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NEAREST-NEIGHBOR MODEL OF MAGNETISM FOR COPPER-NICKEL ALLOYS AND CLUSTERING OF MAGNETIC MOMENTS

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We show that the appearance of a localized moment on Ni atoms in the critical range of concentration is accurately described by a simple environment-dependent model of the Jaccarino-Walker type, and that this model implies a "clustering" of magnetic moments, even on the basis of a random distribution of atoms. The fit with experimental data is promising in view of the approximations made.

Copper-nickel alloys have been extensively studied, particularly in the "critical range" of concentrations between 30 and 60 at.% Ni. High-temperature susceptibility measurements[1] show a strong increase of the susceptibility with concentration, which leads to the supposition of the existence of superparamagnetism. In saturation-moment measurements,[2,3] the plot of the magnetization versus the concentration x of the Ni atoms, linear for $x > 0.6$, exhibits a curvature for $x < 0.6$. This peculiarity has not yet been explained in a satisfactory manner, in spite of several attempts.[4,5] Moreover, the experimental values of σ_s deduced in different ways for the same sample do not agree with one another.[3] Low-temperature specific-heat measurements[3,6] show two anomalies from the usual $c = \gamma T + \beta T^3$ law. The behavior of the specific heat versus temperature is well fitted by the law $c = A + \gamma T + \beta T^3$, A and γ being concentration dependent. Moreover, neutron diffraction patterns have shown the existence of giant moments in Ni-Cu alloys, even in the ferromagnetic range.[7]

All these results have been qualitatively explained by the cluster hypothesis: The nickel atoms tend to cluster into Ni-rich regions in which they can be magnetically coupled; these regions behave like giant moments and give rise to superparamagnetism and anomalies in the specific heat.[8] Although this interpretation has recently been contested, it can be said that no available facts invalidate the model.[8]

Consistent with the cluster hypothesis are the measurements of the effects of heat treatment, plastic deformation, and neutron irradiation on Cu-Ni alloys.[1,3,9]

The short-range order parameters defining the rate of clustering have been correlated with the values of the susceptibilities.[10] There is no doubt now that an alloy slowly cooled from high annealing temperature is not randomly distributed, as shown recently.[11] It could be expected that a perfectly random state never occurred, and that short-range order parameters[12] were necessary to describe the statistical properties of the alloy.[5] However, experiments by one of us[9] tend to show that no short-range order exists at room temperature if the samples are annealed long enough at a temperature higher than 400°C and are very rapidly quenched. It was shown with magnetic measurements that the metastable state obtained from annealing temperatures between 400 and 1000°C seemed to be the same. If there were any short-range order, such a thing could not occur since this phenomenon depends on temperature. Our purpose is, then, to explain the main physical properties of Cu-Ni alloys in the critical range on the basis of a pure-

ly random state.

For Ni-Cu alloys with high Ni concentrations, the linear variation of the saturation magnetization σ_s versus the Ni atomic concentration x has long been taken as a proof of validity of the rigid-band model.[13] However this model fails to explain other properties of the alloys, and an alternative one was recently proposed.[14]

In the critical range, it may be expected that short-range interactions prevail, and that a localized model of magnetism is suitable. Such a model has been predicted to be environment dependent[15] on the basis of interactions between neighboring virtual bound states: It can be said that the minimum polarity model of Ref. 14 is an extension of this model to higher concentrations. An attempt to describe the copper-cobalt alloys in this model was made some years ago,[16] and the appearance of a magnetic moment on dilute Fe atoms in Nb:Mo alloys has been analyzed in this model.[17] Then the model of enviroment-dependent moments was successfully applied to several alloys (a review is given in Ref. 5). Robbins, Claus, and Beck[5] have fitted the whole curve of σ_s vs x with a sophisticated model, including second-neighbor interactions. However, their fit is not very good in the critical range, and their alloy is assumed to be not randomly distributed.

The simplest model of an environment-dependent moment is to assume that one Ni atom has a moment μ_{Ni} if surrounded by at least p Ni atoms as nearest neighbors, and no moment if not. The fixed value of μ_{Ni} is taken as that of pure Ni ($\mu_{Ni} = 0.606\mu_B$). Then the mean moment per atom is given by

$$\bar{\mu} = \mu_{Ni} x \sum_{n=p}^{12} C_{12}{}^{n} x^{n} (1-x)^{12-n},$$

where x is the Ni atomic concentration and $C_{12}{}^{n} = 12!/n!(12-n)!$. The experimental values of $\bar{\mu}$ can be determined from saturation magnetization measurements. It should be noted that taking the extrapolation in zero field gives values of $\bar{\mu}$ necessarily too low, since some localized moments which are paramagnetic or antiferromagnetically coupled are not counted. For this reason, $\bar{\mu}$ has been arbitrarily taken from the extrapolated value at zero temperature of the magnetization in highest available fields (20 kOe). There is no difference for $x > 0.5$, but it increases the values by about 15% for lower x. It has been found with such a method that $\bar{\mu}(0.472) = 0.0436\mu_B$ and $\bar{\mu}(0.422) = 0.0175\mu_B$.[18] All available values are then plotted on Fig. 1, together with theoretical curves for $p = 7$, 8, and 9. Clearly the curve $p = 8$ agrees fairly well with the data.

Now it will be shown that even if the atoms are perfectly randomly distributed, the magnetic atoms are clustered. Hereafter, "a magnetic atom" is defined as "a Ni atom having at least 8 Ni atoms among its 12 nearest neighbors." The basic fact is that in a fcc structure, two sites which are first, second, third, and fourth neighbors have common nearest neighbors; therefore their probabilities of being magnetic are dependent, and four short-range order parameters of magnetic atoms can be computed from the eight-neighbor model of magnetism. First of all, all the configurations of 8, 9, 10, 11, and 12 Ni atoms on the first shell of neighbors of one site have been listed. Calling then A, B, C, and D the shells of the first, second, third, and fourth neighbors of a Ni atom having p Ni atoms in its A shell, the quantities $A(p,q)$, $B(p,q)$, $C(p,q)$, and $D(p,q)$ have been computed. $A(p,q)$ denotes the probability of finding on any site of the A shell a Ni atom surrounded by q Ni-atom nearest neighbors. Similar definitions can be given for $B(p,q)$, $C(p,q)$, and $D(p,q)$. The computation is made by the usual binomial law, assuming a concentration x of Ni atoms on the outer shells, and using the list of atomic configurations on the first one. Then the probability of finding a magnetic Ni atom on any site of the A shell of a mag-

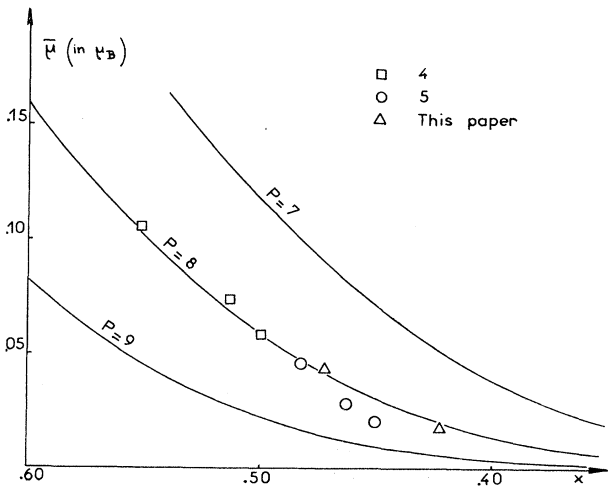

FIG. 1. Saturation moment values versus Ni atomic concentration. Comparison of theoretical curves with experimental data.

Table I. Numerical values of short-range probabilities and order parameters of magnetic atoms. P denotes the probability of magnetism of any atom in the alloy, and N the mean number of magnetic atoms around one magnetic atom.

x	P_A	P_B	P_C	P_D	N	P	α_A	α_B	α_C	α_D
0.40	0.176	0.068	0.041	0.031	3.89	0.0229	0.157	0.046	0.019	0.008
0.42	0.201	0.083	0.054	0.042	4.71	0.0319	0.175	0.053	0.023	0.010
0.44	0.228	0.101	0.069	0.055	5.66	0.0434	0.193	0.061	0.027	0.012
0.46	0.256	0.122	0.087	0.071	6.74	0.0579	0.210	0.068	0.031	0.014
0.48	0.285	0.145	0.108	0.091	7.97	0.0756	0.227	0.075	0.035	0.017
0.50	0.316	0.170	0.132	0.114	9.34	0.0969	0.243	0.081	0.039	0.019

netic Ni atom is given by

$$P_A = [\sum_{p=8}^{12} C_{12}{}^p x^p (1-x)^{12-p} \sum_{q=8}^{12} A(p,q)] \times [\sum_{p=8}^{12} C_{12}{}^p x^p (1-x)^{12-p}]^{-1}.$$

Similar definitions and calculations have been made for P_B, P_C, and P_D. If the probability for a site to be occupied by a magnetic Ni atom is $P = x\sum_8{}^{12} C_{12}{}^p x^p (1-x)^{12-p}$, the short-range order parameters α_A, α_B, α_C, and α_D of magnetic atoms are given by[12]

$$\alpha_A = \frac{P_A - P}{1-P}, \quad \alpha_B = \frac{P_B - P}{1-P},$$

$$\alpha_C = \frac{P_C - P}{1-P}, \quad \alpha_D = \frac{P_D - P}{1-P}.$$

Numerical values of these quantities are shown in Table I. The existence of short-range order parameters prove that the magnetic Ni atoms are clustered, even if the Ni atoms are not.

As the probability of a magnetic moment on any site of the A shell is P_A, it can be said that the mean number of magnetic atoms on this shell is $12P_A$. Similar arguments allow the calculation of the mean number of magnetic atoms in the four first shells of neighbors of one magnetic atom,

$$N = 12P_A + 6P_B + 24P_C + 12P_D.$$

This result is to be compared with the neutron diffraction experiments of Hicks et al.[7] (Fig. 2). They find from magnetic-scattering cross-section measurements that the magnetization in the ferromagnetic state is distributed into "clouds." Using the same approach as for dilute Fe in Pd, they find that the giant magnetic moment of such clouds is about $8\mu_B$ for $x = 0.5$. Such an effect is consistent with our model. An order of magnitude of the giant moment can be given by taking one magnetic atom and its 54 nearest neighbors as the mean cloud. Then, it contains $1+N$ magnetic atoms. For $x = 0.5$ the giant moment of this moment of this model of a cloud is found to be $6.26\mu_B$. This rough approximation gives thus the right order of magnitude, and explains the phenomenon quite well.

Now, the 55 sites composed of one magnetic atom and its 54 nearest neighbors are taken as the mean cluster in the paramagnetic state. If all these clusters are assumed to contribute independently to specific heat and Curie constant, the cluster term of specific heat is found to be proportional to $(1+N)^{-1}$, and about six times higher than experimental data, whereas the Curie constant is found to be proportional to $1+N$ and about three times lower than experimental data. This is consistent with the fact that $1+N$ is too low a value for the mean number of magnetic atoms in a cluster, and that not all the

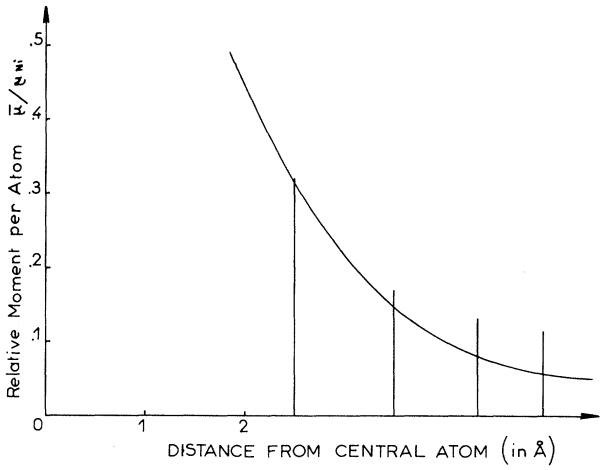

FIG. 2. Distribution of magnetic moment in a "cloud" of 50% Cu-Ni. Continuous curve: after Ref. 7; vertical lines: our approach (vertical lines correspond to the successive position of neighbors).

clusters are independent near the critical concentration.[3]

As a conclusion, it can be said that in any model of environment-dependent moments the magnetic atoms are clustered. With the simplest model and roughest approximation, the main phenomena occurring in the critical concentration range are qualitatively explained, and the quantitative agreement can be regarded as good considering the drastic approximations made. Perhaps "magnetic" clustering is the origin of the tendency to chemical clustering observed during annealing or neutron irradiation below the Curie temperature of pure Ni.

The chosen model of the moment's environmental dependence is good in the critical range. It is probably too simple to represent the behavior of the alloy at extreme concentrations because the strength of interaction of neighboring Ni atoms depends on the local susceptibility on each atom, which can be taken on average as constant only in a limited range of concentration. Nevertheless, available data are too dispersed to allow a more realistic model. Therefore this model can be considered as a good one to explain the main properties of Cu:Ni alloys in the critical range of concentration.

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