JOURNAL OF MATERIALS SCIENCE 20 (1985) 821–826

Mössbauer study of $Li_{0.5}Fe_{2.5-x}Al_xO_4$: cation distribution and noncollinear spin alignment

S. K. KULSHRESHTHA
Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

G. RITTER
*Physikalische Institut Abt II, Universitat Erlangen Nurnberg, D-8520 Erlangen,
Gluck Strasse 10, West Germany*

Based on ^{57}Fe Mössbauer spectroscopic investigations of $Li_{0.5}Fe_{2.5-x}Al_xO_4$ ($x = 0.3$ and 0.8) conducted at 4.2 K under an external magnetic field of 40 kG, the exact cation distribution has been worked out. Both the compositions show spin canting for the octahedral sites, with the Yaffet Kittle angle $\alpha_{yk} \simeq 20°$ for $x = 0.3$ and $\alpha_{yk} \simeq 27°$ for $x = 0.8$. The Al^{3+} ions show some preference for the octahedral sites but the derived cation distribution is quite different from that reported earlier on the basis of magnetization studies. The reported compensation temperature for $x = 0.8$ has not been observed. The origin of the central quadrupole doublet along with the magnetic sextet and the role of canted spin alignment towards the possible observance of compensation point, are discussed.

1. Introduction

The knowledge of exact cation distribution and spin alignment is essential to the understanding of the magnetic characteristics of spinel ferrites and for the preparation of tailor-made compounds. Diamagnetically substituted lithium ferrite has been investigated by a number of authors [1–8] in attempts to understand the magnetic interactions in spinel lattice, because it contains only one type of magnetic ion, namely Fe^{3+}. The crystallographic and magnetic characteristics of the lithium ferrite aluminate system, $Li_{0.5}Fe_{2.5-x}Al_xO_4$, have been investigated by Schulke and Blasse [8]. Stricker and Roy [9] showed that this system forms a complete solid solution when heated above 1200° C. For low Al^{3+} substitution, $x \leqslant 1.0$, the observed values of the saturation magnetic moment [8] were found to be much smaller than that expected theoretically under the assumption that all Al^{3+} ions occupied the octahedral sites. Depending on the value of x, all types of anomalous magnetization curves predicted by Neel's theory of antiferromagnetism, were observed [8]. For $x = 0.8$, the system showed a compensation point at about $T_{CP} \simeq 0.25\, T_N$, above which the net magnetization was along the octahedral (B) sites; but below T_{CP}, the magnetization direction changed towards tetrahedral (A) site Fe^{3+} moments. Assuming a collinear spin alignment between the octahedral and tetrahedral sites, the Al^{3+} concentration at the tetrahedral sites was estimated to be $\simeq 0.2$ for $x = 1.0$.

Subsequently, based on ^{57}Fe Mössbauer studies of this system, Raj and Kulshreshtha [10] showed that for the Al^{3+} substituted compounds, the observed spectra consisted of a central quadrupole doublet in addition to the broad magnetic sextet arising due to the Fe^{3+} ions present at both sites. The relative intensity of the central doublet was found to increase with increasing Al^{3+} concentration. At room temperature the central doublet was clearly visible even for $x = 0.67$. Based on isometric shift (δ) considerations, the central doublet was attributed to those tetrahedral Fe^{3+} ions which were magnetically isolated and did not participate in the long-range magnetic ordering due

0022–2461/85 $03.00 + .12

to a large number of nonmagnetic nearest neighbours placed at the octahedral sites. It was also shown that for a fixed composition, the relative intensity of the central doublet increased with increase in sample temperature. A semiquantitative interpretation of the relative intensity of this doublet was also given in terms of nearest neighbour magnetic interactions, for $0 \leqslant x \leqslant 1.0$, assuming that all the Al^{3+} ions were present at the octahedral sites.

In the present paper, variable temperature ^{57}Fe Mössbauer effect investigations for two additional compositions ($x = 0.3$ and 0.8) are reported to develop a better understanding of the magnetic characteristics of this system. From the 4.2 K studies of these samples, a number of new observations, such as canted spin alignment, exact Fe^{3+} cation distribution and the temperature and external magnetic field dependence of the central doublet, which shed significant light on the magnetic characteristics of this system, are discussed. The role of Yaffet Kittle angles towards the possible origin of the compensation point is also discussed.

2. Experimental details

The samples were prepared by standard ceramic techniques and were characterized by powder X-ray diffraction using monochromatized Cu$K\alpha$ radiation. All the observed reflections could be indexed in terms of a cubic lattice with $a = 0.8304$ and 0.8230 nm corresponding to $x = 0.3$ and 0.8, resepectively. Mössbauer spectra were recorded using a standard constant acceleration drive coupled with a multichannel analyser. The source used was ^{57}Co in a rhodium matrix and was kept at room temperature. The parameters employed for least square fitting of the Mössbauer spectra consisted of a hyperfine field, an axially symmetric quadrupole interaction, isometric shift, width and intensity corresponding to both the crystallographic sites. The width and intensity of the two inner pairs of the magnetic sextet (say S_2S_5 or S_3S_4) of both the sites were related to the outer pair S_1S_6 in terms of four adjustable parameters. This results in equal width and intensity of the two lines of any pair of a sextet.

3. Results and discussion

^{57}Fe Mössbauer spectra for both compositions were recorded at room temperature, liquid nitrogen temperature and at liquid helium temperature, with and without an external longitudinal magnetic field. For both samples, the spectra recorded at 298 and 78 K showed the existence of a small central quadrupole doublet in addition to the partially resolved magnetic sextet, arising due to the magnetically ordered Fe^{3+} ions at the A and B sites. The fractional intensity of this central doublet was found to be more for $x = 0.8$ compared to that of $x = 0.3$, and showed a definite decrease with decrease in temperature. This is in conformity with the results reported earlier [10] and extends the range of aluminium substitution effects to lower x values. For $x = 0.3$, the central doublet disappeared at 4.2 K, but for $x = 0.8$ it was still visible. However, under the application of an external magnetic field of 20 kG, this doublet disappeared completely. This can be clearly seen from Figs. 1 and 2 where the 4.2 K Mössbauer spectra for $x = 0.3$ and 0.8 are shown for $H = 0$, 20 and 40 kG, respectively. Another observation, which

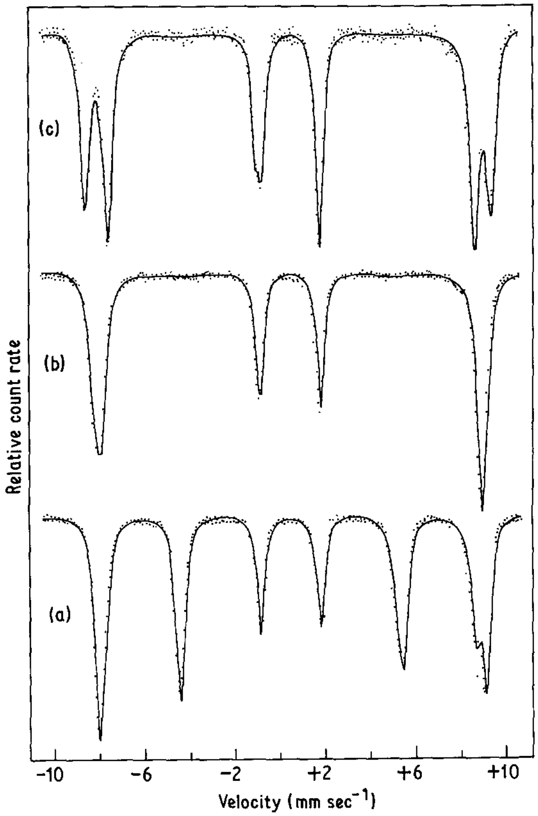

Figure 1 ^{57}Fe Mössbauer spectra of $Li_{0.5}Fe_{2.2}Al_{0.3}O_4$ recorded at 4.2 K with an external longitudinal magnetic field of (a) $H_{ext} = 0$, (b) $H_{ext} = 20$, and (c) $H_{ext} = 40$ kG.

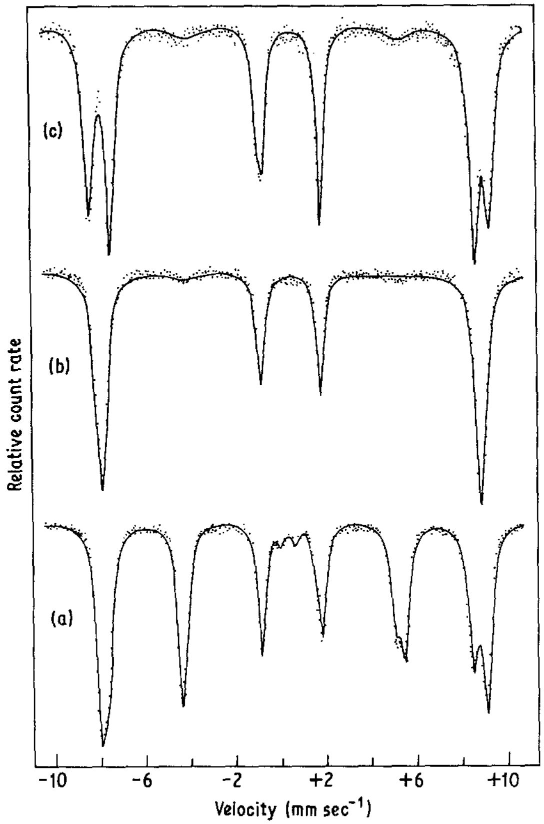

Figure 2 ^{57}Fe Mössbauer spectra of $Li_{0.5}Fe_{1.7}Al_{0.8}O_4$ recorded at 4.2 K under an external longitudinal magnetic field of (a) $H_{ext} = 0$, (b) $H_{ext} = 20$, and (c) $H_{ext} = 40$ kG.

can be made from these figures, is that for $x = 0.8$, the S_2 and S_5 lines which correspond to $\Delta m_I = 0$ transitions, have not disappeared completely under the influence of the external magnetic field. For $x = 0.3$ it is not so clear. This happens because of the existence of spin canting, which we shall prove later from the analysis of observed effective internal hyperfine fields (H_{eff}). The outermost peaks, S_1 and S_6, of both the A and B sites are well resolved for the spectra recorded under 40 kG external magnetic field (H_{ext}).

The results of least square fitting of these spectra are given in Table I. From the table it is clear that, as expected, the values of internal hyperfine field (H_{int}) and isometric shift for the tetrahedral sites are slightly less than those of the octahedral sites. This is in agreement with what has been reported for a number of spinel ferrites [11–13]. The value of the quadrupole shift parameter

$$\epsilon = \frac{e^2qQ}{2}\left(\frac{3\cos^2\theta - 1}{4}\right)$$

was found to be almost zero within experimental error for both sites. This is also a general observation for spinel ferrites, although there exists a finite quadrupole splitting for both octahedral and tetrahedral sites, as can be seen from their paramagnetic state spectra [10, 14]. The reasons for such an observation have been discussed by a number of authors [12, 15]. The other important observation made from this analysis, is that the observed line widths for tetrahedral sites were found to be more than those of the octahedral sites, the effect being more pronounced for $x = 0.8$. This happens because the distribution of hyperfine field values for tetrahedral sites is more, compared to that of the octahedral sites. Since the

TABLE I Mössbauer effect parameters for the $Li_{0.5}Fe_{2.5-x}Al_xO_4$ system

Temp (K)	External field (kG)	Magnetic pattern parameters				Parameters for doublet		$I_{doublet}$
		δ_B* (mm sec^{-1})	δ_A* (mm sec^{-1})	H_B† (kOe)	H_A† (kOe)	δ* (mm sec^{-1})	ΔEq* (mm sec^{-1})	I_{total}
$Li_{0.5}Fe_{2.2}Al_{0.3}O_4$								
298	0	0.34	0.27	512	495	0.22	0.56	0.035
78	0	0.41	0.32	534	512	0.27	0.54	0.020
4.2	0	0.42	0.30	536	513	–	–	–
4.2	20	0.42	0.30	517	534	–	–	–
4.2	40	0.42	0.29	499	554	–	–	–
$Li_{0.5}Fe_{1.7}Al_{0.8}O_4$								
298	0	0.33	0.24	490	459	0.20	0.53	0.052
78	0	0.40	0.28	528	500	0.25	0.57	0.030
4.2	0	0.41	0.28	531	502	0.26	0.61	0.008
4.2	20	0.41	0.29	513	523	–	–	–
4.2	40	0.42	0.29	496	544	–	–	–

*The errors in the estimation are ± 0.02 mm sec^{-1}.
†The errors in the estimation are ± 2.0 kOe.

Al^{3+} ions have a tendency to occupy octahedral sites, the diamagnetic Li^+ and Al^{3+} ions are mainly placed at the octahedral sites and due to the prominent A–B superexchange interaction, the internal hyperfine field at the tetrahedral sites is influenced to a greater extent. For the same reasons, on Al^{3+} substituton the average internal hyperfine field for the tetrahedral Fe^{3+} ions decreases faster as compared to that at the octahedral sites. This is clear from the results listed in Table I and the observed values of the internal hyperfine field for $x = 0.0$, i.e. 537 and 520 kOe, for the octahedral and tetrahedral sites, respectively. In view of the fact that the observed line widths for both the samples are $\simeq 0.5\,\text{mm sec}^{-1}$, no attempt has been made to fit the spectra in terms of near neighbour magnetic ions to obtain the values of super transferred hyperfine fields and near neighbour effects. From the analysis it is also clear that for both compositions the actual decrease in the octahedral site hyperfine field is less than the applied external magnetic field, but for tetrahedral sites, the increase in the hyperfine field value is certainly equal or slightly in excess of the applied field. This implies that at 4.2 K the net magnetization is decided by the octahedral Fe^{3+} ions and there is a definite spin canting for the octahedral Fe^{3+} ions. In fact the positions of residual peaks S_2 and S_5 for $x = 0.8$ in Fig. 2 also correspond to the octahedral sites. For tetrahedral Fe^{3+} ions the spin alignment is parallel to the applied field; the slight excess value of $(H_{\text{eff}}–H_{\text{int}})$ as compared to H_{ext} possibly arises due to the uncertainty in the estimation of H_{int} originating from the significant overlap of the spectra.

The correct Fe^{3+} distribution between the octahedral and tetrahedral sites has been obtained from the analysis of Figs. 1c and 2c where the outermost pair of lines corresponding to both the sites are well resolved. Since the individual areas of both the peaks are comparable and the peaks are reasonably well resolved, the small saturation effects will also be comparable for both sites and can be ignored while calculating the cation distribution. However, an appropriate correction has been made for the residual areas covered by S_2 and S_5 peaks which correspond to the B sites alone. If it can be assumed that (a) all lithium ions, due to their small size, are placed at the octahedral sites, as has been observed from X-ray diffraction [8, 9], neutron diffraction [16], and other studies [17], and (b) the recoil-free fractions for the A and B sites are equal, which has to be particularly true for the 4.2 K studies and has been verified for pure lithium ferrite [18–20] the derived cation distribution can be written as

$$x = 0.3; (Fe_{0.96}Al_{0.04})[Li_{0.5}Fe_{1.24}Al_{0.26}]O_4$$
$$x = 0.8; (Fe_{0.76}Al_{0.24})[Li_{0.5}Fe_{0.94}Al_{0.56}]O_4.$$

This Fe^{3+} cation distribution is different from that derived from magnetization studies. The main cause of this discrepancy lies in the existence of noncollinear spin alignment of the B sites which was not accounted for in the magnetization studies.

In order to obtain an average value of Yaffet Kittle angles, α_{yk}, which the octahedral Fe^{3+} ions make with the net magnetization direction, both the effective hyperfine field and intensity ratios have been used. The resultant hyperfine field in the presence of an external magnetic field can be written as

$$H_{\text{eff}}^2 = H_{\text{int}}^2 + H_{\text{ext}}^2 - 2H_{\text{int}}H_{\text{ext}} \cos \alpha_{yk}.$$

The analysis suggests that for $x = 0.3$ $\alpha_{yk} = (18 \pm 5)^\circ$ and for $x = 0.8$ the value of α_{yk} is $\simeq 27^\circ \pm 5^\circ$. The derived values of α_{yk} for both 20 and 40 kG external magnetic fields are comparable which is also apparent from the intensity of S_2 and S_5 peaks. This is unlike what has been observed for $Ni_{1-x}Zn_xFe_2O_4$ [21] where the value of α_{yk} was found to be external field dependent, particularly for larger H_{ext} values. For $x = 0.8$, the value of α_{yk} has also been estimated from the residual peak intensities of $m_{\text{I}} = 0$ transitions. This value is found to be $(20 \pm 5)^\circ$ which is in reasonable agreement with the value derived from the analysis of observed fields. For $x = 0.3$ the value of α_{yk} could not be estimated from the intensity analysis because of the large uncertainity in its estimation. It is of interest to note that for pure lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$ [2, 3] and $L_{0.5}Fe_{2.3}Sb_{0.2}O_4$ [18–20] the spin canting has not been observed, but as the diamagnetic concentration increases, the spin canting develops as has been observed in the present study and in Zn^{2+}- and Ti^{4+}-substituted systems [4, 7]. This happens because of weakening A–B superexchange interactions.

For diamagnetically substituted ferrites the existence of a central doublet in addition to the well resolved magnetic sextet, has been reported for a number of systems [22–25] but there are many other Zn^{2+}-substituted systems such as

$Ni_{1-x}Zn_xFe_2O_4$ [21, 26] $Co_{1-x}Zn_xFe_2O_4$ [27, 28] $Mn_{1-x}Zn_xFe_2O_4$ [29] where such a doublet has not been observed. The reasons for this inconsistency have not been stressed in either study. It has been stated that the method of preparation is an important factor. In the following discussion we shall try to establish that for the present system this central doublet arises due to the magnetically isolated Fe^{3+} ions located at the tetrahedral sites with a large number of diamagnetic ions as their nearest neighbours and not because of any secondary phase. The only possible impurity phase which can give rise to the central doublet is cubic antiferromagnetic α-$LiFeO_2$ ($T_N \simeq 90°$ K) [30] which could have been produced along with the unreacted α-Fe_2O_3 due to incomplete reaction. The existence of α-$LiFeO_2$ cannot be easily verified from the X-ray diffraction studies as all its intense lines overlap with those of $Li_{0.5}Fe_{2.5}O_4$, however, the room temperature values of isometric shift as reported by Knop *et al.* [31] and Cox *et al.* [30] for α-$LiFeO_2$ are $+0.364$ and $0.35\ \mathrm{mm\,sec^{-1}}$, respectively, with respect to iron metal, which are significantly different from the value of $\delta = +0.21\ \mathrm{mm\,sec^{-1}}$ observed for the central doublet in the present study. In addition the antiferromagnetic α-$LiFeO_2$ should show a paramagnetic doublet at 4.2 K which then changes into a magnetic pattern on application of an external magnetic field. Thus the possibility of α-$LiFeO_2$ is ruled out. It may be pointed out that the value of $\delta = 0.21\ \mathrm{mm\,sec^{-1}}$ for the central doublet is slightly lower than the value of $\delta_A = 0.25$ mm $\mathrm{sec^{-1}}$ derived from the magnetic sextet. This happens because of the large number of Al^{3+} ions as the nearest neighbours for these tetrahedral Fe^{3+} ions. It may be noticed that the reported value [32] of δ_A for Fe^{3+} ions in ^{57}Fe-doped $L_{0.5}Al_{2.5}O_4$ at room temperature is $0.18\ \mathrm{mm\,sec^{-1}}$ with respect to iron metal. The origin of this doublet cannot be visualized in terms of fine particles, as in that case the value of δ should have been the weighted average of δ_B and δ_A with a finite line broadening due to the slight difference in the values of δ and ΔE_Q of the two sites. This is unlike the observations. Under these preparation conditions it is not possible to obtain fine particles ($\simeq 15$ nm) so as to give rise to the superparamagnetically relaxed Mössbauer pattern. For normal superparamagnetic relaxations in the absence of an external magnetic field [26], the number of lines does not exceed more than six for any value of superparamagnetic relaxation frequency. The very fact that the relative intensity of this doublet is a function of composition, temperature and applied external magnetic field as seen from the present and previously reported results [10], implies that it is an inherent property of this system which forms a complete solid solution. The interpretation given earlier is correct. A similar explanation was favoured by Coey [33] of the central doublet in Rare Earth iron garnets, where part of iron is replaced by diamagnetic Ca^{2+} and Sc^{4+} ions. Some authors [24] have proposed that for such a system where a central quadrupole in addition to magnetic sextet is seen, there are two types of spin–spin relaxation smaller magnetic clusters relaxing at a faster rate to give the central doublet, without going into the details of isomeric shift differences as observed in the present study.

The question arises as to why the central loublet for other systems, such as $Ni_{1-x}Zn_xFe_2O_4$ [21, 24, 34], $Co_{1-x}Zn_xFe_2O_4$ [27, 28], $Mn_{1-x}Zn_xFe_2O_4$ [29], etc, are not observed. The possible reason for this is that for all these systems the diamagnetic Zn^{2+} ions are at the tetrahedral sites and, according to this explanation, it is expected that some of the B site Fe^{3+} ions which have large numbers of Zn^{2+} as their nearest neighbours, should have shown the central doublet. However, owing to the fact that each B site Fe^{3+} ion has only six A site ions as its nearest neighbours at a distance of $0.414a$, and the six other nearest neighbours placed actually at the B sites at a distance of $0.353a$, so for such diamagnetically substituted systems the B–B interaction also plays a significant role in addition to the A–B superexchange interaction. This is why these B site Fe^{3+} ions are not magnetically isolated to that extent and contribute to the long-range magnetic ordering, thereby not exhibiting a central doublet well below their magnetic transition temperature. However, close to T_N some of these systems do show the additional central doublet.

From analysis of the 4.2 K data, it is clear that for $x = 0.8$, the net magnetization is along the octahedral sites. The variable temperature magnetic permeablility studies of this sample measured by the a.c. induced method, did not reveal the existence of any compensation temperature. This is unlike the results reported by Schulks and Blasse [8] on the basis of magnetization studies for the same composition. A possible explanation for this discrepancy is suggested below. The amount of

Fe^{3+} on octahedral sites is certainly more than at the tetrahedral sites ($Fe^{3+}_{oct} = 0.94$ and $Fe^{3+}_{tet} = 0.76$), however, due to the existence of $\alpha_{yk} \simeq 27°$ the net magnetization for the octahedral sites is reduced by a factor of $\cos \alpha_{yk} \simeq 0.89$, the octahedral site moment is therefore little more than that of the tetrahedral sites for our samples. It is well known that the cation distribution, and thus also the value of α_{yk} and its temperature dependence, can be slightly affected by the extent of heat treatment, and possibly the sample of Schulke and Blasse [8] had more Fe^{3+} at the tetrahedral sites so as to show the compensation behaviour.

New features, such as the existence of canted spin alignment, the exact cation distribution, the possible explanations for the origin of central quadrupole doublet along with the magnetic sextet and the compensation temperature, etc, have been reported in this study for the first time for the lithium ferrite aluminate system. It is also clear from our work that the observed low value of saturation magnetic moment arises due to spin canting, and not because of the existence of paramagnetic Fe^{3+} centres, which would tend to increase the observed magnetic moment along the octahedral sites.

References

1. J. L. DORMANN, *J. de. Phys.* **41** (1980) 175.
2. C. R. ABEDELO and R. B. FRANKEL, *ibid.* **38** (1977) 135.
3. M. KONWICKI and S. MAKOLAGWA, *ibid.* **38** (1977) 271.
4. M. ROSENBERG, P. DEPPE, S. DEY and U. JANSON, *I.E.E.E. Trans. Mag.* **18** (1982) 1616.
5. J. W. YOUNG and J. SMIT, *J. Appl. Phys.* **42** (1971) 2344.
6. G. F. DIONNE, *ibid.* **45** (1974) 3621.
7. S. M. ZHILYAKOV, V. V. IVOLGA, V. I. MAL'TSER and E. P. NAIDEN, *Sov. Phys. Solid State* **19** (1977) 1817.
8. J. A. SCHULKE and G. BLASSE, *J. Phys. Chem. Solids* **24** (1963) 1651.
9. D. STRICKER and R. ROY, *J. Amer. Ceram. Soc.* **44** (1961) 225.
10. P. RAJ and S. K. KULSHRESHTHA, *J. Phys. Chem. Solids* **31** (1970) 9.
11. F. VANDER WOUDE and G. A. SAWATZKY, *Phys. Rev. B* **4** (1971) 3159.
12. J. M. DANIEL and A. ROSENCWAIG, *Can. J. Phys.* **48** (1970) 381.
13. G. A. SAWATZKY, F. VANDER WOUDE and A. H. MORRISH, *Phys. Rev.* **187** (1969) 747.
14. O. A. BAYUKOV, A. I. DROKIN, V. P. I. KONNIKOV, M. I. PETROV and K. N. SELEZNEV, *Sov. Phys. Solid State* **13** (1972) 2803.
15. H. B. MATHUR, A. P. B. SINHA and C. M. YAGNIK, *Ind. J. Pure Appl. Phys.* **5** (1967) 115.
16. E. PRINCE, *J. de Phys.* **25** (1964) 503.
17. G. A. PETRAKOVSTA and E. M. SOMOKOTIN, *Sov. Phys. JETP* **26** (1968) 718.
18. K. I. ARAI and N. TSUYA, *J. Phys. Soc. Japan* **33** (1972) 1581.
19. G. F. DIONNE, *J. Appl. Phys.* **40** (1969) 4486.
20. B. J. EVANS and L. J. SWARTZENDOUBE, *ibid.* **42** (1971) 1628.
21. S. C. BHARGAVA and N. ZEMAN, *Phys. Rev. B* **21** (1980) 1726.
22. E. De GRAVE, R. VANLEERBERGHE, G. DAUWE, A. GOVAERT and J. De SITTER, *J. de Phys.* **37** (1976) 97.
23. E. D. GRAVE, D. CHAMBAERE and G. ROBBERRECHT, *J. Mag. Magn. Mater.* **15-18** (1980) 643.
24. J. L. DORMANN, D. FIORANI and S. VITICOTE, Proceedings International Conference on Applications of Mössbauer spectroscopy, Jaipur, India (1982) p. 206.
25. J. L. DORMANN, T. MERCERAI and M. NOGUES, *ibid.*, p. 193.
26. S. C. BHARGAVA and N. ZEEMAN, *Phys. Rev. B.* **21** (1980) 1717.
27. S. C. BHARGAVA and P. K. IYENGAR, *Phys Status Solidi B* **46** (1971) 117.
28. *Idem, ibid,* **53** (1972) 352.
29. A. H. MORRISH and P. J. SCHURER, *Physica B* **86-88** (1977) 921.
30. D. E. COX, G. SHIRANE, P. A. FLIN, S. L. RUBY and W. J. TAKAI, *Phys. Rev.* **132** (1963) 1547.
31. O. KNOP, C. AYASSE, J. S. CARLOW, W. W. BORKER, F. W. D. WOODHAMS, R. E. MEADS and W. G. PARKAR, *J. Solid Chem.* **25** (1978) 347.
32. F. De S BARROS, P. J. VICCARS and J. O. ARTMAN, *Phys. Lett.* **27 A** (1968) 374.
33. J. M. D. COEY, *Phys. Rev. B.* **6** (1972) 3240.
34. P. E. CLARK and A. H. MORRISH, *Phys. Status Solidi (a)* **19** (1973) 687.

Received 31 January
and accepted 10 April 1984.