PHYSICAL REVIEW B VOLUME 34, NUMBER 7 1 OCTOBER 1986

Mössbauer study of the local atomic environments in metastable crystalline Fe-B alloys

F. H. Sanchez,* J. I. Budnick, Y. D. Zhang, W. A. Hines, and M. Choi
Department of Physics and Institute of Materials Science,
University of Connecticut, Storrs, Connecticut 06268

R. Hasegawa
Corporate Research and Development Center, Allied Corporation, Morristown, New Jersey 07960

(Received 17 April 1986)

We have applied the Mössbauer effect to study the local atomic environments in metastable crystalline $Fe_{100-x}B_x$ alloys ($1 \leqq x \leqq 12$) produced by rapid quenching from the melt. For concentrations up to 9 at. % B, the spectra revealed the existence of three distinct ^{57}Fe sites, characterized by room-temperature hyperfine fields of 330, 267, and 236 kOe, the first of which is that of Fe in bcc α-Fe. The other two sites were populated in the ratio 1:2, while the total amount of Fe atoms in them was nearly three times the number of B atoms present in the alloys. Furthermore, the temperature dependences of the hyperfine fields at these two sites were the same, although distinctly different from that of the α-Fe site. The Mössbauer results presented here, together with a nuclear-magnetic-resonance investigation previously reported, demonstrate that these alloys are not random solid solutions. Instead, they indicate that the alloys consist of a dispersion of very small regions, which have an orthorhombic-Fe_3B-like structure, embedded in an α-Fe matrix.

I. INTRODUCTION

A few years ago, the production of chill-cast, single-phase body-centered-cubic (bcc) α-Fe(B) alloys with B concentrations up to 12 at. % was reported on the basis of magnetometry, densitometry, and x-ray diffraction (XRD) studies.[1] However, since the first two techniques used in that study are macroscopic in nature and XRD is only very sensitive to well-developed phases, information concerning the B and Fe site occupancy as well as the microstructure of these alloys is not really available. Such information will not only be important in its own right, but perhaps be helpful in understanding the short-range order (SRO) of the amorphous alloys which begin to form for B concentrations greater than 12 at. %.

The equilibrium solubility of boron in iron is extremely low (less than 30 and 60 ppm in α-Fe and γ-Fe, respectively[2]). However, the amorphous alloys referred to above can be produced by a variety of techniques and over a wide concentration range, typically from 12 to 27 at. % B for the case of alloys prepared by rapid quenching from the melt.[3] As a consequence of the research done on the glassy Fe-B system, much knowledge has been gained, and also many questions have been raised. One important question refers to the nature of the SRO. For instance, besides the dense random packing of spheres model,[4] models in which the SRO mimics that found in the related crystalline phases have been suggested.[5–8] In these models, the particular SRO depends on the B concentration as well as the details of the heat treatment and cooling procedures. Furthermore, the existence of two-phase amorphous alloys has been reported, and it was suggested that body-centered-tetragonal (bct) Fe_3B SRO may already exist in the melt.[7]

Aside from the chill-cast, single-phase bcc α-Fe(B) alloys mentioned above,[1] all other work concerning the preparation of Fe-B alloys with low concentrations (< 12 at. % B) by rapid quenching techniques reports inhomogeneous, crystalline materials. For example, mixtures of bcc α-Fe and orthorhombic (*o*) Fe_3B,[9] as well as bcc α-Fe, $Fe_{23}B_6$, *o*-Fe_3B, and bct-Fe_3B (Refs. 10 and 11) have been reported. Furthermore, inhomogeneous alloys containing *o*-Fe_3B, $Fe_{23}B_6$, and amorphous phases were produced by rapidly quenching melts with different compositions.[12]

The Mössbauer effect (ME), a hyperfine interaction technique, provides information about the local neighborhood of certain probe sites. It can distinguish lattice sites which are magnetically, atomically, or electronically inequivalent. In this way, it can also be utilized to identify phases whose dimensions are too small for XRD techniques. In this work, we report the first results of a ME study of the ^{57}Fe hyperfine-field (HF) distribution in rapidly quenched crystalline $Fe_{100-x}B_x$ alloys ($1 \leqq x \leqq 12$) for temperatures up to 550 K. As we will show, these results, along with an earlier nuclear-magnetic-resonance (NMR) investigation,[13] clearly indicate that the alloys are not homogeneous on a microscopic scale, but appear to consist of a dispersion of small *o*-Fe_3B-like complexes embedded in an α-Fe matrix.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

$Fe_{100-x}B_x$ ($1 \leqq x \leqq 12$) alloys were prepared using boron and iron constituents with purities greater than 99.9%. They were rapidly quenched from the liquid state using the chill-casting technique and this resulted in continuous ribbons, 1–5 mm wide and 30–60 μm thick.[1,14] The ribbons were characterized by Cu $K\alpha_I$ XRD using a Norelco diffractometer calibrated against a Si standard. Our XRD results were consistent with those previously reported by Ray and Hasegawa,[1] i.e., the lines could be in-

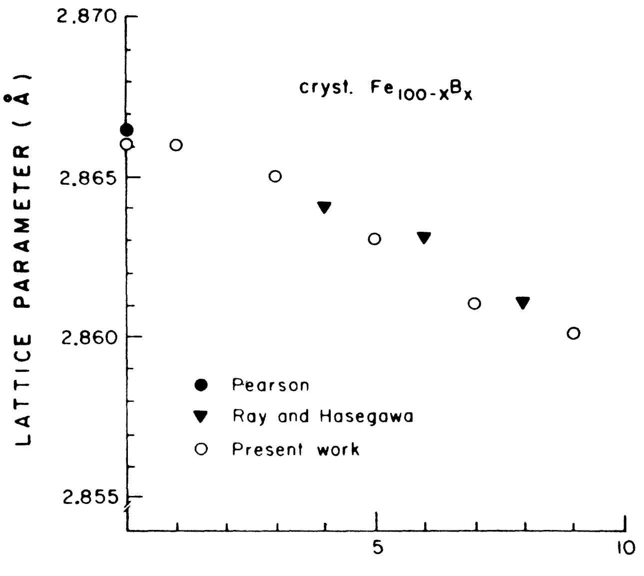

FIG. 1. Room-temperature lattice constant (based on the bcc α-Fe structure) a in Å versus the B concentration x in at. % for the chill-cast crystalline $Fe_{100-x}B_x$ alloys: open circles, this work; solid triangles, Ref. 1; solid circle, Ref. 15.

dexed using a bcc structure with a lattice constant approaching that of α-Fe (2.8660 Å) (Ref. 15) for the $x = 1$-at. %-B sample, and decreasing monotonically with increasing B concentration (see Fig. 1). For the alloys with higher B concentrations, some very weak extra lines were observed from the side of the ribbon which was in contact with the cold substrate wheel during the fabrication process.[14] Except in the case of the 12-at. %-B sample, which is a borderline concentration for the amorphous regime, the extra lines did not appear when either the bulk or the opposite side of the ribbon was analyzed. The extra lines matched those of o-Fe_3B (Ref. 12); however, they accounted for $\lesssim 1\%$ of the total XRD intensity. The ME experiments were performed using the 14.4-keV γ-ray resonance of ^{57}Fe from a 15-mC $^{57}CoPd$ source. The measurements were made under transmission geometry in the constant-acceleration mode. The Mössbauer data were accumulated simultaneously in two halves of 256 channels each corresponding to the positive and negative acceleration of the transducer. The two halves of the spectra were fitted independently with Lorentzian curves on a parabolic base line with respect to the off-resonance background. The velocity calibration was obtained using a 6-μm-thick pure Fe foil as an absorber. The velocity nonlinearity was fitted to a third-degree polynomial. The experimental, data-taking, and spectra-fitting procedures have been described in detail elsewhere.[16]

III. RESULTS AND ANALYSIS

Figure 2 shows the ME spectra obtained from all of the metastable $Fe_{100-x}B_x$ ($1 \leq x \leq 12$) alloys studied in this work. The samples with concentrations of $x = 1$, 3, 5, 7, and 9 at. % B yield spectra which were best fit by consid-

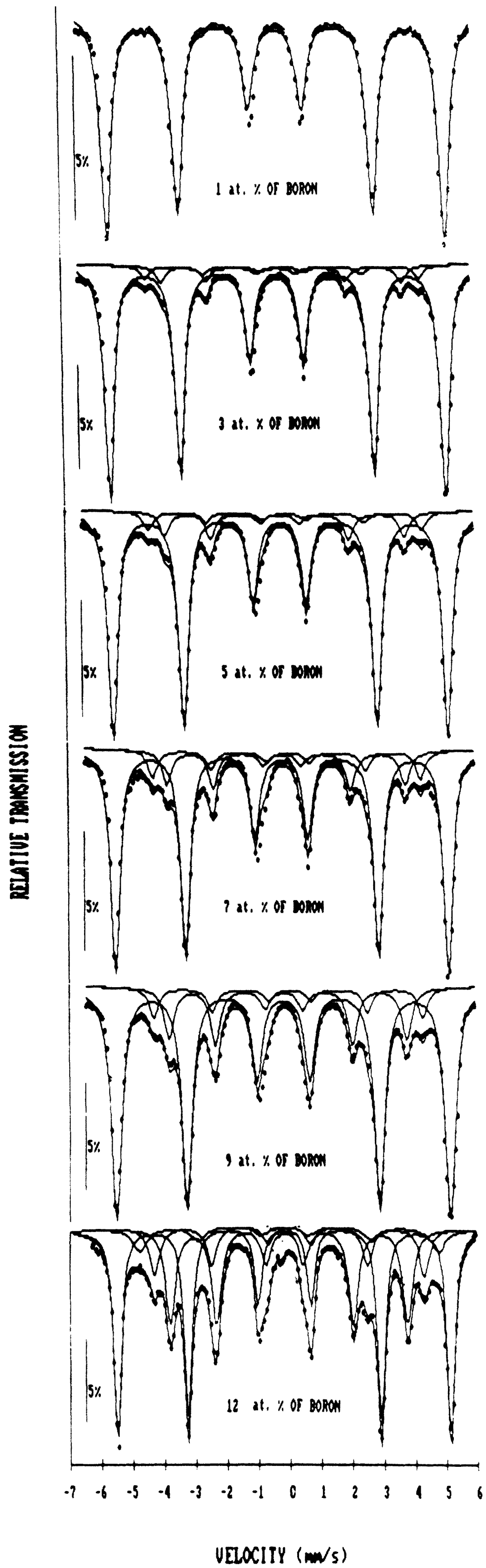

FIG. 2. ^{57}Fe Mössbauer spectra obtained at room temperature for the various chill-cast crystalline $Fe_{100-x}B_x$ alloys. The data are indicated by the open symbols while the solid lines represent the best fit for the three ^{57}Fe subspectra. The vertical bars at the left represent a relative γ-ray absorption of 5%.

ering the existence of three distinct sites for the ^{57}Fe probes, characterized by room-temperature HF values of 330 kOe (site 0), 267 kOe (site 1), and 236 kOe (site 2). The spectrum of the 12-at.%-B sample revealed two additional sites for the ^{57}Fe probes. One of them is characterized by a HF value of 295 kOe, while the other site has a very small population and appears to correspond to a paramagnetic state with zero electric field gradient. (A quadrupole interaction could have also been fit; however, this is unlikely since it would require a high negative isomer shift. This is not expected for the Fe-B system.) The magnetic interaction corresponding to site 0 is identical to that of α-Fe,[16] and hence, is associated with ^{57}Fe probes in regular bcc sites and surrounded by eight nearest-neighbor Fe atoms. A summary of our results for all of the concentrations studied is provided in Table I. An additional spectrum was obtained from a 9-at.%-B sample after it had been thinned to 70% of the original thickness by removing material from the wheel side of the ribbon using a metallography polishing technique. This thinning process was sufficient to eliminate all traces of the very weak extra XRD lines. No change was observed in the hyperfine parameters or the relative populations after the thinning, which indicates that the observed ME spectra correspond to ^{57}Fe probes essentially in the bulk of the sample.

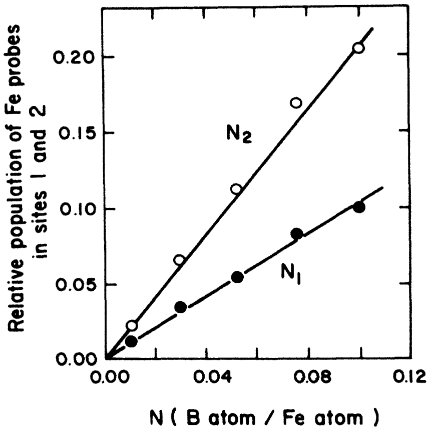

FIG. 3. ^{57}Fe Mössbauer subspectra intensities (relative to the total absorption intensity) N_1 and N_2 corresponding to sites 1 and 2, respectively, versus the number of B atoms per Fe atom in the alloy, N.

Figure 3 shows the relative ME subspectra intensities, N_1 and N_2, corresponding to ^{57}Fe probes in sites 1 and 2, respectively, as a function of the number of B atoms per Fe atom, N. Two empirical relationships can be drawn from the ME results:

$$N_2/N_1=2.1$$

and

$$N_1+N_2=3.0N \ . \qquad (1)$$

If we assume that the recoil-free fraction factor is similar

TABLE I. Room-temperature ^{57}Fe Mössbauer hyperfine parameters for the chill-cast crystalline Fe-B alloys. Isomer shifts are referred to α-Fe at room temperature. Typical uncertainties are as follows: intensity, ±1%; hyperfine field, ±2 kOe; isomer shift, ±0.03 mm/sec; quadrupole splitting, ±0.04 mm/s.

Boron concentration (at. %)	Site	Relative intensity (%)	Hyperfine field (kOe)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)
1	0	96.5	330	0.00	0.00
	1	1.3	269	0.10	0.08
	2	2.2	236	0.11	0.06
3	0	90.0	330	0.00	0.00
	1	3.4	269	0.19	0.01
	2	6.6	236	0.09	0.09
5	0	83.4	330	0.00	0.00
	1	5.4	269	0.18	−0.01
	2	11.2	236	0.09	0.08
7	0	74.9	330	0.00	0.00
	1	8.3	265	0.19	−0.03
	2	16.8	236	0.09	0.06
9	0	69.8	330	0.00	0.00
	1	9.9	266	0.20	−0.03
	2	20.3	235	0.09	0.06
12	0	48.1	330	0.00	0.00
	1	13.5	267	0.17	0.01
	2	29.6	235	0.09	0.06
	3	8.0	295	0.09	0.07
	4	0.8		−0.06	

for these three sites (which will be shown to be the case), we conclude that there are three Fe atoms in non-α-Fe sites for every B atom in the alloy; two in site 2 and one in site 1. This situation, together with the constancy of the hyperfine parameters in this concentration range, indicates that the alloys cannot be considered as random solid solutions. If they were, the relative number of Fe atoms in different sites would be a function of the B concentration. Furthermore, for low B concentrations, the population of Fe atoms with only one B nearest neighbor would be larger than those of Fe atoms with two or more B nearest neighbors. Since the substitution of B atoms into the nearest-neighbor sites of an Fe atom would decrease the Fe magnetic moment, we would expect that for the random solid solution case, the most intense subspectrum (aside from the α-Fe subspectrum) would be the one with the highest HF value. This constitutes a situation which is opposite to that observed. Similar arguments can be raised against the hypothesis of a substitutional pattern in which three B atoms replace two Fe atoms in the bcc lattice, which was proposed earlier for these alloys.[1] Therefore, we conclude that the B atoms must be arranged with those Fe atoms in sites 1 and 2 according to a well-defined pattern. In other words, the rapidly quenched crystalline Fe-B alloys appear to be inhomogeneous in that they are a mixture of α-Fe and some form of Fe_3B. The ME results reported here are completely consistent with recent NMR measurements carried out on both the Fe and B nuclei in these same alloys.[13]

The samples with 3 and 9 at. % B were measured at liquid-helium temperature. Within experimental error, the ME subspectra from the three ^{57}Fe sites had the same relative intensities that they had at room temperature, supporting the assumption of similar recoil-free fraction for the different Fe sites. The measured HF, isomer shift [with respect to α-Fe at 4.2 K (Ref. 16)], and quadrupole splitting values were 341 kOe, 0.00 mm/sec, and 0.00 mm/sec for site 0; 289 kOe, 0.20 mm/sec, and 0.03 mm/sec for site 1; and 253 kOe, 0.07 mm/sec, and 0.08 mm/sec for site 2, respectively.

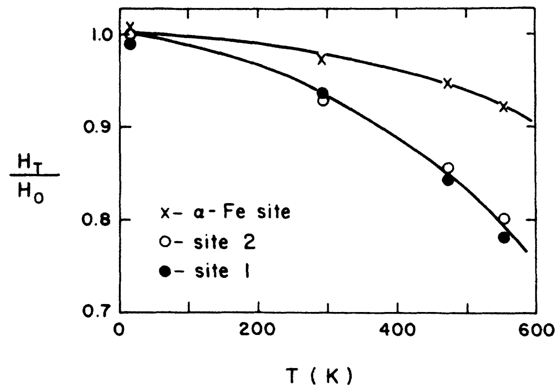

FIG. 4. ^{57}Fe hyperfine field values H_T/H_0, in reduced units versus absolute temperature T in K for the three sites in the chill-cast crystalline $Fe_{91}B_9$ alloy.

In order to gain further insight concerning the existence and exact structure of the postulated Fe_3B regions, the temperature dependences of the HF values were investigated for temperatures up to 550 K using the 9-at. %-B sample. The HF values at sites 1 and 2 possessed the same temperature dependence, although distinctly different from that corresponding to site 0 (the α-Fe site). This is illustrated in Fig. 4. This result strongly suggests that sites 1 and 2 belong to the same structural unit, which is different from bcc α-Fe.

IV. DISCUSSION AND CONCLUSIONS

Table II lists the reported hyperfine parameters for the various iron borides and the relative populations of the different Fe sites. Our HF and isomer-shift values (see Table I) agree quite well with those measured by Choo and Kaplow[9] on a splat-cooled 7-at. %-B sample, which contained regions that were identified as o-Fe_3B on the basis of XRD analysis. The quadrupole shifts almost overlap within experimental error. Furthermore, our

TABLE II. Room-temperature ^{57}Fe hyperfine parameters for various iron borides.

Compound	Site	Relative population	Hyperfine field (kOe)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Ref.
FeB			118	0.26	0.06	22
Fe_2B	1	1	242	0.12	0.04	23
	2	1	232	0.12	0.02	
o-Fe_3B	1	1	264±5	0.13±5	0.11±5	9
	2	2	235±5	0.07±5	0.02±5	
bct-Fe_3B	1	1	288	0.06	0.04	20
	2	1	265	0.03	0.09	
	3	1	226	0.11	−0.06	
$Fe_{23}B_6$	1	8	286			10
	2	12	238			
	3	2				
	4	1				

measured relative populations are consistent with those expected for o-Fe_3B. The comparison with $Fe_{23}B_6$ previously reported for a splat-cooled 5-at.%-B alloy by Franke *et al.*[10] is poorer. However, it should be pointed out that their ME data does not enable a unique fit and thus, the uncertainties in the reported parameters may be large.

Orthorhombic Fe_3B is a very unstable material which, to our knowledge, has never been obtained as a single-phase material. Usually, a careful annealing of Fe-B amorphous alloys with B concentrations slightly less than 25 at.% leads to the formation of bct-Fe_3B.[3] Orthorhombic Fe_3B has been reported to occur on a few occasions in rapidly quenched alloys with mainly Fe-rich compositions.[9–12] Consequently, its hyperfine parameters have been determined from multiphase samples,[9] giving rise to some uncertainty. Part of the uncertainty arises because o-Fe_3C (cementite), which is isostructural with o-Fe_3B, shows essentially the same HF values (207 kOe) for ^{57}Fe in sites 1 and 2.[17] This is in contrast to the HF values for the same two sites in o-Fe_3B which differ by 29 kOe. However, it should be noted that a recent ME study on the $Co_{3-x}Fe_xB$ system ($0 \leqq x \leqq 1.5$),[18] which is also cementite-type, revealed HF values over the range from 268 to 282 kOe for ^{57}Fe in site 1 and from 219 to 236 kOe for ^{57}Fe in site 2, i.e., a situation similar to that found in o-Fe_3B.

As indicated above, we observed only the bcc α-Fe XRD lines from the polished samples. The possibility of having amorphous islands has been ruled out because of the sharpness of the ME spectral lines. Indeed, our results indicate that the "o-Fe_3B phase" is highly dispersed as very small particles or complexes. The intensities of the XRD lines from small particles should be broader and weaker because of the small number of diffracting planes, particularly for those with high Miller indices. The effect would be even more pronounced in the case of crystal structures with large unit cells, such as o-Fe_3B (the o-Fe_3B unit cell is 13.62 times larger than that for bcc α-Fe). Hence, the diffraction intensity from the postulated o-Fe_3B phase would be much weaker than that from the bcc α-Fe phase, even for the 9-at.%-B alloy in which the boride phase accounts for 30% of the sample. Furthermore, ongoing high resolution transmission electron microscopy studies, performed by Zhang and co-workers[19] on the 1- and 7-at.%-B samples showed regions 5–15 Å in diameter which are drastically different from the α-Fe matrix. Selected area diffraction patterns obtained from these regions contained weak components consistent with those of o-Fe_3B. Finally, the observed decrease in the bcc lattice constant with increasing B concentration might be connected with stress introduced into the α-Fe matrix due to the embedded particles of the o-Fe_3B second phase.

As mentioned before, the ME spectrum of the 12-at.%-B sample has two extra components. The HF of 295 kOe does not exactly coincide with any of those listed in Table II; however, it is somewhat close to those of site 1 in bct-Fe_3B (288 kOe) (Ref. 20) and site 1 in $Fe_{23}B_6$ (286 kOe).[10] Consequently, its presence indicates that a mixture of these two iron boride phases might exist in this alloy along with o-Fe_3B. The single-line (paramagnetic) component constitutes an interesting situation. No iron boride has been reported to be paramagnetic or to have a negative isomer shift at room temperature. The lack of a quadrupole interaction suggests a cubic environment for the ^{57}Fe probe in this site. If one takes into account the measured isomer shift of −0.06 mm/sec, this site may belong to metastable γ-Fe [isomer shift of −0.08 mm/sec (Ref. 21)]. Additional work is currently in progress on this interesting composition (12 at.% B), which constitutes the boundary of the amorphous phase for rapidly quenched Fe-B alloys.

In summary, on the basis of the Mössbauer results reported here, we conclude that: (i) the low-B-concentration (< 12 at.% B) metastable crystalline $Fe_{100-x}B_x$ alloys are neither random solid solutions nor interstitial single-phase systems as believed; (ii) for concentrations over the range $1 \leqq x \leqq 9$, there are essentially three Fe atoms in non-α-Fe sites per B atom in the alloy; (iii) also for $1 \leqq x \leqq 9$, the relative populations of the non-α-Fe sites 1 and 2 are nearly 1:2, and the corresponding HF values at room temperature are 267 and 236 kOe, respectively; and (iv) the HF values for the non-α-Fe sites 1 and 2 have the same temperature dependence, but different from that of the α-Fe site. By comparison with the hyperfine parameters of the known iron borides, we further conclude that these alloys are a dispersion of small o-Fe_3B-like particles or complexes embedded in the α-Fe matrix.

Further work on the thermal stability of these alloys is currently in progress, particularly with respect to the evaluation of these minute boride regions as well as the dependence upon annealing of the various iron boride phases.

ACKNOWLEDGMENTS

We would like to thank S. H. Ge, Professor C. L. Chien, and co-workers at Johns Hopkins University for performing the ME measurements at liquid-helium temperature. The authors also wish to express their appreciation to J. C. Ford, C. R. Hummer, and Z. C. Tan for their technical assistance as well as S. H. Ge, G. H. Hayes, J. E. Morral, D. M. Pease, and S. Y. Zhang for many helpful discussions. One of us (F.H.S.) received financial support from the Consejo Nacional de Investigaciónes Científicas y Técnicas, República Argentina.

---

*Permanent address: Departmento de Física, Universidad Nacionalde de La Plata, c. c. 67, 1900 La Plata, Argentina.

[1] R. Ray and R. Hasegawa, Solid State Commun. 27, 471 (1978).

[2] A. Brown, J. D. Garnish, and R. W. Honeycombe, Met. Sci. 8, 317 (1974).

[3] U. Köster and U. Herold, in *Glassy Metals I*, edited by H.-J. Güntherodt and H. Beck (Springer-Verlag, New York, 1981), p. 225.

[4] D. S. Boudreaux, Phys. Rev. B 18, 4039 (1978).

[5] R. Hasegawa and R. Ray, J. Appl. Phys. 49, 4174 (1978).

[6]M. Eibschutz, M. E. Lines, and H. S. Chen, Phys. Rev B **28**, 425 (1983).

[7]J. L. Walter, S. F. Bartram, and I. Mella, Mater. Sci. Engr. **36**, 193 (1978).

[8]I. Vincze, T. Kemeny, and S. Arajs, Phys. Rev. B **21**, 937 (1980).

[9]W. K. Choo and R. Kaplow, Metall. Trans. **8A**, 417 (1977).

[10]H. Franke, U. Herold, U. Köster, and M. Rosenberg, in *Rapidly Quenched Metals III,* edited by B. Cantor (Chameleon, London, 1978), p. 155.

[11]M. Takahashi, M. Koshimura, and T. Abuzuka, Jpn. J. Appl. Phys. **20**, 1821 (1981).

[12]U. Herold and U. Köster, Z. Metallkd. **69**, 326 (1978).

[13]Y. D. Zhang, W. A. Hines, J. I. Budnick, M. Choi, F. H. Sanchez, and R. Hasegawa, J. Magn. Magn. Mater. (to be published).

[14]R. Pond and R. Maddin, Trans. Metall. Soc. AIME **256**, 2475 (1969).

[15]W. D. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon, New York, 1958).

[16]U. Gonser, in *Mössbauer Spectroscopy,* edited by U. Gonser (Springer-Verlag, New York, 1975), p. 1.

[17]M. Ron, H. Schechter, A. A. Hirsch, and S. Niedzwiedz, Phys. Lett. **20**, 481 (1966).

[18]M. Wojcik, H. Lerchner, P. Deppe, F. S. Li, M. Rosenberg, and J. D. Livingston, J. Appl. Phys. **55**, 2288 (1984).

[19]S. Y. Zhang (private communication).

[20]G. L. Caer and J. M. Dubois, Phys. Status Solidi A **64**, 275 (1981).

[21]U. Gonser, C. J. Meechan, A. H. Muir, and H. Widersich, J. Appl. Phys. **34**, 2373 (1963).

[22]T. Shinjo, F. Itak, H. Takaki, Y. Nakamura, and N. Shikagono, J. Phys. Soc. **19**, 1252 (1964).

[23]L. Takacs, M. C. Cadeville, and I. Vincze, J. Phys. F **5**, 800 (1975).