Magnetism and atomic short-range order in Ni-Rh alloys

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Low-field ac susceptibility measurements of Ni-Rh samples of various concentrations are presented. Giant effects of the metallurgical state on the magnetic ordering temperature are associated with changes in the degree of atomic short-range order. By careful control of this degree of short-range order, it is possible to demonstrate the existence of a spin-glass state in Ni-Rh alloys.

The appearance of long-range ferromagnetic order in NiRh alloys at a critical concentration of about $x_{crit} = 63$ at.% Ni originally had been explained in terms of band ferromagnetism and spin fluctuations.[1] However, more recent evidence from elastic neutron scattering,[2] low-temperature specific-heat measurements,[3] and magnetization measurements[4] favors a description in terms of interacting localized moments. These moments called polarization clouds or spin clusters are very large, about $20\mu_B$, and are associated with Ni-rich atomic environments,[4] quite similar to the well-understood Ni-Cu system.[5]

If this local moment description is indeed the correct one, then one would expect the appearance of a spin-glass phase at concentrations less than x_{crit}, as has been observed in other local moment alloys.[6,7]

In this paper we report the first direct observation of a spin-glass transition in NiRh alloys.

In most alloys, the exact nature of the various magnetic phases present near the critical concentration is often obscured by metallurgical problems.[6,7] NiRh is no exception. Figure 1 demonstrates the sensitivity of the magnetic response of a NiRh sample to the metallurgical state of the sample. All alloys for the present study were prepared by arc melting the appropriate amounts of two master alloys of 62 and 64 at.% Ni, respectively.[8] For homogenization, the alloys were subject to severe plastic deformation in three mutual perpendicular directions, followed by a 1200 °C anneal for 3 days. This procedure was repeated once to eliminate all chemical concentration gradients. The samples for magnetization measurements were obtained by compressing a piece, cut from the center of the alloys, to a thickness of about 0.2 mm. Samples were then cut from this compressed piece to a dimension of 2 mm × 1 mm × 0.2 mm, the corners carefully rounded off.

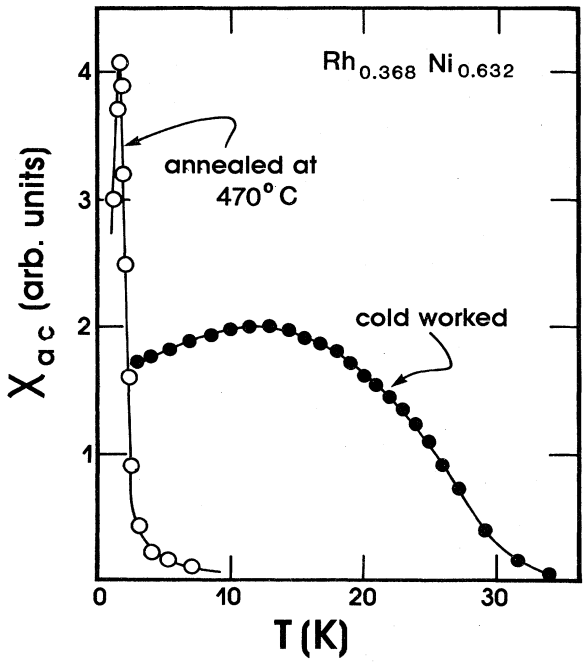

FIG. 1. ac susceptibility in arbitrary units vs temperature for a Ni-Rh sample in two different metallurgical states: cold worked and annealed at 470 °C.

ac susceptibility measurements (at 35 Hz and 0.2-Oe field amplitude) on this "as-made" state are displayed in Fig. 1, marked "cold worked." Also shown are measurements on the same sample after relieving the strain for half an hour at 900 °C, followed by a 10-h anneal at 470 °C. The difference is immense. Cold working increases the magnetic ordering temperature from 2 to about 25 K. The cold-worked state is, however, very nonuniform with a rather "smeared" transition.

Similar effects due to plastic deformations have been observed in other alloys. Examples are Ni-Cu (Ref. 7) and Au-Fe.[9] Here, the changes have been associated with changes in the degree of atomic clustering.[6,7,9] These alloys are not random solid solutions, but show a tendency towards atomic clustering.[6,7] The magnetic moments disordering at the Curie temperature T_C of NiCu and AuFe alloys are large spin clusters associated with Ni- or Fe-rich atomic environments. For both Ni-Cu and Au-Fe, T_C decreases with cold working.[6,7,9] Cold working, in general, makes an alloy more random, i.e., decreases the degree of clustering. As a consequence, the Ni-rich (or Fe-rich) regions are depleted; the magnetic moments decrease and so does T_C. The significant increase of T_C observed in Ni-Rh (see Fig. 1) must mean that Ni-Rh alloys display atomic short-range order (SRO); i.e., Ni atoms like to surround themselves with Rh atoms.[10] Cold working thus increases the number of Ni near neighbors, increasing the magnetic moment and T_C.

A much more controlled way to change the degree of SRO is to quench the samples from various annealing temperature T_A. Figure 2 summarizes a systematic study of this effect. Shown is the magnetic ordering temperature T_C, i.e., the temperature of the maximum in the susceptibility versus the annealing temperature T_A from which the samples were quenched. For all concentrations shown there is a systematic increase in T_C with increasing T_A, i.e., with decreasing degree of atomic SRO. For the sample with 63.2 at.% Ni a

maximum is observed in T_C vs T_A. This effect has been seen, for example, in Au-Fe (Refs. 11 and 12) and is well understood.[11,13] What is happening is that from temperatures $T_A > 750\,^{\circ}C$ we are no longer able to quench-in the high-temperature equilibrium state. Due to vacancy-enhanced diffusion, significant diffusion takes place during the quenching process and the quenched-in state just depends on the quenching rate and not on the initial high-temperature state.[11,13] Also, the samples are inhomogeneous with a "smeared" magnetic transition[12] (error bars in Fig. 2). The data labeled "fast quench" are obtained after shooting the samples from the furnace directly into water by a blast of argon gas. The slow quench refers to a process in which the samples were sealed in quartz capsules, the capsules being pulled from the furnace, stuck into water, and broken as fast as possible.

For the 63.2 at.% Ni sample the highest T_C obtained by fast quenching is only about 12 K compared to 25 K after cold working. Thus, cold working produces a higher degree of disorder than quenching from high temperatures.

It is quite obvious from the results demonstrated in Fig. 2 that there is not a single critical concentration for ferromagnetism similar to other alloys.[6,7] The critical concentration is different for different degrees of atomic SRO. A crude estimate yields values for x_{crit}, anywhere between 60 and 64 at.% Ni depending on the degree of atomic SRO.

Figure 3 displays the actual ac susceptibility curves for two samples quenched from various annealing temperatures. All transitions are sharp, indicating that we were able to quench-in a homogeneous state.[14] The behavior of the two samples is qualitatively different. For the 63.2 at.% Ni sample, the height of the susceptibility maxima remains the same as the ordering temperature is changed. This is indicative of ferromagnetic order, the height being demagnetization limited.[6,7] The other sample with 62 at.% Ni is definitively not ferromagnetic, the height of the susceptibility maxima decreasing dramatically with decreasing ordering temperature.[15] This latter behavior has been observed in other systems and is indicative of spin-glass ordering.[6,7] The sharpening of the ferromagnetic susceptibility cusps at low Curie temperatures for the 63.2 at.% Ni sample is probably due to the manifestation of the "spin-glassiness" already present in the weakly ferromagnetic state.

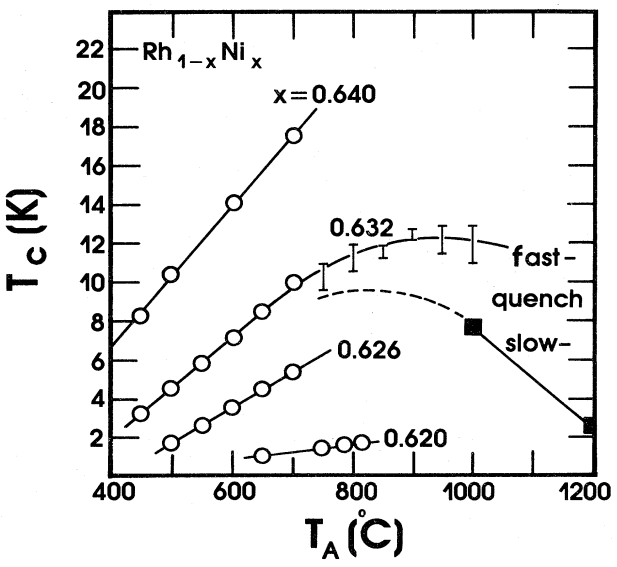

FIG. 2. Magnetic ordering temperature T_C vs annealing temperature T_A from which the samples were quenched. The numbers labeling curves are the Ni concentration in atomic fraction. The two branches for the $x = 0.632$ sample are for different quenching rates (see text). All transition temperatures T_C correspond to paramagnetic to ferromagnetic transitions except for the 62 at.% Ni alloy where T_C represents a paramagnetic to spin-glass transition (see text).

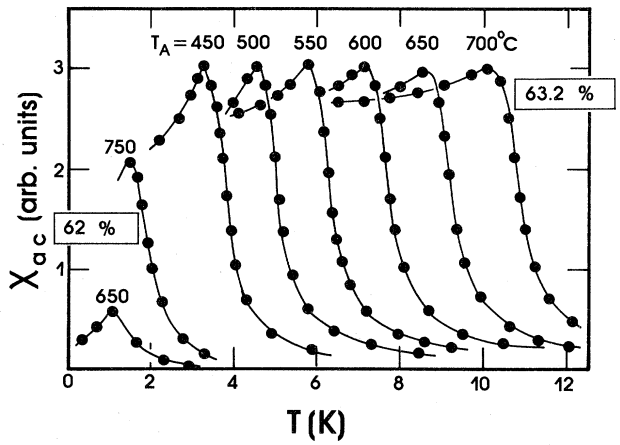

FIG. 3. ac susceptibility in arbitrary units vs temperatures for two Rh-Ni samples quenched from various annealing temperature. The indicated annealing temperatures are in degrees Celsius.

Figure 4 demonstrates that the 63.2 at.% Ni sample is indeed ferromagnetic. The solid squares are taken from hysteresis loop measurements, representing the maximum slope of these loops. As the temperature is lowered below T_C these loops open up immediately. However, the maximum slope remains at the demagnetization limit down to our lowest temperatures. A so-called "reentrant" behavior is not observed. In summary, we have demonstrated that the onset of ferromagnetic order in Ni-Rh alloys is preceded at lower Ni concentrations by a spin-glass ordering. We were able to show this by carefully controlling the gigantic metallurgical effects in Ni-Rh and thus avoiding large inhomogeneities in the degree of atomic SRO.

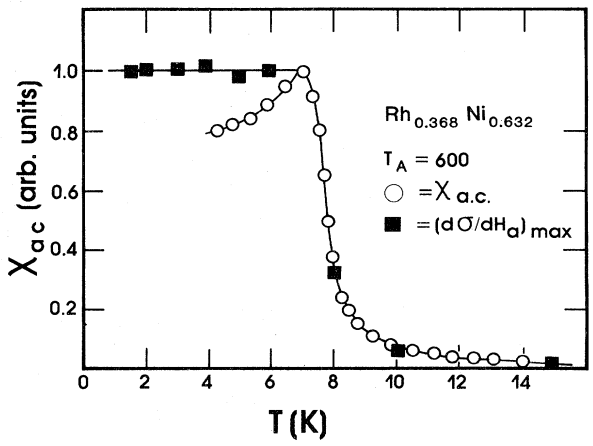

FIG. 4. ac susceptibility (open circles) and dc susceptibility (solid squares) vs temperature; below T_C the dc susceptibility is taken to be the maximum slope of the hysteresis loop.

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[14]Since we first published some preliminary results on Rh-Ni alloys in Ref. 6 we have considerably improved the homogeneity of our samples using the procedure described in the text.

[15]The data below 1.2 K were taken in a dilution refrigerator.