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Mössbauer study of an amorphous magnetic solid containing Cr

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A Cr-containing transition metal based amorphous magnetic solid ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) has been studied by ^{57}Fe Mössbauer spectroscopy in both its amorphous and crystalline states. The magnetic ordering temperatures of $T_C = 249$, 254, and 238 K have been determined for samples from three batches. In the amorphous state at $T > T_C$, well-defined quadrupole spectra are observed. At 4.2 K, the hyperfine-field distribution $P(H)$ is characterized by a two-maxima function of H. It is shown that the high-field component is due to Fe with mainly Fe and Ni as neighbors, whereas the low-field component originates from Fe atoms with Cr neighbors. The temperature dependence of $P(H)$ is studied at various temperatures and unusual features have been observed. In both the amorphous and the crystalline states of the sample, a noticeable amount of Fe is found to be weakly coupled. This is consistent with the results of the magnetic measurements and provides an explanation of the resistivity anomaly.

I. INTRODUCTION

Recently, amorphous magnetic solids with compositions of $(\text{Fe-Ni})_y(\text{P-B})_{100-y}$, where $y \simeq 80$, have been studied by various techniques.[1-4] Amorphous samples with Fe concentration higher than about 20 at.% are generally found to be ferromagnetic. However, the values of the magnetic ordering temperature (T_C) decrease sharply for samples with decreasing Fe content. The rapidly decreasing values of T_C suggest a critical concentration, below which ferromagnetism ceases to occur.[3,4] Indeed, samples with very low Fe concentration often exhibit spin-glass types of magnetic orderings.[4]

In a continuing series of experiments on amorphous magnetic systems using Mössbauer spectroscopy, an amorphous alloy of $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas 2826-*A*) has been studied. As shown in this work, the inclusion of 14 at.% of Cr in an otherwise relatively simple ferromagnetic glassy alloy has drastically altered its properties. The hyperfine anomaly which exists in this Cr-containing amorphous solid also correlates with the unusual characteristics found in magnetization[5] and resistivity[6,7] measurements.

II. EXPERIMENTAL

The amorphous samples of $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$, hereinafter referred to as 2826-*A*, were made by the technique of rapid quenching from the melt. They are in thin-ribbon form with a thickness of about 40 μm. Samples from three different batches, with ribbon widths of 3.2 mm (sample 1, 2 mm (sample 2), and 2.8 mm (sample 3) were used. Apart from a slight difference in the values of T_C, there is no noticeable difference among these samples.

Conventional ^{57}Fe Mössbauer spectroscopy has been used. The experimental details are similar to those described previously.[8]

III. RESULTS

A. Quadrupole interaction

Because of the disordered atomic arrangements in amorphous magnetic solids, the atomic site symmetry is in general lower than cubic. One therefore expects a quadrupole interaction due to the nonzero electric field gradients (EFG). This is evidently observed in 2826-*A* at $T > T_C$ by the quadrupole doublet spectra, as shown in Fig. 1. The fit assumes two independent Lorentzian peaks. The asymmetric rather than symmetric doublets are due to the distributions of EFG's *and* isomer shifts, as has been discussed elsewhere.[9] If one denotes the positions of the two peaks as E_1 and E_2, the average center shift and the average quadrupole splitting are defined as $\frac{1}{2}(E_1+E_2)$ and $E_2 - E_1$, respectively. The temperature dependences of these two quantities are shown in Fig. 2. The values of the center shift are relative to that of α-Fe at 295 K. The quadrupole splitting decreases only slightly with increasing temperature. The center shift decreases linearly with T due to the second-order Doppler effect.[10] The observed rate of decrease agrees well with the expected value of -7.29×10^{-4} (mm/sec)/K, as shown by the solid line.

A number of these measurements were made just above T_C. As shown in Fig. 2, *no* hyperfine anomalies in quadrupole splitting, center shift, or linewidth, suggestive of short-range magnetic ordering or superparamagnetic behavior, were found.

Although a pure quadrupole interaction can be clearly seen at $T > T_C$, the effective quadrupole

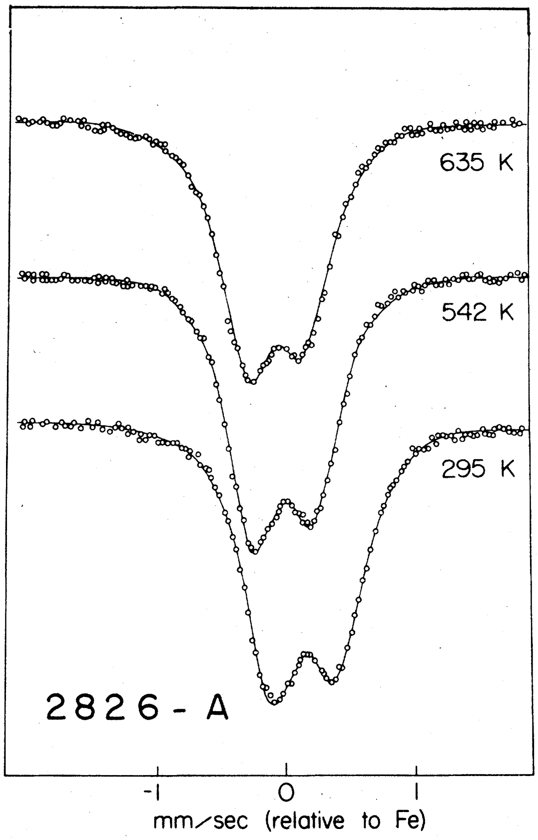

FIG. 1. Mössbauer spectra of amorphous 2826-*A* at $T > T_c$.

interaction at $T < T_C$ is generally negligibly small[11] due to the averaging of the angular factor contained in the effective quadrupole interaction.[10]

B. Magnetic ordering temperature

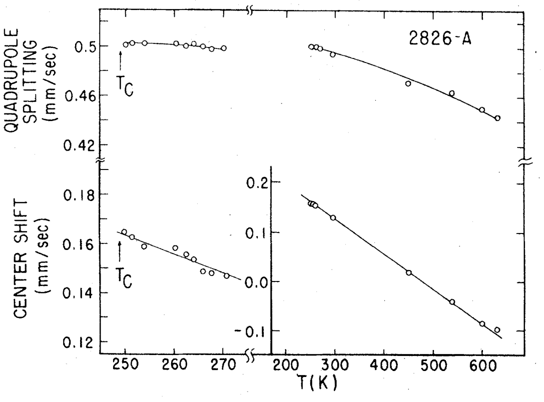

FIG. 2. Temperature dependence of the average quadrupole splitting and the average center shift (relative to α-Fe at 295 K) of 2826-A (sample 1) at $T > T_c$.

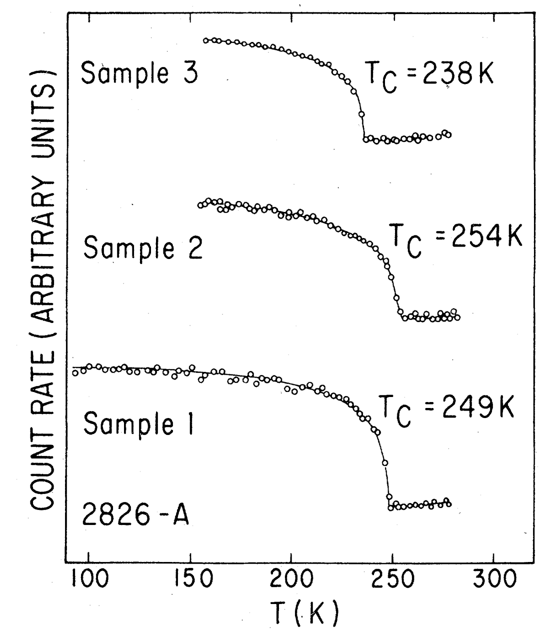

FIG. 3. Determination of T_c of three samples of amorphous 2826-A using the thermal-scan method.

The magnetic ordering temperature (T_C), as measured by the onset of the magnetic hyperfine interaction, can be conveniently determined by the thermal-scan method,[11] in which the velocity of the transducer is set near the centroid of the spectrum. As shown in Fig. 3, the values of T_C can be located by the abrupt rise of the count rate. The values of $T_C = 249$ K (sample 1), 254 K (sample 2), and 238 K (sample 3) have been determined. In all these cases, the transition appears to be very well defined.

The slight difference in the values of T_C for samples from three different batches is likely to be caused by small differences in their compositions. As indicated by the studies of T_C as a function of composition in $Fe_xNi_{80-x}P_{14}B_6$ and $Fe_xNi_{79-x}P_{13}B_8$,[2-4] in the vicinity of 32-at.% Fe, a relative change of 1-at.% Fe affects the value of T_C by more than 15 K. Furthermore, Cr is known to be very effective in reducing the Curie temperature.[12] Thus in the samples of 2826-*A*, a difference of less than 1 at.% in Fe, Ni, and Cr is sufficient to cause the observed difference in the values of T_C.

C. Magnetic hyperfine interaction

The spectra of glassy 2826-*A*, taken below T_C, are shown in Fig. 4. A very unusual behavior, unlike that observed in other transition-metal-based amorphous magnetic solids, is observed. There is a very pronounced central component that persists at $T \ll T_C$. The relative intensity of the central component decreases with decreasing temper-

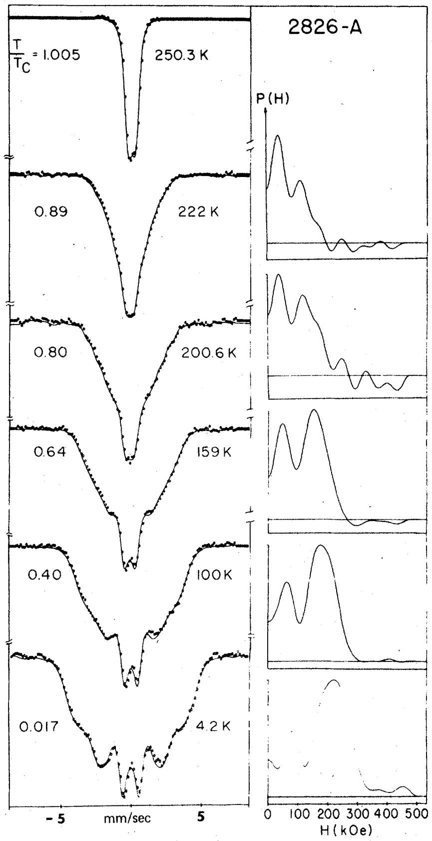

FIG. 4. Mössbauer spectra of amorphous 2826-A (sample 1, $T_c = 249$ K) at 250.3 K and at $T < T_C$. The solid curve for each spectrum is the best-fit result with the inclusion of the deduced $P(H)$ shown on its right-hand side.

ature, but the central component does not disappear even at 4.2 K. An almost identical spectrum has been observed at 2 K, thus indicating that it is unlikely that the spectrum at 0 K would be much different from that of 4.2 K. Apart from a slight difference in the values of T_C, samples from all three batches show almost identical behavior.

Although the central component in the spectrum, especially at low temperatures, appears to be a quadrupole-split doublet, it is highly unlikely that this is the case. This is because its splitting would then be many times larger than the quadrupole splitting observed at $T > T_C$, as shown in the top spectrum of Fig. 4. Furthermore, as shown in Fig. 2, the quadrupole splitting has a very weak temperature dependence at $T > T_C$. It is therefore improbable that its value would increase drastically at $T < T_C$.

To better characterize the unusual behavior in 2826-*A*, we have determined the hyperfine-field distribution $P(H)$ contained in these spectra using the Fourier-series method developed by Window.[13] This method has the distinct advantage of not presupposing any form of $P(H)$.[14] Negligible effective quadrupole interaction and a single center shift have been assumed as approximations to facilitate the deconvolution process. The results of the $P(H)$ analyses using 15 terms of a cosine series are shown on the right-hand side of Fig. 4. The solid curves in each spectrum shown in Fig. 4 are the best-fit results with the inclusion of $P(H)$ shown on its right-hand side. The small oscillatory feature of $P(H)$ at the high-field side is the consequence of the truncated Fourier analyses, and no significance is attached to it. It should be mentioned that the assumption of no effective quadrupole interaction may be troublesome for Fe atoms that have small or zero hyperfine fields. Thus whether the $P(H)$ is finite as indicated in Fig. 4 or zero at $H = 0$ cannot be unequivocally determined. Nevertheless, both the spectra and the $P(H)$ shown in Fig. 4 indicate a substantial number of Fe atoms with very small hyperfine fields.

D. Crystallization and crystalline phases

During measurements at successively higher temperatures, amorphous 2826-*A* (sample 1) began to crystallize at 680 K. The sample was then heated to 1100 K for 24 h to assure complete crystallization. The magnetic ordering temperature (T_C) of the subsequent crystalline phases were then determined by the thermal-scan method. As shown in Fig. 5, there is only one Fe-containing crystalline phase ($T_C = 820$ K) with a magnetic ordering temperature higher than 4.2 K. The spectra of the crystallized sample of 2826-*A* at 295 and 4.2 K are shown in Fig. 6. The six-line pattern originates from the crystalline phase with $T_C = 820$ K. Interestingly, there is a fraction of Fe atoms that remain *nonmagnetic* at 4.2 K, as shown by the central peak. Low-velocity measurements indicate that the central peak actually is a doublet with a quadrupole splitting of about 0.25 mm/sec. Thus in *both* the amorphous and the crystalline states

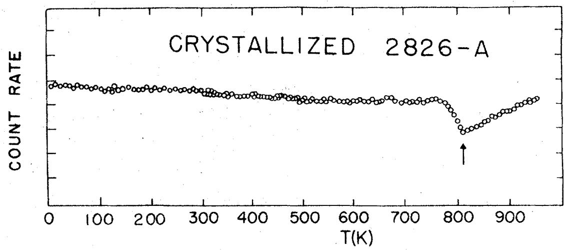

FIG. 5. Determination of T_C in the crystallized sample of 2826-A using the thermal-scan method. The arrow indicates the only T_C (820 K) found between 4.2 and 960 K.

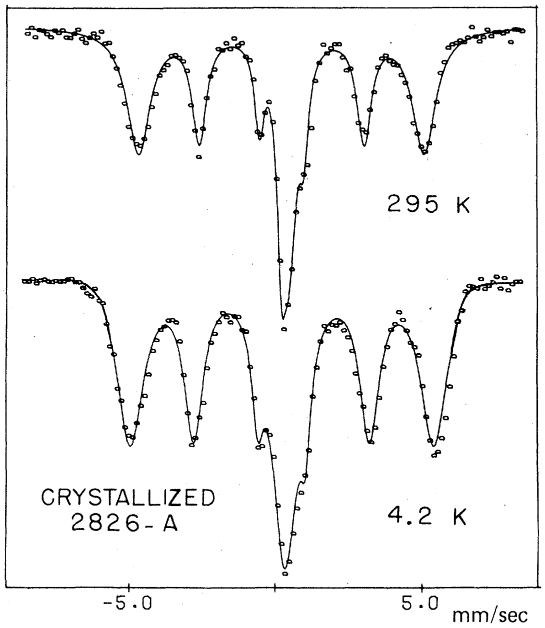

FIG. 6. Mössbauer spectra of the crystallized sample of 2826-A at 295 and 4.2 K.

of 2826-*A* there is a substantial number of Fe atoms that are nonmagnetic or are weakly coupled.

From the spectrum of the crystallized sample of 2826-*A* at 4.2 K, a magnetic hyperfine field of 322 kOe has been measured. This value is larger than almost all the *H* values observed in amorphous 2826-*A*, as shown by the *P*(*H*) at 4.2 K in Fig. 4. On this basis, there is no evidence to suggest that in amorphous 2826-*A* there is distinct short-range crystalline ordering which can be identified with its crystalline state.

IV. DISCUSSION

As shown in Fig. 4, the spectra and the corresponding *P*(*H*) of amorphous 2826-*A* exhibit a number of unusual features. There is a broad range of *H* values with a noticeable population at very low *H* values. The *P*(*H*) can be approximately described by a double-maxima function of *H* with a high-field component and a low-field component. The shape of *P*(*H*) appears to be temperature dependent. The anomalous nature of these spectra and *P*(*H*) becomes apparent when compared with those of other amorphous Fe-Ni-P-B systems, e.g., $Fe_{80}B_{20}$,[15] $Fe_xNi_{80-x}P_{14}B_6$ $(0 \leq x \leq 80)$,[16] and $Fe_{40}Ni_{40}P_yB_{20-y}$ $(0 \leq y \leq 20)$. Although the *P*(*H*) of these samples differs from composition to composition, they are generally well defined single-maximum functions of *H*. More importantly, *none* of these samples with comparable compositions shows the anomalous features exhibited by 2826-*A*. One is therefore led to conclude that the unusual behavior is closely related to the presence of Cr in 2826-*A*. It is particularly fruitful to compare the *P*(*H*) of 2826-*A* with those of other amorphous Fe-Ni-P-B samples with similar compositions and with no Cr. This is shown in Fig. 7, in which the field distributions of 2826-*A* and $Fe_{45}Ni_{35}P_{14}B_6$ at 4.2 K are compared. To facilitate better comparison, the oscillations at the high-field side due to the truncated Fourier analysis have been removed. From Fig. 7 one notes that the high-field component of 2826-*A*, except for a slight shift to smaller *H* values, roughly coincides with the *P*(*H*) of $Fe_{45}Ni_{35}P_{14}B_6$. However, the low-field component of 2826-*A* is not observed in $Fe_{45}Ni_{35}P_{14}B_6$ at all. From this comparison it is reasonable to associate the low-field component of 2826-*A* with those Fe atoms that have a substantial number of Cr neighbors. The high-field component of 2826-*A* is due to those Fe atoms that have primarily Fe, Ni, and possibly some Cr as their neighbors.

To our knowledge there exist no neutron diffraction studies on amorphous 2826-*A*. However, the broad distribution of *P*(*H*) in 2826-*A* suggests a wide distribution of magnetic moments. The appreciable population of very small *H* values in the *P*(*H*) of 2826-*A* indicates the existence of a substantial number of weakly coupled or very small Fe moments. These quasifree moments would then contribute to a high-field magnetic susceptibility as if it had originated from the paramagnetic species. This has indeed been observed in magnetic measurements even at $T \ll T_C$.[5]

The temperature dependence of *P*(*H*) can be more quantitatively described by the peak values and the widths of *P*(*H*). There are two peak values $[(H_{\text{peak}})_1$ and $(H_{\text{peak}})_2]$ and two widths $[(\Delta H)_1$ and $(\Delta H)_2]$, corresponding to the low-field and the high-field components of *P*(*H*), respectively. These values are shown in Fig. 8 as functions of temperature. Of these values, the value of $(H_{\text{peak}})_2$ is most reliable. The values of $(H_{\text{peak}})_1$, especially at T close to T_C, tend to be overestimated because of the assumption of no quadrupole interaction. Due to the substantial overlap of the two components at T close to T_C, the values of $(\Delta H)_1$ and (ΔH_2) are also more

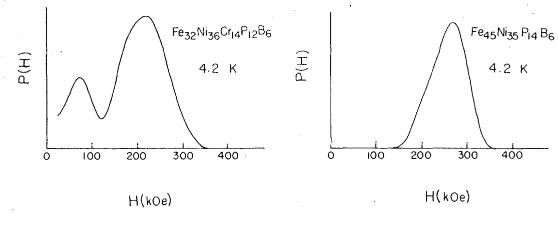

FIG. 7. Hyperfine-field distributions of 2826-A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) and $Fe_{45}Ni_{35}P_{14}B_6$ at 4.2 K.

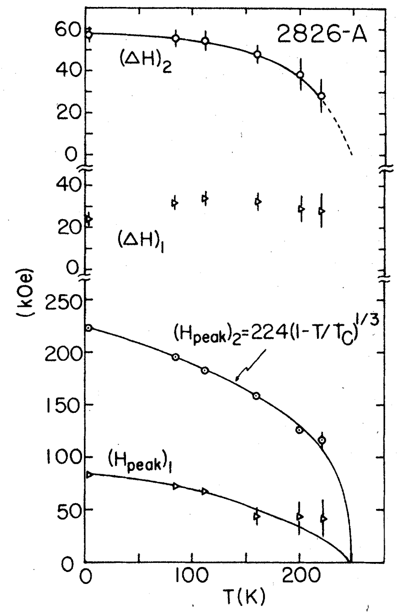

FIG. 8. Temperature dependence of H_{peak} and ΔH, the peak values and width of $P(H)$ of 2826-A. The indices 1 and 2 refer to the low-field and the high-field components, respectively.

difficult to determine.

The peak value of the high-field component $[(H_{peak})_1]$ decreases with T as expected. Its temperature dependence can be *empirically* described by a power law of

$$(H_{peak})_2 = 224(1 - T/T_C)^{1/3} \text{ kOe},$$

as shown by the solid curve in Fig. 8. However, such a power law is generally observed in magnetic system only near the ordering temperature (T_C). It is surprising that such a relation describes the data for the *entire* temperature range. It should be noted that a similar power law relation is also observed in crystalline Fe-Cr alloys, as recently reported.[17]

The temperature dependence of the hyperfine field of an Fe atom reflects the exchange interaction experienced by the Fe atom. Since a well-defined magnetic ordering temperature is shared by all sites and if these sites have the same temperature dependence, then the width of $P(H)$ should decrease with increasing temperatures. This has been observed in amorphous $Fe_{80}B_{20}$, for example.[15] On the other hand, if various Fe sites have rather different temperature dependences, then as T approaches T_C the width of $P(H)$ would be likely to increase.[18] In the case of amorphous 2826-*A*, as shown in Fig. 8, the width of the high-field component $(\Delta H)_2$ is steadily decreasing Thus, various H values in the high-field component have nearly the same temperature dependence as described by that of $(H_{peak})_2$. This perhaps is not too surprising, since the average exchange interactions between Fe and Fe and those between Fe and Ni have been indicated to be ferromagnetic and comparable.[2,3] The width of the low-field component $(\Delta H)_1$ appears to be roughly temperature independent, as shown in Fig. 8. This feature, however, is not conclusive because of the difficulty in ascertaining the shape of the low-field component, as mentioned above. Since the exchange interaction between Cr and Fe is likely to be antiferromagnetic,[19,20] the temperature dependence of $(\Delta H)_1$ may indeed be unusual.

As shown in Fig. 4, the shape of $P(H)$ of 2826-*A* is apparently temperature dependent. Specifically, the proportion of the high-field to the low-field component appears to be monotonically varying with temperatures. However, part of this apparent change is an artifact due to the increasing amount of overlap between the two components and the fact that $H=0$ kOe is the lowest limit. We have earlier identified the two components as Fe with dissimilar neighbors. It is likely that the effective f factors are different for the two components. This would account for the change of the shape of $P(H)$ at various temperatures.

Finally, like most amorphous magnetic solids, amorphous 2826-*A* exhibits a Kondo-type resistivity minimum except with a very larger value of $T_{min} = 270$ K at which the resistivity minimum occurs.[6] Most surprisingly, after crystallizing the sample at temperatures up to 1073 K, the resistivity minimum is reduced but is still present.[7] The present work shows that in both the amorphous state and the crystalline state of 2826-*A* there are a sizable number of Fe atoms that are weakly coupled. Thus the resistivity anomaly in 2826-*A* seems to agree more favorably with the model of conduction-electron scattering by weakly coupled moments as proposed by Tsuei *et al.*,[21,22] than with the model of amorphous structure as proposed by Cochrane *et al.*[6]

V. CONCLUSIONS

An anomalous behavior in the magnetic hyperfine interaction has been observed in a Cr-containing sample of amorphous $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$. The field distribution $P(H)$ exhibits a two-maxima function of H instead of a single-maximum function as usually observed in amorphous Fe-Ni-P-B samples. It is concluded that the extra low-field component originates primarily from the Fe atoms that have some Cr neighbors. It may be particularly interesting to study transition-metal-based amorphous systems that contain various amounts of Cr. This would allow one to study systematically the unusual role played by the Cr atoms. Because of the likelihood of an antiferromagnetic exchange interaction between Cr and Fe, these systems are particularly interesting for their magnetic properties.

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[1] See, e.g., *Amorphous Magnetism II*, edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977).

[2] J. J. Becker, F. E. Luborsky, and J. L. Walter, IEEE Trans. Magn. 13, 988 (1977).

[3] C. L. Chien, D. P. Musser, F. E. Luborsky, J. J. Becker, and J. L. Walter, Solid State Commun. 24, 231 (1977).

[4] J. Durand, in Ref. 1, p. 305.

[5] E. Figueroa, L. Lundgren, D. Beckman, and S. M. Bhagat, Solid State Commun. 20, 961 (1976).

[6] R. W. Cochrane, R. Harris, J. O. Strom-Olsen, and M. J. Zuckermann, Phys. Rev. Lett. 35, 676 (1975).

[7] R. W. Cochrane and J. O. Strom-Olsen, J. Phys. F 7, 1799 (1977).

[8] C. L. Chien and R. Hasegawa, Phys. Rev. B 16, 2115 (1977).

[9] C. L. Chien, J. Hyperfine Int. 4, 869 (1978).

[10] See, e.g., N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy* (Chapman and Hall, London, 1977).

[11] C. L. Chien and R. Hasegawa, Phys. Rev. B 16, 3024 (1977).

[12] A. T. Aldred, Phys. Rev. B 14, 219 (1976).

[13] B. Window, J. Phys. E 4, 401 (1971).

[14] C. C. Tsuei and H. Lilienthal, Phys. Rev. B 13, 4899 (1976).

[15] C. L. Chien, Phys. Rev. B 18, 1003 (1978).

[16] C. L. Chien, D. Musser, F. E. Luborsky, and J. L. Walter, J. Phys. F 8, 2407 (1978).

[17] R. Nemanich, C. W. Kimball, B. D. Dunlap, and A. T. Aldred, Phys. Rev. B 16, 124 (1977).

[18] V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Lett. 13, 752 (1964).

[19] C. G. Shull and M. K. Wilkinson, Phys. Rev. 97, 304 (1955).

[20] A. T. Aldred, B. D. Rainford, J. S. Kouvel, and J. J. Hicks, Phys. Rev. B 14, 228 (1976).

[21] C. C. Tsuei and R. Hasegawa, Solid State Commun. 7, 1581 (1969).

[22] R. Hasegawa and C. C. Tsuei, Phys. Rev. B 2, 1631 (1970).