Superparamagnetism in a nanocrystalline Fe-based metallic glass

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It is shown that rapidly quenched $Fe_{66}Cr_8CuNb_3Si_{13}B_9$ metallic glass, when annealed in a controlled way, shows superparamagnetic behavior at elevated temperatures. This property, as has been demonstrated, is due to the fine crystallites of the bcc-Fe(Si) solid solution created within the amorphous matrix by this annealing. Calculations performed show that the volumetric fraction of these particles is equal to 18%, and that their average dimension is as small as 10 nm. It is also shown that the single particle consists of approximately 10^4 atoms of iron. An analysis performed allows the conclusion that the particles are chemically stable (they do not increase their volumes at the time of measurements at elevated temperatures), and that there are no interactions between them.

INTRODUCTION

In 1988 Yoshizawa, Oguma, and Yamauchi[1] showed that appropriately controlled crystallization of Fe-based metallic glass containing small additions of copper and niobium (nominal composition in at.%: $Fe_{73.5}CuNb_3Si_{13.5}B_9$) leads to a ferromagnetic material with ultrafine grain structure—a nanocrystalline ferromagnet (also known under its trade name FINEMET, introduced by the Hitachi Metals, Ltd.). The material is first cast as an amorphous ribbon and then exposed to the heat treatment above its crystallization temperature. This procedure produces a homogeneous nanocrystalline structure in which the individual ultrafine crystals (typically of the dimension in the range 10–30 nm) of α-Fe(Si) are embedded in an amorphous matrix which can be interpreted as the interfacial component (see, e.g., Ref. 2). Creation of this nanocrystalline structure is ascribed to the addition of Cu and Nb.[1] The main motivation to create this material was to obtain a very soft ferromagnet simultaneously exhibiting vanishing magnetostriction and magnetic anisotropy. It was shown, indeed, that the newly developed nanocrystalline ferromagnets exhibit such behaviors, offering among the existing materials of this class the highest saturation flux density with its value in the range of $B_s = 1.2-1.3$ T (see, e.g., Refs. 3 and 4).

Besides the promising prospects of application, it seems that the nanocrystalline ferromagnets of the type discussed represent a unique object for fundamental research because of the availability of possible coexisting magnetic phases. Since the Curie temperatures of the amorphous and nanocrystalline phases are well separated (in commercial material this separation is typically of the order of 200 K (see, e.g., Ref. 2), with an increase of temperature from the ambient one, the material will first show ferromagnetic behavior of both phases, and then a ferromagnetic phase of the nanocrystalline particles existing within the paramagnetic phase of the amorphous matrix. Finally, for further increase of the temperature and if only the size of these particles is small enough, the superparamagnetic behavior of these crystals embedded in the paramagnetic amorphous matrix can be expected.

The latter case, besides the other interesting experimental possibilities which the material discussed offers, would make it possible to perform an interesting type of experiment (suggested long ago by Bean and Livingston[5]) in which the atomic exchange interaction at the interface can be investigated since the effective field acting on the superparamagnetic particle should include a contribution of the exchange origin. The main goal of the investigations described in the present paper is, however, to show only that the superparamagnetic behavior can, indeed, be created in the considered nanocrystalline magnet.

CHARACTERIZATION OF THE MATERIAL

A metallic glass of the nominal composition of $Fe_{66}Cr_8CuNb_3Si_{13}B_9$, rapidly quenched in the form of a ribbon 5 mm wide and 25 μm thick by means of the single roller melt spinning technique, has been chosen for the experiment (chromium was added to lower the Curie point of the amorphous matrix in order to widen the temperature range within which the search for superparamagnetism might be performed).

The conditions for an appropriate thermal treatment of the glassy sample were defined by means of the differential thermal analysis (Perkin-Elmer DSC-2 unit). The measurements performed (at the temperature rate of 10 K/min) have shown that the first exothermic peak, being identified with formation of the bcc-Fe(Si) solid solution phase (see, e.g., Refs. 6 and 7), occurs within the temperature range 818–890 K (with its peak value at $T = 831$ K). The outset of the second peak appears at $T = 924$ K (this one being identified with creation of the iron boride and/or niobium boride—see, e.g., Refs. 6 and 7), being well separated from the first peak.

In commercial material of the type considered, a volumetric fraction of the nanocrystalline phase is usual-

ly around 0.8. Since a thickness of the interfacial layer of the amorphous matrix is then only of an order of several lattice constants, it can hardly be expected that in such a case "pure" superparamagnetism might be observed because of possible interactions between particles. To avoid this effect and decrease the volumetric fraction of the crystallites, the as-quenched material has been annealed with the heating rate 5 K/min at $T_{ann}=803$ K for 20 min. The x-ray-diffraction study shows that in this case the crystalline phase represents a solid solution of Si in the iron lattice with the lattice constant $a=0.285$ nm corresponding to 14 at. % Si contents in the bcc-Fe(Si) phase.[11]

The resulting microstructure created in this sample is shown in Fig. 1. The micrograph was obtained by means of the transmission electron microscope (JEM 2000EX) on the sample thinned down by ion etching. The inset in this figure shows an electron-diffraction pattern from which the dark field micrograph was taken (from the reflection ring of the bcc phase).

In order to characterize magnetic behavior of the nanocrystallized sample, its temperature dependence of the spontaneous magnetization $M_s(T)$ has been measured at the applied dc magnetic field of 500 kA/m. The measurements have been performed using a Foner magnetometer (EG&G PAR-type 155) equipped with an electric furnace. To protect the sample from eventual oxidation at elevated temperatures, a gaseous helium was used to create an inert atmosphere. The measured dependence is shown in Fig. 2 (curve 1). The same dependence for the as-quenched metallic glass is also shown in this figure (curve 2). It can easily be noticed that the curve for the nanocrystallized sample shows behavior typical for a material containing two ferromagnetic phases (see, e.g., Ref. 8). It is well known that the temperature dependence of spontaneous magnetization $M_s(T)$ of a single-phase ferromagnet can be well described by the following relation:

$$M_s(T)=M_s(0)[1-T/T_c]^{\beta}, \quad (1)$$

where $M_s(0)$ is the spontaneous magnetization at $T=0$ K, T_c is the Curie temperature, and β is the critical exponent. It has also been shown that the above relationship holds even far below the Curie temperature (see, e.g., Refs. 2 and 9). Taking this point into account, the experimental data obtained for temperatures higher than that at which curve 1 (see Fig. 2) shows the distinct kink have been fitted to Eq. (1), assuming that in this temperature range only the nanocrystalline phase contributes to the measured magnetic moment. The best fit was obtained for the following parameters: $\beta=0.364$, $M_s(0)=37.6$ J/T kg (per unit mass of the whole sample), and $T_{cp}=936$ K. It is worth noticing that the calculated value of the critical exponent is very close to $\beta_H=0.36$ showing that the nanocrystalline phase (the particles) behaves like the Heisenberg ferromagnet. The fitted curve is presented in Fig. 2 by a dashed line (curve 4). The fitting procedure allows one to also determine the temperature dependence of the spontaneous magnetization of the amorphous matrix alone (shown in Fig. 2 as curve 3) giving the Curie temperature $T_{ca}=490$ K. Considering both calculated values one can easily notice that the earlier mentioned separation is then twice larger than that in commercial nanocrystalline material.

A knowledge of the T_{cp} value allows one to determine the Si concentration c in the Fe(Si) solid solution, making use of the known T_{cp}(%Si) dependence (see Ref. 10). For the investigated materials it yields $c=15$ at. % Si which is in excellent accordance with x-ray-diffraction data. Taking into account that the saturation induction at room temperature for Fe 15% Si equals $B_s=1.7$ T and its specific density $\rho=7.43\times10^3$ kg/m^3,[10] the volumetric fraction p of the crystalline phase in the sample can be es-

FIG. 1. Transmission electron microscopy micrograph of the annealed metallic glass showing the created fine crystalline structure (inset shows the electron-diffraction pattern).

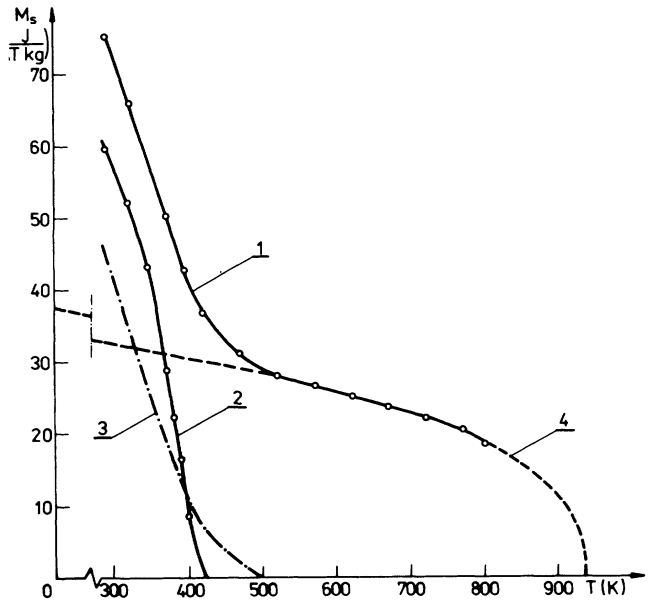

FIG. 2. Temperature dependencies of the spontaneous magnetization of the sample: curve (1), after annealing; (2), for the as-cast state; (3), for the amorphous matrix; (4), for the crystalline phase alone. Curves (3) and (4) were obtained by a numerical fitting to Eq. (1).

timated giving $p=0.18$, since the room-temperature spontaneous magnetization of the crystalline phase taken from the extrapolated curve in Fig. 2 (dashed line) is equal to $M_s=32.5$ J/T kg. Assuming that particles are homogeneously distributed within the volume of the amorphous matrix and that they are of the equal size, the average thickness of the amorphous phase separating particles is of the order of the dimension of the particle itself. The apparent lower crystal density observed in a micrograph (Fig. 1) compared with the one given by the above estimate can be understood since not all the crystallites are visible and, moreover, the ion-etching process causes the selective thinning of the sample.

SEARCH FOR SUPERPARAMAGNETISM

A suitable operational criterion for the occurrence of superparamagnetism includes at least two requirements (see, e.g., Ref. 5). First, the magnetization curve $[M(H)]$ must show no hysteresis. Second, this dependence for an isotropic sample must be temperature dependent to the extent that curves measured at different temperatures T must approximately superimpose when plotted against H/T (with a correction for the temperature dependence of the spontaneous magnetization and under the assumption that the particles do not interact with the others, and that they are chemically stable).

In order to test whether the annealed sample fulfills the requirements mentioned above, and therefore exhibits superparamagnetic behavior, its magnetization M (the component parallel to the applied field direction) has been measured as a function of magnetic field at different temperatures in the range 423–803 K using the Foner magnetometer. Figure 3 shows the measured magnetization curves plotted as a dependence of $M(T)/j_s=f(j_sH/T)$, where $j_s=M_s(T)/M_s(0)$. As is seen in this figure, all the experimental points obtained for temperatures $T\geq 523$ K arrange on practically one curve (within the experimental error) which exhibits no hysteresis. Since both requirements mentioned at the beginning of this section are fulfilled for the investigated sample (in the temperature range $523\leq T\leq 803$ K), this fact entitles one to state that the nanocrystallized Fe-based metallic glass shows, indeed, superparamagnetic behavior as was expected. For the temperatures below the Curie point of the amorphous matrix, the magnetic exchange interactions between the particles and the matrix switch on, and the superparamagnetism cannot be observed (see the curve for $T=423$ K in Fig. 3).

It is well known that an analysis of the thermal equilibrium magnetization properties of an assembly of, in principle, isotropic single domain particles is analogous to the Langevin approach of atomic paramagnetism. The only difference is that, whereas in the latter case one is dealing with the magnetic moment of a single atom, in the case of superparamagnetism this magnetic moment is usually composed of 10^5 atomic moments coupled ferromagnetically. Therefore, the temperature dependence of magnetization for a superparamagnetic sample can formally be described by the familiar Langevin function given by

$$M(T)=n\mu[\coth(\mu H/k_BT)-k_BT/\mu H]\ , \qquad (2)$$

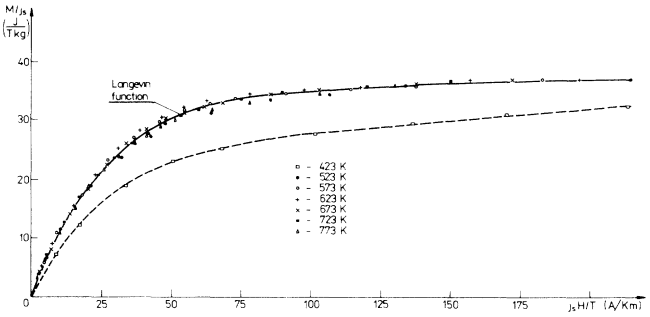

FIG. 3. Comparison of magnetization curves on a j_sH/T basis as a demonstration of superparamagnetic behavior of nanocrystalline bcc-Fe(Si) particles embedded in an amorphous matrix.

where n is the number of single domain particles per unit volume, μ is the magnetic moment of the single particle, and k_B is the Boltzmann constant.

The experimental points given in Fig. 3 have been fitted to the Langevin function (assuming that all the particles have the same volume) resulting in the solid-line curve shown in Fig. 3. Since this fit is really very good, it entitles one to conclude that the particles investigated are chemically stable (they do not change their dimensions at the time of measurements) and that there are no interactions between them. This conclusion can additionally be confirmed by plotting the dependence of j_s^2/χ_0 vs temperature [$\chi_0=(dM/dH)_{H\to 0}$ is the initial susceptibility], as shown in Fig. 4. For temperatures $T\geq 523$ K (where the amorphous matrix is in the paramagnetic state), this dependence has the form of a straight line through the origin, thus the Curie law is fulfilled.

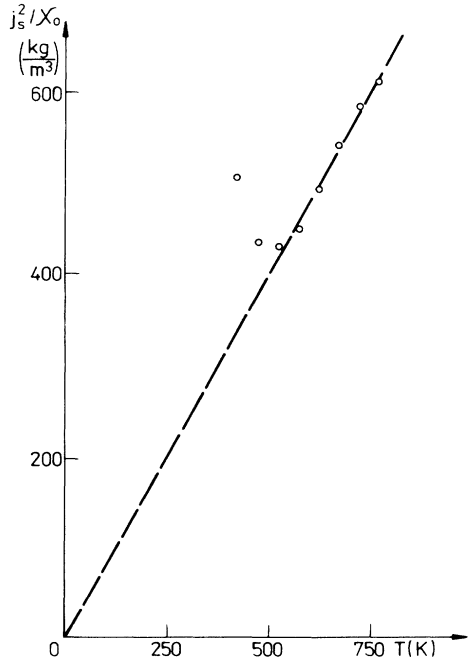

FIG. 4. Temperature dependence of inverse initial (low field) magnetic susceptibility. The dashed line represents the Curie law.

In the course of the fitting procedure of the magnetization curves to the Langevin function, the magnetic moment μ of a single particle as well as the number n_t of these particles in the sample have been determined. The best fit was obtained for $n_t = 2.57 \times 10^{14}$ (independent of the temperature of measurements). A knowledge of this value allows to estimate an average volume of a single particle V_s according to the relation $V_s = pV_{\text{tot}}/n_t$. The total volume of the sample $V_{\text{tot}} = 7.5 \times 10^{-10}$ m^3 has been calculated measuring its mass ($m_{\text{tot}} = 5.44 \times 10^{-3}$ g) and assuming that its average specific density after crystallization does not differ significantly from the one for amorphous state ($\rho_{\text{am}} = 7.25$ g/cm^3). The estimated value in this way of an average volume of a single particle is equal to $V_s = 525$ nm^3. Assuming that the particles have a spherical shape, their diameter is equal to $d_p \simeq 10$ nm, the value which is in a good agreement with the one determined directly from the micrograph shown in Fig. 1.

The other parameter of the fitting procedure, namely, the magnetic moment of the particle, decreases with increasing temperature from $\mu(523\text{ K}) = 63000\mu_B$ to $\mu(773\text{ K}) = 47000\mu_B$ (Bohr magnetons). The particle volume V_s' can thus be determined from the relation $V_s' = \mu(T)p/M_s(T)$ and its value is $V_s' = 548$ nm^3, being very close to the value previously obtained.

Knowledge of the particle's magnetic moment allows one to also find the average number of iron atoms being contained in each particle. Since the magnetic moment of the individual iron atom is equal to $2.2\mu_B$, this very rough estimate gives 10^4 iron atoms per particle.

Finally, it would be instructive to estimate the critical temperature T_{cr} (so-called "blocking" temperature) at which an ideal superparamagnetism sets in for an isolated particle of the type considered here (or an assembly of particles embedded into nonmagnetic matrix). This can be done using the well-known criterion given by

$$T_{\text{cr}} = KV_p/25k_B \ , \tag{3}$$

where K is the anisotropy constant of the particle. Assuming that the magnetocrystalline anisotropy constant of the bcc-Fe-15% Si material is of the order of 10^4 J/m^3 (see, e.g., Ref. 12), an estimate gives the value $T_{\text{cr}} \simeq 15$ K, far below the Curie temperature of the amorphous matrix above which the superparamagnetic behavior of the crystallites is observed.

CONCLUSIONS

It has been shown that the nanocrystalline Fe-based metallic glass exhibits superparamagnetic behavior at elevated temperatures. The effect is due to the Fe-Si particles of the nanometer scale, created by an appropriate thermal treatment and being embedded in the amorphous paramagnetic matrix. According to the present author's opinion, the above results may open new opportunities to study the fundamental magnetism.

Besides the expected importance for basic research, the results presented here may also be utilized for practical purposes. In a number of publications appearing quite recently a variety of possible material compositions yielding nanocrystalline structure was reported (see, e.g., Ref. 13). Since their properties are not fully known yet, it seems that the methods described in the present paper might also be useful for testing, for example, chemical stability of the particles as well as their size and distribution in these novel materials.

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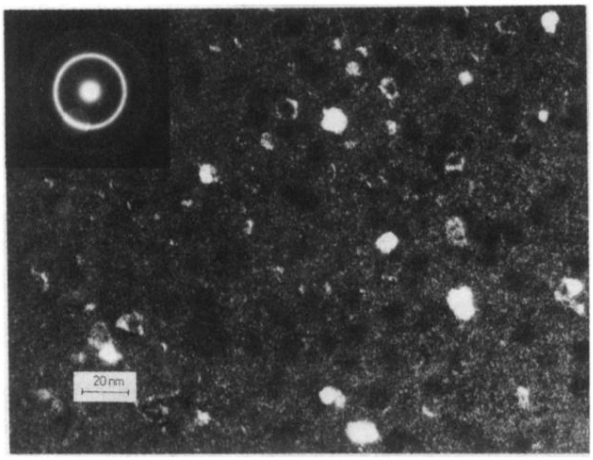
[1] Y. Yoshizawa, S. Oguma, and K. Yamauchi, J. Appl. Phys. **64**, 6044 (1988).
[2] G. Herzer, IEEE Trans. Magn. **MAG-25**, 3327 (1989).
[3] Y. Yoshizawa and K. Yamauchi, IEEE Trans. J. Magn. Jpn. **5**, 530 (1990).
[4] H. R. Hilzinger, Mater. Sci. Forum **62-64**, 515 (1990).
[5] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, 120S (1959).
[6] K. Hono, A. Inoue, and T. Sakurai, Appl. Phys. Lett. **58**, 2180 (1991).
[7] T. Kulik, Mater. Sci. Eng. (to be published).
[8] A. E. Berkowitz, in *Magnetism and Metallurgy*, edited by A. Berkowitz and E. Kneller (Academic, New York, 1969), Vol. **1**, p. 331.
[9] S. N. Kaul, J. Magn. Magn. Mater. **53**, 5 (1985).
[10] R. M. Bozorth, *Ferromagnetism* (van Nostrand, New York, 1953), pp. 75–79.
[11] M. Müller, N. Mattern, and L. Illegen, Z. Metallkd. **82**, 895 (1991).
[12] K. Suzuki, A. Makino, N. Kataoka, A. Inoue, and T. Masumoto, Mater. Trans. JIM **32**, 93 (1990).
[13] H.-Q. Guo, T. Reininger, H. Kronmüller, M. Rapp, and V. Kh. Skumrev, Phys. Status Solidi A **127**, 519 (1991).



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