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A. Amamou and J. Durand

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THE APPROACH TO FERROMAGNETISM IN AMORPHOUS Ni-P-B ALLOYS*

A Amamou[†] and J. Durand[†]

W. M. Keck Laboratory of Engineering Materials,
California Institute of Technology
Pasadena, California 91125

Magnetization was measured between 1.7 and 300°K in fields up to 70 kOe on splat-cooled Ni-P-B amorphous alloys in the critical concentration range for the appearance of ferromagnetism. The onset of ferromagnetism is attributed to interactions between giant moments. For the composition range investigated, the magnetic contribution is arising mainly from moments of $5-6\mu_B$ with a Kondo-type characteristic temperature of 1°K.

The inhomogeneous character of the paramagnetic-ferromagnetic transition was first emphasized by magnetic measurements on Ni-Cu¹ and Ni-Rh² disordered alloys. The ferromagnetic ordering was showed to occur from the coupling of giant moments whose concentration increases when the Ni content goes up to the critical composition. Such a behavior seems to be the most common case in disordered alloys such as Ni-Cr, Ni-V, Ni-Mo³, Fe-V⁴, Co-Re⁵....., as well as in compounds CoGa⁶, CoAl, FeAl, NiAl⁷..... The homogeneous model has been found applicable to a relatively small number of alloys⁸ i.e. Ni-Pt, ZrZn₂, Ni₃Ga...

The appearance of ferromagnetic order was already investigated in some amorphous alloys (Fe-Pd-Si⁹, Co-Pd-Si¹⁰, Ni-P¹¹). But because of the low fields used for the magnetic susceptibility measurements (7 kOe max.) these previous studies were not conclusive. For instance, the Arrott plots (M^2 vs M/H) for Ni-P alloys are linear at low fields¹¹, but they exhibit large deviations from linearity for fields up to 150 kOe.¹²

We present magnetic data on amorphous Ni-P-B alloys with compositions close to the critical concentration for the para-ferro transition. Our experiments performed over temperatures ranging from 1.7 to 300°K and in fields up to 70 kOe allow us to conclude unambiguously that the ferromagnetic order occurs in an inhomogeneous way.

The Ni-P-B samples were obtained by rapid quenching from the liquid state using the "piston and anvil technique".¹³ Full details of the alloy preparation may be found elsewhere.¹⁴ We studied three samples with a constant B content: Ni₈₀P₁₂B₈, Ni₇₉P₁₃B₈ and Ni₇₈P₁₄B₈. Concentrations are nominal. Each foil was checked with

a Norelco X-ray diffractometer. Magnetization was measured by Faraday method with an Oxford Instruments Magnetometer (description in ref. 15).

The three samples we measured are not ferromagnetic. But the magnetization (M) behavior as function of field H and temperature T is typically that of alloys in the critical concentration range for the occurrence of ferromagnetism (fig. 1). For $T < 20^{\circ}\text{K}$, the isotherms $M = f(H)$ exhibit a strong magnetic contribution almost saturated for $H > 50 \text{ kOe}$ at 1.7°K . For $T > 40^{\circ}\text{K}$, we still found a small magnetic component, but roughly temperature independent and saturated for $H \leq 10 \text{ kOe}$; for $H > 10 \text{ kOe}$, M vs H is linear. This latter magnetic contribution is attributed to macroscopic grains of crystalline Ni, whose concentration is too small to be detected by X-ray analysis. Such an interpretation is justified as follows: i) the residual magnetization is lowered by less than 10% between 40 and 300°K , which implies a high Curie Temperature; ii) the saturation field is small and temperature independent; iii) this magnetic contribution is larger in the center of the foils (up to 1%) than in the edges (about 0.03%) where the cooling rate is known to be faster; iv) after subtracting this small contribution, the remaining part of M defined as the amorphous contribution is the same for different parts of a given foil. For $T < 40^{\circ}\text{K}$, this crystalline component is mixed up with the strong amorphous contribution. For subtracting it, we assume that it remains constant between 40 and 1.7°K . From now on, our analysis will be dealing only with the amorphous contribution.

Arrott plots for our three samples exhibit strong departures from the linearity at both small and large fields, so that the magnetization

Fig. 1. Magnetization vs field for the $\text{Ni}_{78}\text{P}_{14}\text{B}_8$ alloy at various temperatures.

behavior has to be understood by an inhomogeneous model. We analyzed our data in a similar way and with the same notations used for Ni concentrated alloys.¹⁻³ The temperature dependence of the initial susceptibility χ_o can be expressed by the phenomenological law:

$$\chi_o = \chi' + C_{cw}/(T + \theta_o) \quad (1)$$

in which χ' is temperature independent for a given concentration, but increases substantially with the Ni content (fig. 2). The second term of Eq. (1) follows a Curie-Weiss law, with a constant C_{cw} and a characteristic temperature θ_o negative and increasing with Ni concentration (Table I). At low temperature and within the high-field limit, the magnetization varies according to:

$$M(H, T) = \sigma_o(T) + \chi_H H \quad (2)$$

where $\sigma_o(T)$ is the saturation magnetization and χ_H the high-field susceptibility. For a given concentration, the value of χ_H is higher than that of χ' , but the departure is considerably smaller than in crystalline cases.^{2, 3, 6} The two previous laws imply that the magnetization is the sum of two main components: a non magnetic contribution ($\chi'H$) arising from P, B and non magnetic Ni atoms, and a magnetic contribution originating from magnetic impurities whose characteristics are defined by C_{cw} , σ_o and θ_o . Assuming that the impurities moments have the same size, their value μ^* and their concentration c^* are deduced from $C_{cw} = c^* \mu^{*2} / 3k$ (k is the Boltzmann constant) and $\sigma_o = c^* \mu^*$. If they are different types of magnetic

Fig. 2. Product of initial susceptibility and temperature vs temperature for Ni-P-B alloys (compositions in at. % Ni).

TABLE I. Magnetic properties of amorphous Ni-P-B alloys.

Alloy (at.%Ni)	σ_0 (emu/g)	χ_H (10^{-6} cgs)	χ' (10^{-6} cgs)	θ_0 ($^{\circ}$ K)	C_{cw} (10^{-6} $^{\circ}$ K/cgs)	c^* (10^{-1} at.%)	μ^* (μ_B)	J_1	c_1 (10^{-1} at.%)	J_2	c_2 (10^{-1} at.%)
78	0.76	2.85	1.60	≈ 0	116	1.0	6.8	2.5	1.38	-	-
79	0.78	3.05	1.96	≈ 0	118	1.0	6.7	-	1.38	4.6	0.06
80	0.83	3.30	2.30	-5	125	1.2	6.7	-	1.38	4.7	0.13

moments, μ^* and c^* represent only average values. From this analysis, we obtained a moment per cloud roughly constant (6.5 to 7 μ_B) and a concentration slowly increasing with the Ni concentration (0.10 to 0.12 at. %).

The behavior of the magnetic impurities may be analyzed in more detail by considering the magnetization data at low temperatures. The magnetic contribution can be written as:

$$M_{\text{mag}}(H, T) = M(H, T) - \chi' H$$

The term $M_{\text{mag}}(H, T)$ for the three alloys can be expressed by a unique function of $H/(T + \theta)$, where the characteristic temperature θ ($1 \pm 0.1^\circ\text{K}$) does not vary substantially with Ni content. For the Ni_{78} sample, this function is the Brillouin function $B_{J_1}(x)$, with $x = \mu_1 H/k(T + \theta_1)$, $J_1 = 2.5$, $\theta_1 = 1^\circ\text{K}$, $\mu_1 = g J_1 \mu_B = 5 \mu_B$ (assuming $g = 2$) (fig. 3). For the Ni_{79} and Ni_{80} samples, $M_{\text{mag}}(H, T)$ does not follow a Brillouin function, but after subtracting the experimental values for the Ni_{78} alloy, the remaining data can be roughly expressed by a Brillouin function B_{J_2} with $\mu_2 \approx 9 \mu_B$, $J_2 \approx 4.5$, and a value for θ_2 between 0 and 1°K . The results of the previous separation are listed in Table I. According to this analysis, all the magnetic clouds in the Ni_{78} alloy have roughly the same moment of $5 \mu_B$. When the critical concentration is approached, there is some evidence for a larger distribution of magnetic clouds. Let us note that a small discrepancy (20%) between the values of C_{cw} for the Ni_{80} sample, as determined at low and high temperatures, can be explained by the dissociation of large moments into smaller moments when the temperature is increased³ (see fig. 2).

Fig. 3. Variation of the magnetic impurities magnetization ($M - \chi'H$) vs ($H/T + 1.0$). Full line represents a Brillouin function ($g = 2$; $J = 2.5$).

The positive value we obtained for θ_1 must be compared with the critical temperatures determined for isolated magnetic impurities in Kondo alloys. In both cases, the same mechanism seems to hold: s-d exchange interactions result in antiferromagnetic coupling between the impurity moment and the conduction electrons.¹⁰ In a classical Kondo alloy like Au-Fe, the value of θ_1 (0.40°K) as determined from the magnetic data¹⁶ on isolated Fe impurities corresponds fairly well to the Kondo temperature $T_K = 0.24^\circ\text{K}$ obtained from resistivity ρ measurements.¹⁷ Resistivity measurements above 4.2°K on our samples gave a logarithmic decrease of ρ down to a minimum between 15 and 20°K. Measurements at lower temperatures are needed in order to determine whether this minimum corresponds to a Kondo behavior and to compare this T_K with the value of θ_1 obtained from our magnetic data.

Let us compare now the results of our analysis with the main features reported on disordered alloys and compounds near the para-ferro transition. In both cases, the ferromagnetic approach was found to arise in an inhomogeneous way by the occurrence of polarization clouds. Nevertheless, the amorphous alloys exhibit two particular features. First, the temperature dependent contribution can be interpreted by the existence of only two types of magnetic moments, μ_1 and μ_2 , whose values are not very different, whereas for Ni-Cu, Ni-V.... disordered alloys, a similar analysis showed the existence of a larger number of impurity types which vary with T and H in very different ways. In particular, in amorphous Ni-P-B alloys, there is no evidence for the existence of nearly magnetic impurities.^{3, 6} Thus, the average moment μ^* (6.5 to 7 μ_B per cloud) is relatively

small and close to the moment μ_1 ($5 \mu_B$) obtained by a Brillouin-function analysis. In contrast, the high values of μ^* (10 to $40 \mu_B$) determined for concentrated alloys arise mainly from an average of magnetic impurities with very different moments. Second, the non-magnetic contribution χ' varies substantially with the Ni content for the Ni-P-B alloys, whereas χ' is roughly constant in crystalline Ni alloys.^{3, 6} This variation of χ' seems to be fairly linear, so that its extrapolation is nearly zero for $c_{Ni} = 74\%$, a concentration close to that of Ni_3 (PB). In addition, from structural studies on Ni based amorphous alloys¹⁸, it is known that the short-range order of the crystalline counterpart is essentially preserved. In our case, this short-range order should be of the Ni_3P or Ni_3B type. In these crystal structures, Ni atoms in different sites have 2 or 3 P or B atoms as first neighbors. These compounds are both paramagnetic. So the magnetic properties of amorphous Ni-P-B alloys may be tentatively explained by an environmental model where the electronic state of a given Ni atom is assumed to depend on its neighboring atom. For a Ni concentration close to 75 at.%, all the Ni atoms would be paramagnetic with a small value of χ' . When c_{Ni} is increased, the probability for Ni atoms to have 1 or 0 metalloid first neighbor is also increased. The magnetic clouds might appear among the Ni atoms having no metalloid atom as nearest neighbor. The increasing χ' contribution might originate from Ni atoms having one metalloid first neighbor.

In conclusion, the approach to ferromagnetic order seems to be rather simpler in amorphous Ni-P-B alloys than in most concentrated Ni alloys. The effect of long-range structural disorder does not occur, since the magnetization process in Ni alloys is mainly determined by

short-range interactions. So the main differences observed between amorphous and crystalline cases arise from the existence and the nature of the short-range order in amorphous alloys.

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REFERENCES

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† On leave from Laboratoire de Structure Electronique des Solides,
E.R.A. 100, 4, rue Blaise Pascal, 67000 Strasbourg, France.

1. J. S. Kouvel and J. B. Comly, Phys. Rev. Letters 24, 598 (1970).
2. W. C. Mueller and J. S. Kouvel, Phys. Rev. B 11, 4552 (1975).
3. A. Amamou, F. Gautier, and B. Loegel, J. Phys. F 5, 1342 (1975).
4. P. Pataud, J. P. Perrier, and R. Tournier, J. Phys. (Paris) 35,
C4-189 (1974).
5. S. Mishra, E. J. Hayes, R. Tustison, and P. Beck, J. Phys. (Paris)
35, C4-195 (1974).
6. A. Amamou and F. Gautier, J. Phys. F 4, 563 (1974).
7. A. Parthasarathi and P. A. Beck, Sol. State Commun. 18, 211 (1976).
8. E. P. Wohlfarth, Comments Sol. State Phys. 6, 123 (1975).
9. R. Hasegawa, J. Appl. Phys. 41, 4096 (1970); J. Phys. Chem.
Solids 32, 2487 (1971).
10. R. Hasegawa and C. C. Tsuei, Phys. Rev. B 3, 214 (1971).
11. D. Pan and D. Turnbull, AIP Conf. Proc. 18, 646 (1974).

12. A. Berrada (to be published, 1976).
13. P. Duwez and R. Willens, Trans. AIME 227, 362 (1963).
14. P. L. Maitrepierre, J. Appl. Phys. 40, 4826 (1969).
15. G. Tangonan, Ph.D. Thesis, Caltech (1975).
16. J. L. Tholence and R. Tournier, J. Phys. (Paris) 35, C4-229 (1974).
17. J. W. Loram, T. E. Whall, and P. J. Ford, Phys. Rev B 2, 857, (1970).
18. G. S. Cargill III, Solid State Physics, ed. Seitz et al. (Academic Press, New York, 1975), Vol. 30, p. 225.