Mössbauer study of amorphous $Fe_{78}B_{12}Si_{10}$

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Amorphous $Fe_{78}B_{12}Si_{10}$ in ribbon form has been investigated over a large temperature range from 4.2 to 750 K using the Mössbauer technique. The average isomer shift, although less than that for crystalline iron at 4.2 K, has a similar temperature dependence. The average quadrupole shift is zero below the Curie temperature T_F. The average hyperfine field is proportional to $(T/T_F)^{3/2}$ for $0.03 \leq T/T_F \leq 0.5$, but varies more slowly for $T/T_F \leq 0.03$. The conduction electrons appear to play an important role in reducing the importance of the amorphous nature of the alloy. The magnetization of a clamped sample, nearly randomly oriented at or below room temperature, lies mainly in the plane of the ribbon between 500 and 700 K. On returning to room temperature after annealing at 706 K, the magnetization has a large out-of-plane component.

I. INTRODUCTION

The investigation of amorphous magnetic materials has revealed a variety of interesting properties. From the viewpoint of applications, ferromagnetic amorphous alloys consisting of transition metals and metalloids are important because they are magnetically soft, possessing very small coercive force and anisotropy. For these materials a Mössbauer study is useful since information is obtained about the magnetic anisotropy and its dependence on parameters such as temperature and stress without the need to apply an external field.

From a theoretical point of view the effect of nonperiodicity in the atomic positions is of interest. The random atomic arrangement has been studied by x-ray diffraction and electron microscopy. To a first approximation, the atomic distribution can be considered as a random packing of hard spheres.[1] The inequivalency of atomic sites is observable through hyperfine interactions which can be studied with Mössbauer spectroscopy. The Mössbauer spectra of a large variety of amorphous alloys are very similar, and consist of structureless absorption lines that are broadened by the combined effect of nonperiodicity and the random distribution of metal and metalloid atoms. In the present work the hyperfine interactions and the magnetic anisotropy in amorphous $Fe_{78}B_{12}Si_{10}$ have been studied between 4.2 and 750 K.

II. EXPERIMENTAL

The amorphous $Fe_{78}B_{12}Si_{10}$ was prepared with the roller quenching technique at the Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai. The samples were in the form of ribbons, 1.1 cm wide and 35 μm thick.

The Mössbauer measurements were performed with an Elscint constant acceleration spectrometer that had linewidths of 0.30 mm/s for the outer lines of an iron calibration absorber 10 μm thick. The differential linearity[2] of the spectrometer is 0.2%. The measurements above room temperature were made in a furnace with a temperature stability of $\sim$0.5 K/24 h. Those below room temperature were obtained in a cryostat with a stability of 0.1 K/24 h. During the measurements the sample was clamped on a beryllium plate with stainless-steel rings. The measuring time was typically 20 h.

III. RESULTS AND DISCUSSION

A. General

The Mössbauer spectra of amorphous $Fe_{78}B_{12}Si_{10}$, shown in Fig. 1, have the same appearance as those of other amorphous materials with iron as the only magnetic atom present. Clearly, the spectra consist of several overlapping absorption patterns, the result of a distribution of isomer shifts, δ, quadrupole shifts, ϵ or ϵ', and hyperfine field, H_{hf}. The outer absorption lines are broadened the most and the inner ones the least. The outer linewidths $\Gamma(T)$ decrease monotonically with decreasing $H_{hf}(T)$ (Fig. 2). It follows that the line broadening largely has its origin in a distribution in the hyperfine fields.

In an external magnetic field a Mössbauer spec-

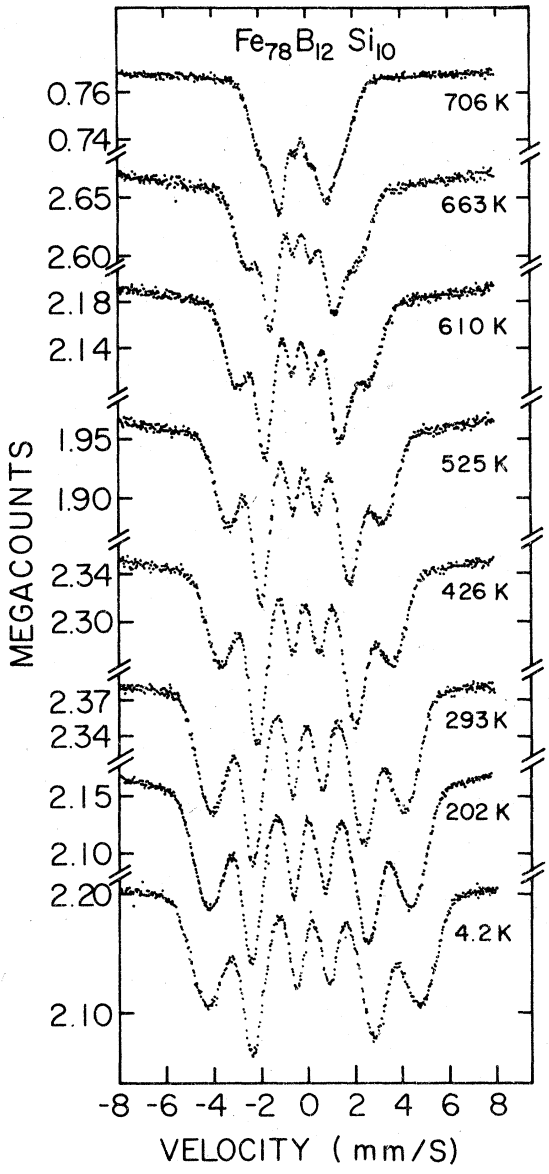

FIG. 1. Mössbauer spectra of amorphous $Fe_{78}B_{12}Si_{10}$ at different temperatures.

trum below the Curie temperature T_F is reduced to four absorption lines that are well separated.[3] Analysis of this spectrum shows that the absorption line shape is to a good approximation Gaussian. Consequently a fit of the present spectra with only one six-line absorption pattern will give average values of δ, ϵ', and H_{hf}.

For crystalline iron-metalloid alloys, e.g., *Fe*Si,[4] the values of δ increase and of H_{hf} decrease proportional to the number of Si atoms in the neighboring shell; hence the average value of δ is larger and the average value of H_{hf} is smaller. A similar result is found for amorphous $Fe_{78}B_{12}Si_{10}$. At 4.2 K an isomer shift

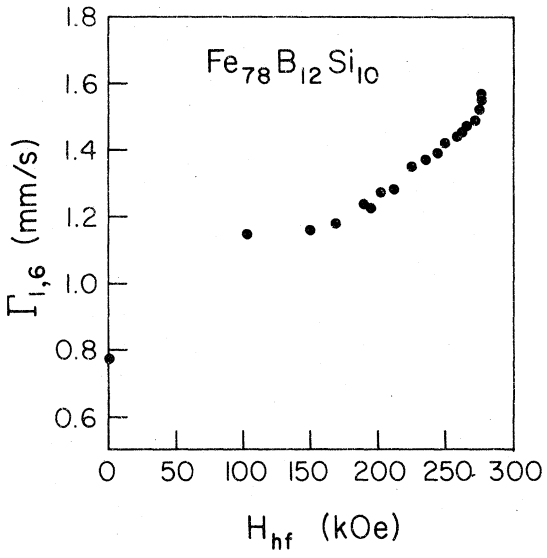

FIG. 2. Change of the linewidth Γ of the outer Mössbauer absorption lines with hyperfine field.

$\delta = 0.076(2)$ mm/s with respect to iron and a hyperfine field $H_{hf} = 280.5(2)$ kOe are observed. Here the numbers in brackets represent the error in the last significant number. The average δ and H_{hf} values indicate that compared to crystalline iron, the *d*-electron density increases; consequently the magnetic moment will be lowered and the nucleus will be better screened from the outer electrons. This prediction is confirmed by magnetization measurements which give a value of $1.67\mu_B$ per iron atom at 4.2 K. The mechanism by which the magnetic moment decreases as compared to pure iron is thought to be a transfer of metalloid *s* and *p* electrons to the conduction band and the *d* holes of the transition metal, respectively.[5,6]

B. Isomer shifts

The isomer shift has a temperature-dependent contribution which is caused by the motions of the emitting and absorbing nuclei. The second-order Doppler shift is given by $\Delta E_\gamma/E_\gamma = -\langle v^2\rangle/2c^2$ where E_γ is the energy of the unshifted γ ray, ΔE_γ is the shift in energy, v is the velocity of the emitting nucleus in the direction of the γ ray, and c is the velocity of light. For a crystalline material, in which harmonic forces are assumed, the temperature dependence of the shift becomes

$$\frac{1}{E_\gamma}\frac{\partial\delta(T)}{\partial T} = -\frac{C_L}{2Mc^2} ,$$

where M is the atomic mass and C_L is the specific heat of the lattice. For crystalline iron at high tem-

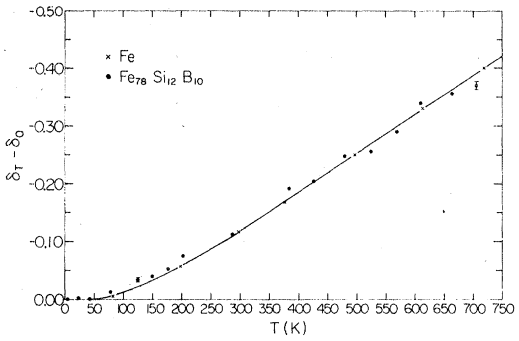

FIG. 3. Temperature dependence of the isomer shift δ. δ_0 is the isomer shift at 4.2 K.

peratures $\delta(T)$ becomes linear with a slope which agrees closely with $C_L = 3k$, where k is Boltzmann's constant.[7] For amorphous materials Cochrane *et al.*[8,9] propose that many atoms find themselves in atomic wells which are corrugated on a scale of a fraction of the average atomic spacing. For such atoms the atomic forces are not expected to be in good approximation harmonic, at least not at low temperatures. However, as shown in Fig. 3, a difference between the temperature dependence of $\delta(T)$ for amorphous $Fe_{78}B_{12}Si_{10}$ and for crystalline iron is not observed. This result indicates either that the forces are indeed harmonic or that the distortions leading to anharmonicity are not important for the behavior of $\delta(T)$. It is possible that the conduction electrons play a significant role in screening the atoms from the effects of nonperiodicity.

C. Quadrupole shifts

The screening by the conduction electrons reduces the quadrupole splitting in crystalline metals; in amorphous metals and alloys this effect can be expected to be important as well. Above T_F, the quadrupole shift is given by

$$\epsilon = \tfrac{1}{4} eQV_{zz}(1 + \tfrac{1}{3}\eta)^{1/2} \ ,$$

where e is the electronic charge, Q is the quadrupole moment of the nucleus, V_{zz} is the electric field gradient along the quantization axis, and η is the asymmetry parameter. Near the Curie temperature partial crystallization occurs in $Fe_{78}B_{12}Si_{10}$. It is possible to separate the absorption corresponding to the amorphous part of the sample from the hyperfine-split pattern associated with the crystalline part. Then, the average quadrupole shift a few degrees above T_F is found to be $\epsilon = 0.34(1)$ mm/s. Even this value should be treated with reserve however since some atomic rearrangement may also have taken place in the amorphous part.

Below T_F an average quadrupole shift has been calculated from $\epsilon' = \frac{1}{2}(\Delta_{56} - \Delta_{12})$, where Δ_{ij} is the difference in the positions of the absorption lines i and j. As demonstrated in Fig. 4 ϵ' is found to be zero within the error of measurement. Apparently the directions of the z axis of the electric-field-gradient tensor and the hyperfine field are uncorrelated throughout the sample.

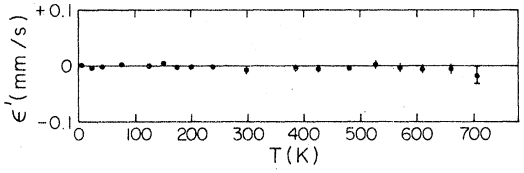

FIG. 4. Temperature dependence of the quadrupole shift ϵ' below the Curie temperature.

D. Hyperfine fields

The hyperfine-field distribution, which is primarily responsible for the large linewidth broadening, has been studied between 4.2 and 706 K. After cooldown to room temperature no indication of crystallization was observed. Annealing at 600–700 K led to an increase in the hyperfine field; specifically, $H_{hf} = 253.2(2)$ kOe for the as quenched sample whereas $H_{hf} = 256.5(2)$ kOe for the annealed one. The transition from the ferromagnetic to the paramagnetic state occurred within a narrow temperature range of less than 2 K at $T_F = 745$ K. At this temperature the alloy crystallizes partially.

The distribution in hyperfine fields may well have more than one source. Since the average magnetic moment per iron atom in amorphous alloys, such as $Fe_{78}B_{12}Si_{10}$, depends on the concentration of the metalloid atoms,[10] a distribution of magnetic moments is probably present. Such a distribution must be at least partially responsible for the variation in hyperfine fields. In addition, spin polarization of the conduction electrons by neighboring atoms may also lead to a significant variation in $H_{hf}(0)$.

The random nonperiodic atomic distribution suggests also a distribution in exchange interaction because the exchange interaction constant J depends on distance. However, the temperature dependences of the various hyperfine-field components are the same within the errors of measurement for amorphous $Fe_{78}B_{12}Si_{10}$.[11] The same result was observed for $Fe_{80}B_{20}$.[12,13] These data support a model in which conduction electrons couple spins over large distances. As a consequence, the effects of nonperiodicity average out and a large distribution of exchange interactions is not observed.

For all amorphous ferromagnets investigated so far,[14,15] the hyperfine field at low temperatures

decreases as

$$\frac{H_{hf}(T)}{H_{hf}(0)} = \frac{H_{hf}(T) - H_{hf}(0)}{H_{hf}(0)} = B_{3/2}(T/T_F)^{3/2} + C_{5/2}(T/T_F)^{5/2} ,$$

where $B_{3/2}$ and $C_{5/2}$ are coefficients that can be related to fundamental quantities. The leading $(T/T_F)^{3/2}$ term is characteristic of long-wavelength spin-wave excitations for which the nonperiodic arrangement is not important.[16] This term was found to be dominant from 4.2 K up to temperatures as high as $T/T_F = 0.5$.

As can be seen from Fig. 5, the behavior of amorphous $Fe_{78}B_{12}Si_{10}$ is not quite the same. In the temperature region $0.03 \leq T/T_F \leq 0.5$, $H_{hf}(T)$ indeed decreases in proportion to $(T/T_F)^{3/2}$; the value of 0.42 determined for $B_{3/2}$ is in good agreement with those found for the other alloys. However, for $T/T_F < 0.03$, $H_{hf}(T)$ decreases much slower with increasing temperature. To confirm this behavior, two or three spectra were taken at each of the temperatures 4.2, 23.0, 42.6, and 77.3 K. Some spectra had a parabolic background from the solid-angle effect, and others had a flat background, obtained after folding spectra collected with a triangular drive. The spectral lines were fitted with independent Gaussian-shaped curves by least squares using a computer routine. To illustrate the consistency of the data, at $T = 4.2$ K values of 280.9(2) and 280.2(2) kOe were obtained for the hyperfine field. Then, at $T = 77.3$ K, values of 279.0(2) and 278.6(2) kOe were found. Clearly the reproducibility is within 0.7 kOe. The difference in H_{hf} between $T = 4.2$ and 77.3 K is then -1.7 kOe. For the hyperfine field at 4.2 K to lie on an extrapolation of the higher temperature $T^{3/2}$ straight line, the difference would have had to be about 3 kOe; the additional 1.3 kOe required appears to lie well outside the uncertainties. It is not clear whether the behavior for $T/T_F < 0.03$ implies a smaller value of $B_{3/2}$ or whether exponents of T/T_F lower than $\frac{3}{2}$ must be considered.

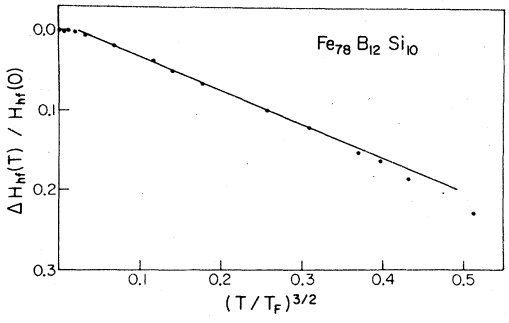

FIG. 5. Fractional change of the magnetic hyperfine field as a function of $(T/T_F)^{3/2}$ at low temperatures.

E. Magnetic anisotropy

Information about the magnetization direction in the ribbon can be obtained from the areal ratios of the six absorption lines in the Mössbauer spectrum. For an infinitely thin absorber the area ratios of the six lines are $A_{1,6}:A_{2,5}:A_{3,4}::3:A_{2,5}:1$. Here $A_{2,5} = 4\sin^2\theta/(1+\cos^2\theta)$ and θ is the angle between the γ-ray and magnetic hyperfine-field directions. $A_{2,5}$ increases from 0 to $\frac{4}{3}$ as θ changes from 0 to 90°. For a completely random distribution of magnetic-moment directions $A_{2,5}/A_{1,6} = \frac{2}{3}$.

Calculations of the spin direction can be misleading if a large overlap of the absorption lines occurs. If the shape of the hyperfine-field distribution is not known to be close to Gaussian, then the area ratios obtained with Gaussian line shapes may contain systematic errors. Therefore it is important to investigate first the line shape. The best approach is to eliminate the second and fifth absorption lines by applying a large external magnetic field longitudinally. Such an investigation for the present sample indeed showed that the absorption line shape at room temperature is to a good approximation Gaussian.[3]

In Fig. 6 the experimental values of $A_{2,5}/A_{1,6}$ are presented. The values do not change much below room temperatures and indicate that the hyperfine-field directions have some preference for the ribbon plane.

Above room temperature $A_{2,5}/A_{1,6}$ increases until about $T = 450$ K and thereafter decreases somewhat. The stress induced by thermal expansion of the clamped sample may be the cause of this increase.

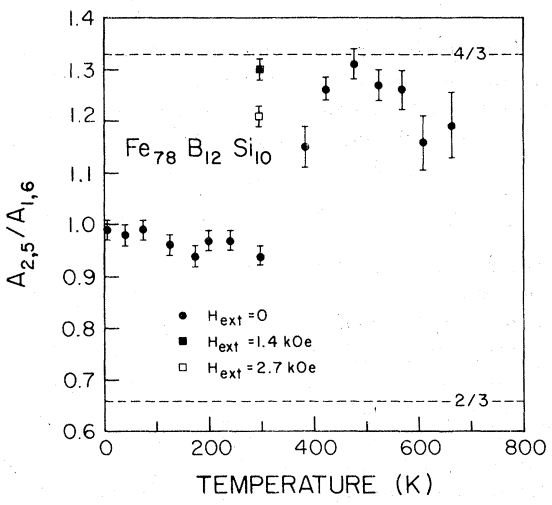

FIG. 6. Areal ratio $A_{2,5}/A_{1,6}$ of the absorption lines 2 and 5 to the outer lines 1 and 6 as a function of temperature, shown as circles. The same ratio when magnetic fields of 1.4 and 2.7 kOe are applied in the ribbon plane are indicated by the squares.

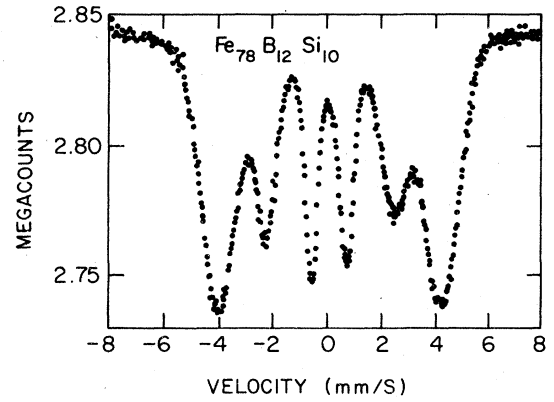

FIG. 7. Mössbauer spectrum of $Fe_{78}B_{12}Si_{10}$ at room temperature after annealing at 706 K.

For $T \gtrsim 450$ K the hyperfine-field directions are mainly in the plane of the ribbon. Support for this conclusion comes from room-temperature spectra obtained with two external magnetic fields, H_{ext}, applied parallel to the ribbon plane. The data analyses yielded $H_{hf}=249.1(6)$ for $H_{ext}=1.4$ kOe and $H_{hf}=247.5(6)$ for $H_{ext}=2.7$ kOe, to be compared with the value $H_{hf}=250.4(2)$ for $H_{ext}=0$. Since the relationship $H_{hf}(H_{ext})=H_{hf}(0)-H_{ext}$ is well satisfied by these values, it follows that the sample was completely saturated. The area ratios $A_{2,5}/A_{1,6}$ deduced were 1.30(2) and 1.21(2) for $H_{ext}=1.4$ and 2.7 kOe, respectively, (also plotted in Fig. 6) and are somewhat less than the value of 1.33 expected theoretically.

When a sample is returned to room temperature after annealing at 706 K, the spectrum shown in Fig. 7 is observed. The data yield $A_{2,5}/A_{1,6}=0.44(2)$, which is significantly lower than the original value of 0.94(2) found before annealing. A similar change from a magnetization direction in the plane to a direction out of the plane has been observed for $Fe_{40}Ni_{40}P_{14}B_6$ after annealing for two days at 545 K.[14] These authors suggested that the annealing relieved the stresses and as a result the magnetic moments become directed more randomly. However, for the present sample the annealing produces a change from a direction between an in plane and a random distribution to one with a direction largely perpendicular to the ribbon. A similar result was observed for $Fe_{80}B_{20}$.[13]

The increase in $H_{hf}(0)$ after annealing at high temperatures suggests that an atomic rearrangement or changes in the atomic distances may have taken place. Possibly such changes have also altered the magnetic anisotropy properties.

IV. CONCLUSIONS

It is difficult to distinguish between the effects of nonperiodicity and the random distribution of metal and metalloid atoms in amorphous $Fe_{78}B_{12}Si_{10}$. Both effects are diminished and averaged out through the screening and the long-range interactions via the conduction electrons. An annealing at high temperatures changes the magnetic hyperfine field slightly and the magnetic anisotropy considerably. The reason for this behavior has not been determined yet and more study is needed.

ACKNOWLEDGMENTS

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