MAGNETIC SUSCEPTIBILITY AND SPECIFIC HEAT OF NEARLY FERROMAGNETIC NiRh ALLOYS

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(Received 3 May 1967)

Recent theoretical predictions by Doniach and Engelsberg[1] and Berk and Schrieffer[2] have shown that in a nearly ferromagnetic metal the interaction between the low-energy spin fluctuations and the conduction electrons gives rise to an increase in the specific heat. According to these authors, whenever the Stoner enhancement of the susceptibility $(1-\bar{I})^{-1}$ becomes large, the effective mass of the conduction electrons will also be enhanced by a factor proportional to $-\ln(1-\bar{I})$. Here $\bar{I}=IN(0)$ is the product of the effective interaction and the bare density of states at the Fermi surface. This change in the effective mass gives rise to a corresponding increase in the linear term in the specific heat. Doniach and Engelsberg have also shown that because of the variation of the electron self-energy as one moves away from the Fermi surface, the specific heat will have an additional term $\propto T^3 \ln(T/T_S)$, $k_B T_S$ being the characteristic spin fluctuation energy. In order to verify these predictions we have measured the specific heat and magnetic susceptibility of a series of Rh-Ni alloys from 0 to 100% Rh with particular emphasis on the region around the critical concentration at which the system becomes ferromagnetic.

The Ni-Rh system forms an uninterrupted series of solid solutions in which no decomposition or ordering occurs.[3] To prepare the alloys each sample was remelted many times in an arc furnace and then annealed for 70 h at 1100°C at pressures below 10^{-6} Torr. The samples close to the critical concentration showed a remanence of the order of $(10^{-2}\text{-}10^{-3})\mu_B$ per atom that was sensitive to sample preparation. However the high-field slope $d\sigma_m/dH$ was independent of these effects. The specific heat was measured by a heat-pulse technique[4] and the susceptibility by a pendulum magnetometer.[5]

Figure 1 shows the specific heat and magnetic susceptibility as a function of temperature for the alloy which has the largest enhancement effects, $Ni_{0.63}Rh_{0.37}$. The susceptibility has a maximum at ~40°K where the system becomes ferromagnetic. Although the theoretical predictions were made in the paramagnetic region, one can show that if the density of states varies linearly with change in concentration the enhancement effects should by symmetric about the critical concentration. It appears that the $Ni_{0.63}Rh_{0.37}$ sample is just on the ferromagnetic side of the critical concentration.

As illustrated in Fig. 1, the specific heat shows an anomaly below 8°K. This anomaly decreases on either side of the critical concentration, disappearing, within our accuracy, at $Ni_{0.55}Rh_{0.45}$ on the parametric side and at $Ni_{0.70}Rh_{0.30}$ on the ferromagnetic side. The solid curve is a fit using the expression

$$C_v/T=\gamma+aT^2+bT^2\ln T^2.$$

The steep slope at low temperatures is due to the fact that $T^2\ln T^2$ vs T^2 has an infinite derivative at $T=0$. It should be noted that the enhanced value of γ is given by the intercept at $T=0$ and not an extrapolated intercept from the higher temperature data. It should also be pointed out that the anomaly does not fit a T^{-2} law that might be characteristic of local-

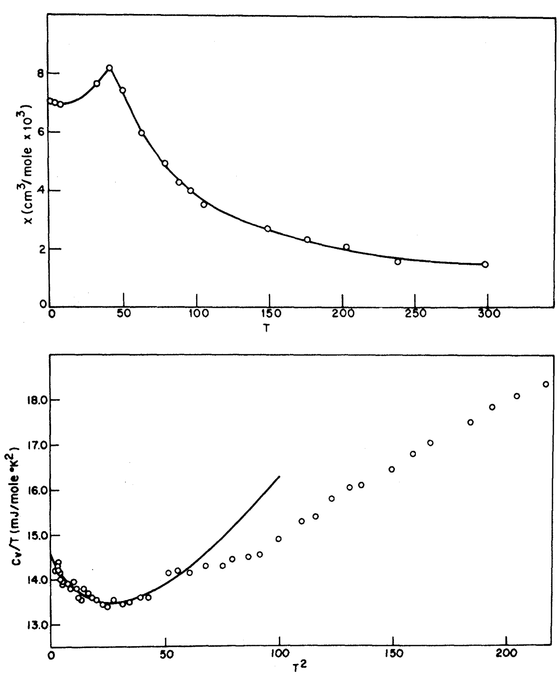

FIG. 1. The magnetic susceptibility and specific heat of $Ni_{0.63}Rh_{0.37}$, the sample with the largest enhancement effects.

ized spins.

In Fig. 2 the γ values obtained as described above are plotted against concentration along with the magnetic susceptibility. The susceptibility and γ values have been written in units of states/eV atom to facilitate making comparisons. One sees a sharp peak in both curves at 63% Ni. The susceptibility behaves as $|C-C_F|^{-1}$ while the specific heat qualitatively follows $-\ln|C-C_F|$ in the region of the critical concentration, $C_F = 63\%$ Ni, giving an excellent confirmation of the theory. Several more specific features of the data are explanable in terms of the bare density of states given by Ehrenreich et al.[6] and others.[7] The simplest is the small decrease in γ for low concentrations of Rh. This is simply due to the fact that the majority-spin Fermi surface is some distance above the top of the d band so that the first effect on adding Rh is to reduce the number of minority-spin carriers increasing the magnetization[8] and, because the minority-spin Fermi energy is in a region of rapidly increasing density of states, decreasing the γ value. Another feature obtainable from an examination of the band structure is the symmetry of the peak in the γ value. As already stated, the enhancement of both the specific heat and the susceptibility is symmetrical about the critical concentration if the density of states is a linear function of energy in the region of the relevant Fermi energy. However, the critical concentration occurs when the Fermi energy is just below the peak value of the d-band density of states so that in the ferromagnetic region the majority-spin Fermi surface increases rapidly at first and then begins to decrease, thus giving rise to the asymmetry of γ. These two facts along with the temperature variation of the susceptibility for various samples indicate that the band calculations give reasonable values for the underlying bare density of states. If this is the case the enhancement of the electronic specific heat for the sample $Ni_{0.63}Rh_{0.37}$ is ~2 while the enhancement of the susceptibility $(1-\bar{I})^{-1} \simeq 70$. This value of the enhancement of the specific heat is considerably smaller than the value given by the model calculation [~13 for $(1-\bar{I})^{-1} = 70$].[9] In these calculations the enhancement of γ is roughly speaking dependent on two parameters for a given value of $(1-I)$, the magnitude of the coupling of the electrons to the spin fluctuations and the width of the peak of the dynamic susceptibility in re-

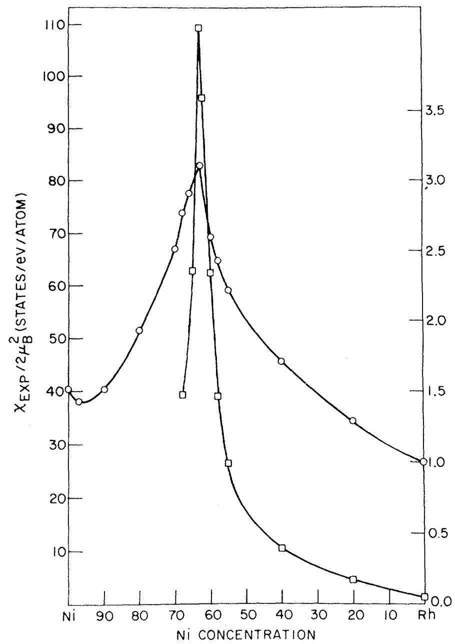

FIG. 2. The magnetic susceptibility (squares) at 1.4°K and the γ value (circles) of the specific heat versus concentration. The results are plotted in states/eV atom in order to facilitate comparisons of the enhancement effects.

ciprocal space. Doniach[10] has shown that intra-atomic Hund's-rule exchange reduces the coupling of the electronic excitations to the spin fluctuations. However, the most one can obtain from this effect is a reduction of γ by a factor of 3 which is insufficient here. In a zero-range model the width of the peak in the susceptibility is overestimated, as any q dependence of the interaction will surely tend to narrow the peak. This narrowing appears to be important in explaining the induced magnetization around an Fe impurity in Pd[11] so that it is probably also important here. Some combination of these two effects could possibly lead to the observed value of γ. With these differences in the linear term it is probably not meaningful to compare the coefficient of the $T^2 \ln T$ term in the specific heat, although the value used in Fig. 1 of 9.4×10^{-3} (states/eV atom°K^2) is not unreasonable as it gives $\epsilon_F \sim 2 \times 10^4$ °K and $T_S \sim 250$°K. The unique feature of this term is that the logarithmic singularity becomes evident only at low temperatures relative to T_S.

In conclusion, we feel the results give a good qualitative confirmation of the theoretical predictions. We also point out that there is nothing unique about NiRh alloys in this context; for example, CuNi alloys show a similar anomaly. However, we prepared several CuNi alloys near the critical concentration and found that the susceptibility measurements were quite sensitive to sample preparation, probably indicating superparamagnetism. Thus for metallurgical reasons RhNi appears to be the better material.

We would like to thank E. Corenzwit and L. D. Longinotti for technical assistance and S. Strässler, W. L. McMillan, and P. W. Anderson for useful discussions.

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FURTHER EVIDENCE OF NAGAOKA'S BOUND STATE FOR CONDUCTION ELECTRONS IN DILUTE ALLOYS

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The temperature dependence of the solute magnetic susceptibility of very dilute Cu-Fe alloys shows an anomaly at a temperature in the range 6-17°K. The effective Bohr-magneton value of the localized moment is appreciably reduced below this temperature. It is suggested that this anomaly can be interpreted as further evidence of the formation of a quasibound election state as suggested by Nagaoka.

Daybell and Steyert[1] have recently pointed out that their measurements of the electrical resistivity and magnetic susceptibility of very dilute Cu-Fe alloys in the temperature range 0.040-40°K can be interpreted in terms of Nagaoka's theory.[2] This theory predicts the occurrence below a certain critical temperature (T_c) of a quasibound state arising from the negative s-d exchange interaction between the localized moment of the solute ion and the conduction electron spins. For the Cu-Fe system Daybell and Steyert conclude from their resistivity data that $T_c = 16°$K. The Nagaoka theory also predicts a significant reduction in the effective moment of the solute ion as the quasibound state is formed, and this should be evident from measurements of the magnetic susceptibility of an alloy. Preliminary susceptibility measurements for one alloy (110-ppm Fe) are presented by Daybell and Steyert, and it is shown that the results are not in disagreement with the Nagaoka theory. However, these authors feel that, because of the experimental difficulties of such magnetic measurements (which were made by a low-field induction method), further experiments are required before their magnetic data can be interpreted with complete confidence.

In the course of a magnetic study of very dilute α-phase Cu-Fe and Au-Fe alloys (6- to 220-ppm atomic Fe) in this laboratory by a high-precision Faraday method[3] in the range 6-300°K, we have observed an anomaly in the temperature dependence of the magnetic susceptibility of the solute in the Cu-Fe system. Because of the spacing of our data, we can presently say only that the anomaly occurs at a temperature in the range 6-17°K. However, since the experimental evidence for the existence of Nagaoka states in alloys is so meagre and in view of the present low ratio of experimental to theoretical publication on this