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Clustering Effects and the Rigid-Band Model in Cu-Ni Alloys

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Owing to the heat treatment of the samples, the results of the photoemission work on Cu-rich Cu-Ni alloys might not be representative of these solid solutions.

IN their comments on the x-ray work on clustering in Cu-Ni alloys,[1] Seib and Spicer show that their experimental observations are consistent with the virtural-bound-state model.

To minimize clustering, Seib and Spicer have annealed their samples at a high temperature. This, in principle is a good procedure. But it is now becoming more and more clear that Cu-Ni alloys contain clusters rich in Ni even when the samples are not annealed at a relatively low temperature (i.e., around 300°C). Hicks *et al.*[2] find clustering in Cu-Ni alloys ("magnetization clouds"). These authors homogenized their samples at 1000°C for 3 days and then quenched them to room temperature. They found clouds of magnetization with a magnetic moment of about 8 μ_B and a concentration of 70% Ni in alloys with nominal concentrations around 50%.

Also, Robbins *et al.*[3] find a magnetic moment due to Ni-rich clusters after quenching the specimens from 1000°C. This magnetic moment rose by about 10% only after annealing the specimen at 325°C for 24 h. The magnetization in a 50% Cu-Ni alloy is then appreciable even if the samples are not annealed at 350°C, as was done in the x-ray work.

As for Cu-Ni alloys rich in Cu, Van Elst *et al.*[4] have shown that a 70%-Cu alloy (quenched from high temperature and not annealed) exhibits strong superparamagnetism. They find clusters with a magnetization of 25 μ_B, and 30% of the Ni atoms in the alloy seem to be in clustered form. These authors even find some superparamagnetism in an 80%-Cu alloy. Clustering effects seem to be appreciable in Cu-Ni alloys rich in Cu even when the samples are quenched from high temperatures to room temperature.

There is also another important point to consider about the heat treatment of the specimens. In preparing Cu-Ni alloys one has first of all to homogenize them at high temperatures for a long time. We have done magnetic measurements on different Cu-Ni alloys and have seen irregularities in the results when we used alloys that have been homogenized for 3 h at 900°C. Only after heating the samples for 5 days at 1000°C could we reproduce the room-temperature results given in the literature. Indeed, we can see in the work of Ryan *et al.*[5] how these authors take great precautions to ensure the homogeneity of the alloys.

Failure to homogenize the specimen before the measurements should lead to regions with concentrations of nearly pure Ni and pure Cu. This should be the reason why in the work on photoemission measurements the Ni content changed in one of the samples between 19 and 27% instead of being constant. This was seen by Seib and Spicer using microprobe analysis and it is in itself surprising because Seib and Spicer note in their comments that their specimens were homogenized for a long time at a temperature about 1000°C. We must conclude that the homogenization was not done adequately. Now the occurrence of regions rich in one type of atom has a statistical character. There is a distribution of the size of these regions, and there should be small regions along the big ones. This distribution is highly dependent on the heat treatment and cannot be estimated unless the exact heat treatment is known.

Seib and Spicer conclude that the rigid-band model does not hold for the Cu-rich Cu-Ni alloys from the fact that the Cu *d*-state-to-Fermi-level separation remains constant upon alloying. They show, in their paper, that if the rigid-band model holds, almost all of the Ni in the alloy would be contained in Ni-rich clusters.

We have shown here that their specimens were presumably highly inhomogeneous. Accordingly, it is very probable that in their samples most of the Ni was in clustered form, and the rigid-band model might still hold.

On the other hand, we agree with Seib and Spicer that the energy distribution curves are not a superposition of the results from pure Cu and pure Ni. The observation of a peak at 1 eV below E_F may be really a consequence of the existence of virtual bound states. But it might also be possible that some kind of superposition of the photoemission from different clusters containing different percentages of Ni and all of them behaving according to the rigid-band model would give the measured photoemission curves.

To sum up, we do not know whether the results of

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[5] F. M. Ryan, E. W. Pugh, and R. Smoluchowski, Phys. Rev. **116**, 1106 (1959).

the photoemission measurements are characteristic of Cu-rich Cu-Ni alloys because the samples used in this study were not homogenized. Nevertheless, the comments of Seib and Spicer show with some confidence that the virtual-bound-state model is more likely to be the right one. It would be very desirable to repeat the photoemission measurements, this time using well-homogenized samples which are subsequently very quickly quenched from high temperature to room temperature.

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Supplementary Results on "Low-Temperature Resistivity of Dilute Magnetic Impurities in the Presence of Internal Fields"

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Previous calculations on the effect of random internal fields on the Kondo resistivity are extended to cover a wider range of variation of internal field parameters and exchange constants. An error in the previous calculated results is also corrected.

In a previous work[1] we have examined the low-temperature resistivity associated with scattering of electrons by magnetic impurities dispersed in a nonmagnetic solvent. The calculation was done in an effective field approximation using the second Born approximation to obtain the relaxation times. Because of an error[2] in one of the expressions, we recalculated the values of the resistivity and have taken this opportunity to extend our calculations to a wider range of values of the *s-d* exchange constant J. In the previous calculation,[1] a particular choice of the width of the truncated Lorentzian field distribution Δ was used, where Δ is proportional to the impurity concentration. Whereas in the previous work Δ/c was taken to be a constant determined from specific-heat data, in the present paper we regard Δ/c as a parameter, and give the resistivity for several values of Δ/c. This will allow for effects of differing geometrical and degeneracy factors in the internal fields entering the resistivity and the specific-heat calculations. The distribution of internal fields is still assumed to be independent of the temperature. This is not strictly correct,[3] but is reasonable at low temperatures. The general features of the resistivity calculations will be recalled: As the temperature is lowered from the T^5 region the resistivity exhibits a minimum at $T_{\min}$ and then rises approximately logarithmically in temperature to a maximum at $T_{\max}$, finally falling approximately linearly at still lower temperatures.[4] For higher concentrations of magnetic impurities the extrema in the resistivity are replaced by inflection points.

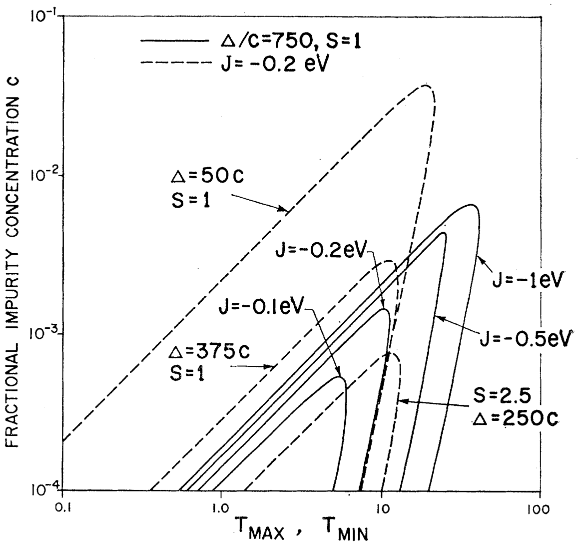

FIG. 1. Values of $T_{\max}$ and $T_{\min}$ as a function of the impurity concentration, where $T_{\max}$ is the temperature of the resistivity maximum and $T_{\min}$ that of the minimum. The lower temperature is associated with the maximum. The solid lines all have the same internal field parameter Δ/c and S, and indicate the variation with J, whereas the dashed lines all have the same value of J.

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[4] It is assumed throughout that the temperature is such that perturbation theory is valid. See Footnote 20, Ref. 1. Also see R. More and H. Suhl, Phys. Rev. Letters **20**, 500 (1968).