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Heat Capacities of Dilute Alloys of Fe in Cu Below 1°K*

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Abstract

The heat capacities of five alloys containing between 0.0081 and 0.27 at.% Fe in Cu have been measured between 0.06 and 1°K. It is concluded that the low-temperature heat capacity characteristic of the spin-compensated state is proportional to T, and that Fe-Fe interactions are important, even in the most dilute alloy, at the lowest temperature.

A number of recent theoretical investigations have dealt with the heat capacity associated with the thermal breakup of the spin-compensated state in dilute magnetic alloys. For temperatures well below the Kondo temperature T_K, expressions have been derived that predict heat capacities proportional to T,[1,2] to $T\ln T/T_K$,[3] and to $T^{\frac{1}{2}}$.[4] Daybell, Pratt, and Steyert[5] have reported measurements on two dilute solutions of Fe in Cu in which a heat capacity contribution approximately proportional to $T^{\frac{1}{2}}$ was observed, and they suggested that this result provided a basis for choosing between the various theoretical approximations. We report here the results of similar measurements that cover a greater range of concentration. The new results show that the heat capacity observed by Daybell, Pratt, and Steyert included a contribution from Fe-Fe interactions, and that the heat capacity characteristic of the spin-compensated state is more nearly proportional to T. At the higher concentrations and lowest temperatures our measurements also show an approximately concentration-independent heat capacity similar to that expected for Fe-Fe interactions, possibly modified by the formation of the spin-compensated state on some Fe atoms.

Several observed properties of dilute Fe in Cu solutions verify the existence of the spin-compensated state.[6-9] For this reason, and also because the magnitude of T_K ($\approx 6°K$) makes the associated heat capacity relatively large compared with other contributions, it is logical to choose this system for measurements of the energy and entropy changes accompanying the formation of the spin-compensated state. The experimental problem is that of separating the effects of Fe-Fe and Fe-conduction electron interactions, each of which contributes to the heat capacity.

It is clear that the heat capacity that is characteristic of the Fe-conduction electron interaction would be identifiable as a heat capacity in excess of that of pure copper that is proportional to concentration. Earlier low-temperature measurements have been at concentrations too high to satisfy this criterion.

The samples were prepared under vacuum in an induction furnace and chill-cast from the melt. Chemical analysis of portions from opposite ends of the samples, and microprobe analysis, failed to show any evidence of inhomogeneity or precipitation of Fe. The 4.2-°K resistivity also suggested that the Fe was in solution and free of oxidation. The compositions reported were obtained by chemical analysis.[10] The measurements were made in an adiabatic demagnetization cryostat, except for those above 0.4°K on the 0.0081-at.% sample, which were made in a ^{3}He cryostat using a previously calibrated germanium thermometer.

The heat capacities of five alloys are compared with that of pure copper in Fig. 1. For the more concentrated alloys at the lowest temperatures, the heat capacity is the sum of terms proportional to T^{-2} and to T. The T^{-2} term, which is approximately proportional to concentration, is presumably a hyperfine contribution. Figure 2 compares the coefficient of the linear term with values found for more concentrated solutions at higher temperature[11,12] and exhibits its weak concentration dependence. The heat capacity contribution associated with Fe-Fe interactions has been predicted to be proportional to T and independent of concentration.[13,14] As the temperature increases above a characteristic temperature proportional to concentration, this contribution is expected to disappear gradually. The behavior illustrated in Figs. 1 and 2 is strikingly similar to these predictions, and suggests that the heat capacity of the solutions (with the possible exception of the 0.0081 at .% solution) is dominated by Fe-Fe interactions at the lowest temperatures. Even in the absence of competing interactions it is not clear how rigorously independent of concentration this heat capacity should be, but the observed decrease at concentrations below 0.3 at .% may be an indication of the formation of the spin-compensated state on some of the Fe atoms. As a consequence of the random arrangement of the Fe atoms, the number contributing to the heat capacity (those experiencing an effective interaction $\lesssim kT$) is independent of concentration.[13,14] Formation of the spin-compensated (singlet) state on an Fe atom would reduce the heat capacity by eliminating the contribution of that atom. This effect would be more important the more dilute the solution, because the spin-compensated state is spatially extended and its formation inhibited by the presence of near magnetic neighbors.

Figure 3 shows, for the three most dilute alloys, the excess heat capacity ΔC, reduced by the amount of the hyperfine term and divided by temperature and concentration. The relatively large systematic deviations from a smooth curve for the 0.0081 - at .% sample below 0.4°K are a consequence of the small magnitude of ΔC and the use of a carbon thermometer. The heat capacities measured by Daybell, Pratt, and Steyert[5] on 0.011 and 0.038 - at .% samples are consistent with those reported here. They are intermediate between those of our 0.0081 and 0.0070 - at .% samples, and show a similar dependence on temperature and concentration. The concentration dependence, however, was not clearly resolved and was not taken into account in interpreting the data. The low-temperature rise in $\Delta C/T$ occurs in a concentration and temperature range in which ΔC is not proportional to concentration dependence shown in Fig. 3 suggests that the concentration-proportional limit characteristic of the spin-compensated state is that exhibited by the 0.0081 - at.% sample above about 0.4°K: $\Delta C/T = 0.9 J/deg^2$-mole Fe. This temperature dependence is that calculated by Nagaoka[1] and Klein,[2] and the magnitude is reasonable for ions with spin 3/2 and $T_K \approx 6°K$.

According to the above interpretation, the low-temperature rise in $\Delta C/T$ reflects a reduction in energy associated with the Fe-Fe interactions. It does not appear possible to achieve a reduction by breaking up spin-compensated configurations that were formed at higher temperatures, and it is therefore probable that the only Fe ions involved are those that are close enough together for their interactions to quench the spin-compensated state. For the 0.070 - at.% sample, entropy considerations show that 3% of the Fe atoms would account for the observed rise; for the 0.0081 - at.% sample, the extrapolation of $\Delta C/T$ to 0°K is uncertain, but the corresponding quantity could be less than 1%. Such small numbers of uncompensated Fe spins would not have been detected in the low-temperature resistivity measurements made to date.[6,15] Nuclear-magnetic-resonance studies of the ^{63}Cu line width do, however, show evidence for the presence of uncompensated spins. The low-temperature line width is linear in magnetic field and extrapolates to the pure copper value for a 0.013 - at.% sample, but to a significantly higher value for a 0.076 - at.% sample,[7] suggesting that interactions become important in quenching the spin-compensated state in this concentration range. It also seems possible that the low-field temperature-dependent part of the low-temperature susceptibility[16] is associated with small clusters of uncompensated and weakly interacting spins.

A more extensive investigation of the heat capacities of these alloys, including their dependence on magnetic field, is in progress and will be reported later.

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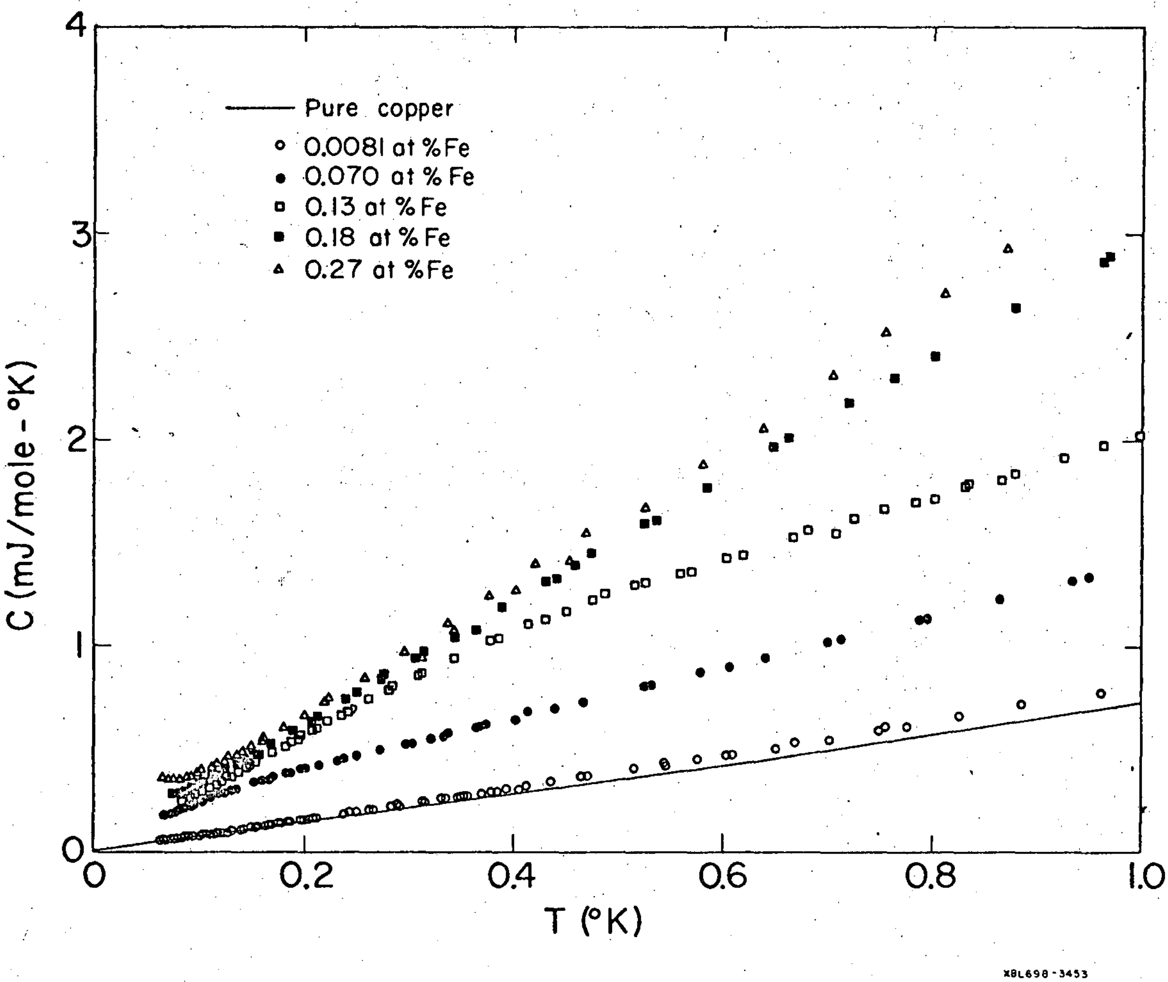

Figure 1. Heat capacities of five dilute alloys of Fe in Cu.

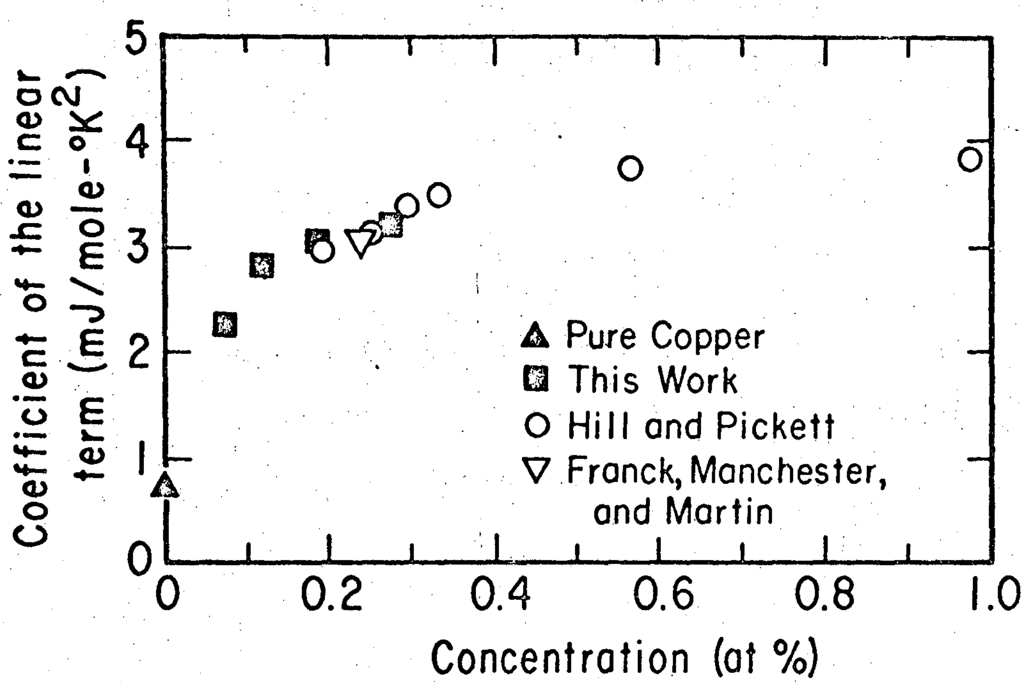

Figure 2. Concentration dependence of the heat capacity contribution proportional to temperature that is observed at low temperature in the higher concentration alloys.

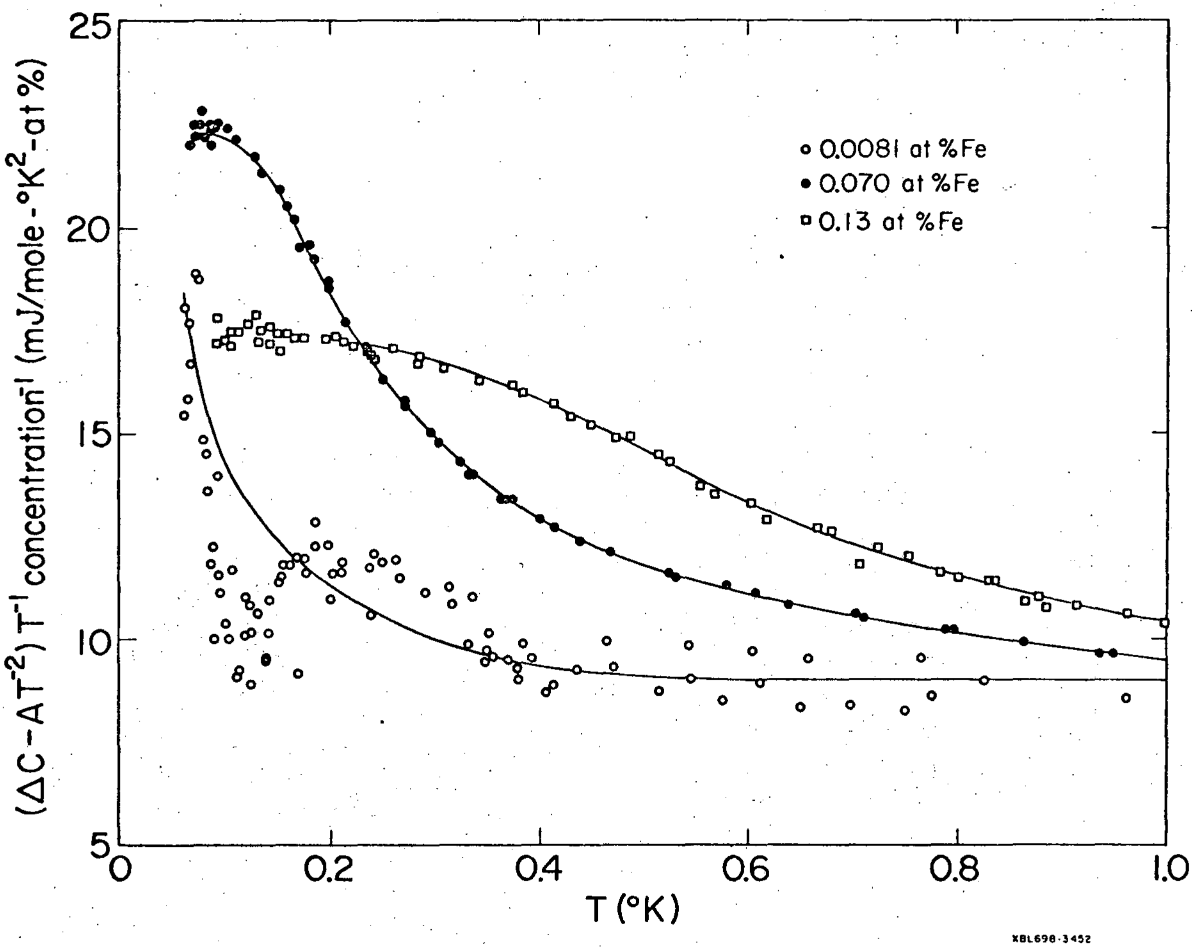

Figure 3. The heat capacity in excess of that of pure copper. For the 0.13 and 0.070 - at .% samples at T^{-2} term has been subtracted; for the 0.0081 - at .% sample, this term was too small to be measured and no correction has been made.