Title
LOW TEMPERATURE HEAT CAPACITIES OF DILUTE SOLUTIONS OF Fe AND Cr IN Cu

Permalink
https://escholarship.org/uc/item/5xc2h44r

Authors
Triplett, B.B.
Phillips, Norman E.

Publication Date
1970-08-01
LOW TEMPERATURE HEAT CAPACITIES
OF DILUTE SOLUTIONS OF Fe AND Cr IN Cu

B. B. Triplett and Norman E. Phillips

August 1970
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Low Temperature Heat Capacities
of Dilute Solutions of Fe and Cr in Cu.*

B. B. Triplett and Norman E. Phillips

Inorganic Materials Research Division
of the Lawrence Radiation Laboratory,
and Department of Chemistry,
University of California, Berkeley,
California 94720.

Abstract

Heat capacity measurements on Cu-Cr samples give \((1.05 \pm 0.10) \ln 4\) for the entropy associated with the formation of the Kondo state. On the high-temperature side of the anomaly the Cu-Fe data are less accurate but are also consistent with an entropy of \(\ln 4\). The field dependence of the heat capacity suggests that the \(T^{-1/2}\) term in the susceptibility is associated with Fe-Fe interactions.
Although Cu-Cr and Cu-Fe appear to be spin 3/2 systems, the entropies associated with the formation of the Kondo state have been reported to be significantly less than $\ln 4$.\(^1\) To check this discrepancy, and to test theoretical expressions for the heat capacity at temperatures near its maximum, we have extended our measurements\(^2\) on Cu-Fe to higher temperatures and made new measurements on Cu-Cr.

The Cr concentrations of the Cu-Cr samples were determined to ± 5% by a spectrophotometric method.\(^3\) Within that accuracy, the 4.2 K resistivities were linear in concentration; $\rho_{4.2} = 1.08 \times 10^{-3} \, \mu\text{ohm cm/ at ppm}$. The reported compositions were assigned from $\rho_{4.2}$ and that relation. The heat capacity in excess of that for pure copper $\Delta C$, divided by concentration $c$, is shown in Fig. 1 for three Cr-Cr samples. Above 0.15 K $\Delta C$ is proportional to $c$, showing that $\Delta C$ is characteristic of the Kondo state. At lower temperatures $\Delta C/c$ for the 21-at. ppm sample is less than for the 51-at. ppm sample. The difference is small, however, and it is reasonable to assume that the 21-at. ppm sample exhibits the Kondo-state heat capacity. The solid curve in Fig. 1 is the theoretical heat capacity derived by Blochfield and Hamann,\(^4\) scaled to fit the data near the maximum. The curve corresponds to $T_K = 2.1$ K, in excellent agreement with the value derived\(^5\) from resistivity data. The dashed curve is an extrapolation to 0 K suggested by the Cu-Fe measurements,\(^2\) and proportional to $T$ for $T < 0.05$ K. This curve and the theoretical curve at higher temperatures given an entropy of $1.05 \ln 4$. In view of the uncertainties in absolute concentrations and extrapolations, the discrepancy with $\ln 4$ is not significant.

Figure 2 shows the heat capacity of the 51-at. ppm Cu-Cr sample in magnetic fields. In 83 kOe the maximum occurs at the temperature expected for a spin 3/2 satellite anomaly, but the peak height is only \(\approx 80\%\) of
the Schottky peak. There is an additional contribution similar in shape to the zero-field heat capacity, suggesting that the spin-compensated state is only partially destroyed in 38 kOe.

Figure 3 shows zero-field heat capacities of two Cu-Fe samples. The solid curves are similar to the smooth curve through the 21 at. ppm Cu-Cr data, but scaled and shifted in different ways. Curve (a) which gives the best fit corresponds to high values of $T_K$ and entropy, 47.3 K and 1.22 R ln 4, respectively. A combination of curve (d), the Bloomfield-Hamann curve, above 4 K and curve (a) below 4 K gives a good fit to the data, an entropy of 1.01 R ln 4, and $T_K = 28$ K. However, the deviations from the Bloomfield-Hamann curve below 0.1 $T_K$ are more pronounced than for Cu-Cr.

Figure 4 shows the heat capacity of a 640 at. ppm Fe in Cu sample in magnetic fields. The dashed curve represents the dilute-impurity limit characteristic of the Kondo state in zero field. At low temperatures and low fields the heat capacity increases with increasing field, corresponding at least qualitatively to the $T^{-1/2}$ susceptibility. For the 81 and 195 at. ppm samples at the same temperatures, the zero-field heat capacity is very close to the dashed curve, and the heat capacities decrease with increasing field for all fields. This suggests that the increase in heat capacity with applied field and the $T^{-1/2}$ susceptibility are associated with Fe-Fe interactions rather than with the Kondo state.
References

*Work supported by the U. S. Atomic Energy Commission.


3. The analysis was carried out by Mr. R. D. Giauque, of the Lawrence Radiation Laboratory, University of California, Berkeley, California 94720.


Fig. 1. The heat capacities of dilute solutions of Cr in Cu. Measurements in different calorimeters on the same sample are distinguished by different symbols. The error bars represent the effect of 0.1% error in the total heat capacity for the 51 at. ppm sample.
Fig. 2. The heat capacities of 51 at. ppm Cr in Cu in magnetic fields.
Fig. 3. The heat capacities of dilute solutions of Fe in Cu. The error bars represent the effect of a 0.1% error in total heat capacity for the 195 at. ppm sample.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.