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Crystal, magnetic and electric behaviour of $CoMn_xFe_{2-x}O_4$ cubic ferrites

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Six powder samples of $CoMn_xFe_{2-x}O_4$ ($0 \leqslant x \leqslant 1$) were synthesized by using a ceramic sintering technique. X-ray powder diffraction patterns were obtained and confirmed the presence of single-phase spinel structure with no evidence of impurities. Lattice constants were determined. Differential thermal analysis measurements showed no variation in crystal phase with temperature. AC conductivity measurements at the temperature range (300–950 K) and for the frequency range (10^2–10^5 Hz) were also carried out and the Néel transition temperatures for all samples were determined. Mössbauer effect patterns revealed magnetic ordering for all compositions at room temperature. The obtained spectra were successfully analysed into two Zeeman sextets, could be attributed to the tetrahedral and octahedral sites. The different Mössbauer effect parameters were deduced and discussed. Neutron diffraction measurements were also performed where oxygen parameters and cation distributions were determined, and magnetic structure were studied. All obtained results from the different techniques support the Néel model of ferrimagnetism for such compounds.

1. Introduction

A large number of spinel type ceramics have been investigated because of the important applications where their magnetic properties are of academic and technical interest. Ferrimagnetic in pure $CoFe_2O_4$ was studied by several authors [1, 2]. Mixed solid solution ferrites $CoMn_xFe_{2-x}O_4$ ($0 \leq x \leq 1$) are of interest. Six compounds were prepared to study their magnetic order and to obtain the exchange integral values of their magnetic cell. It is necessary at first to determine their crystallographic hyperfine parameters and their magnetic transition temperatures, and this is the subject of this paper. Since X-ray diffraction technique is less precise for the determination of the cationic distribution, and since oxygen anions have a barely measurable effect on X-ray diffraction intensities, the accuracy of determination of the oxygen coordinates is rather low. Therefore, it was interesting to utilize the diffraction of thermal neutrons, where the heavy cations and the oxygen atoms have comparable scattering amplitudes and there is the possibility of neutron magnetic scattering. Moreover, our aim was to understand the role of the magnetic Mn and Fe cations, and to distinguish their distribution in these mixed oxides, by studying the Mössbauer effect and the electrical conductivity of these compounds.

2. Experimental procedure

Solid solutions of six of $CoMn_xFe_{2-x}O_4$ ($0 \leq x \leq 1$) were prepared by using the usual ceramic method [3]. Stoichiometric amounts of the powders CoO, Mn_2O_3 and αFe_2O_3 were mixed in desired proportions, having been air fired for 48 h at 1100 °C followed by slow cooling. The resulting powders were then compressed in the form of pellets and fired at 1200 °C for 4 h, and then left to cool slowly. The powder X-ray diffraction patterns indicate that all compositions have spinel structure with no evidence of impurities or separate phases. The lattice constants for the six compositions were found to be around 0.8353 nm. Samples of the prepared compositions were in the form of a disc with diameter 2 cm and thickness 4 mm were used for electrical conductivity measurements by using an RC circuit. These measurements were carried out in an evacuated cell (0.133 Pa) at frequencies of 10^2–10^5 Hz by using a low-frequency lock-in amplifier over a temperature range of 300–950 K.

The neutron diffraction data for the prepared polycrystalline samples were obtained at both room temperature and at their transition temperatures by using a neutron diffraction spectrometer placed at one of the horizontal channels of the Egyptian Reactor running at 2 MW. The neutron diffraction patterns at 300 and

650 K for the compound $CoMn_{0.6}Fe_{1.4}O_4$ are shown in Fig. 1.The temperature dependence of intensity for the reflection (3 1 1) was measured by following the peak height as the sample cooled slowly from 740 K down to room temperature for the compound ($x = 0.6$) (Fig. 2). The transition point was found to be 550 K. All transition points obtained in this way are in good agreement with those obtained from electrical conductivity measurements. Mössbauer resonance spectra of the studied compounds at room temperature (Fig. 3) were taken by using a time mode Mössbauer effect spectrometer of the constant acceleration driving system coupled to 1024 multichannel analyser (PCA). The source used was 50 mCi ^{57}Co diffused in a Pd matrix. The Mössbauer spectra clearly showed the absence of any uncreated αFe_2O_3.

3. Results and discussion

The measured Mössbauer spectra for the studied compounds at room temperature showed that the average full-width at half-maximum for the Mössbauer lines is large compared to that for αFe_2O_3, suggesting overlapping sextets. In fact the analysis of the spectral lines shows a good fit to two six-line Zeeman patterns of different populations and confirms the occupations of the two different crystallographic sites by ferric ions, one due to the Fe^{3+} ions at the [B] site and the other due to Fe^{3+} ions at the (A) site. Each Zeeman compound is approximated by an asymmetric spectrum with six Lorentzian distribution peaks. The spectra are shown in Fig. 3, and indicate a magnetic ordering at room temperature. In the figure the black dots represent the experimental points and the continuous lines through the data points are the results of the least squares fit to the data of the two mixed magnetic dipole and electric quadrupole ^{57}Fe hyperfine patterns for each site. The vertical line above each spectrum indicates the position of the individual line. The dashed line represents the best fit to a sextet spectrum for each site. The deduced Mössbauer parameters are given in Table I. The determined isomeric shift values from the Mössbauer spectra at room temperature of the studied samples relative to iron metal for the ferric ions at (A) and [B] sites lie between 0.20 and 0.40 mm s^{-1}. These values are very similar to those reported by Evans and Hafner [4] in spinel systems and are characteristic of the high spin Fe^{3+} charge state. Within experimental errors the isomer shift values for Fe^{3+} ions in the different site configurations obtained from the present study are independent of x concentration, thus indicating that we can attribute the patterns to the same ions in each sample. Moreover, the s electron charge distribution of the Fe ions is negligibly influenced by manganese substitution.

The hyperfine fields, H_{eff}, measured by the Mössbauer effect consists of three contributions: $H_{\text{eff}} = H_{\text{cor}} + H_{\text{dip}} + H_{\text{steff}}$. H_{cor} results from the polarization of s electrons by the magnetic moments of the d electrons. This field is larger for free ions than for

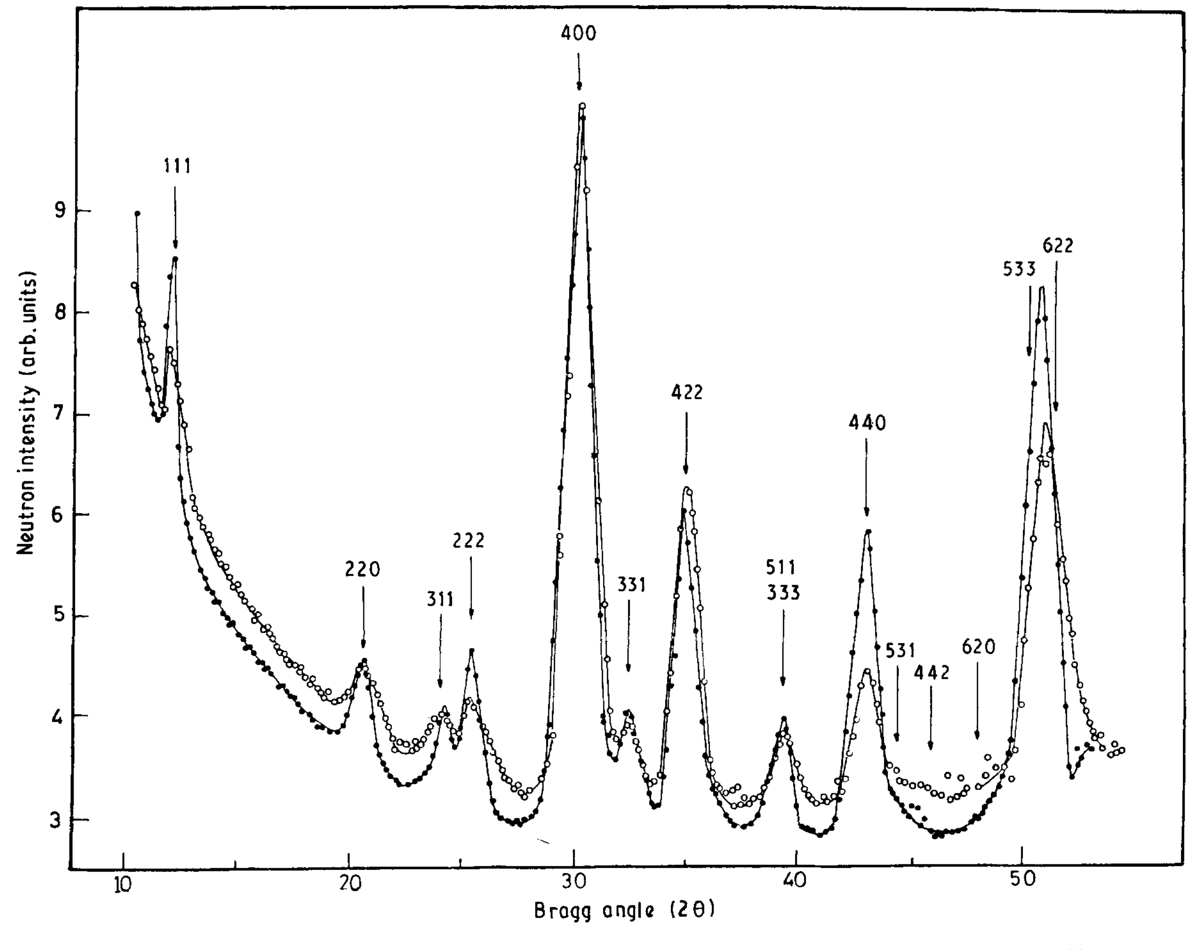

Figure 1 Neutron diffraction patterns for the sample $CoMn_{0.6}Fe_{1.4}O_4$ at room temperature (●) and 650 K (○); $\lambda = 0.108$ nm.

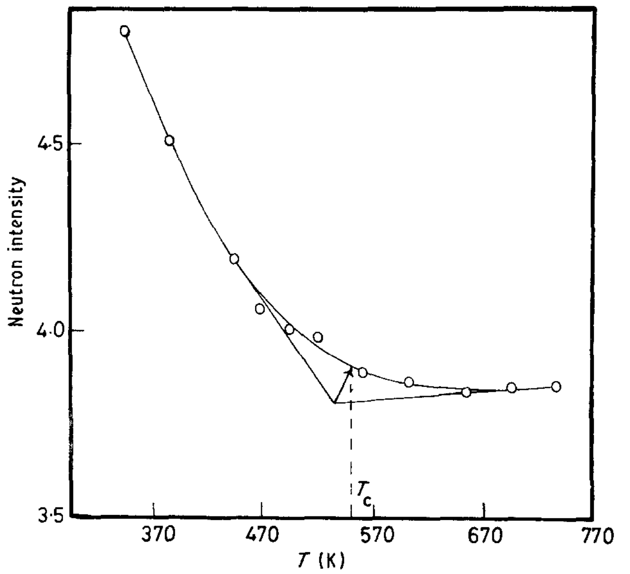

Figure 2 Variation of the intensity of (3 1 1) reflection as function of temperature for the sample $CoMn_{0.6}Fe_{1.4}O_4$.

ions in a crystal because of covalency. H_{dip} represents the dipolar fields produced by the surrounding magnetic ions. This field will depend on the distribution of the cations in (A) and [B], i.e. it will also change if one of these ions is replaced by an ion with a different magnetic moment. Supertransferred hyperfine fields H_{steff} at a central cation originate from the magnetic moments of nearest neighbouring cations, i.e. from the inter sublattice contributions h_{AA} and h_{BB} and the inter sublattice contributions h_{AB} and h_{BA}. The hyperfine fields at ^{57}Fe nuclei in the two sites are sufficiently different. The decrease in the magnetic field for both (A) and [B] sites as x increases can be explained on the basis of charge interactions between and within the sublattices.

The EFG may be due to: (i) departure of the six nearest anion neighbours from their ideal octahedral symmetry, and (ii) the non-spherical distribution of charges on the next nearest cation and anion neighbours of the octahedral site. Thus, although the over-

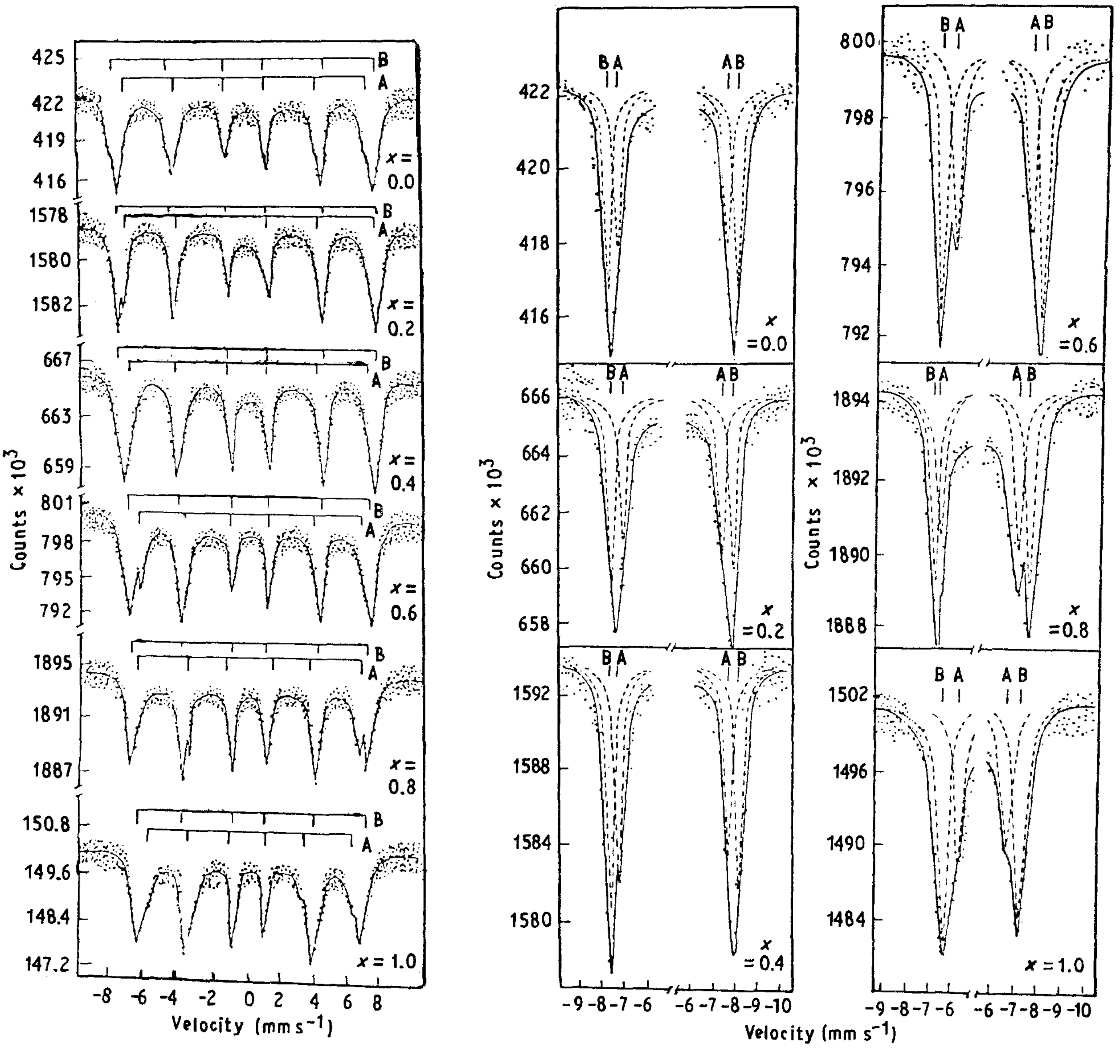

Figure 3 Mössbauer effect spectra and its analysis of the outer peaks for the ferrite system $CoMn_xFe_{2-x}O_4$ at room temperature.

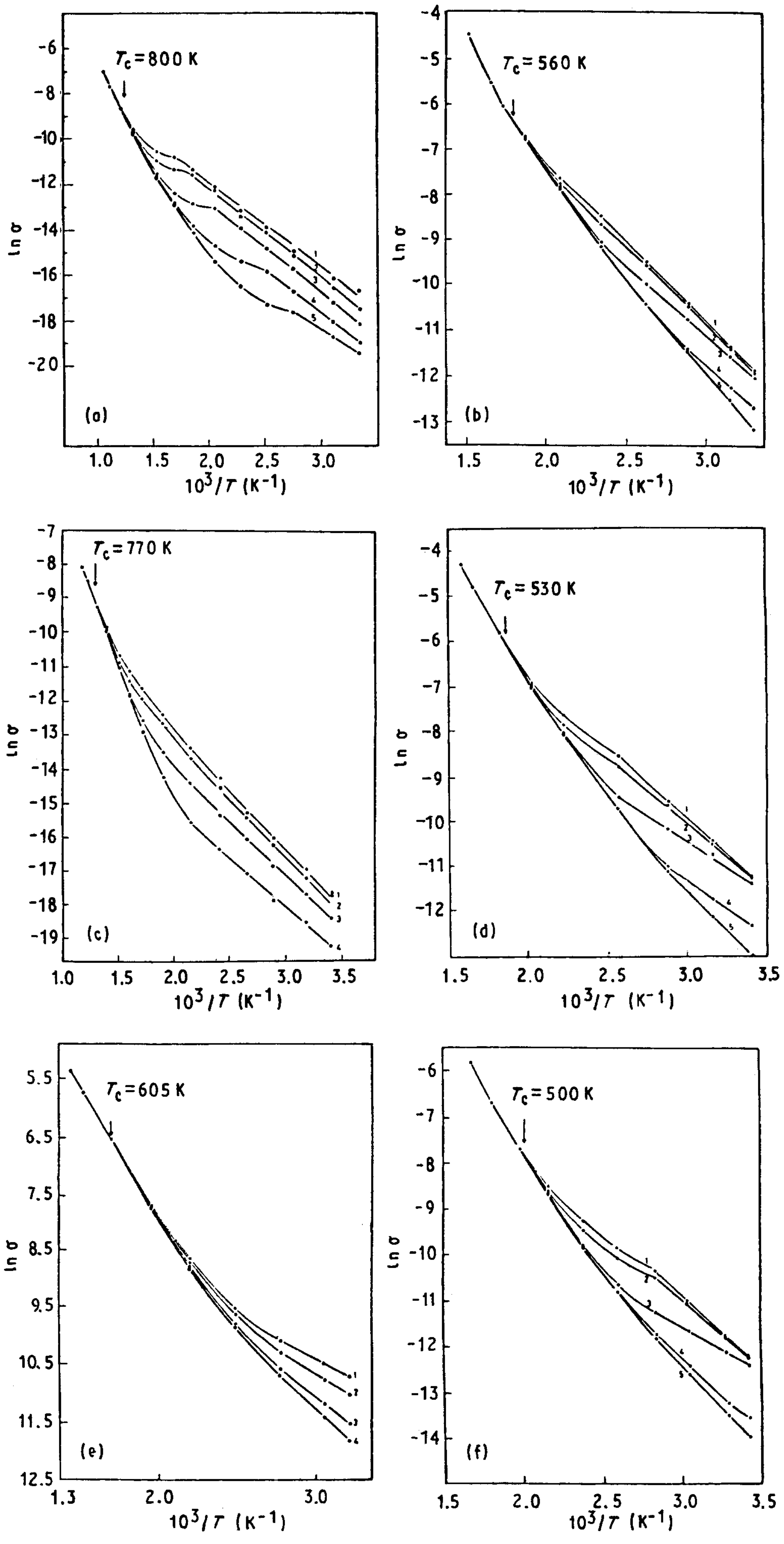

Figure 4 AC conductivity as ln σ versus $10^3/T$ for the ferrite system $CoMn_xFe_{2-x}O_4$. (1) 100 kHz, (2) 50 kHz, (3) 10 kHz, (4) 1 kHz, (5) 170 Hz. (a) $x = 0$, (b) $x = 0.6$, (c) $x = 0.2$, (d) $x = 0.8$, (e) $x = 0.4$, (f) $x = 1.0$.

TABLE I Mössbauer effect parameters of the ferrite system $CoMn_xFe_{2-x}O_4$ at room temperature

Sample x	A site			B site			Site occupancy ratio
	H_{eff} kOe	IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)	H_{eff} kOe	IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)	I/II
0.0	453	0.30	0.060	481	0.25	0.075	0.614
0.2	454	0.28	0.035	479	0.33	0.030	0.700
0.4	447	0.30	0.015	475	0.34	0.020	0.727
0.6	411	0.36	0.025	447	0.33	0.015	0.431
0.8	411	0.32	0.065	432	0.33	0.045	0.714
1.0	370	0.37	0.070	408	0.38	0.014	0.646
Error	± 2	± 0.02	± 0.02	± 2	± 0.02	± 0.02	

TABLE II Cation distribution in the ferrite system $CoMn_xFe_{2-x}O_4$ as calculated from Mössbauer effect studies

Sample	Cation distribution
$CoFe_2O_4$	$Co^{2+}_{0.24}Fe^{3+}_{0.76}[Co^{2+}_{0.76}Fe^{3+}_{1.24}]O^{2-}_4$
$CoMn_{0.2}Fe_{1.8}O_4$	$Co^{2+}_{0.26}Fe^{3+}_{0.74}[Co^{2+}_{0.74}Fe^{3+}_{1.06}Mn^{3+}_{0.20}]O^{2-}_4$
$CoMn_{0.4}Fe_{1.6}O_4$	$Co^{2+}_{0.33}Fe^{3+}_{0.67}[Co^{2+}_{0.67}Fe^{3+}_{0.93}Mn^{3+}_{0.40}]O^{2-}_4$
$CoMn_{0.6}Fe_{1.4}O_4$	$Co^{2+}_{0.58}Fe^{3+}_{0.42}[Co^{2+}_{0.42}Fe^{3+}_{0.98}Mn^{3+}_{0.60}]O^{2-}_4$
$CoMn_{0.8}Fe_{1.2}O_4$	$Co^{2+}_{0.50}Fe^{3+}_{0.50}[Co^{2+}_{0.50}Fe^{3+}_{0.70}Mn^{3+}_{0.80}]O^{2-}_4$
$CoMn_{1.0}Fe_{1.0}O_4$	$Co^{2+}_{0.61}Fe^{3+}_{0.39}[Co^{2+}_{0.39}Fe^{3+}_{0.61}Mn^{3+}_{1.0}]O^{2-}_4$

TABLE III Activation energies of the ferrite system $CoMn_xFe_{2-x}O_4$

Sample x	Below transition temperature				Above transition temperature
	100 kHz	50 kHz	10 kHz	1 kHz	
0.0	0.33	0.34	0.35	0.33	0.86
0.2	0.30	0.29	0.27	0.25	0.82
0.4	0.11	0.13	0.17	0.20	0.36
0.6	0.29	0.29	0.25	0.33	0.59
0.8	0.27	0.25	0.20	0.17	0.54
1.0	0.27	0.27	0.18	0.29	0.50

all symmetry of the partly inverse spinel ferrites $CoMn_xFe_{2-x}O_4$ ($0 \leq x \leq 1$) is cubic, its two sublattices may suffer non-cubic charge ions occupying these two sublattices.

The ratio of areas under the well-resolved outermost lines belonging to (A) and [B] sublattices as fitted in this study (where the recoil fractions f_A and f_B for the absorber are relatively small) confirms that Co^{2+} ions usually give rise to inversion in spinel [5, 6], and that Mn^{3+} ions are located in an octahedral site [7]. The cation distribution proposed for these compounds is given in Table II, where the ions in the parentheses are located at A-sites and those in square brackets at B-sites. The neutron diffraction patterns were used for the refinement of the oxygen parameter, which shows that it differs from its usual value of 0.25. As the oxygen parameter is greater than this value it implies a contraction of the oxygen lattice about the octahedrally coordinated metal atoms, and a corresponding expansion about the tetrahedrally coordinated ones. The oxygen ions move apart in the [1 1 1] direction from the nearest position. Co, Mn, and Fe cations are distributed among the tetrahedral and octahedral sites of the face centred cubic oxygen lattice. The cation distribution is determined mainly by polarization and site preference. Cation distributions for the compounds obtained from neutron diffraction patterns are in good agreement with those obtained from Mössbauer effect patterns given in Table II. The magnetic ordering was studied from the neutron diffraction patterns below the Néel point and there was good agreement with the Néel model [8] of ferrimagnetism where the spins are directed along the [1 1 1] direction. From the conductivity measurements the Néel point of every sample was determined (Fig. 4) and confirmed the preceding results [9]. The activation energies are given in Table III. The dielectric constant and dielectric loss tangent were also deduced and showed a normal behaviour for the samples ($x = 0.0$, 0.2 and 0.4) and a relaxation spectrum for the samples ($x = 0.6$, 0.8, and 1.0).

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