_K)^2]$ at $T \ll T_K$.

The Cr content of the CuCr samples was determined to ± 5% by a spectrophotometric method.[8] Within that accuracy the 4.2 K resistivities were fitted by $\rho_{4.2}/c = 1.08 \times 10^{-3} \mu\,\Omega$-cm/at ppm where c is the concentration, and that relation was used to assign the reported concentrations

from values of $\rho_{4.2}$. The CuFe samples were the same ones used in an earlier investigation.[6] All measurements were made with a reproducible germanium thermometer that permitted a high sample-to-sample precision. The heat capacities of the sample holder and the pure copper from which the samples were made were measured in separate experiments.

The zero-field CuCr data are shown in Fig. 1 as $\Delta C$, the heat capacity in excess of that of pure copper divided by the concentration. Within the precision of the measurements, $\Delta C \propto c$, as it must be in the single impurity limit, except below 0.15 K. At the lowest temperatures the 51 at ppm sample exhibits effects of impurity-impurity interactions similar to those observed[6] in CuFe. The dashed curve represents a linear extrapolation to T = 0 as suggested by measurements[6,9] on CuFe at lower reduced temperatures. Above 0.15 K there are no systematic differences between the samples, and we have taken the 51 ppm data, for which the precision is best, as defining the shape of the peak. The peak is better defined than in earlier work[3] and is broader. The solid curve represents the theory of Bloomfield and Hamann,[7] scaled and shifted in temperature to fit the peak. As drawn it corresponds to $T_K = 2.1$ K, and provides an excellent fit to the data for $T/T_K > 0.07$. The linear extrapolation to T = 0 and extrapolation to high temperature by the theoretical curve give $\Delta S = 1.05\ R \ln 4$. Since the spin is 3/2,[10] this corresponds to the complete removal of the degeneracy, to within the uncertainty in the concentrations.

For 81 and 195 at ppm CuFe $\Delta C/c$ is independent of concentration for $T > 0.12$ K. The maximum $\Delta C/c$, which occurs near 9 K, is greater than

that found by Franck, Manchester, and Martin[11] for more concentrated samples, but is consistent with the trend in their data. At higher temperatures the lattice heat capacity obscures the shape of $\Delta C$, but an extrapolation to $T = \infty$ with a Bloomfield-Hamann curve adjusted to fit the data near the peak in $\Delta C$, which requires $T_K = 28$ K, gives $\Delta S = 1.01\ R \ln 4$. In this case approximately 50% of the entropy is under the extrapolation, but by analogy with CuCr it seems probable that the entropy is $R \ln 4$. The significance of the new data is in showing that the anomaly is broader than that observed at higher concentrations, and that there is probably a greater contribution to $\Delta S$ at high temperatures.

The heat capacities of 81 and 640 at ppm CuFe samples in magnetic fields are shown in Figs. 2 and 3. The data for the 81 at ppm sample in low fields were indistinguishable from the zero-field data, and have been omitted for clarity. Measurements on a 195 at ppm sample have shown that $\Delta C/c$ is the same as for the 81 at ppm sample for the fields and temperatures in Fig. 2. The dependence of $\Delta C/c$ on magnetic field shown in Fig. 2 is therefore characteristic of single-impurity behavior. In Fig. 3 the dashed curve represents the single-impurity zero-field limit established by measurements at lower concentrations.[6,9] The zero-field heat capacity in excess of that represented by the dashed curve is not proportional to concentration and must therefore be associated with impurity-impurity interactions.[6] The application of a magnetic field broadens the interaction contribution to $\Delta C$ and shifts it to higher temperatures. Qualitatively, the effect of magnetic field on $\Delta C$ for the 640 at ppm sample can be easily understood. In zero field uncompensated spins contribute

to $\Delta C$ at temperatures corresponding to the effective fields (generated by other uncompensated spins) they experience. For the 640 at ppm sample the zero field heat capacity shows that these field are $\lesssim 1.5$ kOe.[6] In an applied field greater than this value their contribution to $\Delta C$ is shifted to higher temperatures. In 38 kOe it is almost entirely determined by the applied field and occurs at temperatures above 1 K. Thus, the reduction of $\Delta C/c$ at low temperatures by a 38 kOe applied field is the sum of two effects -- the shift of the impurity-impurity interaction contribution to higher temperatures and the small reduction of the impurity-conduction electron interaction contribution shown by the data for the 81 at ppm sample.

The field dependence of the heat capacity is related to the temperature dependence of the magnetization M by the thermodynamic equality

$$\frac{\partial(C/T)}{\partial H} = \frac{\partial^2 M}{\partial T^2} = H\,\frac{\partial^2 \chi}{\partial T^2}\,, \qquad (1)$$

where $\chi = M/H$. At temperatures below 1 K the <u>differential</u> susceptibility of dilute <u>Cu</u>Fe is the sum of a $T^{-\frac{1}{2}}$ term that saturates in fields of the order of 1 kOe and a constant term.[2] M is therefore the sum of a $T^{-\frac{1}{2}}$ term that is independent of field in high field and a temperature independent term. The large positive values of $\partial(C/T)/\partial H$ predicted by Eq.(1) for the $T^{-\frac{1}{2}}$ term are observed, but only in regions of c and T where interaction effects are important. They are apparent in Fig. 3, for example, for $H \approx 1$ kOe and $0.4 < T < 1.5$ K. In a 195 at ppm sample they occur at lower temperatures and correspondingly lower fields. For the 81 at ppm sample they presumably occur at very low temperatures and

fields where they are lost in the scatter of the data. Since the positive values of $\partial(C/T)/\partial H$ are not proportional to c they cannot be associated with the impurity-conduction electron interaction. We conclude that they, and the associated $T^{-\frac{1}{2}}$ susceptibility, are a consequence of impurity-impurity interactions and are not characteristic of the spin-compensated state. Similar conclusions have been drawn from the concentration dependence of the susceptibility.[5,12]

Above 1.3 K the single-impurity susceptibility, established by a careful study of the concentration dependence,[5] has the form $\chi = \chi_o \cdot 29/(T + 29)$. Substitution of this expression into Eq.(1) gives a small positive value of $\partial(C/T)/\partial H$ and an effect on $\Delta C$ comparable to the scatter in the data for 38 kOe. This is in agreement with the experimental $\Delta C/c$ for 81 at ppm above approximately 2 K. At lower temperatures, however, the larger negative observed values of $\partial(C/T)/\partial H$ require a change in the curvature of $\chi$ vs. T. The change is in the direction suggested by the third law of thermodynamics which requires $[\partial\chi/\partial T]_{T=0} = 0$. Thus, there is a clear indication that near $T_K/15$ the temperature dependence followed by $\chi$ over a wide range of higher temperatures[4,5] is modified in the direction required by the third law. Theoretical evidence for an effect of this type has recently been reported.[13] If the third law is assumed, the field dependence observed below 0.7 K, $\partial(C/T)\partial H \propto$ constant x H, can be integrated to give $\chi = \chi_o[1 - 15(T/29)^2]$. Below 2 K the difference between this expression and $\chi = \chi_o\, 29/(T + 29)$ is less than 2% and would not have been observed in the direct susceptibility measurements,[5] which are dominated by the copper nuclear susceptibility below 1.3 K. The

field dependence of the heat capacity, however, is very sensitive to the difference between the two expressions because it measures $\partial^2\chi/\partial T^2$, which is very different for the two expressions.

The form suggested for the temperature dependence of $\chi$ in the low-temperature single-impurity limit is particularly interesting in connection with other recent experimental results. For $T \ll T_K$, $C \propto T$[6,9] and recent measurements on the resistivity $\rho$ of very dilute CuFe show[14] that $\rho = \rho_o[1 - \beta(T/T_K)^2]$ where $\beta$ is a constant. Thus, for CuFe, a pattern is emerging for the temperature dependences of physical properties at $T \ll T_K$ that is very different from that of a few years ago. Recent results on AuV suggest the same pattern.[14,15] It is also interesting that several theoretical treatments of the Kondo effect predict this pattern, or parts of it.[1]

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