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Comparison of amorphous and crystalline FeB

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We have studied amorphous FeB made by high-rate sputtering. The results are compared with those of crystalline FeB containing a *single* Fe site. The quadrupole splittings and the isomer shifts measured in the paramagnetic state and the hyperfine-field distribution measured in the ferromagnetic state show considerable differences between amorphous and crystalline FeB. These results indicate dissimilar short-range order in the amorphous and crystalline states. The hyperfine field of amorphous FeB decreases more rapidly with temperature than that of crystalline FeB. This clearly illustrates the effects of a distribution of exchange interactions in an amorphous ferromagnet as opposed to a single-site crystalline ferromagnet.

I. INTRODUCTION

Recently there has been considerable interest in amorphous magnetic systems.[1] Of particular interest are amorphous solids that have crystalline counterparts. In such cases a direct comparison can be made between the amorphous and crystalline states, allowing the effects of structural disorder to be more clearly elucidated. Several comparisons have already been reported in the case of rare-earth—transition-metal systems and large differences have been observed between the crystalline and amorphous states.[2]

Most crystalline transition-metal (T)—metalloid (M) systems form the compounds T_3M (although, as for example in Fe_3B, they may be unstable at high temperatures), T_2M, and TM.[3–7] The liquid-quench techniques yield amorphous samples in the composition range near $T_{80}M_{20}$ and could, in principle, provide samples for a comparison of T_3M in the crystalline and amorphous states. However, the T_3M compounds are poor candidates for such a comparison for a variety of reasons. The crystalline T_3M compounds have several inequivalent structural sites. In the magnetically ordered state an even greater number of magnetically inequivalent sites are possible.[7] Mössbauer spectra of the T_3M compounds contain, therefore, a large number of lines, complicating data analysis.[8] Further complications arise because of the possibility of forming interstitial solids. Inconsistencies in reported properties reflect these difficulties. From the standpoint of the amorphous solid, the T_3M compositions have high Curie temperatures which are close to the crystallization temperatures.[1] In these cases, sample crystallization makes measurements in the paramagnetic state difficult or impossible.

In this work, we report a study of FeB in its crystalline and amorphous states. This composition does not present the difficulties described above. The crystal structure, Curie temperature, and hyperfine interactions of the stable crystalline FeB (β-FeB) are well known.[3–10] More importantly, all the Fe sites in this crystalline FeB state are equivalent and Mössbauer-effect experiments indicate only one magnetic site in the ferromagnetic state. In addition, the Curie temperatures of crystalline and amorphous FeB are sufficiently low so that the paramagnetic state is easily accessible and, in the case of amorphous FeB, far from the crystallization temperature. Thus by comparing various properties of crystalline β-FeB and amorphous FeB one has the opportunity to study the effects of structural disorder in both ferromagnetic and paramagnetic states.

II. EXPERIMENTAL

Amorphous samples of FeB (hereafter referred to as *a*-FeB) cannot be formed by the liquid-quench techniques, but can be made by vapor-deposition techniques.[11–14] Our samples were made by a high-rate sputtering device using Ar as the sputter gas. Sputtering rates were typically 500—1000 Å/min and samples were made with thickness from 5 to 15 μm. The films were deposited either on water-cooled or liquid-nitrogen—cooled substrates of copper or Kapton. The sputtering targets were made from appropriate homogeneous mixtures of pure Fe (99.9% purity) and pure B (99.5% purity). Consistent results were determined from all the samples made in this manner.

During the course of this work we also made several targets and samples from commercially available, supposedly single phase, crystalline FeB.[15] These samples exhibited considerably different magnetic properties (e.g., a substantially lower Curie temperature). However, subsequent analyses of the commercial crystalline FeB revealed the presence of free boron, resulting in a true Fe content of only about 46 at.%.[16] This accounted for the observed differences. Only the results from samples made from targets of homogeneous mixtures are reported here.

It should be mentioned that certain properties (e.g., the Curie temperature and the hyperfine field) of amorphous Fe_xB_{100-x} depend sensitively on the composition x. Because of the low atomic number of boron, it is difficult to determine the *absolute* samples composition better than a few atomic percent. Consequently, relatively small compositional variations most likely account for the differences in the results of several studies of vapor-deposited Fe-B systems.[11–14] Despite these small compositional uncertainties, amorphous samples of nominally *a*-FeB can still be profitably compared with crystalline FeB if the properties of the samples with compositions near *a*-FeB can be shown to be considerably different from those of crystalline FeB.

All the measurements were made using a conventional Mössbauer spectrometer with a ^{57}Co in Rh source. Samples were immersed in liquid helium for the 4.2-K measurements and variable-temperature inserts were used for temperatures up to 300 K. Above room temperature a variable-temperature vacuum oven was used.

III. RESULTS AND DISCUSSIONS

A. Magnetic ordering temperatures (T_C)

The value of $T_C = 598$ K has been determined for crystalline β-FeB (hereafter referred to as *c*-FeB). This is in good agreement with the values of 597.5±0.1 K (Ref. 4) and 594 K (Ref. 9) reported in the literature. In the present case a smaller value of $T_C = 550$ K has been determined for *a*-FeB. Other studies indicate even lower values of T_C for *a*-FeB.[12] This apparent discrepancy is due to the high sensitivity of T_C on *x* and uncertainties in the sample composition.[11] Nevertheless it is reasonable to conclude that T_C of *a*-FeB is substantially lower than that of *c*-FeB. It should be noted that amorphous alloys do not always have smaller values of T_C than their crystalline counterparts. Even in amorphous Fe-metalloid systems, the amorphous state can have a much higher T_C (e.g., *a*-FeSi, *a*-Fe_3C),[17,18] comparable T_C [e.g., *a*-Fe_3B (Ref. 3)] or much lower T_C [e.g., *a*-Fe_2B (Ref. 11)] than that of the crystalline state.

B. Quadrupole splitting and isomer shift

The quadrupole spectra of *a*-FeB and *c*-FeB at 605 K (above T_C in both cases) are shown in Fig. 1. It is clear that the isomer shifts and the quadrupole splittings are noticeably different. To eliminate the possibility of any unexpected temperature dependences, we have measured the quadrupole spectra of both *a*-FeB and *c*-FeB over an extended temperature range in the paramagnetic region. As shown in Fig. 2, the quadrupole splittings of *a*-FeB and *c*-FeB are essentially temperature independent within the temperature range measured. The quadrupole splitting of 0.425±0.01 mm/sec for *c*-FeB is in excellent agreement with the value of 0.434±0.01 mm/sec reported previously.[4] A substantially larger quadrupole splitting of 0.55±0.01 mm/sec is observed in *a*-FeB. Furthermore, our measurements indicate that the quadrupole splittings for amorphous samples from $x = 40$ to $x = 50$ are within 5% of 0.55 mm/sec.[18] Thus, even allowing for compositional uncertainties, the quadrupole splitting of *a*-FeB is considerably larger than that of *c*-FeB.

As shown in Fig. 2, the isomer shifts decrease with temperature as $-\alpha T$ due to the second-order Doppler effect.[8] The theoretical value of $\alpha = 7.29 \times 10^{-4}$ mm/sec K, indicated by the straight lines in Fig. 2, is in excellent agreement with the experimental results. The isomer shift of *c*-FeB is greater than that of *a*-FeB by about 0.05 mm/sec. For metallic systems, this represents a rather large difference in isomer shift.[8] Similar differences have also been observed at 4.2 K. We have earlier reported the isomer shift of amorphous Fe_xB_{100-x} over a wide composition range.[19] A maximum in the isomer shift has been observed near $x = 50$. Thus the isomer shift of *c*-FeB is substantially larger than *all* compositions of *a*-Fe_xB_{100-x}.

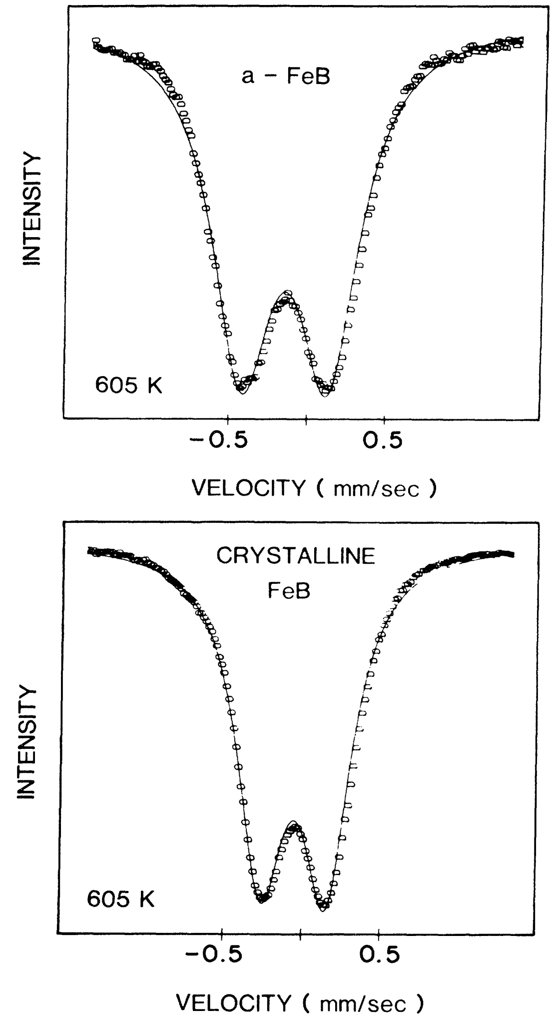

FIG. 1. Mössbauer spectra of *a*-FeB and *c*-FeB at 605 K which is above the T_C of both samples. Slight asymmetry in the spectrum of *c*-FeB is caused by an impurity phase.

C. Magnetic hyperfine interaction

A Mössbauer spectrum of *a*-FeB at 4.2 K without external field is shown in the upper half of Fig. 3. Figure 4 shows the spectrum measured with an external magnetic field of about 1 kOe applied in the sample plane. In the case without an applied field the magnetic moments tilt substantially out of the sample plane. Consequently, the 2 and 5 spectral lines are considerably suppressed and noticeably improve the resolution of the spectrum. This effect, observed in many amorphous ferromagnets made by

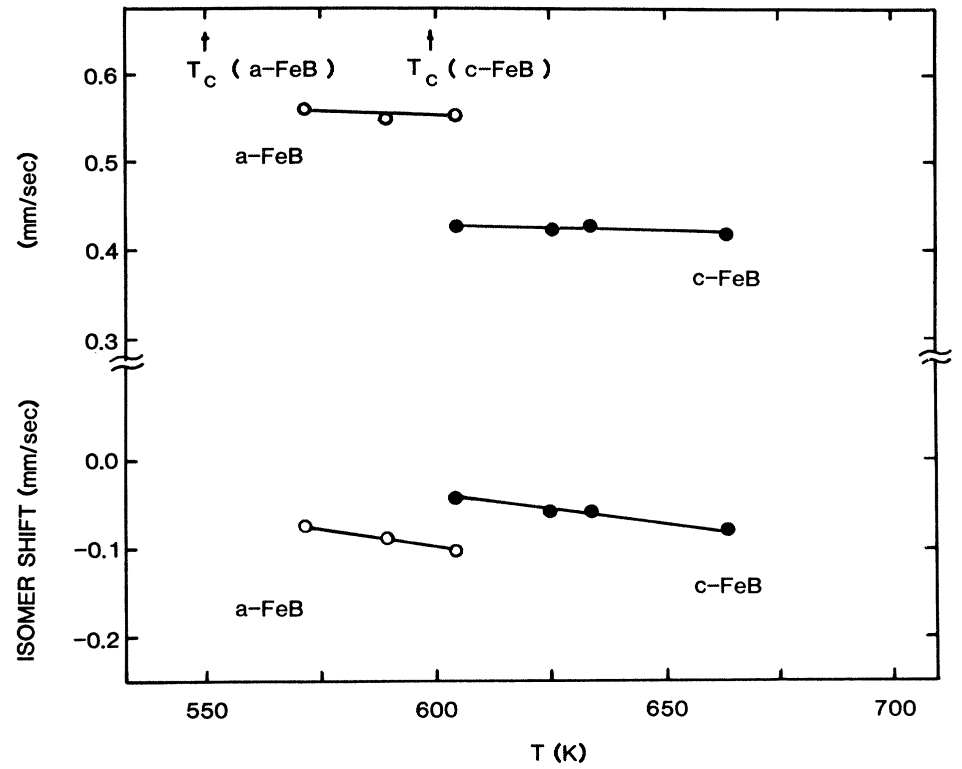

FIG. 2. Quadrupole splittings and isomer shifts of *a*-FeB and *c*-FeB as a function of temperatures. Arrows indicate the values of T_C.

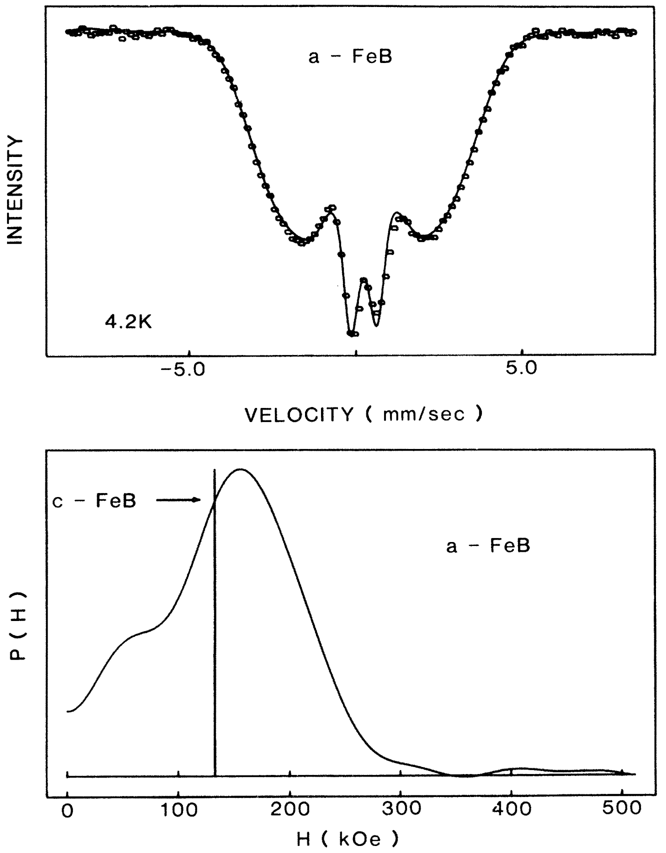

FIG. 3. Mössbauer spectrum and field distribution of *a*-FeB at 4.2 K without an external magnetic field.

vapor deposition, is often attributed to substrate stresses.[19,20] The fact that a small applied field can substantially realign the moments back into the sample plane, greatly increasing the 2 and 5 line intensities, indicates that the magnetic ordering is ferromagnetic and rather soft.

The hyperfine-field distribution $[P(H)]$ of *a*-FeB has been deduced by a variation of Window's method[21] and is shown in the lower half of Fig. 3. The observed asymmetry of the spectral lines is accounted for by a linear correlation between the isomer shift I and the hyperfine field of the form $I = \text{const} + \beta|H|$. The value of β is about 2×10^{-4} mm/sec kOe. The $P(H)$ of *a*-FeB is rather

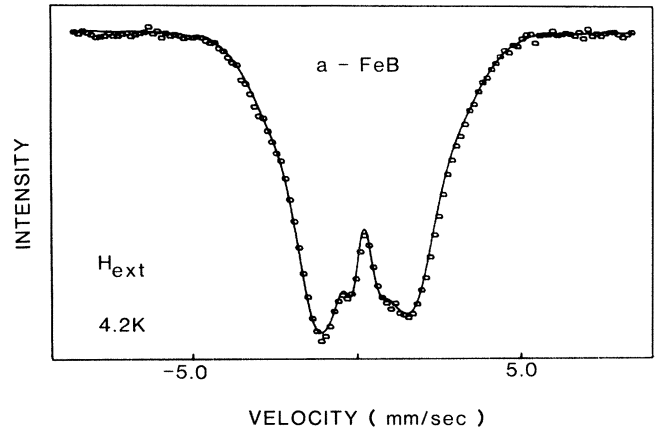

FIG. 4. Mössbauer spectrum of *a*-FeB at 4.2 K with an external magnetic field of about 1 kOe applied in the sample plane.

broad and is centered about a value noticeably larger than $H = 131$ kOe (indicated by the heavy vertical line in Fig. 3) characteristic of *c*-FeB.[4] Korecki *et al.* have arrived at similar conclusions.[14] As also shown in Fig. 3, a considerable fraction of Fe atoms in *a*-FeB experience very small hyperfine fields and therefore are only quasiparamagnetic or even nonmagnetic. This, in fact, is a common feature of all amorphous samples with compositions near *a*-FeB and below, as has also been observed by Blum *et al.*[12]

D. Temperature dependence of the hyperfine field

The temperature dependence of the effective hyperfine field of *a*-FeB and *c*-FeB in reduced units is shown in Fig. 5. It is well established that in both amorphous and crystalline Fe-B the hyperfine field is, to a good approximation, proportional to the Fe moment.[1,3] Thus the temperature dependence shown in Fig. 5 can be taken to be that of the magnetization. It is clear that the curve for *a*-FeB falls off with temperature much more rapidly than that of *c*-FeB.

The temperature dependence of the hyperfine field in Fe-based crystalline alloys has been extensively discussed.[21] In amorphous ferromagnets, a lower or "flatter" magnetization curve is often observed.[1] A large coefficient of the $T^{3/2}$ term for the hyperfine field and magnetization at low temperatures also reflects this fact.[1] This feature is generally attributed to the presence of a distribution of exchange interactions in the amorphous ferromagnets.[1–3] Such a situation is not, however, exclusive to amorphous solids but is also present in crystalline systems with many inequivalent sites and occurs in disordered alloys as well.

On the other hand, the existence of a distribution of exchange interactions has been disputed by a few studies. Schurer and Morrish fit the broad spectra of amorphous $Fe_{78}B_{12}Si_{10}$ with two six-line patterns, the physical meaning of which is not clear.[22] Based on this analysis, they claim the distribution of exchange interactions is very narrow, if a distribution exists at all. Instead, the lower magnetization curve is indicated to be similar to those of crystalline Fe_3Si and Fe_3Al. More recently, Ok *et al.* compared amorphous $Fe_{75.4}B_{14.2}Si_{10.4}$ with the crystalline phases of Fe_2B and $Fe_{47}Si_{10.4}$ and noted a similar temperature dependence for the hyperfine fields.[23] The lower hyperfine-field curve is attributed to the metalloid species and its content. In both cases two very similar amorphous alloys have been compared to several very different crystalline solids, both with respect to their elemental constituents and compositions. In addition, these crystalline compounds contain several distinct magnetic sites further complicating the comparison of the amorphous and crystalline states.[23]

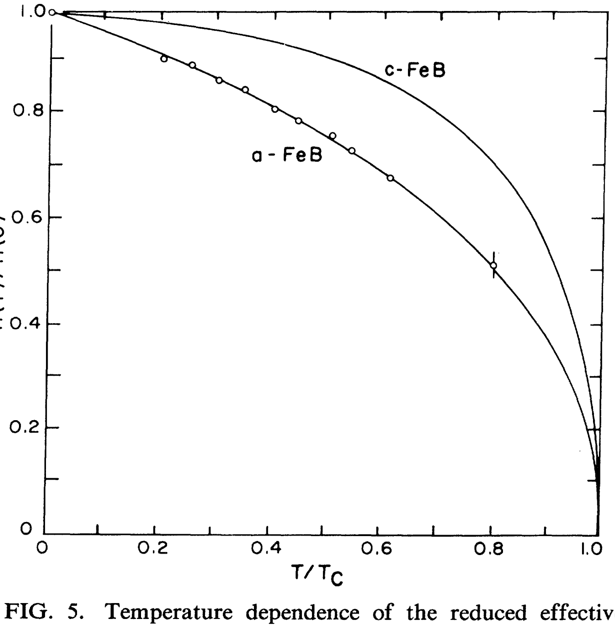

FIG. 5. Temperature dependence of the reduced effective field of *c*-FeB and *a*-FeB.

In the present case of FeB, such difficulties do not exist. *c*-FeB, having a single site, exhibits a magnetization curve which is very much higher than that of *a*-FeB. The lower curve for *a*-FeB cannot be attributed to the specific metalloid content nor to its crystalline counterpart. Instead, this direct comparison clearly illustrates the effects of structural disorder.

E. Short-range order

Studies of short-range order (SRO) in amorphous systems can be approached by structure models, structural determination and hyperfine-interaction measurements.[24–29] In amorphous *T*-*M* alloys, the readily available compositions near the eutetic point ($T_{80}M_{20}$) are by far the most extensively studied. One of the first such models was the microcrystalline model in which the SRO is the same in both amorphous and crystalline solids; a prediction not compatible with experimental results. More recently a quasicrystalline model has been proposed.[25] This model originated from the observation that the hyperfine-field distributions of amorphous samples with compositions near that of Fe_3B could be reasonably reproduced by summing broad Gaussians centered about the three field values of crystalline Fe_3B. Similar arguments have been made with respect to the quadrupole spectra.[26] However, it is unclear to what extent the apparent success of this model for these samples is convenienced by the number of Fe_3B sites from which the distributions are constructed. It is also noted that the ^{59}Co NMR results indicate that the SRO in amorphous Co_3B is not compatible with that in crystalline Co_3B.[28]

In the present case, a comparison of single-site crystalline FeB and the corresponding amorphous state provides a better test of these SRO models. As described above, the quadrupole splitting, isomer shift, and hyperfine-field distributions of *a*-FeB show very substantial differences which cannot be reconciled within the framework of the quasicrystalline model.

With vapor-deposition techniques, many binary amorphous systems can be made over wide composition ranges. In such systems, simple SRO models based on crystalline compounds become even more inadequate. The results of measurements on most compositions without crystalline counterparts cannot be reproduced by distributions about the crystalline values.[19] Even for compositions with crystalline counterparts, very large differences have been observed in many cases.[30,31] Finally, it has recently been shown that amorphous alloys comprised of mutually insoluble elements as Fe-Ag and Fe-Pb can be fabricated.[32] In these systems, the complete absence of crystalline alloys and compounds clearly illustrates the deficiencies of SRO models which are based on the crystalline solids.

IV. CONCLUSIONS

Amorphous FeB exhibits considerable differences in T_C, quadrupole splitting, isomer shift, and hyperfine-field distribution when compared to those of crystalline FeB. These results are therefore not compatible with the quasicrystalline model of amorphous solids which predicts very similar short-range order in an amorphous solid and its crystalline counterpart. Very much different temperature dependences of the hyperfine fields have been observed in *a*-FeB and *c*-FeB illustrating the different behavior of a single-site ferromagnet and an amorphous ferromagnet.

ACKNOWLEDGMENT

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