CALT-822-84

MAGNETISM AND LOCAL ENVIRONMENT MODEL IN $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ AMORPHOUS ALLOYS

A. Amamou

JUNE 1976

A REPORT ON RESEARCH CONDUCTED UNDER CONTRACT FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

W. M. KECK LABORATORY OF ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

DISCLAIMER

CALT-822-84

California Institute of Technology

W. M. Keck Laboratory of Engineering Materials

MAGNETISM AND LOCAL ENVIRONMENT MODEL IN $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ AMORPHOUS ALLOYS

by

A. Amamou

Energy Research and Development Agency Report No. 74, under Contract No. AT(04-3)-822

Professor Pol Duwez, principal investigator.

JUNE 1976

NOTICE

ABSTRACT

The magnetic properties of amorphous alloys $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ have been investigated. The samples were prepared by the splat-cooling method. The Curie temperatures have been determined and the magnetization measurements performed for $1.7^{\circ}K \leq T \leq 270^{\circ}K$ and fields up to kOe. $Ni_{0.78}P_{0.14}B_{0.08}$ is paramagnetic, whereas $Co_{0.78}P_{0.14}B_{0.08}$ is ferromagnetic until the crystallization temperature ($678^{\circ}K$). The average moment per cobalt atom is $1.15\mu_B$. In $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ the critical concentration for the paramagnetic-ferromagnetic transition is $c \simeq 0.15$, this transition occurs in an inhomogeneous way. The saturation magnetization in the whole concentration range can be interpreted (as for some crystallized alloys and compounds) by a local environment model, when a reasonable short range order is assumed. In such a model the magnetic moment per cobalt atom is related merely to the number of its Co first neighbors n_{Co}. For $n_{Co} = 0$ and 1 the cobalt atom is not magnetic, for $n_{Co} = 2$ and 3 it carries a small moment $\mu_1 = 0.50\mu_B$ and for $n_{Co} > 3$ it is magnetic with $\mu_2 = 1.15\mu_B$ as in $Co_{0.78}P_{0.14}B_{0.08}$; the nickel atoms do not carry a substantial moment in the entire concentration range. These features are comparable to those obtained in some crystalline alloys.

INTRODUCTION

In recent years a number of studies on amorphous alloys of transition metals (Mn, Fe, Co, Ni) have been performed and show a large variety of magnetic behaviours. For instance Mn-P-C[1] is antiferromagnetic, Ni-P-B alloys are non magnetic although a behaviour characteristic of the existence of magnetic impurities is observed[4]; hitherto few studies on cobalt amorphous alloys have been performed.[5] Many studies have shown that the structure of amorphous alloys is characterized by the absence of long range order, but in most cases there is a well established short range order. In alloys containing transition elements of the first long period (Cr, Mn, Fe, Co and Ni) it is possible to substitute one of these elements by another. Amorphous alloys can therefore be obtained with a wide range of continuously varying magnetic properties

In this paper we study the magnetic properties of $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ $(o \leq c \leq 1)$ amorphous alloys obtained by "splat cooling". The Curie temperatures have been determined and the magnetizations were measured in a wide range of magnetic fields and temperatures. $Ni_{78}P_{14}B_8$ is "paramagnetic"[4] whereas $Co_{0.78}P_{0.14}B_{0.08}$ is ferromagnetic; a para-ferro transition occurs at a cobalt critical concentration c_{cr} of $\simeq 0.15$ at.%. We show that the saturation magnetization can be interepreted by a local environment model (LEM). For concentrations near c_{cr} the characteristics of the magnetization below and above the Curie temperature are determined and discussed.

EXPERIMENTAL RESULTS

Foils of $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ were obtained by rapid quenching from the liquid state using the "piston and anvil technique". Full details of the alloys preparation can be found in ref. 7. The concentrations given in this paper are nominal. The X-ray diffraction spectrum of each foil was checked with a Norelco diffractometer. The Curie temperatures were determined by an induction method using an ac bridge; the heating rate above room temperature was about $5^{\circ}K$/min; the magnetic measurements were performed by the Faraday method using an Oxford Instrument magnetometer described in ref. 8; the magnetic field was varying up to 70 kOe and the temperature between $1.70^{\circ}K$ and $270^{\circ}K$. When necessary the variation of the magnetization at low fields ($H < 0.5$ kOe) was measured in detail, in order to determine the real initial susceptibility.

Curie Temperatures

For cobalt concentrations c below 0.15 no Curie transition was observed; for higher cobalt concentrations a transition occurs at a temperature T_c which increases rapidly with c. This temperature was determined as the temperature at which the permeability drop presents an inflexion point; T_c curve versus c exhibits roughly an S shape(Fig. 1), and is linear with a slope of about $11.5^{\circ}K$/at.% Co for $0.30 \lesssim c < 0.70$. The width ΔT_c of the Curie transition is rather large for $c \leq 30$ ($\Delta T_c \simeq 20^{\circ}K$) and decreases when the cobalt concentration is increased; $\Delta T \simeq 7^{\circ}K$ for $c = 0.70$. Such a width variation

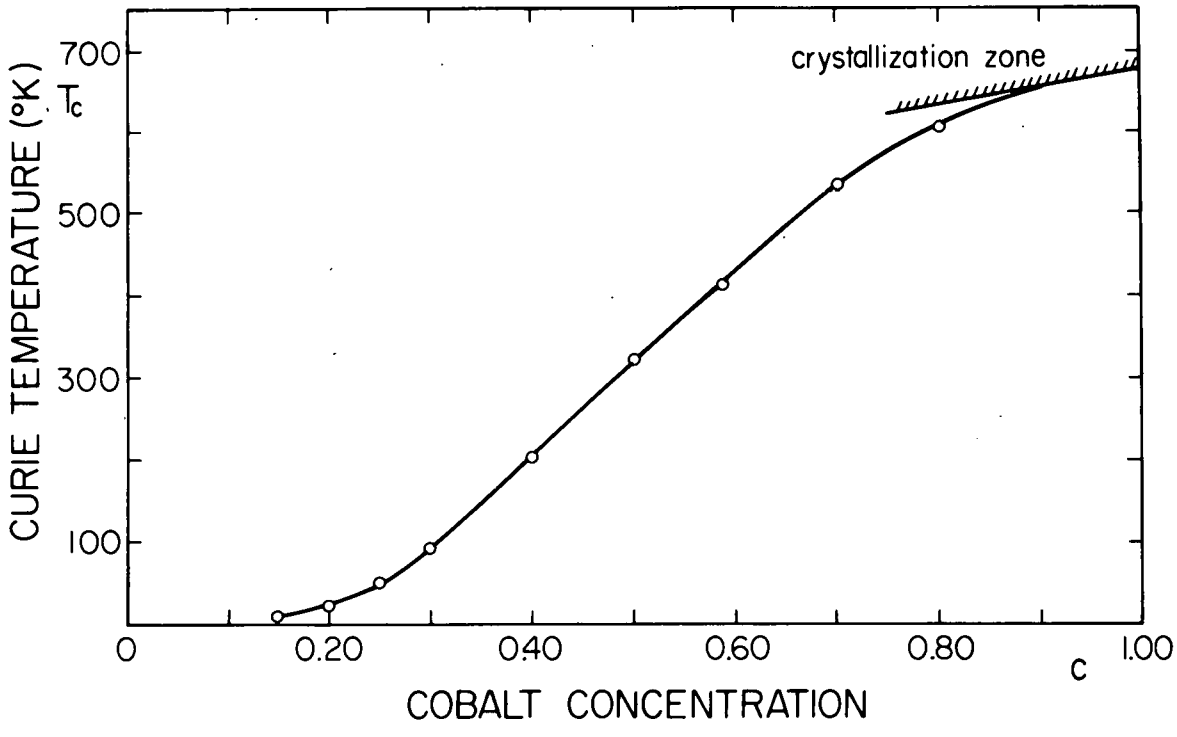

Fig. 1. Variation of the Curie temperature T_c with the cobalt concentration for $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ alloy.

suggests that large magnetic inhomogeneities occur at low cobalt concentration; this will be discussed in the next section.

For high cobalt concentrations ($c > 0.90$) the permeability drop is not reversible, suggesting the occurrence of a crystalline transformation. Since crystallization of an amorphous alloy is accompanied by a relatively high heat release, this explanation was tentatively confirmed by observing a heat release at a temperature close to that of the permeability drop. The release was observed by the method described in ref. 9 with a rate of heating of about $300^{\circ}K/min$. To study the exact nature of this crystallization requires additional measurements such as electrical resistivity, X-ray diffraction and specific heat.

Magnetization Properties

The amorphous alloys $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ for $c \leq 0.30$ were measured in fields up to 70 kOe and between $1.7^{\circ}K$ and $270^{\circ}K$, for higher cobalt concentrations the saturation magnetization M_o was determined at $4.2^{\circ}K$. Without cobalt, the saturation magnetization is quite small (0.7 emu/g); the curve M_o versus c deviates from linearity for $c \leq 0.20$ and $c \geq 0.70$. For $Co_{0.78}P_{0.14}B_{0.08}$ the average magnetic moment per cobalt atom is $1.15\,\mu_B$. The magnetization M(H, T) for $c \leq 0.30$ varies considerably with H and T in the investigated range; we observed the existence of a small contribution which has to be related to a precipitate of Ni, Co or Co-P-B. Such an interpretation is mainly justified by the same way as previously reported[4]; this contribution was subtracted from the experimental data. This subtraction is necessary in order to obtain the correct magnetization of the amorphous alloy, particulary in the determination of the initial susceptibilities.

For $0.15 \leq c \leq 0.30$, a remanent magnetization appears below T_c.

DISCUSSION

The $M^2(H, T)$ curves versus $H/M(H, T)$ (Arrott plots) for all the investigated samples, present large deviations from linearity; this shows that the para-ferro transition occurs in an inhomogeneous way as in many crystalline alloys and compounds (Ni-Cu, Ni-Rh[10], Ni-V[11] Fe-V[12], CoGa[13] Gd$(Co\text{-}Ni)_2$[14]. In the present case the saturation magnetization results can be explained by a local environment model LEM where it is assumed that: i) the interaction of the atoms occurs between near neighbors; ii) the electronic state on a given atom depends on the nature of its neighbors. Previous structural studies on transition amorphous alloys[6] show that the short range order of the crystalline counterpart is essentially preserved. In the Ni-Co-P-B alloys it is reasonable to assume a short range order of Ni_3P or Ni_3B type; so a transition atom should have 2 or 3 metalloid atoms and 12 transition atoms as near neighbors. By assuming 11 or 13 instead of 12 neighbors the conclusions of the LEM are not significantly changed although the agreement with the experimental data is not as good. The nickel and cobalt atoms are supposed to be randomly distributed on the transition sites. The experimental data can be roughly explained by a very simple LEM where the cobalt atom carries a magnetic moment of $1.15\,\mu_B$ (as in $Co_{0.78}P_{0.14}B_{0.08}$) when surrounded by 3 or more Co atoms, otherwise it is not magnetic; the nickel atoms do not carry any noticeable moment. However some discrepancies with the experimental data are observed for $0.15 \lesssim c \lesssim 0.40$.

A good agreement with the saturation magnetization results over the entire concentration range is obtained (Fig. 2), when it is assumed that the magnetic state of a cobalt atom depends on the number n_{Co} of its cobalt near neighbors, as follows: for $n_{Co} = 0$ or 1 it is non magnetic, for $n_{Co} = 2$ or 3 it carries a small moment $\mu_1 = 0.50\ \mu_B$ and for $n_{Co} > 3$ it carries its full moment $\mu_2 = 1.15\ \mu_B$. The examination of M_o for $c \gtrsim 0.80$ suggests that a nickel atom with 11 or 12 cobalt near neighbors may have a small moment of about $0.4\ \mu_B$; but the contribution of such atoms is too small, compared to those of the cobalt atoms, to be experimentally accurately determined.

The previous results can be compared to those obtained for crystalline alloys and compounds. For instance, the cobalt atom is magnetic when surrounded by 3 or more cobalt atoms in CuCo[16] and $Gd(Co\text{-}Ni)_2$[14]; the nickel atom in Ni-Cu[15], requires 8 or more Ni nearest neighbors to be magnetic; meanwhile in Ni-Cr, Ni-Mo and Ni-V[13] alloys the nickel atom even surrounded by 12 Ni nearest neighbors is not magnetic. In the present case the low values of the cobalt moment and the absence of a significant Ni moment can be related to the strong perturbation introduced by the metalloid atoms. Finally we point out that, unlike the crystalline alloys and compounds, a LEM accounts for the observed saturation magnetization over the entire concentration range. This suggests that the main assumption of the LEM is fulfilled i.e. the atom interactions occur essentially between near neighbors.

The experimental results show that for $c \leq 10$, the initial susceptibility χ_o can be separated into a temperature independant contribution $\chi' \simeq 2.0$ emu/g attributed to the non-magnetic atoms, and a magnetic impurities contribution which is varying according to a Curie-Weiss law. For $c > 10$ the magnetic contribution becomes larger when c increases, so no χ'

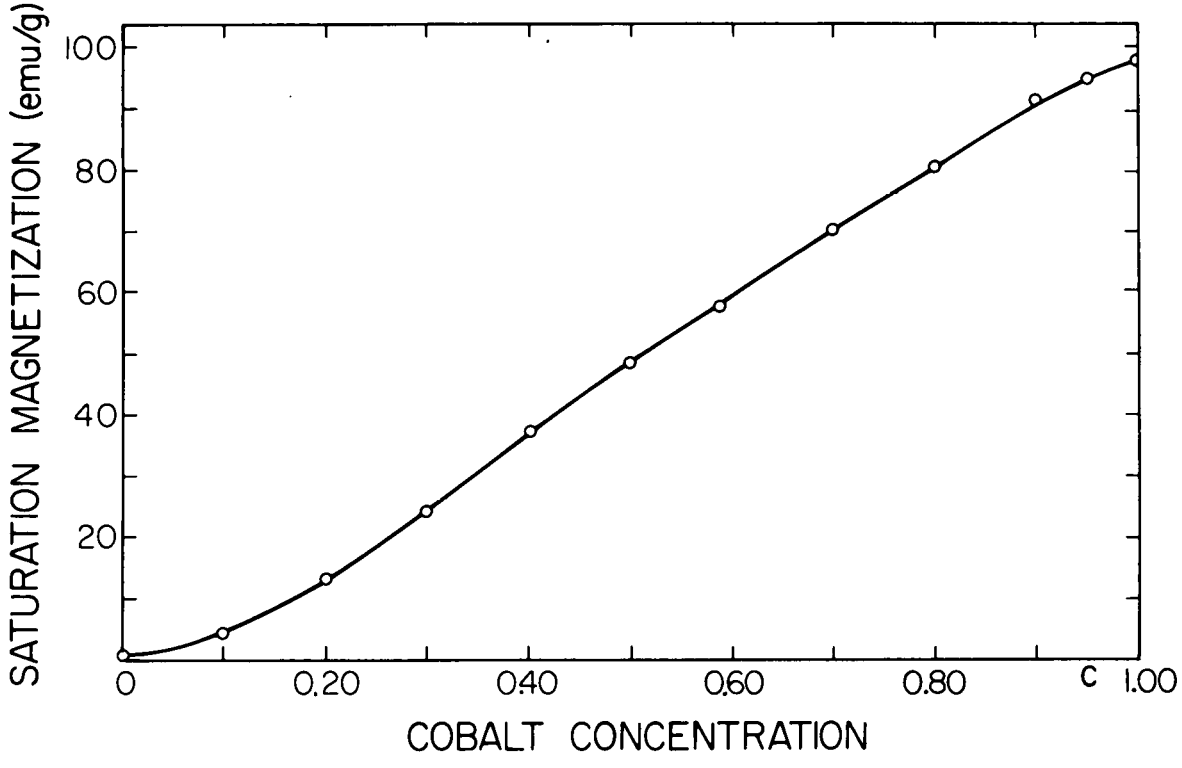

Fig. 2. Saturation magnetization versus cobalt concentration at low temperature for $(Ni_{1-c}Co_c)_{0.78}P_{0.14}P_{0.08}$ alloy. The circles represent the experimental results, the solid line is the magnetization calculated by the LEM.

is detected. The inverse susceptibility versus T is linear in a temperature range which is narrower with increasing cobalt concentration; for instance, at c = 0.30, $(\chi_o)^{-1}$ is linear between 220°K and 270°K. The paramagnetic Curie temperatures θ are significantly higher than the corresponding T_c.

In addition, for a given amorphous alloy which has a well defined T_c the remanent magnetization and M(H, T) at low fields decrease slowly with T, then rapidly near T_c; this decrease becomes smoother at higher field (Fig. 3). The saturation magnetization and the magnetization at high fields (H > 20 kOe) decrease linearly with T. The previous susceptibility and magnetization features of $(Ni_{1-c}Co_c)_{0.78}P_{0.14}B_{0.08}$ near the critical concentration, suggest that an important ferromagnetic coupling occurs at T_c; but this coupling does not involve all the magnetic atoms. Such a process probably occurs in a wide temperature range. As a result, below T_c some magnetic moments are not included in the ferromagnetic order and above T_c the alloy is characterized by the existence of large magnetic clusters. A further analysis and NMR measurements have to be performed in order to provide quantitative details on this ferromagnetic transition.

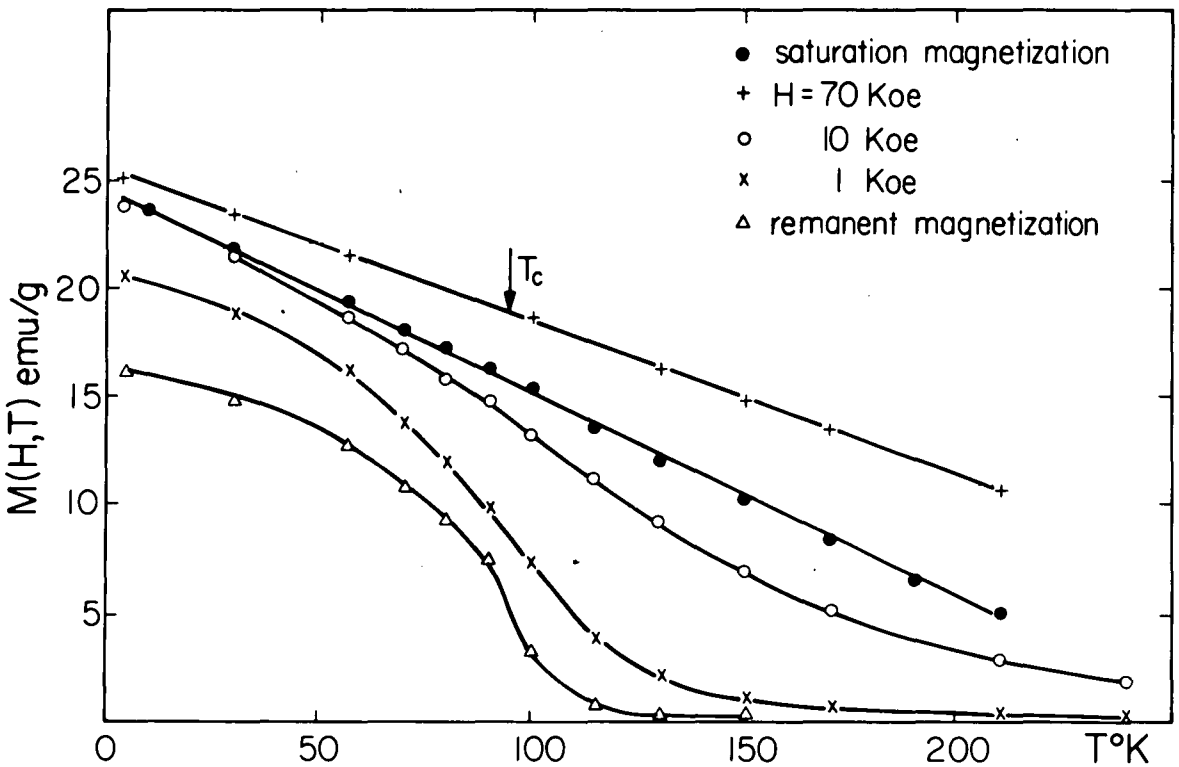

Fig. 3. Magnetization M(H, T) versus temperature curves for $(Ni_{0.70}Co_{0.30})_{0.78}P_{0.14}B_{0.08}$ alloy.

REFERENCES

1. A. K. Sinha: J. of Appl. Phys. 42, 338 (1971).

2. C. C. Tsuei, G. Longworth and S. C. H. Lin: Phys. Rev. 170, 603 (1968).

3. J. Durand: IEEE Trans. on Magnetics, MMM-Intermag Conf., June 1976, Pittsburgh, Pa.

4. A. Amamou and J. Durand: to be published.

5. R. C. Sherwood et al. 20th annual conf. Mag. and Mag. Mat. San Francisco (U.S.A.) (1974).

6. P. Duwez: "Annual Review of Materials Science" 6, 83 (1976).

7. P. L. Maitrepierre: J. Appl. Phys. 40, 4826 (1969).

8. G. Tangonan, Ph.D. Thesis Caltech (1975).

9. P. K. Rastogi and P. Duwez: J. of Non-Cryst. Sol. 5, 1 (1970).

10. W. C. Muellner and J. S. Kouvel: Phys. Rev. B11, 4552 (1975).

11. A. Amamou, F. Gautier and B. Loegel: J. Phys. F5, 1342 (1975).

12. P. Pataud, J. P. Perrier and R. Tournier: J. Phys. (Paris) 35, C4-189 (1974).

13. A. Amamou and F. Gautier: J. Phys. F4, 563 (1974).

14. J. A. Cannon, J. I. Budnick and T. J. Burch: Sol. State Com. 17, 1385 (1975).

15. J. W. Garland and A. Gonis: "Magnetism in Alloys" Publication of the Metallurgical Society of A.I.M.E., 79 (1972).

16. P. Costa-Ribeiro, J. Souletie, D. Thoulouze and R. Tournier: J. Phys. Paris 32, C1, 753 1971.