

scribing a surface with a variable thickness of the electron density.²⁴ We feel, therefore, that the results of our analysis together with the observations of Kunz indicate a serious systematic deficiency in existing microscopic models of surface-plasmon dispersion which predict $C_1 \cong 5 > 0$ and $\Gamma_s = 0$ for electron fluids of density comparable to that of aluminum. Both measurements of C_1 are consistent with Bennett's model calculation provided a suitable electron-density profile is used in the model.

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Calorimetric Evidence for a Singlet Ground State in $CuCr$ and $CuFe^{\dagger}$

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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 $\chi = \chi_0 \times [1 - 15(T/T_K)^2]$, 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 ΔS , 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 susceptibility²⁻⁵ χ , if extrapolated to $T=0$, does not satisfy the requirement of the third law of thermodynamics that $[\partial \chi / \partial T]_{T=0} = 0$. 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 measurements⁶ 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 theory⁷ for $T/T_K > 0.07$ and give $\Delta S = R \times \ln(2S + 1)$. The CuFe data are consistent with $\Delta S = R \ln(2S + 1)$. Their field dependence shows that the low-temperature single-impurity χ deviates from an extrapolation of the data^{4,5} above 1 K 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 $\pm 5\%$ by a spectrophotometric method.⁸ Within that accuracy the 4.2-K resistivities were fitted by $\rho_{4.2}/c = 1.08 \times 10^{-3} \mu\Omega \text{ cm/at. ppm}$, 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 ΔC , 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 observed⁶ 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-

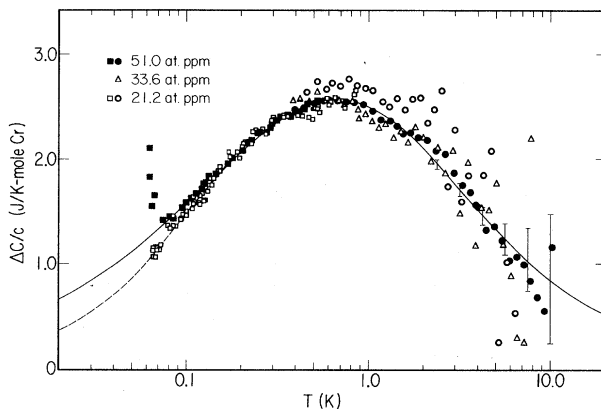


FIG. 1. The heat capacity of CuCr per mole of Cr. The solid curve represents the Bloomfield-Hamann theory, and the dashed curve is a linear extrapolation to $T = 0$. The error bars represent the effect of a 0.1% error in the total heat capacity.

ppm data, for which the precision is best, as defining the shape of the peak. The peak is better defined than in earlier work³ 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 $\Delta S = 1.05R \ln 4$. Since the spin is $\frac{3}{2}$,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 Martin¹¹ for more concentrated samples, but is consistent with the trend in their data. At higher temperatures the lattice heat capacity obscures the shape of ΔC , but an extrapolation to $T = \infty$ with a Bloomfield-Hamann curve adjusted to fit the data near the peak in ΔC , which requires $T_K = 28$ K, gives $\Delta S = 1.01R \ln 4$. 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 ΔS 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 sam-

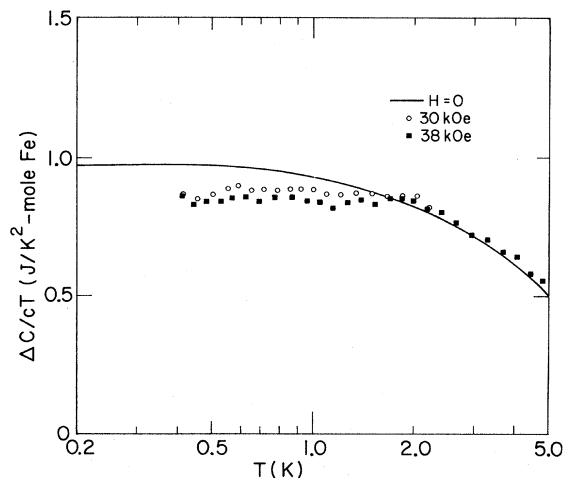


FIG. 2. The heat capacity of 81-at.-ppm CuFe per mole of Fe, as a function of magnetic field.

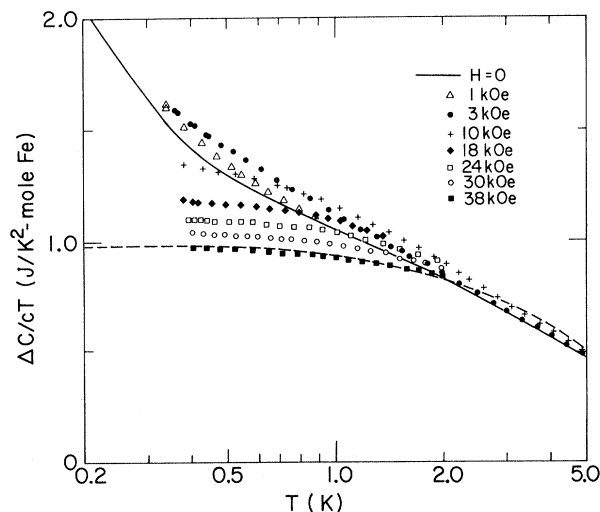


FIG. 3. The heat capacity of 640-at.-ppm CuFe per mole of Fe, as a function of magnetic field. The dashed curve represents the single-impurity zero-field behavior.

ple 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 ΔC and shifts it to higher temperatures. Qualitatively, the effect of magnetic field on ΔC for the 640-at.-ppm sample can be easily understood. In zero field, uncompensated spins contribute to ΔC 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 fields are ≤ 1.5 kOe.⁶ In an applied field greater than this value their contribution to ΔC 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

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

where $\chi = M/H$. At temperatures below 1 K the differential susceptibility of dilute CuFe is the sum of a $T^{-1/2}$ term that saturates in fields of the order of 1 kOe and a constant term.² M is therefore the sum of a $T^{-1/2}$ 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 $T^{-1/2}$ 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 $T^{-1/2}$ 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 $\chi = \chi_0[29/(T+29)]$. Substitution of this expression into Eq. (1) gives a small positive value of $\partial(C/T)/\partial H$ and an effect on ΔC 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 χ 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 χ 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, $\partial(C/T)\partial H \propto \text{const}H$, can be integrated to give $\chi = \chi_0[1 - 15(T/29)^2]$. Below 2 K the difference between this expression and $\chi = \chi_0[29/(T + 29)]$ 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 χ 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 ρ of very dilute CuFe show¹⁴ that $\rho = \rho_0[1 - \beta(T/T_K)^2]$ where β 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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Induced Absorption in the Presence of High Electronic Excitation

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Experimental evidence is presented for the existence of an absorption continuum in CdS which is probably caused by the high density of electron-hole pairs and free excitons. The magnitude of this absorption is largest near the absorption edge and tails off toward lower energies. The presence of this continuum causes a change of the line shape of the A_1 exciton absorption.

Several semiconductors have shown stimulated light emission when excited with either photons of energy greater than the band gap or electron beam sources of high enough power. Numerous studies of this kind have been reported recently

on CdS and other II-VI materials.¹⁻⁵

Whenever the wavelength distribution of the stimulated emission as a function of the exciting light intensity is studied, one particular feature always appears to be present: At low exciting