JOURNAL OF SOLID STATE CHEMISTRY 63, 16–22 (1986)

# Mössbauer Studies of $Fe_{1-x}M_xBO_3$ ($x = 0, 0.1$; $M = Al^{3+}, Ga^{3+}, Cr^{3+}$) close to the $T_c$

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Received June 17, 1985; in revised form October 3, 1985

The results of a Mössbauer study on the effect of substitution of $Al^{3+}$, $Ga^{3+}$, and $Cr^{3+}$ in ferromagnetic $FeBO_3$ close to the $T_c$ are presented. The Curie temperatures of $FeBO_3$, $Fe_{0.9}Al_{0.1}BO_3$, $Fe_{0.9}Ga_{0.1}BO_3$, and $Fe_{0.9}Cr_{0.1}BO_3$ have been determined to be 352, 317, 319, and 335 K, respectively. "Anomalous" spectra have been found to appear just 1° below the $T_c$ for $FeBO_3$, but 15° below the $T_c$ for substituted borates. The inadequacy of static models in explaining these spectra has been pointed out. These spectra have been simulated using relaxation models and estimates of activation energy obtained for spin–flip processes. The results are attributed to dominant superparamagnetic relaxation effects due to the presence of clusters. Mössbauer spectra of $FeBO_3$ substituted by a magnetic ion, viz., $Cr^{3+}$, are found to differ significantly from those of the above-mentioned samples.

## Introduction

Attempts to understand situations giving rise to "anomalous" Mössbauer spectra exhibiting a superposition of "magnetic" and "paramagnetic" profiles have been made both from theoretical and experimental points of view (*1–11*). These studies of magnetically ordered materials have been made mainly on oxide systems such as the ferrites, where the preparatory techniques introduce nonstoichiometry and inhomogeneity. $FeBO_3$ and substituted $FeBO_3$, on the other hand, can be prepared in good purity and stoichiometry as the method involves the use of $B_2O_3$ as flux. The system permits a close comparison of the parent and solid solutions. The other noteworthy features for the selection of $FeBO_3$ are (i) it has a single site and therefore gives a simple Mössbauer spectrum (*12*), (ii) it has a convenient Curie temperature of 348 K and measurements can be made without difficulty near $T_c$ (*13*), and (iii) it is a material with potential magnetooptic applications (*14–16*). In this paper we present the results of our Mössbauer studies on $FeBO_3$ and the solid solutions $Fe_{0.9}M_{0.1}BO_3$ ($M$ = Al, Ga, Cr) close to their Curie temperatures. An attempt is made to computer simulate the spectra employing (i) the static model of Coey and co-workers (*17, 18*) and (ii) relaxation models due to Blume and Tjon (*1*), Dattagupta (*3*) and van der Woude and Dekker (*4*). Relaxation phenomena have been theoretically handled at various levels of approximations by different authors. We have used the relatively simple treatment due to the above-mentioned authors, who employ the random frequency modulation theory and consider the spin state to vary between two levels. The models are shown to account well for the experimental observations. The results

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0022-4596/86 $3.00

for the parent compound were compared with those for solid solutions and estimates of activation energies for the spin–flip processes in the substituted $FeBO_3$ were obtained. Differences between the spectra for substitution of diamagnetic and magnetic ions are reported. In the course of our work a related study on $Fe_{1-x}Cr_xBO_3$ ($x = 0.11$, 0.5) was reported by Ruckman *et al.* (*19*).

## Experimental

$FeBO_3$ and the solid solutions $Fe_{0.9}M_{0.1}BO_3$ ($M$ = Al, Ga, and Cr) were prepared according to the method of Muller *et al.* (*20*). Stoichiometric amounts of metal nitrates were dissolved with 400% excess $H_3BO_3$ in hot deionized water. A small amount of $LiNO_3$, preferably 5 moles for every 50 moles of ferric nitrate, was added to this solution. After the solution was evaporated to dryness, the resultant material was mixed thoroughly under acetone and heated in a platinum crucible at 500°C for 4 hr and at 810°C for 2 days. After the material was cooled to room temperature it was dissolved in deionized water to remove excess $B_2O_3$, separated, and dried under vacuum.

X-Ray powder diffractograms of $FeBO_3$ and its solid solutions confirmed the formation of these compounds and the absence of starting materials as impurities (*20*). The photoacoustic and infrared spectra of these samples were found to agree quite well with those reported (*14, 21*). Mössbauer spectra showed the absence of $Fe_2O_3$, $Fe_3BO_6$, and any other iron-bearing materials.

The Mössbauer measurements were carried out as reported earlier (*22*).

## Results and Discussion

### (*i*) $FeBO_3$

Mössbauer spectra of $FeBO_3$ have been recorded in the temperature range 80–352 K. The room temperature spectrum gave rise to relative intensities of 3 : 3 : 1 : 1 : 3 : 3 which may be compared with those reported for the single crystal, viz., 3 : 4 : 1 : 1 : 4 : 3, in the study pertaining to determination of critical exponent and magnetic parameters from spin wave theory (*13, 23*). That the relative intensities are close to those obtained for the single crystal indicates strong anisotropy in the system under investigation. The anisotropy may arise due to preferred orientation of the microcrystallites, texture effects, or anisotropy in the recoilless fraction. Pronounced anisotropy in this system is also evident in the observation of an asymmetric doublet with narrow linewidth ($\approx$0.33 mm/sec) even at 400 K, much higher than the $T_c$ (352 K). Mössbauer spectra recorded close to the $T_c$ for the powder sample also showed similarities with those of Eibschutz *et al.* (*13*). The profiles were found to be quite characteristic of time-dependent relaxation effects. These spectra were analyzed using Blume and Tjon's relaxation model (*1*). The theoretical spectra thus obtained are compared with experimental spectra measured between 350 and 352 K in Fig. 1.

### (*ii*) $Fe_{0.9}Al_{0.1}BO_3$

Mössbauer spectra of 10 metal atom percent $Al^{3+}$ substituted $FeBO_3$ have been recorded from 80 to 317 K. The low-temperature spectra showed no anomalous features. However, spectra measured from 305.5 to 317 K clearly exhibited profiles typical of the time-dependent hyperfine field.

Unlike the case of $FeBO_3$, the spectra for the diamagnetically substituted system, such as in the present case, can also be accounted for in the light of Coey's model, which takes into account the probabilities of different coordinations due to substitution and the consequent distributions in the hyperfine field (*17, 18*). With this view in mind, attempts were made in this case to

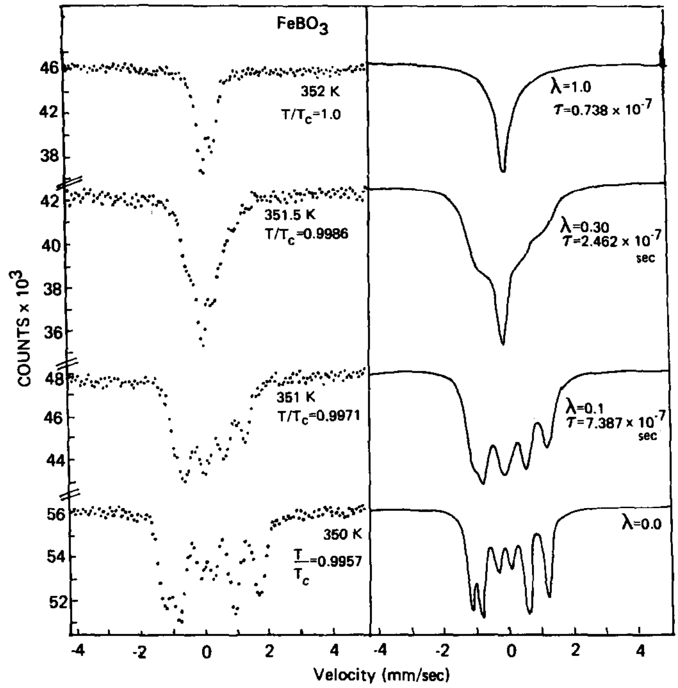

FIG. 1. Comparison of experimental spectra of $FeBO_3$ close to the $T_c$ with theoretical spectra based on relaxation effects of Blume and Tjon's model (*1*).

simulate the spectra for $Fe_{0.9}Al_{0.1}BO_3$ in octahedral symmetry. It was found, however, that the theoretical spectra based on this model agreed poorly with experimental observations.

Attempts to simulate the theoretical spectra employing the relaxation model of Blume and Tjon (*1*) showed that unlike the parent $FeBO_3$ the profile of the experimental spectra could not be reproduced in these cases. Hence we tried the model of van der Woude and Dekker (*4*), which is basically the same as that of Blume and Tjon (*1*) but includes an order parameter, $\eta$ $(0 < \eta < 1)$, which differentiates the probability of spins being present up or down. Theoretical spectra obtained using the latter model are compared with experimental spectra in Fig. 2. The theoretical profiles show good agreement with the measured spectra. Spectra recorded at 317 K and above were found to be doublets with linewidths typical of paramagnetic spectra. The spectra, however, showed unequal intensities for the doublet. For this system an estimate of the activation energy of $9.936 \times 10^{-13}$ erg deg$^{-1}$ is obtained for the spin–flip process using the expression

$$\Omega = \Omega_0 e^{-E_a/kT}$$

where $E_a$ is the activation energy for the spin–flip process.

### (*iii*) $Fe_{0.9}Ga_{0.1}BO_3$

Mössbauer spectra of $Fe_{0.9}Ga_{0.1}BO_3$ recorded in the range 80–320 K showed features similar to those of $Fe_{0.9}Al_{0.1}BO_3$. The theoretical spectra simulated on the basis of the relaxation model of van der Woude and Dekker (*4*) showed good agreement with experimental spectra (Fig. 3). Line profiles of spectra recorded at and above 319 K indicated that the $T_c$ for this sample is 319 K. An estimate of the activation energy of

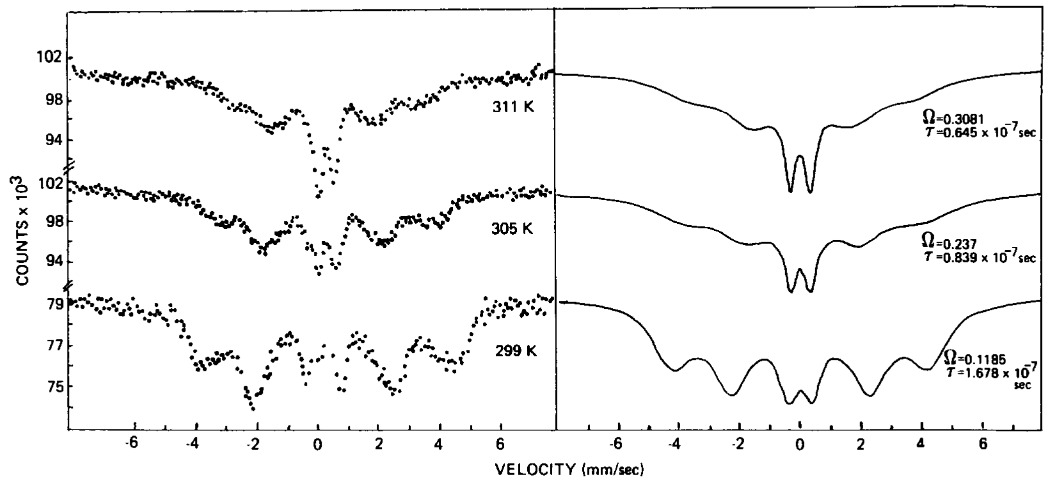

FIG. 2. Comparison of experimental spectra of $Fe_{0.9}Al_{0.1}BO_3$ close to the $T_c$ with theoretical spectra based on relaxation effects of van der Woude and Dekker's model (*4*).

$5.87 \times 10^{-13}$ erg $deg^{-1}$ was obtained in this case and is nearly the same as that found for $Fe_{0.9}Al_{0.1}BO_3$.

### (*iv*) $Fe_{0.9}Cr_{0.1}BO_3$

Mössbauer spectra of $Fe_{0.9}Cr_{0.1}BO_3$ were recorded in the range 80–335 K. Spectra recorded at and above 335 K showed that the $T_c$ for this sample is 335 K. Spectra recorded far from the $T_c$ were similar to those of the parent and other solid solutions. However, those recorded close to the $T_c$, reproduced in Fig. 4, showed significant differences from those of both the parent and the $Ga^{3+}$ and $Al^{3+}$ substituted systems, particularly in the region −2 to +2 mm/sec. Attempts to simulate these experimental spectra using the relaxation models which

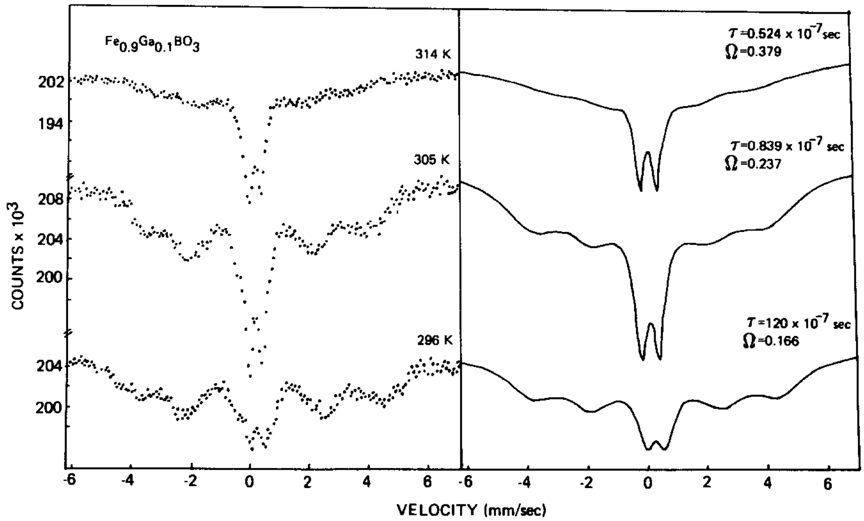

FIG. 3. Comparison of experimental spectra of $Fe_{0.9}Ga_{0.1}BO_3$ close to the $T_c$ with theoretical spectra based on relaxation effects of van der Woude and Dekker's model (*4*).

TABLE I

SPIN–FLIP FREQUENCY ($\Omega_s$), CORRELATION TIME ($\tau_s$), AND ACTIVATION ENERGY ($E_a$) FOR THE SPIN–FLIPPING PROCESS FOR 10% $Ga^{3+}$ AND $Al^{3+}$ SUBSTITUTED $FeBO_3$

| Compound | Temperature (K) ±1 | $\Omega_s$ | $\tau_s$ (sec) × $10^7$ | $E_a \times 10^{13}$ (erg degree$^{-1}$) |
|---|---|---|---|---|
| $Fe_{0.9}Ga_{0.1}BO_3$ | 296 | 0.166 | 1.20 | 5.87 |
| | 305 | 0.237 | 0.84 | |
| | 314 | 0.379 | 0.52 | |
| $Fe_{0.9}Al_{0.1}BO_3$ | 299 | 0.118 | 1.678 | 9.93 |
| | 305.5 | 0.237 | 0.84 | |
| | 311 | 0.3081 | 0.64 | |

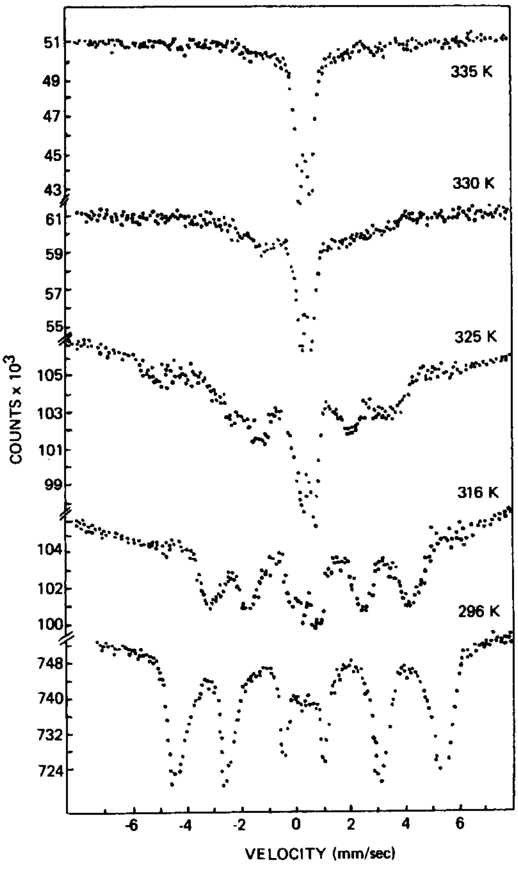

FIG. 4. Mössbauer spectra of $Fe_{0.9}Cr_{0.1}BO_3$ close to the $T_c$.

successfully reproduced spectra for other solid solutions gave unsatisfactory results, particularly in the above-mentioned velocity region.

The Ω values, the spin–flip frequency, $\tau_s$, the correlation time, and the activation energy obtained for $Al^{3+}$ and $Ga^{3+}$ substituted samples are given in Table I. The hyperfine field at 80 K, the lowest temperature measured, the isomer shifts and quadrupole splittings for the spectra measured in the paramagnetic states, and the Curie temperatures for the parent and substituted systems are given in Table II.

Our results show that relaxation effects influence the profiles of the spectra close to the $T_c$. In the case of the parent compound, viz., $FeBO_3$, they become pronounced only very close to the $T_c$ (1° below $T_c$). The data

TABLE II

QUADRUPOLE SPLITTING (QS), ISOMER SHIFT (IS), $H_{eff}$ (80 K), AND $T_c$ VALUES FOR $FeBO_3$ AND $Fe_{0.9}M_{0.1}BO_3$ ($M$ = Ga, Al, AND Cr)

| Compound | QS[a] (mm/sec) ±0.02 | IS[b] (mm/sec) ±0.02 | $H_{eff}$ (80 K) ±2 kOe | $T_c$ (K) |
|---|---|---|---|---|
| $FeBO_3$ | 0.36 | 0.30 | 545 | 352 |
| $Fe_{0.9}Al_{0.1}BO_3$ | 0.45 | 0.28 | 533.5 | 317 |
| $Fe_{0.9}Ga_{0.1}BO_3$ | 0.40 | 0.35 | 530.7 | 319 |
| $Fe_{0.9}Cr_{0.1}BO_3$ | 0.38 | 0.32 | 539 | 335 |

[a] Data for paramagnetic spectra measured above the $T_c$.
[b] Relative to Fe foil, at room temperature.

in this case could be fitted well using the expression of Blume and Tjon (*1*) without invoking the order parameter $\eta$. In the case of the solid solutions pronounced relaxation effects are evident close to the $T_c$ but appear even as far away as 15° below their respective $T_c$'s. In these cases it was found necessary to use the expression of van der Woude and Dekker (*4*) which includes the order parameter, and the value of $\eta$ is significant, i.e., 0.45. The order parameter is proportional to the magnetization. A finite value of $\eta$ thus indicates polarization of the spin states, implying that the collective behavior of the spins has broken down but partial order is present to a significant extent in the solid solutions.

Our observations can be well accounted for in terms of relaxation effects due to superparamagnetic fluctuations (*2*). These effects occur due to the presence of small regions, otherwise called clusters, in a solid which are more magnetic than the rest of the solid. The flip time of the cluster magnetization is given by (*6, 9*)

$$\tau_s = \tau_0 \exp(KV_{eff}/k_BT)$$

where $V_{eff}$ characterizes a spread in effective volume due to the inhomogeneity intrinsic to the substituted materials, $K$ is the anisotropy energy per unit volume, and $k_B$ is the Boltzmann constant. Thus a plot of $\log \tau_s$ vs $1/T$ leads to an estimate of $\tau_0$ which is found to be $5.4 \times 10^{-8}$ and $5.0 \times 10^{-8}$ sec for $Fe_{0.9}Al_{0.1}BO_3$ and $Fe_{0.9}Ga_{0.1}BO_3$, respectively, which is in the order expected for superparamagnetic relaxation effects (*2, 4, 7*). Further, according to the superexchange relaxation model the spin–flip time $\tau_s$ has been shown to decrease with increase in temperature which is found to be the case in our own observations in the systems under investigation (Table I). In the absence of clusters, where the behavior resembles the case of large particle size, anisotropy and hence $kV$ tend to zero and hence the relaxation effects appear only very close to the $T_c$, the phenomenon being referred to as "critical superparamagnetism" (*6*). This happens to be the case for $FeBO_3$ in the present study. On the other hand substitution by nonmagnetic ions such as $Al^{3+}$ and $Ga^{3+}$ causes a significant change in the material, giving rise to clusters with a wider distribution in the value of $V_{eff}$. This, in turn, gives rise to a large relaxation region with the effects seen even up to $(T_c - 15)°$ in solid solutions. Observation of anomalous spectra over a wide range of temperature does not imply a distribution of $T_c$ but does signify a spread in the temperature close to $T_c$ where size effects become important (*6*).

It was found that the line profiles of the solid solution $Fe_{0.9}Cr_{0.1}BO_3$ could not be closely reproduced particularly in the central portion of the spectrum using either of the expressions used for other cases. The influence of substitution by another magnetic ion with a different spin state such as $Cr^{3+}$ may result in observations not easily accounted for (*24–28*).

## Conclusions

A Mössbauer study of $FeBO_3$ and the solid solutions $Fe_{0.9}Ga_{0.1}BO$, $Fe_{0.9}Al_{0.1}BO_3$, and $Fe_{0.9}Cr_{0.1}BO_3$ shows that their Curie temperatures are 352, 319, 317, and 335 K, respectively. A static model such as the one due to Coey is found to be inadequate in explaining the spectra measured close to the $T_c$ in these cases. Relaxation models account well for the profiles close to the $T_c$. Estimates of activation energies for the spin–flip have been found to be $9.93 \times 10^{-13}$ and $5.87 \times 10^{-13}$ erg deg$^{-1}$ for $Fe_{0.9}Al_{0.1}BO_3$ and $Fe_{0.9}Ga_{0.1}BO_3$, respectively. In the parent material, viz., $FeBO_3$, relaxation effects are important only very close to the $T_c$, i.e., 1° below the $T_c$. In the solid solutions relaxation effects dominate even 15° below the $T_c$. It was found necessary to include $\eta$, the order parameter signifying a differentiation in the probabilities of different spin states and a partial order, in the lineshape expression for simulating spectra close to experimentally observed results. The results show that the superparamagnetic relaxation effects due to the presence of clusters produced by substitution of magnetic by nonmagnetic ions are important.

## Acknowledgment

One of us (M.V.) thanks CSIR, New Delhi, for the award of a Senior Research Fellowship.

## References

1. M. Blume and J. A. Tjon, *Phys. Rev.* **165,** 446 (1968).
2. J. K. Srivastava, S. C. Bhargava, P. K. Iyengar, and B. V. Thosar, *in* "Advances in Mössbauer Spectroscopy" (B. V. Thosar, P. K. Iyengar, J. K. Srivastava, and S. C. Bhargava, Eds.), p. 1, Elsevier, New York (1983), and references therein.
3. S. Dattagupta, *in* "Advances in Mössbauer Spectroscopy" (B. V. Thosar, P. K. Iyengar, J. K. Srivastava, and S. C. Bhargava, Eds.), p. 586, Elsevier, New York (1983).
4. F. van der Woude and A. J. Dekker, *Phys. Status Solidi* **9,** 775 (1965).
5. S. Morup, "Paramagnetic and Superparamagnetic Relaxation Phenomenon Studied by Mössbauer Spectroscopy," thesis, Lyngby, Denmark (1981), and references therein.
6. L. M. Levinson, M. Luban, and S. Shtrikman, *Phys. Rev.* **177,** 864 (1969).
7. V. U. S. Rao, F. E. Huggins, and G. P. Huffman, *J. Appl. Phys.* **50,** 2408 (1979).
8. C. M. Srivastava, S. N. Shringi, and R. G. Srivastava, *Phys. Rev. B* **14,** 2041 (1976).
9. R. Nagarajan and J. K. Srivastava, *Phys. Status Solidi B* **81,** 107 (1977).
10. F. van der Woude and A. J. Dekker, *Phys. Status Solidi* **13,** 181 (1966).
11. M. Eibschutz, S. Shtrikman, and D. Treves, *Phys. Rev.* **156,** 562 (1967).
12. R. Diehl, *Solid State Commun.* **17,** 743 (1975).
13. M. Eibschutz, L. Pefiffer, and J. W. Nielsen, *J. Appl. Phys.* **41,** 1276 (1970).
14. A. J. Kurtzig, R. Wolfe, R. C. LeCraw, and J. W. Nielsen, *Appl. Phys. Lett.* **14,** 350 (1969).
15. R. C. LeCraw, R. Wolfe, and J. W. Nielsen, *Appl. Phys. Lett.* **14,** 352 (1969).
16. R. Wolfe, A. J. Krutzig, and R. C. LeCraw, *J. Appl. Phys.* **41,** 1218 (1970).
17. J. M. D. Coey and G. A. Sawatzky, *Phys. Status Solidi B* **44,** 673 (1971).
18. J. M. D. Coey, *Phys. Rev. B* **6,** 3240 (1972).
19. M. W. Ruckman, R. A. Levy, and R. Chennettee, *J. Appl. Phys.* **53,** 1694 (1982).
20. O. Muller, M. P. O'Horo, and J. F. O'Neill, *J. Solid State Chem.* **23,** 115 (1978).
21. J. C. Joubert, T. Shirk, W. B. White, and R. Roy, *Mater. Res. Bull.* **3,** 671 (1968).
22. M. Vithal and R. Jagannathan, *Trans. Met. Chem.* **9,** 73 (1984).
23. M. Eibschutz and M. E. Lines, *Phys. Rev. B* **7,** 4907 (1973).
24. L. M. Corliss, J. M. Hastings, and W. Kunnmann, *Phys. Rev.* **160,** 408 (1967).
25. A. Tauber, W. M. Moller, and E. Banks, *J. Solid State Chem.* **4,** 138 (1972).
26. A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyp. Int.* **1,** 265 (1975).
27. T. Birchall and A. F. Reid, *J. Solid State Chem.* **13,** 351 (1975).
28. J. K. Srivastava and B. W. Dale, *Phys. Status Solidi B* **90,** 391 (1978).