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MAGNETIC CLUSTERS ASSOCIATED WITH ISOLATED Fe ATOMS IN PARAMAGNETIC Cu-Ni ALLOYS*

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A small magnetic cluster is shown to exist around an isolated Fe atom in $Cu_{1-x}Ni_x$ alloys with a magnetic moment and saturation hyperfine field depending on the number n of Ni near neighbors. This small cluster changes abruptly from moments of $(2.85+0.6n)\times\mu_B$ to large moments [(~17 to 20)μ_B] for Ni concentrations near the critical composition. The moment compensation (Kondo effect) found for isolated Fe in Cu appears to persist in Cu-Ni up to at least 10 at.% Ni.

Giant moment clusters (~$10\mu_B$) with large spatial extent have been reported[1-4] in the critical region ($0.4 \lesssim x \lesssim 0.5$) bounding the ferromagnetic Ni-rich $Cu_{1-x}Ni_x$ alloys. In the present Letter we report Mössbauer-effect results for isolated Fe atoms (i.e., sources) in both the Cu-rich ($x \lesssim 0.33$) and in the critical region of Cu-Ni alloys. In the critical region the presence of an Fe atom nucleates a giant moment of 17-20μ_B. In the nonferromagnetic Cu-rich alloys, the data are readily understood in terms of a distinctly different small cluster confined largely to the Fe atom and the nearest-neighbor shell of surrounding atoms. We find that a simple model of the cluster, with near-neighbor Cu atoms magnetically inert and Ni atoms active,[5] predicts the complex Mössbauer spectra observed at compositions of $x=0.1$, 0.21, and 0.33. The data also suggest that the Kondo effect is present in the $x=0.1$ alloys, with a Kondo temperature T_K of ~3 K. This is to be compared with T_K ~16 K (as defined from Mössbauer data) for Fe in pure Cu.[6,7]

Any investigation of the $Cu_{1-x}Ni_x$ system raises the obvious question of atomic clustering. The small amount of short-range order found[8-10] in slow-cooled alloys with x near 0.5 would not substantially alter our conclusions. Our alloys were rapidly quenched from high temperature, with correspondingly less clustering.[11]

Our "small"-cluster model assumes a moment μ_n for an Fe atom having n Ni nearest neighbors of

$$\mu_n = (2.85 + 0.6n)\mu_B. \quad (1)$$

This moment determines the paramagnetic behavior of the cluster as a function of applied field H_0 and temperature. The Fe magnetic hyperfine fields at saturation, H_{sat}^n, are also assumed to be functions of n. The distribution in the population of n is taken to be that appropriate to a random alloy of the concentration in question. Models of this type are not new. What is unique here is that this particularly simple model, effectively with one adjustable parameter,[12] predicts both the splitting and the complex shapes[13] of spectra for a variety of fields, temperatures, and alloy compositions, as seen in Fig. 1. (The induced and applied fields are opposed, hence the net average hyperfine field can, and does, go through a minimum. Note the ability to predict the temperatures at which these minima occur.) While satisfactory, the agreement between the model and experiment is inferior to that often obtained in parametrized fits of Mössbauer spectra. Fits of similar quality could be made here by the explicit inclusion of additional adjustable parameters, attributed to more-distant-neighbor or other effects. Such will not be done here. As is true with almost all such fits, the fitting would not be unique and the "improvements" would be within the noise of the model and the experiments.

The giant moment clusters of the critical re-

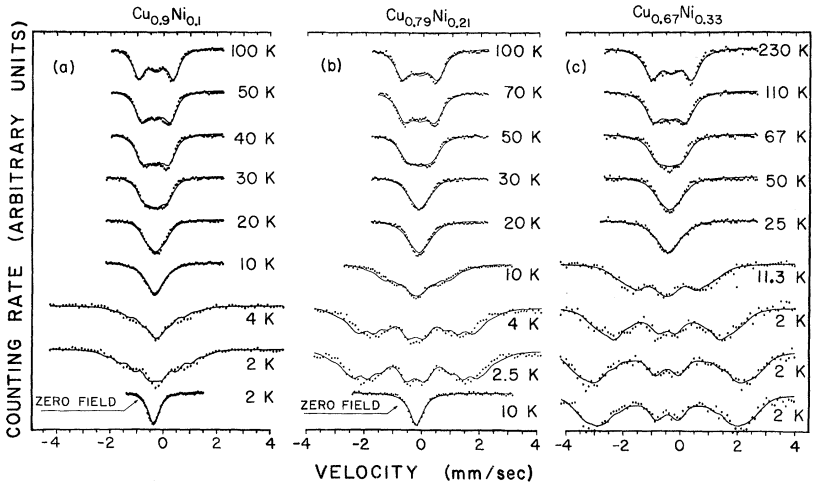

FIG. 1. Mössbauer effect data (points) and theoretical spectra (solid lines). The theoretical spectra have not been parametrized [e.g., by using second-neighbor effects, clustering $T_K(n)$, etc.] to fit the data, but are generated as described in the text. The 2-K spectra for $Cu_{0.67}Ni_{0.33}$ are for an external field of, from bottom to top, 50 kOe (3.98 MA m^{-1}), 30 kOe (2.38 MA m^{-1}), and 10 kOe (0.80 MA m^{-1}). All other spectra were taken in an external field of 50 kOe (3.98 MA m^{-1}), except for the zero-field spectra. The $Cu_{0.9}No_{0.1}$ theoretical spectra use $T_K = 2.7$ K.

gion appear[1,2] to extend over ~100 lattice sites, with a cluster moment occurring if a region of the crystal is Ni rich. The critical local Ni concentration is probably in excess of 65%. Ferromagnetism occurs when there is sufficient overlap between clusters (namely at $x \sim 0.43$). The Fe site enhanced moments appearing in the Cu-rich alloys have smaller dimensions. We have observed[14] alloys containing 3% Fe to order ferromagnetically with $T_c \sim 10$ K for $0.1 \leq x \leq 0.3$ whereas $\frac{1}{2}$% Fe alloys do not order down to 4 K. The clusters are thus of limited spatial extent, i.e., the moment is limited to one or two shells of neighbors (consistent with the model used to describe the Mössbauer spectra), in contrast to the giant clusters in the critical region.

Consider Eq. (1). The value $2.85\mu_B$ is characteristic of an Fe atom moment in either pure Cu[15] or pure Ni[16] and $0.6\mu_B$ is characteristic of a Ni moment. A zero moment is expected for Cu.[5] The average cluster moments predicted by Eq. (1) (setting n equal to the average nearest-neighbor Ni count) are in agreement with the values obtained from a standard plot[17] (see Fig. 2) of the average hyperfine splitting as a function of $H_0/(T-T_C)$, with $T_C = 0$ for the nonferromagnetic alloys. For example, this yields an average moment of $\sim 5.4\mu_B$ for the $x = 0.33$ alloy, as compared with $5.25\mu_B$ given by setting $n = 4$ in Eq. (1). The moment values derived from Fig. 2 are plotted in Fig. 3. It is seen that there is a sharp break in moment behavior between the Cu-rich and critical regions. Given the moment appropriate to a particular near-neighbor environment, the magnetic field at the Fe nucleus is the sum of the applied field and an induced field. The induced hyperfine field is given by

$$H_{eff}{}^n = -H_{sat}{}^n B_J(\mu_n H_0/kT), \qquad (2)$$

where B_J is a Brillouin function and $J = \mu/(g\mu_B)$. We have used $g = 2$, a result appropriate to the behavior[15] of Fe in pure Cu. The present results are not very sensitive to the value of g.

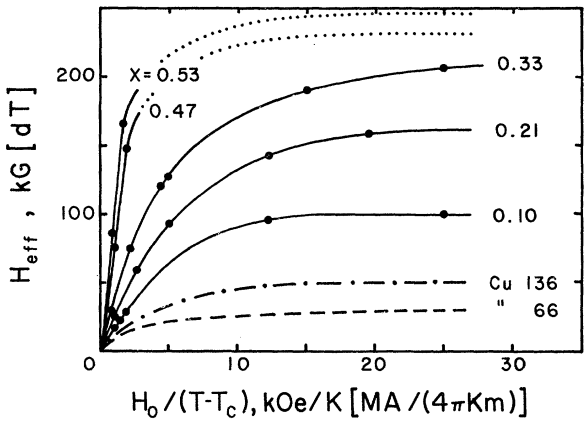

FIG. 2. Average Fe-site internal field versus $H_0/(T-T_C)$ for $Cu_{1-x}Ni_x$ (^{57}Co) alloys. H_0 is the externally applied field ($H_0 = 50$ kOe for all the data points shown). The Curie temperatures, T_C, are 79 K for $Cu_{0.47}Ni_{0.53}$, 16 K for $Cu_{0.53}Ni_{0.47}$, and zero for the remaining alloys. The $x = 0.53$ and 0.47 curves have been extended to the saturation fields as determined below the Curie temperature. The Cu data for $H_0 = 66$ and 136 kOe are from Ref. 7.

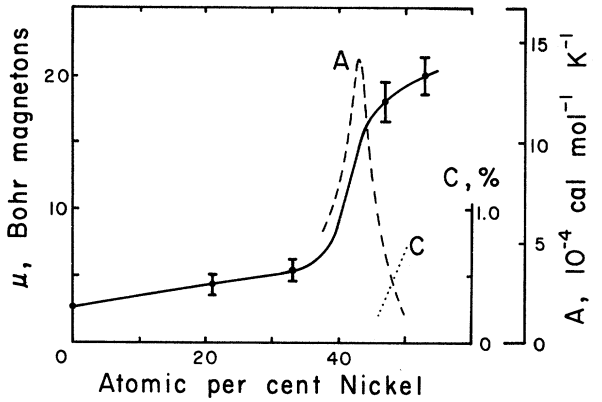

FIG. 3. Measured average moment μ versus percent Ni for isolated Fe in Cu-Ni. The point for pure Cu is from Ref. 9. Also shown are the cluster specific heat A (Ref. 2), and the concentration C of magnetic clusters as measured by neutron diffraction (from Ref. 1).

Changes in the Fe hyperfine field with alloying are most sensitive to the near-neighbor environment in ferromagnetic metals.[18] In a case such as that under consideration, where the magnetic cluster moment is largely limited to near neighbors, it appears reasonable to assume $H_{sat}{}^{n}$ is a function of n alone with only minor contributions from further neighbors. We utilize the data of Wertheim and Wernick[19] to obtain $H_{sat}{}^{n}$ values of 250, 262, 270, 276, 280, and 282 for $n=7$ to 12 (i.e., the Ni-rich ferromagnetic alloys), respectively. For $n=6$ our source data for ferromagnetic alloys below their Curie temperatures show $H_{sat}{}^{6}=240$. $H_{sat}{}^{0}$ was obtained[7,20] from source data for Fe in Cu as 80 kG. The remaining $H_{sat}{}^{n}$ are very nearly what one would obtain by drawing a smooth curve through the above mentioned fields. The values utilized[21] are 130, 155, 185, 205, and 225 for $n=1$ to 5, respectively.

Given these $H_{sat}{}^{n}$ values and the assumption of a random alloy (i.e., a binomial probability distribution for n), all the data of Fig. 1 are well described except the low temperature (i.e., $T=2$ and 4 K) results for $Cu_{0.9}Ni_{0.1}$. In this case the assumed $H_{sat}{}^{n}$ values are too large. This apparent reduction in saturation hyperfine field at low temperature is also present[6] for Fe in pure Cu and has been explained as due to a moment fluctuation[6] or compensation,[7,22] i.e., the Kondo effect. Assuming this, we replace[23] T by $T+T_K$ in Eq. (2) and, retaining the above $H_{sat}{}^{n}$ values, we obtain $T_K=2.7$ K, yielding the $x=0.1$ spectra plotted in Fig. 1. The presence of the Kondo effect is, of course, not proven by this. However, granting the presence of the Kondo effect for Fe in pure Cu, it is present in this alloy as well. Measurements at higher fields would be useful. With T_K (for $x=0.1$) and the above values for $H_{sat}{}^{n}$ we obtain the predictions shown as solid lines in Fig. 1. The ability to predict a large variety of spectra supports the essential correctness of the model. Note that only a small amount of second-neighbor, atomic clustering, or other effects would be allowed in an attempt to improve the theoretical spectra by parametrization.

The cluster-moment data at Fe sites deduced from Fig. 2 is compared in Fig. 3 with data on binary Cu-Ni alloys. [No datum point is shown for the enhanced Fe moment for $x=0.1$ since the moment value from Eq. (1) was assumed in the process of obtaining $T_K=2.7$ K.] We see that the small cluster moments go over sharply to values of $(17\text{-}20)\mu_B$ when the Fe is in the presence of the giant clusters of the critical region. The cluster specific-heat (A) results[2] sample the number of uncoupled paramagnetic giant clusters. The neutron diffraction results[1] C sample those clusters which are ferromagnetically coupled (hence the concentration C rises at a larger Ni concentration than either A or our data). Susceptibility studies[3] have also shown the onset of the uncoupled giant cluster moments. Taken with magnetization data, the neutron diffraction results yield a cluster-moment value of $(8\text{-}10)\mu_B$ for a giant iron-free cluster, while our results yield $(17\text{-}20)\mu_B$ for a cluster in which an Fe moment is imbedded. These enhanced moments are somewhat larger than the simple sum of the iron-free Cu-Ni alloy giant moment [with its average of $(0.1$ to $0.2)\mu_B$ per Ni site] plus the local Fe near-neighbor cluster including its $0.6\mu_B$ for the nearest-neighbor Ni sites as described by Eq. (1). One might expect that an Fe moment nucleates a giant cluster moment. Giant moments which are larger than the simple sum are consistent with this expectation and with the model, advanced by Hicks et al.,[1] for the moment in the pure Cu-Ni alloy.

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[21]These $H_{sat}{}^n$ were adjusted slightly by fitting the $x = 0.21$ and 0.33 spectra taken at largest H_0/T (i.e., when all moments are nearly saturated). The $x = 0.21$ spectrum is most sensitive to $H_{sat}{}^n$ for $n = 1$, 2, and 3 while that for $x = 0.33$ is sensitive to $n = 3$, 4, 5.

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