DISCONTINUOUS OCCURRENCE OF LOCALIZED MOMENTS IN METALS

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The conditions under which an impurity ion in a metallic host system will acquire a localized magnetic moment have recently received considerable attention, experimentally[1] and theoretically.[2-5] The theories, while differing in their description of the local state, are in agreement in predicting that the formation of the local moment will depend upon the width Δ of the localized state and its position E_0 with respect to the Fermi level E_F. They also agree that once certain threshold conditions are met, any localized moment from zero to a definite maximum may appear. In the Nb-Mo alloys containing 1% Fe the apparent moment per iron atom appears,[1] in fact, to increase from 0 μ_B below 40% Mo to 2.2 μ_B above 90% Mo (see Fig. 1). Since it is known that in this region the electronic density of states $N(E)$ has a rapid variation, and Δ and E_0 are directly related to $N(E)$, it is natural to associate this with the continuous change in moment per atom.

We present evidence here which suggests that the magnetization process may, on the contrary, be essentially a discontinuous one, the moment being either zero or having some maximum value. The apparently continuous change in average moment is then associated with the probability that individual impurity ions have magnetized. This probability we further associate with that of certain neighboring configurations of ions in the alloy system.

Compelling evidence for this idea of discontinuous magnetization is to be found in the Rh-Pd system. Small amounts of Fe in $Th_{1-c}Pd_c$ alloys are always magnetic[1]; for $c \sim 1$, giant moments of ~12 μ_B per Fe atom indeed appear. Cobalt in similar concentrations magnetizes strongly at the Pd-rich end of this system. However, Co in pure Rh is nonmagnetic[6]—χ is essentially temperature independent—and so, it has been found in the nmr of Co^{59}. With

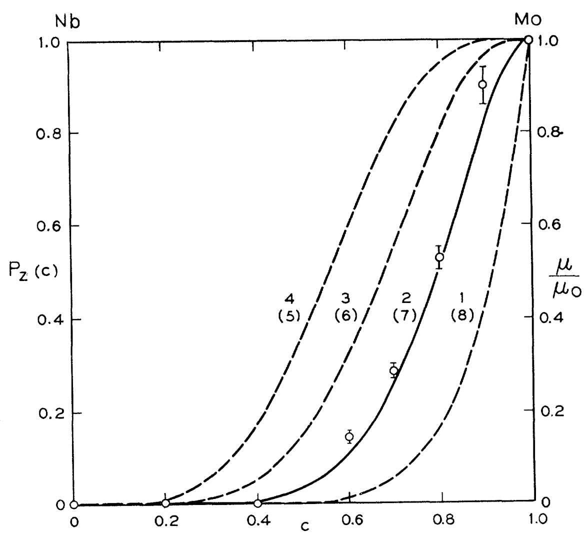

FIG. 1. The observed effective magnetic moment of 1% Fe in the $Nb_{1-c}Mo_c$ bcc alloy system, normalized to value $\mu_0 \simeq 2.1$ Bohr magnetons of Fe in pure Mo, is shown as a function of c (see Reference 1). Superimposed on this data are curves which give the probability $P_z(c)$ that an Fe impurity will have at least $z=5$, 6, 7, or 8 Mo near neighbors as a function of c. No matrix polarization effects are included as are necessary for the Rh-Pd system.

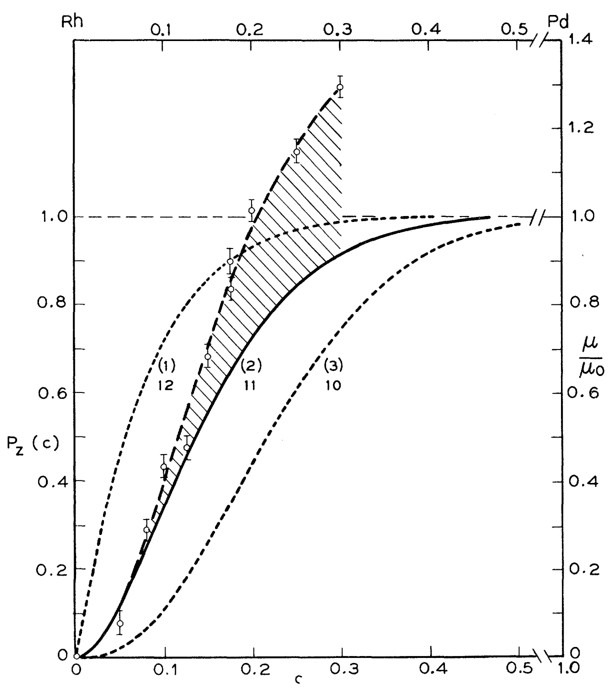

FIG. 2. The observed effective magnetic moment of 1% Co in the $Rh_{1-c}Pd_c$ fcc alloy system, normalized to the value $\mu_0 = 1.7$ Bohr magnetons (see text). Superimposed on this data are curves which give the probability $P_z(c)$ that a Co impurity will have at least 1, 2, or 3 Pd nearest neighbors. The additional moment induced in the matrix, which is proportional to Co-free susceptibility of the Rh-Pd alloys, is shown by the shaded region.

increasing Pd concentration a definite Curie-like behavior develops in χ and the associated effective moment per Co ion increases as shown in Fig. 2. The Co^{59} resonance, however, continues to be visible to at least 12.5% Pd concentration with negligible temperature variation or concentration dependence to the resonance frequency—only the intensity of the resonance falls steadily. This behavior implies very strongly that some of the Co atoms remain unmagnetized, the number of such survivors decreasing as the Pd concentration increases.

The most obvious distinction between different impurity ions is the nature of their local environment in the disordered alloy, and we consider the possibility that in some environments they are unmagnetized and in all others they have their full moment. The simplest model of this type is the following. Let the binary alloy system, with nearest-neighbor coordination member Z, be written as $A_{1-c}B_c$, where by convention the impurity does not magnetize in A alone. Let us suppose the impurity to magnetize if it has at least z B-type near neighbors, and write $P_Z(z,c)$ for the probability of this event. We have[7]

$$P_Z(z,c)=\sum_{x=z}^{Z}\binom{Z}{x}c^x(1-c)^{Z-x}$$

$$=1-\sum_{x=0}^{z-1}\binom{Z}{x}c^x(1-c)^{Z-x}.$$

In Figs. 1 and 2, $P_Z(z,c)$ is shown for $Z=8$ (bcc) and $Z=12$ (fcc) for certain values of z. In Fig. 1 we also show the observed results for the Nb-Mo system, and it is clear that $z=7$ gives a good fit and that the choice of z is unequivocal. This can also be expressed by saying that two or more Nb near neighbors demagnetize the Fe. For the Co in Rh-Pd as shown in Fig. 2 it is apparent that $z=2$ gives a unique initial fit or, correspondingly, that 11 or more Rh neighbors demagnetize the Co. Here we utilize the fact that the giant moments observed for Fe and Co in the Pd-rich end of the Rh-Pd system correspond to an appreciable polarization of the Pd matrix but a negligible increase, if any, of the impurity magnetic moment beyond that found for the primary metals, Fe and Co; i.e., $\mu_0 \simeq 2.2$ and 1.7 μ_B/atom, respectively. Thus we assume the maximum moment on the Co in Rh-Pd to be 1.7. The difference (indicated by the shaded region) between the experimental observations and the curve for $z=2$, $\Delta\mu=\mu_{\rm exp}(c)-\mu_{z=2}(c)$ we attribute to the increased polarizability of the matrix with increasing Pd concentration. The latter supposition is in accord with the fact that (1) $\Delta\mu$ is proportional to the impurity-free matrix susceptibility, within the experimental error, in the range of concentrations investigated, and (2) the giant moments at the Pd-rich end have their maximum value where the matrix susceptibility has its maximum ($Rh_{0.05}Pd_{0.95}$).

To the authors' knowledge no experimental data exist which are in conflict with the discreteness concept. In those alloy systems, other than the ones discussed above, which have so far been investigated,[1] either the local moment remains constant until a phase change occurs (e.g., Fe in Mo-Re) or such variations as do take place unfortunately are also accompanied by a change in phase (e.g., Fe in Ru-Rh). It would be desirable to have further magnetization studies of single-phase binary systems where the impurity is known to be nonmagnetic and magnetic in the primary metals A and B, respectively (e.g., Co in Rh-Pt). Other experimental tests of the notion of discreteness versus a continuously varying local moment are (1) Fe^{57} high-field Mössbauer-effect studies of the Fe in Nb-Mo system, and (2) heat-capacity measurements of the total spin entropy in a large magnetic field.

The relevance of near-neighbor effects on the formation of a local moment to the present state of the theory is, as yet, not apparent.

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[7]In the sum,

$$\binom{Z}{x}=\frac{Z!}{x!\,(Z-x)!},$$

the binomial coefficient.