Influence of a small addition of Nd on the magnetic properties of amorphous Fe-B alloys

B. X. Gu and H. R. Zhai
Department of Physics, Nanjing University, Nanjing 210 008, Jiangsu, China

B. G. Shen
Institute of Physics, Academia Sinica, P.O. Box 603, Beijing 100 080, China
(Received 29 January 1990; revised manuscript received 22 June 1990)

The influence of the addition of a few atomic percent of Nd on the Curie temperature, crystallization temperature, and magnetic properties of amorphous iron-boron alloys was investigated. With increasing Nd content, the crystallization temperature increases linearly, but the Curie temperature and the magnetic moment of the Fe atom decrease. The change of the crystallization temperature and the magnetic properties of amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \le x \le 6)$ alloys can be explained by the atomic size effect and the chemical properties of neodymium. On annealing, the coercivity H_c and the magnetic energy $(BH)_{max}$ of the samples (except $x=0$) increase, depending strongly on the Nd concentration. A hard magnet with $H_c=2.3$ kOe and $(BH)_{max}=8$ MG Oe was obtained.

I. INTRODUCTION

In previous papers[1-4] we have reported the magnetic properties, structure, Mössbauer spectra, and demagnetization behavior of a new hard-magnetic $Nd_3Fe_{81}B_{16}$ alloy prepared by the crystallization of rapidly quenched amorphous ribbons. This hard-magnetic alloy contains only a small amount of Nd, but it exhibits better hard-magnetic properties. Its room-temperature coercivity is ${}_bH_c=2$ kOe, remanence $B_r=12$ kG, and magnetic energy $(BH)_{max}=8$ MG Oe. The B_r and $(BH)_{max}$ values are much higher than those of the widely used anisotropic $(Ba,Sr)Fe_{12}O_{19}$ ferrites. Therefore it may be developed as a new inexpensive permanent magnet. In order to study the influence of the addition of a few atomic percent Nd on the magnetic properties of Fe-B alloys, we prepared amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \le x \le 6)$ alloys and investigated their magnetic properties and crystallization temperatures.

II. EXPERIMENTAL

Iron (99.98% purity), boron (99.9% purity), and neodymium (99.9% purity) were melted in an argon atmosphere into homogeneous buttons. The ingot of about 3 g in weight was rapidly quenched from the melt onto a rotating copper wheel with a rotational velocity of 35 m/s. The melt-spun alloys were in the form of long ribbons, typically 0.02 mm thick and 0.8 mm wide. All samples were found to be amorphous by x-ray diffraction.

Annealing of the samples was performed in a quartz tube which was evacuated to 1×10^{-5} mbar and backfilled with flowing helium gas of high purity evaporated from liquid He. The samples were heated quickly to the desired temperatures and kept for 10 min and then cooled rapidly to room temperature.

Differential-thermal-analysis (DTA) measurements were performed under an argon atmosphere with a heating rate of 20 K/min. The structural analysis was made by x-ray diffraction using Cu $K\alpha$ radiation. Low-temperature and high-field magnetization measurements were performed using an extracting sample magnetometer in a superconducting solenoid with 60 kOe. The room-temperature hysteresis loops were measured by a vibrating-sample magnetometer (VSM) with a maximum applied magnetic field of 20 kOe. The Curie temperature was measured in a weak field of about 0.75 Oe under an argon atmosphere.

III. RESULTS AND DISCUSSION

A. Crystallization temperature

The crystallization temperatures of amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \le x \le 6)$ alloys were determined from the DTA curves. A typical DTA curve is shown in Fig. 1. Figure 2 shows the dependence of the crystallization temperature T_x on the Nd concentration x. T_x increases linearly with increasing x from 459 °C for $x=0$ to 631 °C for $x=6$. The change of T_x amounts to an increase of about 29 °C for each additional 1 at. % of Nd. This demonstrates that a small percentage of Nd additives in amorphous Fe-B alloys has a substantial stabilization effect on the amorphous state. The influence of Nd on the stability of amorphous Fe-B alloys originates from the atomic size and the chemical effects of Nd. The Nd atom has a larger atomic radius and a great affinity to boron,[5] and so it hinders the diffusion of the boron atoms in the crystallization process of amorphous Fe-B alloys.

B. Curie temperature

The dependence of the Curie temperature T_c on the Nd concentration x is shown in Fig. 3. It can be seen that T_c decreases almost linearly with increasing x from 390 °C for $x=0$ to 244 °C for $x=6$. The decrease of T_c may result from the influence of both Nd and B. In amorphous Fe_xB_{100-x} $(72 \le x \le 86)$ alloys, T_c decreases

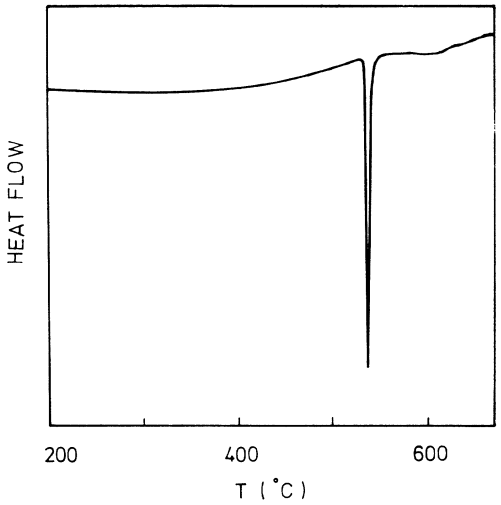

FIG. 1. DTA curve for amorphous $Nd_2Fe_{81}B_{17}$ alloy.

with decreasing B content with a rate of about 15 °C/at. % B.[6] For amorphous $Nd_xFe_{81}B_{19-x}$ ($0 \leq x \leq 6$) alloys, the change of T_c from amorphous $Fe_{81}B_{19}$ to $Nd_6Fe_{81}B_{13}$ alloys amounts to a decrease of about 24 °C for each at. % of B, which is larger than that for amorphous Fe_xB_{100-x} alloys. This result suggests that Nd has an influence on the T_c of amorphous Fe-B alloys. Nd causes T_c to decrease with a rate of about 9 °C/at. % Nd. It can be interpreted by the size effect of the Nd atoms. According to mean-field predictions the Curie temperature is given approximately by

$$T_c = \frac{2\langle Z \rangle J_{\text{Fe-Fe}} S(S+1)}{3k} , \tag{1}$$

where S is the spin, k is the Boltzmann constant, $\langle Z \rangle$ is the average number of Fe nearest neighbors of the Fe atom, and $J_{\text{Fe-Fe}}$ is the exchange interaction between the Fe atoms. For simplicity we neglect the exchange interaction between the Fe and Nd atoms ($J_{\text{Fe-Nd}}$) and between the Nd atoms ($J_{\text{Nd-Nd}}$) in Eq. (1). It has been reported that in amorphous Nd-Fe alloys $J_{\text{Fe-Nd}} = 7 \times 10^{-16}$ erg and $J_{\text{Nd-Nd}} = 2 \times 10^{-16}$ erg,[7] and in amorphous Fe-B alloys $J_{\text{Fe-Fe}} = 1.4 \times 10^{-14}$ erg.[8] Thus we assumed that in amorphous $Nd_xFe_{81}B_{19-x}$ ($0 \leq x \leq 6$) alloys $J_{\text{Fe-Fe}}$ is also much larger than $J_{\text{Fe-Nd}}$ and $J_{\text{Nd-Nd}}$ and we neglected the latter two contributions in Eq. (1). It can be seen from (1) that the value of T_c is directly proportional to $\langle Z \rangle$ and $J_{\text{Fe-Fe}}$. Nd has a larger atomic radius, so when the Nd atom enters into amorphous Fe-B alloys, it changes the mean interatomic distances between the iron atoms, and causes a reduction of the average number of the Fe nearest neighbors of the Fe atoms and the ferromagnetic exchange interaction between the iron atoms. Therefore the value of T_c decreases with increasing Nd content.

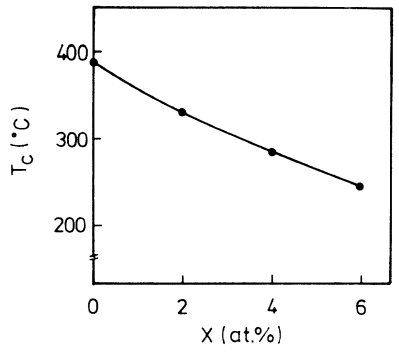

FIG. 3. Curie temperature as a function of Nd concentration.

C. Low-temperature magnetic properties

Figure 4 shows the magnetization curves of amorphous $Nd_xFe_{81}B_{19-x}$ ($0 \leq x \leq 6$) alloys measured at 1.5 K. The curves are linear in the high-field range of 30–60 kOe. From these curves the spontaneous magnetization $\sigma_s(0)$ can be obtained by extrapolating the linear portion of the

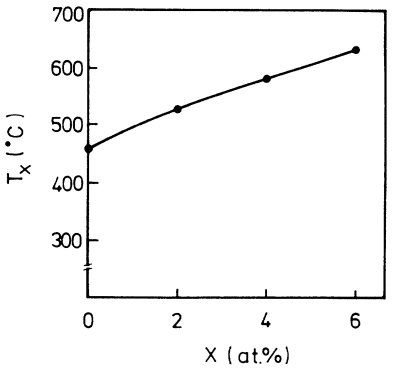

FIG. 2. Crystallization temperature as a function of Nd concentration.

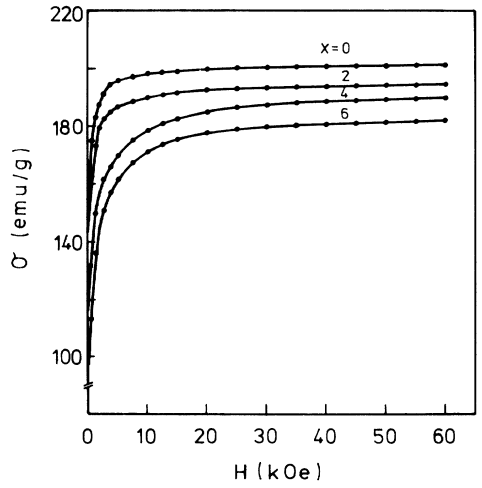

FIG. 4. Magnetization curves of amorphous $Nd_xFe_{81}B_{19-x}$ ($0 \leq x \leq 6$) alloys at 1.5 K.

magnetization curve to $H=0$. The results are shown in Fig. 5. With increasing Nd content the values of $\sigma_s(0)$ decrease almost linearly with a rate of about 3.5 (emu/g)/at. % Nd. Thus the concentration dependence of $\sigma_s(0)$ can be written as

$$\sigma_s(0)=199.5-3.5x \text{ emu/g} . \quad (2)$$

The $\sigma_s(0)$ at 1.5 K is very close to the value of $\sigma_s(0)$ at 0 K, so we let $\sigma_s(0)$ at 1.5 K equal $\sigma_s(0)$ at 0 K. Thus the average magnetic moment $\bar{\mu}$ per $Nd_xFe_{81}B_{19-x}$ ($0\le x\le 6$) alloy atom can be calculated by using both the mean-field theory and the 1.5-K magnetization data $\sigma_s(0)$,

$$\bar{\mu}=\frac{\sigma_s(0)A}{N\mu_B} , \quad (3)$$

where N is Avogadro's number, μ_B the Bohr magneton, and A the molecular weight of the $Nd_xFe_{81}B_{19-x}$ alloys. The Nd-content dependence of A can be written as

$$A=4729+133.43x \text{ g/mol} . \quad (4)$$

Because of the ferromagnetic alignment of the effective moment of the Nd and the Fe atoms, we have

$$\bar{\mu}=81\bar{\mu}_{Fe}+x\bar{\mu}_{Nd} . \quad (5)$$

It has been shown that in amorphous Nd_xFe_{1-x} alloys, the moment of the Nd atoms exhibits a noncollinear structure.[7,9] When the Nd content $x\le 0.1$, the Nd moments are distributed on a cone of half-angle $\theta=105°$.[10] From the formula[11]

$$\bar{\mu}_{Nd}=\tfrac{1}{2}\mu_{Nd}(1+\cos\theta) , \quad (6)$$

where $\mu_{Nd}=3.27\mu_B$ is the moment of the free Nd atom, $\bar{\mu}_{Nd}=1.21\mu_B$ can be obtained. So using Eqs. (2)–(5) the concentration dependence of the effective moment $\bar{\mu}_{Fe}$ per Fe atom in amorphous $Nd_xFe_{81}B_{19-x}$ ($0\le x\le 6$) alloys can be obtained with the expression

$$\bar{\mu}_{Fe}=2.085+0.0073x-0.001x^2 , \quad (7)$$

which is shown in Fig. 5. From Fig. 5 we can see that $\bar{\mu}_{Fe}$ increases almost linearly with increasing Nd content (decreasing B content) up to $x=4$ and then it decreases. This behavior is similar to the amorphous Fe-B alloys,[12] but the increasing rate of $\bar{\mu}_{Fe}$ with decreasing B content in amorphous $Nd_xFe_{81}B_{19-x}$ alloys is smaller than that in amorphous $Fe_{100-x}B_x$ alloys. In amorphous $Fe_{100-x}B_x$ alloys, with decreasing B content $\bar{\mu}_{Fe}$ increases with a rate of about $0.008\mu_B$/at. % B, while in amorphous $Nd_xFe_{81}B_{19-x}$ alloys, the increasing rate of $\bar{\mu}_{Fe}$ is about $0.004\mu_B$/at. % B. It demonstrates that the addition of the Nd atom has an influence on the magnetic moment of the Fe atoms in amorphous Fe-B alloys. Therefore the change of $\bar{\mu}_{Fe}$ in amorphous $Nd_xFe_{81}B_{19-x}$ alloys may be due to the influence of both B and Nd. As the Nd content increases, the B content decreases, leading to an increase of $\bar{\mu}_{Fe}$ because of the decreasing number of *sp* electrons transferred from the B atoms to the *d* band of iron. On the other hand, the addition of Nd atoms may cause a noncollinear alignment of the Fe magnetic sublattice in the Nd-Fe-B alloys. Taylor *et al.*,[7] based on magnetization, Mössbauer, and Hall-effect data, concluded that in Nd-Fe amorphous alloys the moment

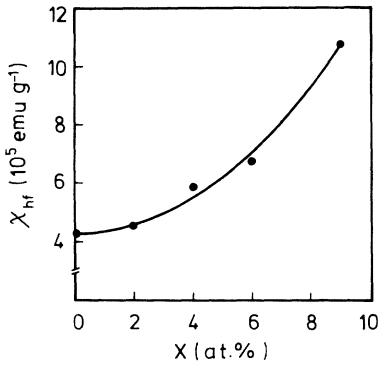

FIG. 6. Concentration dependence of the high-field susceptibility of amorphous $Nd_xFe_{81}B_{19-x}$ ($0\le x\le 6$) alloys.

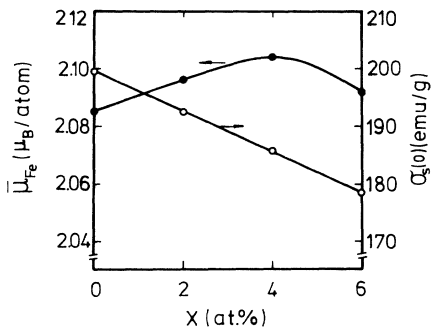

FIG. 5. Concentration dependence of the spontaneous magnetization at 1.5 K at 60 kOe and the effective moment per Fe atom for amorphous $Nd_xFe_{81}B_{19-x}$ ($0\le x\le 6$) alloys.

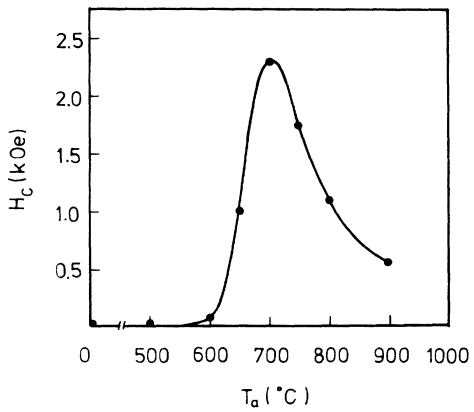

FIG. 7. Dependence of the coercivity H_c on annealing temperature T_a for amorphous $Nd_4Fe_{81}B_{15}$ alloy.

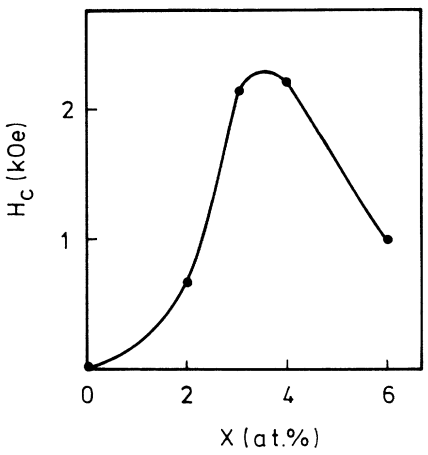

FIG. 8. Concentration dependence of the maximum coercivity of annealed samples.

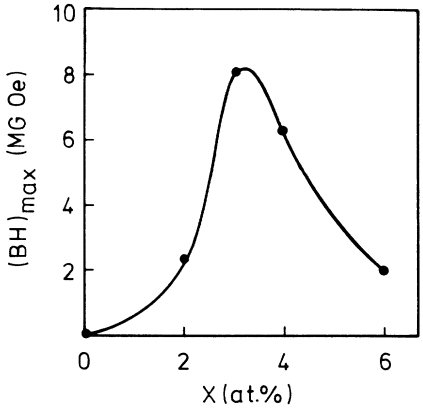

FIG. 9. Concentration dependence of the maximum magnetic energy of annealed samples.

of the Fe subnetwork is not collinear, and indicated that the best evidence is provided by the large high-field slopes observed for the M-H curves. We have measured M-H curves for amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \leq x \leq 6)$ alloys and obtained the concentration dependence of the high-field susceptibility χ_{hf} shown in Fig. 6. The χ_{hf} increases with increasing Nd content. Since the Nd content is much smaller than the B content in amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \leq x \leq 6)$ alloys, the influence of the B atoms on the Fe moment is predominant. Therefore the concentration dependence of the Fe moment is similar to that in amorphous Fe-B alloys.

D. Influence of annealing on magnetic properties

After annealing above the crystallization temperature, the coercivity of amorphous $Nd_xFe_{81}B_{19-x}$ $(0 \leq x \leq 6)$ alloys increases rapidly with increasing annealing temperature and reaches a maximum at temperatures between about 650 °C and 750 °C, depending on the Nd concentration. Figure 7 shows an example of the dependence of the coercivity H_c on annealing temperature T_a for the $Nd_4Fe_{81}B_{15}$ alloys. The maximum values of the coercivity H_c and the magnetic energy $(BH)_{max}$ obtained by annealing depend strongly on the Nd concentration x, as can be seen from Figs. 8 and 9. The higher H_c and $(BH)_{max}$ are obtained only within a narrow range of about $3 \leq x \leq 4$. The maximum magnetic properties of the annealed samples are as follows: the intrinsic coercivity ${}_iH_c = 2.3$ kOe, the coercivity ${}_bH_c = 2$ kOe, the remanence $B_r = 12$ kG, and the magnetic energy $(BH)_{max} = 8$ MG Oe. The hard-magnetic properties can be further enhanced by varying the composition. For example, a $(BH)_{max}$ as high as 14 MG Oe has been obtained in $Nd_4Fe_{77}B_{19}$ alloys. Compared with the widely used anisotropic $(Ba,Sr)Fe_{12}O_{19}$ ferrites, B_r and $(BH)_{max}$ are much higher. The Nd-Fe-B alloys contain a small amount of Nd (3–4 at. %), therefore it may be developed as a new inexpensive permanent magnet. It is of interest to note that the addition of a few atomic percent (3–4 at. %) Nd in the $Fe_{81}B_{19}$ alloy causes a substantial change of the magnetic properties from magnetically soft to hard with H_c as high as 2.3 kOe. The experimental data showed that the magnetization and demagnetization behavior for the low-Nd-content Nd-Fe-B alloys with relatively high coercivity may be interpreted by domain-wall pinning.[3] However, the hard-magnetic property requires high anisotropy of main phase in the material. Our x-ray diffraction and Mössbauer data showed that only Fe_3B and α-Fe exist as the main phases in the annealed samples.[2,4] The origin of the high anistropy in this material is not understood, on which a detailed study is now being undertaken.

ACKNOWLEDGMENTS

This work was supported by the Magnetism Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing.

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