

## Neutron investigation of ferrites

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**Abstract.** This article reviews the work carried out at Trombay in a variety of single and mixed spinel ferrites. The use of polarised neutrons in the elucidation of cation distribution and magnetic structures in powder specimens is emphasised. Magnetic form factor studies in single crystal specimens of  $\text{Fe}_3\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  are described. Evaluation of dominant exchange interactions in a few powder specimens in their paramagnetic phase using the cold neutron scattering technique is described. Measurements of the acoustic magnon dispersion in  $\text{MnFe}_2\text{O}_4$  and  $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$  are outlined.

**Keywords.** Ferrites; neutron diffraction; magnetic structure; spinel ferrites; magnetic form factor; spin density distribution; polarised neutron.

### 1. Introduction

Ferrites constitute an important class of technologically useful ferrimagnetic materials having high permeability coupled with high electrical resistivity. Soft magnetic ferrites (those which are demagnetised at zero field) have many uses in high frequency electrical and electronic devices such as transformers, aerials, dynamos, motors, modulators, amplifiers and as memory elements in earlier computers. Hard magnetic ferrites, on the other hand, find application in devices such as loudspeakers, recording head and magnetic tapes. Most of the soft ferrites belong to the cubic spinel structure (space group  $\text{O}_h^7\text{-F3dm}$ ) in which the magnetic ions occupy two inequivalent lattice sites with tetrahedral (*A*) and octahedral (*B*) oxygen coordination. The magnetic structure of such crystals essentially depends upon the type of magnetic ions residing on the *A* and *B* sites and the strengths of the inter ( $J_{AB}$ ) and intra sublattice exchange interactions ( $J_{AA}$ ,  $J_{BB}$ ) of the *A* and *B* sublattices. Neutron diffraction offers several advantages in the determination of the magnetic properties of spinel ferrites. The marked difference in the nuclear scattering amplitudes of the cations and the interaction of their magnetic moments with the neutron magnetic moment make possible accurate determination of the cation distributions as well as detailed magnetic structure. Dynamical neutron scattering studies, on the other hand, provides crucial information about the strengths of the exchange interactions in these systems. The neutron scattering group at Trombay was one of the earliest groups to have embarked upon a systematic study of a variety of ferrites, single and mixed. Some major contributions in this area will be reviewed. It is well known that the polarised neutron technique is a powerful and indeed a unique tool to probe magnetic moment density distributions in ferro and ferrimagnetic crystals. Such studies carried out at Trombay in the archetypal ferrite,  $\text{Fe}_3\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  will also be briefly described. Some dynamical neutron scattering studies in a few spinels to evaluate exchange interactions will be touched upon. For more details, however, the reader may refer to the original papers cited at the end of this article.

## 2. Magnetic structures of some spinel ferrites determined by polarised and unpolarised neutron diffraction

Elucidation of magnetic structures in ferrites is always preceded by an accurate determination of the cation distribution between the tetrahedral (*A*) and octahedral (*B*) sites. By a fortunate circumstance, the nuclear scattering amplitudes across the transition metal series vary appreciably (and even changes sign as in Mn) as compared to the x-ray scattering amplitudes. Therefore neutron diffraction is more reliable than x-ray diffraction in arriving at the cation distribution. However, the data are often scanty for the complete solution of magnetic structures, especially in the case of the mixed ferrite systems, because of the unavailability of good single crystals. At Trombay, we exploited the technique of polarised neutron diffraction to offset this, and the additional data thus provided have, as shown below, helped in a more accurate and unambiguous determination of the cation distributions and the magnetic structures. Although Takei *et al* (1960) and Satya Murthy *et al* (1969a) did use polycrystalline polarised neutron diffraction earlier to resolve ambiguities of moment orientation in magnetic structures, this was the first systematic use of this technique for magnetic structure determination in ferrites.

In the case of unpolarised neutrons, the Bragg reflection intensity is given by the formula

$$I_{hkl}^0 = \text{constant} \times jL(N^2 + \frac{2}{3}M^2)\exp(-2W), \quad (1)$$

for a cubic crystal with both chemical and magnetic long range ordering, where *j* is the multiplicity of the planes  $\{hkl\}$ , *L* the Lorentz factor, *N* and *M* the nuclear and magnetic structure amplitudes, and  $\exp(-2W)$  the Debye-Waller factor. We have neglected the absorption factor. For polarised neutrons with polarisation parallel (+) and antiparallel (-) relative to the magnetisation of the crystal, on the other hand, the Bragg intensities are given by the formulae

$$I_{hkl}^+ = \text{constant} \times jL(N^2 + M^2 + 2PDNM)\exp(-2W), \quad (2)$$

and

$$I_{hkl}^- = \text{constant} \times jL(N^2 + M^2 - 2PD\overline{2f-1}NM)\exp(-2W). \quad (3)$$

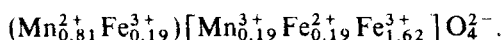
The cross terms in the parenthesis arise from the coherence between the nuclear and magnetic scattering process in the case of polarised neutrons, *P* is the beam polarisation, *D* is the polarisation transmission through the crystal, and *f* is the neutron polarisation reversal efficiency. It is thus seen that using unpolarised and polarised neutron diffraction patterns, the amount of intensity data can be tripled, enabling one to arrive in a self-consistent manner to an accurate determination of cation distribution and magnetic structure factors.

### 2.1 Single ferrites

2.1a *MgFe<sub>2</sub>O<sub>4</sub>*: A detailed neutron diffraction study of *MgFe<sub>2</sub>O<sub>4</sub>* was attempted in view of the fact that two earlier studies (Bacon and Roberts 1953; Corliss and Hastings 1953) did not investigate the migration of Mg ions to the *A* sites as suggested by magnetization studies. The cation distribution was determined at six different temperatures, ranging from liquid nitrogen to 625 K. The results show that the degree of inversion in *MgFe<sub>2</sub>O<sub>4</sub>* is 0.860 and the cation distribution remains unchanged in this

temperature range. The other properties of this ferrite are listed along with those of other ferrites in table 1. The Néel temperature was determined to be  $680 \pm 5$  K.

2.1b  $MnFe_2O_4$ : This ferrite was reported to be 81 % normal by Hastings and Corliss (1956). Harrison *et al* (1958) proposed the following valency formula to explain the observed ferrite moment of  $4.6 \mu_B$ /molecule:



However, Lotgering (1964) studied the electrical conductivity and Seebeck effect in the system  $Fe_3O_4$ - $MnFe_2O_4$ - $Mn_2FeO_4$  and concluded that the presence of  $Mn^{3+}$  ions on the *B* sites in  $MnFe_2O_4$  is very unlikely. In order to throw light on this controversy we used both polarised and unpolarised neutrons to arrive at the following cation distribution in  $MnFe_2O_4$  (Satya Murthy *et al* 1971b):

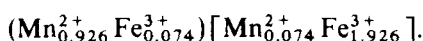


Figure 1 shows the diffraction patterns of  $MnFe_2O_4$  taken with polarised neutrons. These are typical of the patterns that can be obtained with fairly thin samples and the striking difference between the patterns for the two states of neutron polarisation is obvious. The magnetic intensities at each temperature were analysed on a Néel model and the temperature dependence of the magnetic intensities yield 560 K as the transition temperature. The magnetic moment values on the *A* and *B* sites extrapolated to 0 K indicate that Mn is in the divalent state and has nearly the 'spin only' magnetic moment of  $5 \mu_B$ . As we shall see later, the cation distribution established by us in this spinel was useful in the interpretation of the exchange interactions from our spinwave dispersion measurement in  $MnFe_2O_4$ .

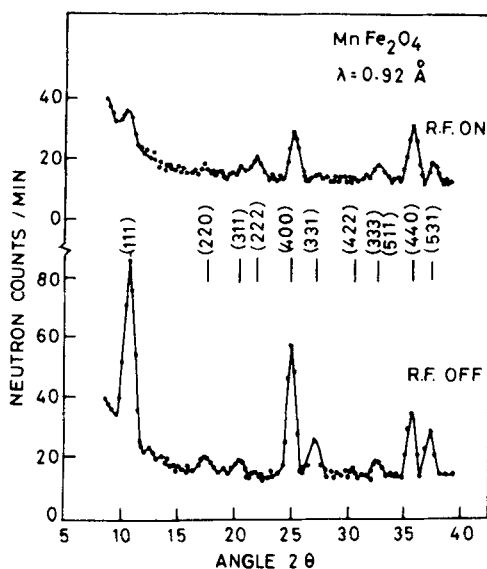


Figure 1. Polarised neutron diffraction patterns of  $MnFe_2O_4$  for the two neutron spin states.

Table 1. Magnetic and structural properties of ferrites

Ferrite	Lattice constant (Å)	Oxygen parameter	Cation distribution		Magnetic moment ( $\mu_B$ ) (300°K)		$T_N$ (°K)	$T_{VK}$ (°K)
			A site	B site	A site	B site		
NiFe <sub>2</sub> O <sub>4</sub>	8.325	0.2573	(Fe <sup>3+</sup> )	[Ni <sup>2+</sup> Fe <sup>3+</sup> ]	4.87	3.48	873	—
MgFe <sub>2</sub> O <sub>4</sub>	8.385	0.2571	(Mg <sup>2+</sup> <sub>1.4</sub> Fe <sup>3+</sup> <sub>0.86</sub> )	[Mg <sup>2+</sup> <sub>0.86</sub> Fe <sup>3+</sup> <sub>1.14</sub> ]	3.89	2.48	680	—
MnFe <sub>2</sub> O <sub>4</sub>	8.525	0.2600	(Mn <sup>2+</sup> <sub>0.926</sub> Fe <sup>3+</sup> <sub>0.074</sub> )	[Mn <sup>2+</sup> <sub>0.074</sub> Fe <sup>3+</sup> <sub>0.926</sub> ]	3.95	3.74	560	—
CoFe <sub>2</sub> O <sub>4</sub>	8.381	0.2568	(Co <sup>2+</sup> <sub>0.118</sub> Fe <sup>3+</sup> <sub>0.882</sub> )	[Co <sup>2+</sup> <sub>0.882</sub> Fe <sup>3+</sup> <sub>1.118</sub> ]	4.31	3.44	790	—
Mg <sub>0.25</sub> Mn <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub>	8.464	0.2592	(Mg <sup>2+</sup> <sub>0.03</sub> Mn <sup>2+</sup> <sub>0.29</sub> Fe <sup>3+</sup> <sub>0.68</sub> )	[Mg <sup>2+</sup> <sub>0.22</sub> Mn <sup>2+</sup> <sub>0.48</sub> Fe <sup>3+</sup> <sub>1.32</sub> ]	4.01	3.36	615	—
Mg <sub>0.5</sub> Mn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	8.450	0.2588	(Mg <sup>2+</sup> <sub>0.09</sub> Mn <sup>2+</sup> <sub>0.387</sub> Fe <sup>3+</sup> <sub>0.523</sub> )	[Mg <sup>2+</sup> <sub>0.41</sub> Mn <sup>2+</sup> <sub>0.113</sub> Fe <sup>3+</sup> <sub>1.477</sub> ]	3.83	3.06	640	—
Mg <sub>0.75</sub> Mn <sub>0.25</sub> Fe <sub>2</sub> O <sub>4</sub>	8.414	0.2581	(Mg <sup>2+</sup> <sub>0.11</sub> Mn <sup>2+</sup> <sub>0.10</sub> Fe <sup>3+</sup> <sub>0.79</sub> )	[Mg <sup>2+</sup> <sub>0.64</sub> Mn <sup>2+</sup> <sub>0.13</sub> Fe <sup>3+</sup> <sub>1.21</sub> ]	3.70	2.81	660	—
Zn <sub>0.25</sub> Ni <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub>	8.346	0.2561	(Zn <sup>2+</sup> <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.75</sub> )	[Ni <sup>2+</sup> <sub>0.75</sub> Fe <sup>3+</sup> <sub>1.25</sub> ]	3.60	3.50	725	300
Zn <sub>0.5</sub> Ni <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	8.374	0.2573	(Zn <sup>2+</sup> <sub>0.5</sub> Fe <sup>3+</sup> <sub>0.5</sub> )	[Ni <sup>2+</sup> <sub>0.5</sub> Fe <sup>3+</sup> <sub>1.5</sub> ]	2.30	2.75	550	400
Zn <sub>0.75</sub> Ni <sub>0.25</sub> Fe <sub>2</sub> O <sub>4</sub>	8.400	0.2598	(Zn <sup>2+</sup> <sub>0.75</sub> Fe <sup>3+</sup> <sub>0.25</sub> )	[Ni <sup>2+</sup> <sub>0.25</sub> Fe <sup>3+</sup> <sub>1.75</sub> ]	1.10	1.30	375	375

2.1c  $\text{CoFe}_2\text{O}_4$ : The unpolarised neutron diffraction work of Prince (1956) on  $\text{CoFe}_2\text{O}_4$  showed it to be completely inverted while the Mössbauer data (Sawatzky *et al* 1968) contradicted this. Our results show that  $\text{CoFe}_2\text{O}_4$  is 88% inverted. This structure was solved using polarised neutrons only (Satya Murthy *et al* 1971a). The fact that the magnetic form factors of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions are appreciably different made it possible to determine the individual magnetic moments of these ions on the *A* and *B* sites and these indicate that the Co moments have a small orbital contribution on both the sites.

2.1d  $\text{NiFe}_2\text{O}_4$ : The nuclear scattering amplitudes of Ni and Fe are very close to each other and hence the cation distribution cannot be ascertained using nuclear intensities alone. Using unpolarised neutrons, Hastings and Corliss (1953) had concluded that the intensities are not sensitive to complete inversion and they could only state that  $\text{NiFe}_2\text{O}_4$  is at least 80% inverted. Our results with polarised neutrons conclusively prove that  $\text{NiFe}_2\text{O}_4$  is a completely inverted spinel (Youssef *et al* 1969). It has been possible to estimate the inversion to within an accuracy of 1% using polarised neutron intensities. Mössbauer data on this ferrite were given (Kedem and Rothen 1967; Chappert and Frankel 1967) conflicting interpretations regarding the collinearity of the moment arrangement in this ferrite. Our results from polarised as well as unpolarised data show clearly that  $\text{NiFe}_2\text{O}_4$  is a collinear ferrimagnet at all temperatures. This was confirmed from the study of the systematics of the Zn-Ni ferrite system as discussed below.

## 2.2 Mixed ferrites

2.2a  $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ : The first neutron diffraction work (Nathans *et al* 1957) on the system with  $x = 0.25, 0.50, 0.75$  and  $0.90$  had been interpreted as showing the cation distribution in the system to be quite regular with about 90% of manganese always going to the *A* site. However the Trombay results (Satya Murthy *et al* 1971b) indicate that the fraction of  $\text{Mn}^{2+}$  ions going to the *A* sites is 38.7%, 77.4% and 40% respectively for  $x = 0.25, 0.50$  and  $0.75$ . Though these values are in direct conflict with the observations of Nathans *et al* (1957) they corroborate the findings of Yamzin *et al* (1962) who investigated the cation distributions in the systems  $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$  and found an anomalous distribution of the Mn and Fe ions over the two sites. Moreover, the Trombay results on the lattice constant and the transition temperature indicate a strong similarity of behaviour and lend strong support to the correctness of the cation distribution obtained. The various parameters of the system as determined in our study are listed in table 1. These were further confirmed from our room temperature data using polarised neutrons on these ferrites.

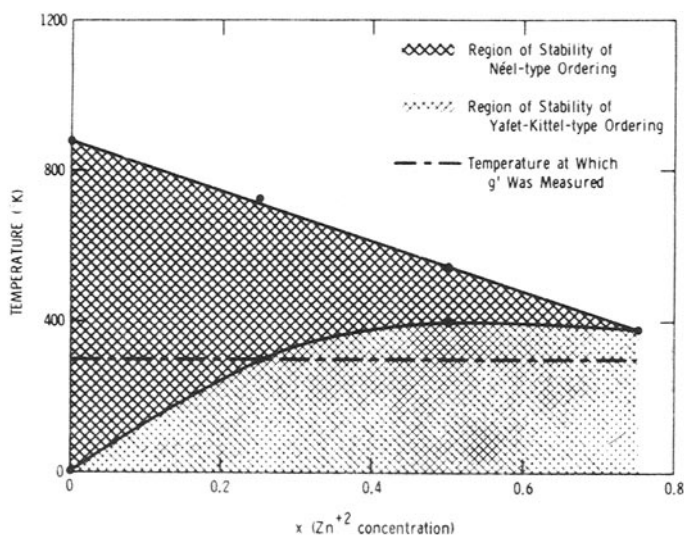
2.2b  $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ : The variations of the net moment as a function of  $x$  in this system were puzzling and had been unsatisfactorily explained by several previous workers (Sobota and Voigtlander 1963; Gilleo 1960). It was shown by the Trombay group from a detailed analysis that some of the intermediate compositions in this ferrite system exhibit the Yafet-Kittel ( $\gamma\text{K}$ ) type of magnetic structure (Satya Murthy *et al* 1969). In such a structure the *B* sublattice moments are split into two groups having equal magnitudes but making angles  $\alpha_{\gamma\text{K}}$  and  $-\alpha_{\gamma\text{K}}$  with the net magnetisation as well as with the *A* site magnetic moment. The salient features of magnetic ordering seen in this ferrite system were as follows: (i) The  $\gamma\text{K}$  angles increase with  $x$  and for a given  $x$

decrease with increasing temperature. It is  $0^\circ$  for  $\text{NiFe}_2\text{O}_4$  and when extrapolated gives a value of  $90^\circ$  for  $\text{ZnFe}_2\text{O}_4$  i.e. predicts a collinear antiferromagnetism for  $\text{ZnFe}_2\text{O}_4$ . (ii)  $\gamma_K$  angles are strongly temperature-dependent and there is a transition from the  $\gamma_K$  to the Néel type before the paramagnetic transition in some cases. The region of Néel configuration decreases with increasing  $x$ . Thus, while  $\text{NiFe}_2\text{O}_4$  has the Néel type of ferri-magnetic arrangement at all temperatures below its  $T_N$ ,  $\text{Zn}_{0.75}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4$  has the Yafet-Kittel type of ordering at all temperatures below its paramagnetic transition. On the other hand,  $\text{Zn}_{0.25}\text{Ni}_{0.75}\text{Fe}_2\text{O}_4$  has the Néel arrangement above 300 K but the Yafet-Kittel arrangement below that temperature. These features are illustrated in figure 2. The observed  $\alpha_{\gamma_K}$ 's were related to the concentration  $x$  and the various molecular field coefficients operative in the system using a three sublattice molecular field theory. From the minimum energy condition, the following expression for  $\alpha_{\gamma_K}$  were obtained:

$$\cos \alpha_{\gamma_K} = \frac{m_A m_{B1} \lambda_{AB1} + m_A m_{B2} \lambda_{AB2}}{2m_{B2}^2 \lambda_{B1B2} + 2m_{B1}^2 \lambda_{B1B2} + 4m_{B1} m_{B2} \lambda_{B1B2}} \quad (4)$$

The relative signs and magnitudes of the various molecular field constants  $\lambda$  were got from the 0 K extrapolated values of  $\alpha_{\gamma_K}$  for the various compositions. The solid lines in figure 3 are the calculated temperature dependence curves using these values. The values of  $\alpha_{\gamma_K}$  along with other parameters are given in table 1.

These results of the Ni-Zn ferrite system were also confirmed using polarised neutrons. In the case of  $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$  the polarised neutron diffraction intensities lead to a room temperature value of  $\alpha_{\gamma_K} = 13^\circ$  which is the same as obtained from the unpolarised case. This incidentally established the applicability of the polarised neutron method even in the case of noncollinear structures provided there is complete saturation of the moments in the field direction.



**Figure 2.** Magnetic order in  $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$  system as determined from neutron diffraction measurements.

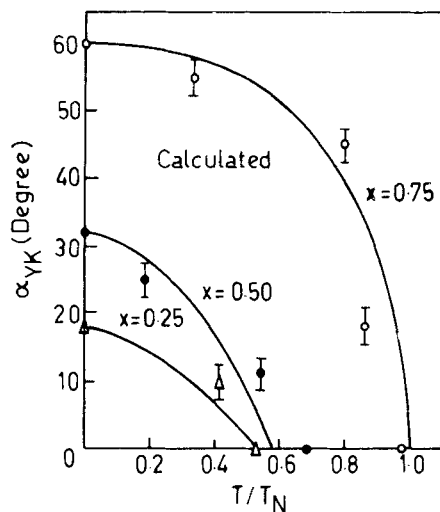


Figure 3. The temperature dependence of the Yafet-Kittel angles in  $Zn_xNi_{1-x}Fe_2O_4$ .

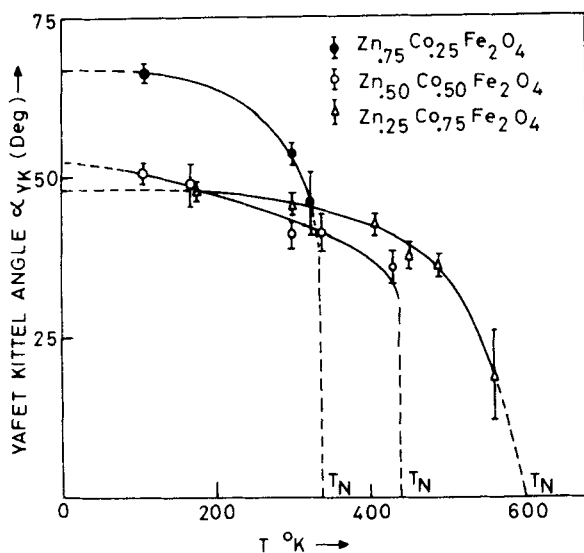


Figure 4. Variation of the Yafet-Kittel angle with temperature in  $Co_xZn_{1-x}Fe_2O_4$  for  $x = 0.25, 0.50$  and  $0.75$ .

2.2c  $Zn_xCo_{1-x}Fe_2O_4$ :  $ZnFe_2O_4$  is a completely normal spinel exhibiting a complicated antiferromagnetic ordering while  $CoFe_2O_4$  on the other hand shows Néel type of magnetic ordering (see table 1) with 88% inversion. Given the strong preference on the  $Zn^{2+}$  ion to occupy the A site it was thought interesting to undertake neutron diffraction studies on the mixed ferrite  $Zn_xCo_{1-x}Fe_2O_4$  for different values of  $x$ . This mixed ferrite system was seen to exhibit a non-collinear, Yafet-Kittel type of spin ordering (Radhakrishnan *et al* 1972). Figure 4 summarises the variation of  $\alpha_{YK}$  with

temperature for this mixed ferrite system. An interesting feature observed here is the absence of a Néel region as in Ni-Zn ferrites.

### 3. Magnetic form factor and spin density distribution in ferrite using polarised neutrons

In the foregoing section, the determination of magnetic structures in powder specimens was discussed in which the role of the polarised neutron was to enhance the quality of the data and thus help in removing any possible ambiguity in deriving the magnitude and orientation of the magnetic moment at the appropriate lattice sites. However, the most powerful use of the polarised neutron beam technique is in the measurement of magnetic form factors and spin density distributions in ferro, ferri and some types of antiferromagnetic materials. The principal motivation in such investigations is to gain a better understanding of solid state electronic wave functions. Using thin single crystal specimens one measures with considerable precision the three-dimensional magnetic structure amplitudes both in magnitude and phase, since as remarked earlier, in this technique one essentially measures the interference between magnetic and nuclear scattering. The data is then analysed in Fourier space (form factor approach) using suitable theoretical models or a Fourier summation with suitable averaging procedures is performed to obtain magnetic moment density contours in various sections of the crystal lattice quite similar to what is done in building electron density maps in x-ray diffraction. The technique and its potentialities have been described in detail elsewhere (Madhav Rao 1980, 1982).

#### 3.1 Ionic systems

Magnetic scattering from ionic crystals is generally discussed in terms of molecular orbitals of transition metal complexes. The ionic wave functions that take part in the bonding are the metal  $3d$  orbitals and the ligand  $2s$  and  $2p$  orbitals.  $\sigma$  bonding occurs between the  $e_g$  metal orbitals and the six  $p$  orbitals while the  $\pi$  bonds are formed between the  $t_{2g}$  metal orbitals and the twelve ligand  $p\pi$  orbitals. We recall that bonding orbitals being predominantly ligand in character are filled and do not directly contribute to magnetic scattering while the antibonding orbitals being predominantly  $d$  in character are the ones responsible for magnetic scattering. As an example of the molecular orbital approach to interpret covalency effects from polarised neutron data, we shall discuss briefly the interpretation of the experiments on single crystals specimens of  $Fe_3O_4$  done at Trombay a few years ago.

3.1a  $Fe_3O_4$ :  $Fe_3O_4$  is an inverted cubic spinel ferrite in which the tetrahedral ( $A$ ) sites are occupied by  $Fe^{3+}$  ions and the octahedral ( $B$ ) sites are randomly occupied at room temperature by  $Fe^{2+}$  and  $Fe^{3+}$  ions. The first polarised neutron study on natural crystal specimens (Srinivasan *et al* 1974) gave evidence of a small moment residing on the oxygen atom near the  $A$  site  $Fe^{3+}$  ion with the magnetisation density of the  $A$  site being more extended than in the free ion  $Fe^{3+}$  case. These experiments were later repeated using much thinner single crystal specimens (to minimise extinction and multiple Bragg effects). Using the form factor approach, attention was specifically focussed on the moment distribution of the  $Fe^{3+}$  ion on the  $A$  site (Rakhecha and



Satya Murthy 1978). The tetrahedral crystal field splits the  $d$  level into two groups but with the  $E$  set lower than  $T_2$ . We recall that in a pure crystal field situation, even in the absence of a centre of symmetry the moment density at  $A$  will remain centrosymmetric (see figure 5), and its form factor will be real. However, when one allows for covalency this is no longer true. The magnetic form factor will have an imaginary component  $f_3(\kappa)$

$$f(\kappa) = f_0(\kappa) - iB(hkl)f_3(\kappa) + A(hkl)f_4(\kappa), \tag{5}$$

where  $f_n(\kappa)$  is defined as

$$f_n(\kappa) = \int_0^\infty [4\pi\rho n(r)]j_n(\kappa r)r^2 dr. \tag{6}$$

The overlap form factors corresponding to a given overlap density were calculated using Slater type orbitals for  $Fe^{3+}$  given by Clementi (1965) and those for  $O^{2-}$  given by Watson (1958). The admixture coefficients which remain as adjustable parameters then determine to what extent the overlap form factors for the  $E^{\pi}$ ,  $T_2^{\sigma}$  and  $T_2^{\pi}$  states

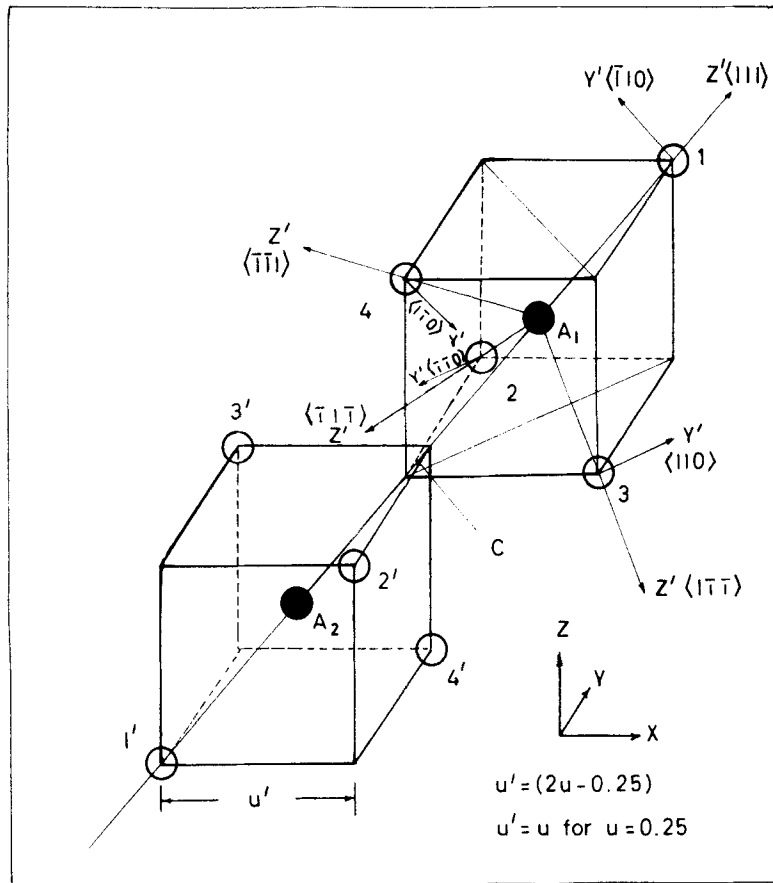


Figure 5. Two neighbouring  $A$  sites in the unit cell, denoted by  $A_1$  and  $A_2$  together with their nearest neighbour oxygen ion tetrahedra.

contribute to the net form factor for the  $A$  site density. The covalency parameters for the  $A$  site were sought by direct comparison of the calculated magnetic structure factors with experimental ones by a least squares procedure. A least squares refinement of these parameters starting from the full temperature corrected moment of  $4.7 \mu_B$  gave values of 0.6, 0.0 and 0.4 for  $A_{\sigma}^T$ ,  $A_{\pi}^T$  and  $A_{\pi}^E$  respectively (see figure 6). These values lead to the conclusion that about 28% of the moment density is transferred from the  $A$  site  $\text{Fe}^{3+}$  ion to the neighbouring four oxygen ligands. To our knowledge, this is the first quantitative evaluation of covalency on a  $\text{Fe}^{3+}$  ion in a tetrahedral environment. The analysis of the  $B$  site magnetisation distribution was less satisfactory since it corresponds to some average of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  distributions. Indeed the NM model was considered to be rather inappropriate for this site owing to the large conduction on these sites. Moreover, groups of reflections to which only the  $B$  site contributes are quite small and weak and could not be measured with the desired precision.

3.1b  $\text{MnFe}_2\text{O}_4$ : Polarised neutron diffraction measurements were carried out on single crystal specimens of  $\text{MnFe}_2\text{O}_4$  to obtain the three-dimensional magnetic structure amplitudes (Srinivasan *et al* 1974; Paranjpe 1980). This study was preceded by

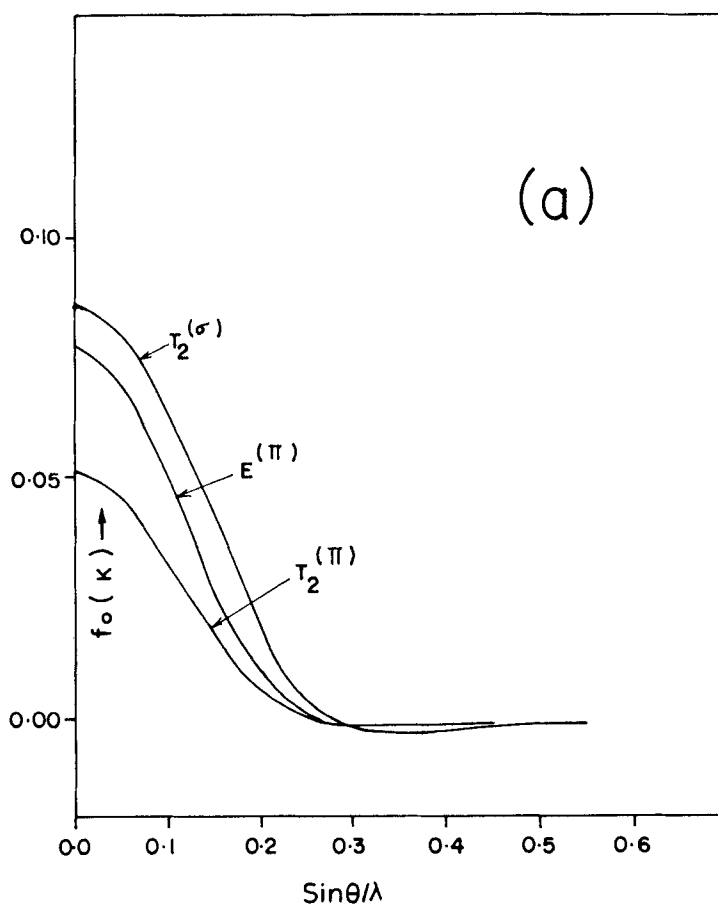


Figure 6(a). For caption, see p. 314.

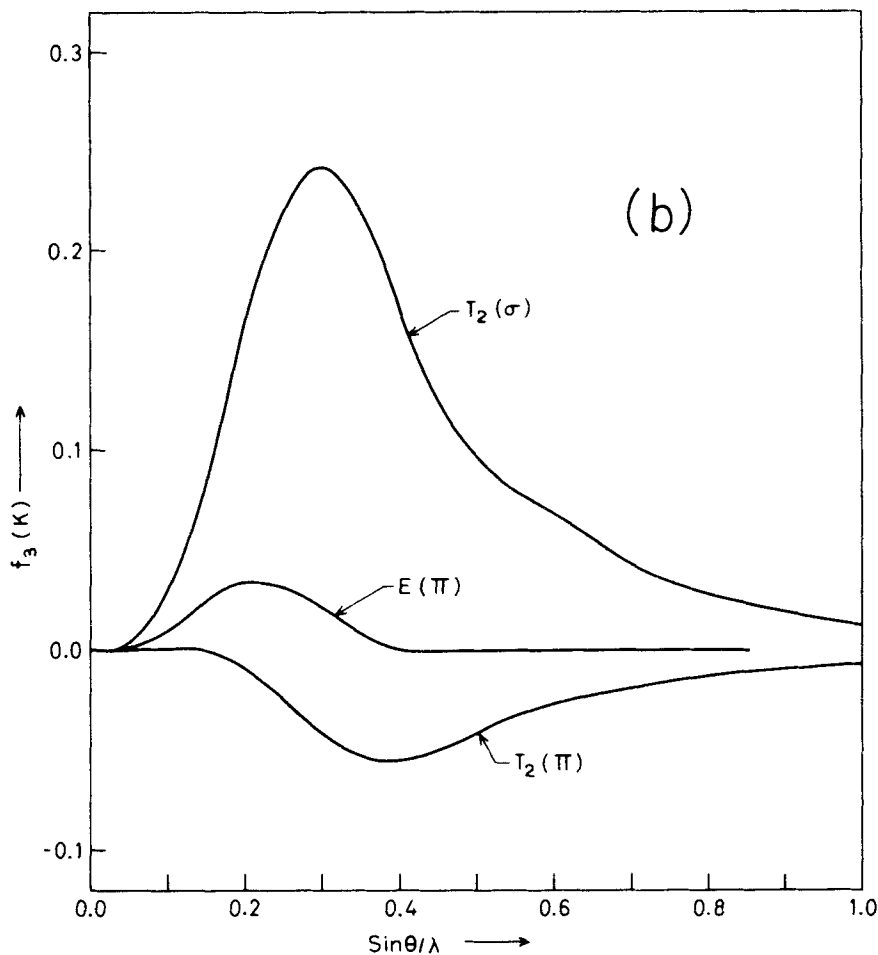
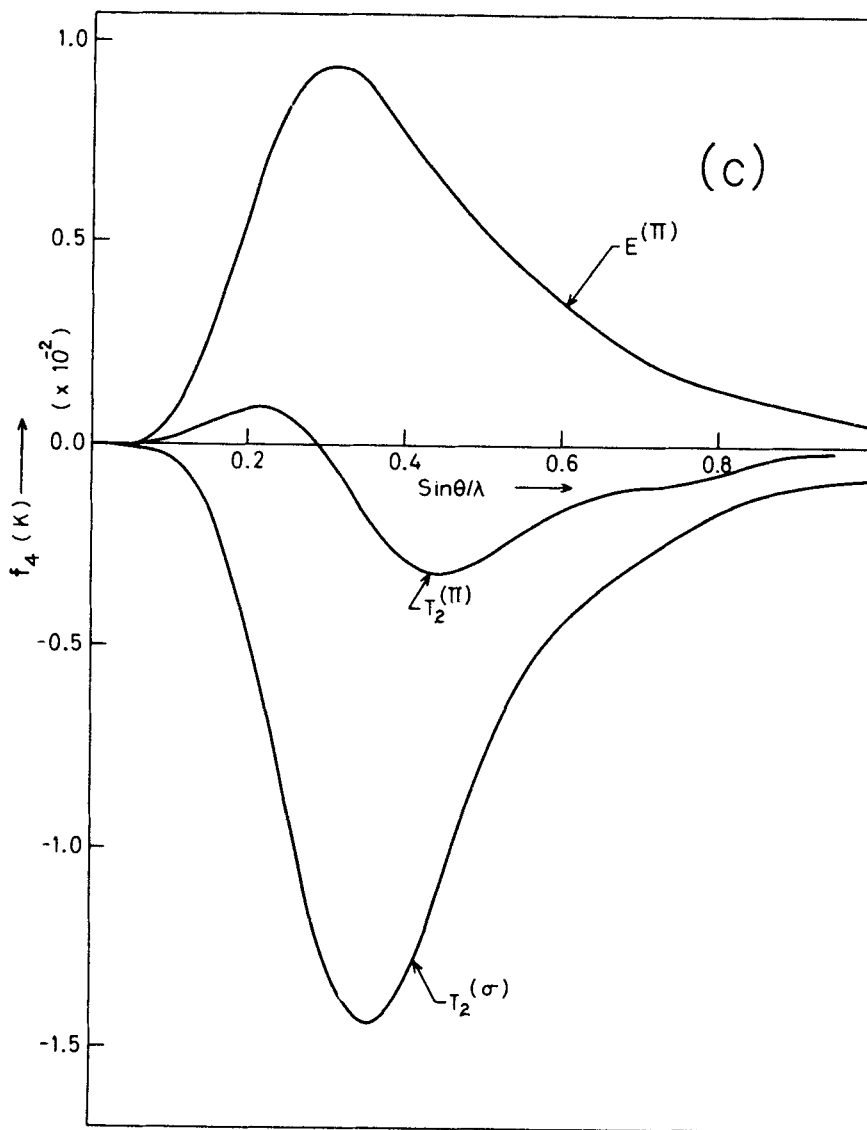


Figure 6(b). For caption, see p. 314.

an unpolarised neutron diffraction study wherein the high angle Bragg intensities were analysed to obtain the cations distribution. It was found that these specimens were about 92% normal, confirming a similar conclusion drawn earlier from powder specimens of  $\text{MnFe}_2\text{O}_4$  (vide § 2.1b). The magnetic structure amplitudes were analysed in Fourier space to obtain the site moments on the *A* and *B* sites as also their asphericity. We recall that the situation in  $\text{MnFe}_2\text{O}_4$  is more complicated than in  $\text{Fe}_3\text{O}_4$  in the sense that in the former both the *A* and *B* sites are randomly occupied (albeit in different proportions) by  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions. The magnetic moment on the *A* site was found to be  $4.22 \mu_B$  with an excess of about 10% of  $T_2$  symmetry. The *B* site moment on the other hand was found to be less i.e.  $3.16 \mu_B$  with a deficiency of about 4% of  $T_{2g}$  symmetry. These are the room temperature values which when normalised to  $0^\circ\text{K}$  turn out to be  $5 \mu_B$  and  $3.88 \mu_B$  for the *A* and *B* sites respectively. It must be remarked, however, that while the *A* site moment was refined from purely the *A* site reflections, the *B* site moment was refined from the mixed reflections (the *B* site reflections being few and quite weak and hence difficult to observe). Therefore, while the rather low moment on



**Figure 6.** The form factors for the overlap densities  $\langle d_T | \psi_{T^*} \rangle \langle d_T | \psi_x \rangle$  and  $\langle d_E | \psi_{E^*} \rangle$ . (a)  $f_0$  (b)  $f_3$  (c)  $f_4$ .

the  $B$  site (predominantly occupied by  $\text{Fe}^{3+}$ ) may point out to important covalent effects, a full quantitative evaluation of the covalency parameters may not be justified. The principal conclusion one can draw from this study is that unlike the  $\text{Fe}^{3+}$  ion on the  $A$  site in  $\text{Fe}_3\text{O}_4$ , the  $A$  site ion (predominantly the  $\text{Mn}^{2+}$  ion) in  $\text{MnFe}_2\text{O}_4$  is almost fully ionic in character with practically no covalent character.

#### 4. Paramagnetic studies in mixed ferrites

An experimental knowledge of the exchange integrals is basic to the understanding of the various magnetic properties of solids such as its magnetic structure and transition

temperature. In spinel ferrites particularly, where the cation distribution and the relative values of the exchange interactions influence the nature of magnetic ordering, such a knowledge is extremely useful. Temperature dependence of sublattice magnetisation as well as paramagnetic susceptibility data are often insensitive to some of the exchange interactions and their analysis takes recourse to molecular field theory. However, as Smart (1963) has pointed out the molecular field method is a poor approximation for evaluating exchange integrals in spinels. On the other hand, the paramagnetic neutron scattering technique offers itself as a simple yet powerful tool in directly evaluating exchange integrals in powder specimens in their paramagnetic phase. The theory underlying this technique is quite general and is applicable to any ionic system coupled together by the Heisenberg Hamiltonian. At Trombay we had exploited this technique extensively to evaluate exchange integrals in a number of magnetic insulators (Satya Murthy and Madhav Rao 1968; Madhav Rao 1970). It is especially suitable to those systems characterised by just one or two important exchange interactions.

Following Van Hove (1954) we can express the double differential scattering cross-section for neutrons scattered from an assembly of spins as follows:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{2\pi} A(\mathbf{k}, \mathbf{k}') \mathcal{S}(\mathbf{Q}, \omega) \quad (7)$$

where

$$A(\kappa, \kappa') = \left( \frac{e^2 r}{mc^2} \right)^2 \frac{\kappa'}{\kappa} S(S+1) |F(Q)|^2; \quad \mathbf{Q} = \kappa' - \kappa, \quad (8)$$

and

$$\mathcal{S}(\mathbf{Q}, \omega) = \sum_{\mathbf{R}} \int_{-\infty}^{+\infty} \langle S_{\mathbf{0}}(0) \cdot S_{\mathbf{R}}(t) \rangle \exp[i(\mathbf{Q} \cdot \kappa - \omega t)]. \quad (9)$$

$\kappa$  and  $\kappa'$  are the initial and final wave vectors of the neutron,  $F(Q)$  in the magnetic form factor,  $\hbar Q$  and  $\hbar\omega$  are the momentum and energy transfers respectively suffered by the neutron in the process of scattering,  $\mathcal{S}(\mathbf{Q}, \omega)$  called the scattering law is the spatial and temporal Fourier transform of the spin correlation function  $\langle S_{\mathbf{0}}(0) \cdot S_{\mathbf{R}}(t) \rangle$ . The spin correlation function physically signifies the probability that a spin at  $\mathbf{R}$  and at time  $t$  is parallel to another spin at  $\mathbf{O}$  and  $t = 0$ . In the paramagnetic phase where there is no static spin structure  $\langle S_{\mathbf{0}}(0) \cdot S_{\mathbf{R}}(t) \rangle = 0$  for  $\mathbf{R} \neq 0$  and  $t = 0$ . However, for all other values of  $t$ , the spins are dynamically coupled through exchange forces and the correlation function is finite. De Gennes (1958) was the first to have examined several interesting features of the scattering law  $\mathcal{S}(\mathbf{Q}, \omega)$  by the method of moments. He showed that for large momentum transfers i.e.  $Qb \gg \pi$  (when  $b$  is the separation distance between the magnetic ions), the scattered neutron energy distribution is essentially Gaussian and independent of  $Q$ . That is

$$\mathcal{S}(Q, \omega) = \frac{1}{[2\pi \langle \omega^2 \rangle]^{1/2}} \exp\left(\frac{-\omega^2}{2\langle \omega^2 \rangle}\right) \quad (10)$$

where the second moment  $\langle \omega^2 \rangle$  is given as

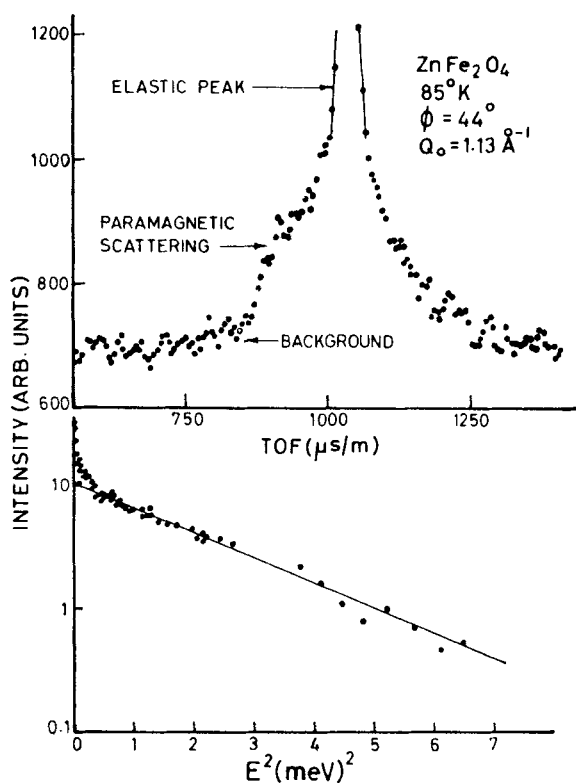
$$\langle \omega^2 \rangle = \frac{8}{3} S(S+1) \sum_i z_i J_i^2 \quad (11)$$

$z_i$  is the number of  $i$ th neighbours of a magnetic ion and  $J_i$  is the corresponding exchange integral. Clearly, the paramagnetic neutron scattering technique is suitable for magnetic systems characterised by very few exchange interactions and most suitable when only one exchange integral is dominant.

Paramagnetic neutron scattering studies were carried out on powder specimens of  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$  and  $\text{MnAl}_2\text{O}_4$  with a view to determining the exchange interactions between  $\text{Fe}^{3+}$ - $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ - $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ - $\text{Mn}^{2+}$  (Satya Murthy *et al* 1971b). These experiments were performed on the rotating crystal spectrometer at the CIRUS reactor which furnishes a cold neutron beam of 4.1 Å. The energy analysis was done by the time-of-flight technique.

#### 4.1 Results and discussion

Figure 7 shows the typical time-of-flight distribution of 4.1 Å neutrons scattered by  $\text{ZnFe}_2\text{O}_4$ .  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  were completely normal from room temperature diffraction patterns (Satya Murthy *et al* 1971b) and hence the only exchange integrals operating are those between the  $B$  sites ions. The experiments yielded the dominant interactions in the two cases as  $J_{BB}(\text{Fe}^{3+}$ - $\text{Fe}^{3+}) = 1.04$  K and  $J_{BB}(\text{Cr}^{3+}$ - $\text{Cr}^{3+})$



**Figure 7.** At the top is shown the "raw" time-of-flight spectrum of 4.1 Å neutrons scattered from  $\text{ZnFe}_2\text{O}_4$  powder at 85 K and at scattering angle  $44^\circ$ . The final corrected intensity plotted on a semi-logarithmic scale against the square of the energy transfer is shown at the bottom. The gaussian nature of the energy distribution is clearly seen. The inverse of the slope of the straight line yields the second moment.

= 2.38 K. Both  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  are known to have complicated types of ordering at low temperatures and these have been argued as due to the influence of distant neighbour  $B$ - $B$  interactions. However, we can expect these interactions to be atleast an order of magnitude smaller than the dominant nearest neighbour  $B$ - $B$  superexchange. In the paramagnetic scattering experiments the energy exchange with the neutron can be reasonably assumed to arise mainly from this dominant interaction (especially as the second moment involves the squares of  $J$ 's).

In the case of  $\text{MnAl}_2\text{O}_4$  the sample was found to have a small inversion of 9% and hence there is, in addition to  $J_{AA}$  a significant  $J_{AB}$  interaction between the  $\text{Mn}^{2+}$  ions. Using therefore a molecular field expression for  $T_N$  (= 18 K) along with the second moment of the scattered energy distribution, it was found that  $J_{AA}(\text{Mn}^{2+}-\text{Mn}^{2+}) = -0.21$  K and  $J_{AB}(\text{Mn}^{2+}-\text{Mn}^{2+}) = -16$  K. It is interesting to recall that in  $\text{MnAl}_2\text{O}_4$ , Friedman and Goland (1966) also using a neutron scattering method derived  $J_{AA}(\text{Mn}^{2+}-\text{Mn}^{2+})$  as 2.2 K ignoring the small inversion. Although we used a molecular field expression for  $T_N$ , the widely different values of  $J_{AA}$  underline the importance of taking into account inversion in view of the dominant nature of  $J_{AB}$ .

## 5. Spin wave dispersion in $\text{MnFe}_2\text{O}_4$ and $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$

While the paramagnetic neutron scattering technique is admittedly a powerful tool to probe exchange interactions only in a specific class of magnetic insulators, the most detailed informations of exchange interactions (their relative strength and range) and other dynamical features can be had only from mapping of spinwave dispersion relations. Such measurements are however difficult and time-consuming since they need fairly large single crystal specimens and good neutron fluxes. In this section we shall briefly describe such measurements done at Trombay on two single crystals specimens:  $\text{MnFe}_2\text{O}_4$  (Rakhecha *et al* 1972, 1974) and  $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$  (Rakhecha *et al* 1976).

### 5.1 $\text{MnFe}_2\text{O}_4$

The  $\text{MnFe}_2\text{O}_4$  single crystal used was pyramidal in form, 20 mm high and 15 mm in diameter at the base. A diffraction measurement made on a small chip of this block confirmed that this specimen was 92% normal. The acoustic spinwave dispersion measurements were performed on the polarised neutron diffractometer using the Bragg misset method. This technique facilitates easy isolation of pure spinwave scattering. The measurements essentially consisted of measuring the angular width of the diffuse spinwave scattering (i.e. by calipering the spinwave "scattering surface") and then deducing the spinwave dispersion  $h\omega$  versus  $q$  ( $q$  is the wavevector and  $h\omega$  the energy) by an indirect iterative procedure which assumes an isotropic polynomial dispersion relation. Thus in this technique no explicit energy analysis of the scattered neutron is involved. The effective inter-sublattice exchange constant  $J_{AB}$  between the  $A$  and  $B$  magnetic sublattices was evaluated at all temperatures of measurement (300 K, 393 K, 450 K with  $T_N = 560$  K) in the framework of spinwave theory for ferrites in the Heisenberg model. (We recall that in  $\text{MnFe}_2\text{O}_4$  there is exchange disorder but no spin disorder since both  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  have  $S = 5/2$ .) It may be pointed that the acoustic spinwave branch is most sensitive to  $J_{AB}$ , and the value of this parameter at room

temperature was evaluated to be  $-15.1 \pm 0.5$  K. Extrapolating this value of 0 K, from the known magnetisation curve,  $J_{AB}$  at 0 K turns out to be  $-18.9$  K. This value of exchange constant represents closely the  $\text{Mn}^{2+}(A)\text{-Fe}^{3+}(B)$  exchange integral and is probably the first such direct measurement of this quantity in a ferrite. The spinwave dispersions at three different temperatures are shown in figure 8. Distinct softening of the spin-waves due to spinwave renormalization is seen as one approaches  $T_N$ . This renormalization was found to scale essentially as  $\langle S_z \rangle$ , the sublattice magnetisation with a very weak dependence on the wavevector  $q$ .

### 5.2 $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$

The motivation for exploring the spinwave dispersion in this crystal stemmed from similar measurements done on  $\text{Fe}_3\text{O}_4$  (Brockhouse and Watanabe 1963) and on  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  (Wanic *et al* 1972). The  $\text{Li}^+$  ions go substitutionally to the octahedral  $B$  sites and affect the cation distribution only on their sites. In particular, the proportion of  $\text{Fe}^{3+}$  ions is increased at the expense of  $\text{Fe}^{2+}$  ions and for  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  only  $\text{Fe}^{3+}$  ions are left on the  $B$  site. Despite the introduction of nonmagnetic  $\text{Li}^+$  ions on the  $B$  sites, the Néel temperature is higher for  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  than in  $\text{Fe}_3\text{O}_4$  and so are the spinwave energies. This may be construed as showing the larger value of  $J_{AB}$  ( $\text{Fe}^{3+}\text{-Fe}^{3+}$ ) exchange as compared to  $J_{AB}$  ( $\text{Fe}^{3+}\text{-Fe}^{2+}$ ). It seemed interesting to explore this point further with the ferrite  $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$  which has an intermediate composition.

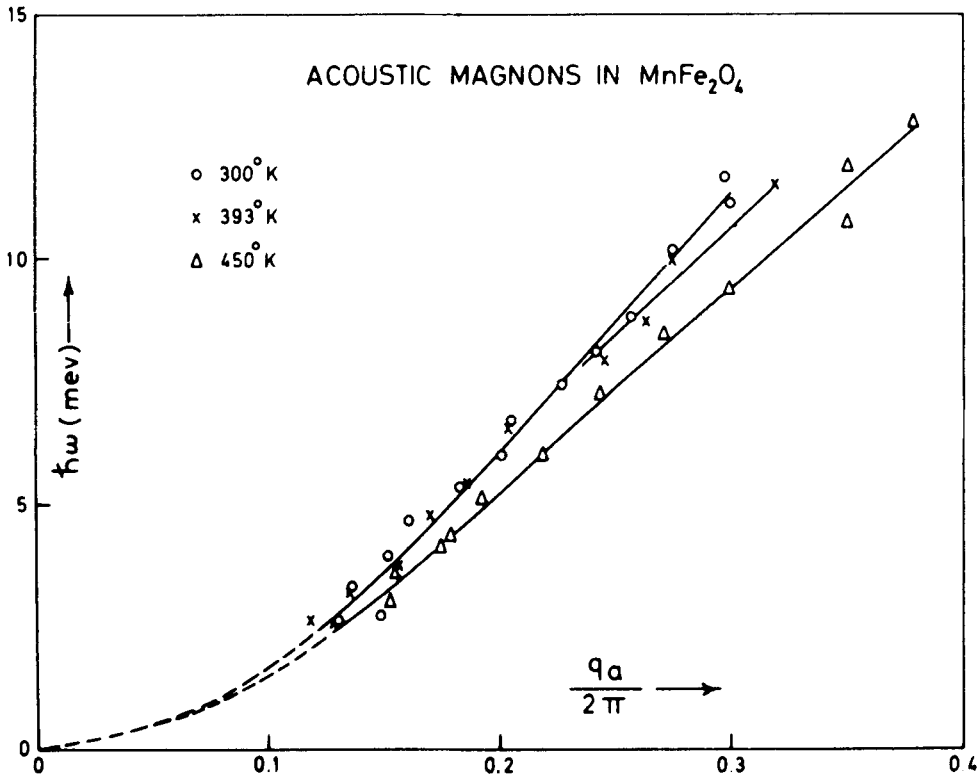


Figure 8. Acoustic spinwave dispersion curves in  $\text{MnFe}_2\text{O}_4$  at three temperatures. Note the 'softening' of the spinwaves as  $T_N$  is approached.



Unlike in the case of  $\text{MnFe}_2\text{O}_4$ , the acoustic spinwaves were measured by an explicit energy analysis on the triple axis spectrometer at Trombay, along the  $\langle 001 \rangle$  direction using the 'constant  $Q$ ' 'constant  $E$ ' modes. The dispersion was measured upto 0.55 of the Brillouin zone boundary and upto much higher spinwave energies ( $\sim 50$  meV) as compared to  $\sim 15$  meV in the previous technique on  $\text{MnFe}_2\text{O}_4$ . For a given  $q$  value the spinwave energies in  $\text{Li}_{0.13}\text{Fe}_{2.87}\text{O}_4$  were seen to be slightly higher than in  $\text{Fe}_3\text{O}_4$  but lower than in  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ . The effective exchange integral  $J_{AB}$  deduced, in the Heisenberg model was  $-30.1 \pm 0.75$  K and was seen to be practically the same as that for  $\text{Fe}_3\text{O}_4$  and for  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  within the experimental accuracy.

## 6. Concluding remarks and acknowledgement

This article has attempted to give an overview of the investigations carried out by the Trombay group in a variety of ferrites spanning a period of nearly a decade. The author thanks the Editorial Board for inviting him to contribute this article in honour of his respected colleague and friend, the late Dr N S Satya Murthy who initiated and guided these neutron investigations in ferrites and whose scientific influence was felt in other spheres as well. Thanks are also due to Drs V C Rakhecha, S K Paranjpe and R Chakravarty for their help in this work.

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