

Fe⁵⁷ MOSSBAUER STUDY IN COBALT SUBSTITUTED MAGNETITE

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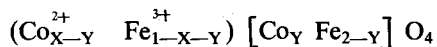
ABSTRACT

The Mossbauer effect has been studied in the mixed ferrites $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ (for $x = 0.8, 0.9$ and 1) with the spinel structure in the temperature range between 78 and 830K . The composition with $x = 1$, showed an expected Zeeman spectrum with two overlapping magnetic hyperfine patterns related to the Fe^{3+} ions in tetrahedral and octahedral sites. While for samples with $x = 0.8$ and 0.9 the Mossbauer spectrum for each compound was successfully analysed into three different patterns corresponding to the ferric ions placed at the tetrahedral and octahedral sites and ferrous ions at the octahedral sites, indicating no electron transfer between Fe^{3+} and Fe^{2+} , where the quantity of cobalt sufficiently large to be located at the six nearest neighbours to ferrous ions. The Mossbauer effect parameters were calculated for these observed sites and their variation with temperature reported. The reduced hyperfine magnetic fields of the Fe^{3+} (B) ions were found to follow the one third power law. The magnetic ordering temperature was determined to be $\approx 815\text{K}$ and the possible magnetic interactions were discussed.

INTRODUCTION

In the past few years, the interest for mixed valence compounds has been growing because of their particular electrical properties, due to the possibility of an electron delocalization, and because of the possibility of ferromagnetic ordering due to a double exchange process. The spinel structure is very good system to study two valences of the same ion either on different crystallographic sites, i.e. tetrahedral and octahedral or on the same site, i.e. octahedral. The most well known example of this situation is magnetite, Fe_3O_4 , which has been extensively studied by different methods and especially by Mossbauer spectroscopy [1-5]. Substituted magnetites have been also studied: non magnetic impurities in A-site (Zn and Cd) [6], and in B-site (Al, Sn and Ti) [7-9], magnetic impurities (Ni and Co) or vacancies in B-site [10]. Mixed Cobalt ferrites of the type $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ have been the subject of numerous investigation owing to both the interesting physical properties and the importance as a constituent of more complicated mixed ferrites, utilized in technical applications [11]. One of the basic aspects in understanding the physical properties of such ferrites, is that of their electronic structure. A special interest deserve those ferrites, which contain, distributed over the same type of cationic sites (either tetrahedral A-sites or octahedral B-sites), both Fe^{2+} and Fe^{3+} ions in variable proportions.

$\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ system crystallizes in the cubic spinel structure. Crystallographic and magnetic studies of many workers [11] on this system of compounds revealed that it may have the cation distribution formula:



where () indicates tetrahedral A-site ions and [] refers to octahedral B-site ions. Neutron diffraction data suggested that in these ferrites, the spin arrangement could be explained by the Neel scheme of antiferromagnetic coupling between the octahedral and tetrahedral sites [12, 13]. The composition with $X = 0$, i.e. Fe_3O_4 possess the highest Curie temperature 860K and the largest room temperature electrical conductivity $250 \Omega^{-1} \text{cm}^{-1}$ [11]. The unit cell has the formula $(\text{Fe}_8^{3+}) [\text{Fe}_8^{3+} \text{Fe}_8^{2+}] \text{O}_{32}^{2-}$

There are equal numbers of ferrous and ferric ions in the octahedral sites. There is an exchange of electrons between neighbouring cations and this is believed to be responsible for the high electrical conductivity of this material [14]. In addition to the unusual electrical properties of magnetite, the distribution gives rise to strong intersublattice $\text{Fe}^{3+}(\text{A}) - \text{O}^{2-} - \text{Fe}^{3+}(\text{B})$ antiferromagnetic super-exchange interactions, which lead to the high Ne'el temperature of the collinear ferrimagnetic spin structure of Fe_3O_4 . At the Verwey temperature $T_V \approx 120\text{K}$, magnetite exhibits distortion from cubic to orthorhombic symmetry [14]. The Mossbauer spectrum for this compound above that temperature was detected by several authors [15-17] and consists of two overlapping Zeeman patterns, one of which is due to ferric ions on tetrahedral A-sites of the spinel lattice, while the second pattern is due to octahedral (B) ferric and ferrous cations, rendered indistinguishable by rapid electron exchange, which produces a completely average spectrum from these latter ions, without a quadrupole effect. The frequency of this hopping is faster than that of the Larmor precession of the iron nuclei in the hyperfine field [18, 19]. On the other hand, below T_V , the crystal symmetry distortion prevents the electronic exchange and the ordering of Fe^{2+} and Fe^{3+} ions sets in. The Mossbauer spectrum is complicated and two sites appear, one of which is attributed to the Fe^{3+} ions on both sites and the other to Fe^{2+} ions [20]. Associated with this transition is anomaly in both specific heat and electrical conductivity of magnetite at this temperature.

Generally, electron diffusion (or transfer) is always expected to take place as long as iron ions both valencies can be found at least in pairs in different regions of the crystal. Substitution of other atoms in Fe_3O_4 will influence the super-exchange, the values of local moments and the electron diffusion.

For pure CoFe_2O_4 , Co^{2+} and Fe^{3+} cations are unequally distributed among the tetrahedral A and octahedral B lattice sites and the distribution is temperature dependent. Mossbauer spectra of this composition showed that this spinel is not complete inverse and that the degree of inversion depends on the heat treatment of the material. The structural formula has been found to be: $(\text{Fe}_{1-a} \text{Co}_a) [\text{Fe}_{1-a} \text{Co}_{1-a}] \text{O}_4$

where $a = 0.24$, and the Mossbauer spectrum had only six unresolved peaks [21].

The ferrite CoFe_2O_4 orders ferrimagnetically at temperatures below the transition temperature $T_V \approx 860\text{K}$ [11], the value of which depends on the distribution parameter a .

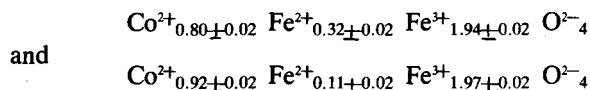
Previous Mossbauer effect measurements on the cobalt substituted magnetite system showed that electronic exchange among octahedral sites occurs up to $x = 0.7$ [22]. Metallic conductivity behaviour Fe_3O_4 is therefore to continue up to that composition. Beyond this, the

system has semiconducting behaviour, due to the uncorrelated electron hopping (as x increases, the relative number of ferrous ions in octahedral sites decreases, and there is a gradual change of the transport properties from metallic behaviour of (Fe_3O_4) to an insulating one $(\text{CoFe}_2\text{O}_4)$. Investigation of the compounds with $x \geq 0.7$, which is the subject of this work, allows us to distinguish the magnetic distribution of both Fe^{2+} and Fe^{3+} ions in these mixed oxides. The present studied mixed ferrite samples are taken with a quantity of cobalt ($x = 0.8$ and 0.9) sufficiently large to be located at the six nearest neighbours to ferrous ions. Therefore, no transition between Fe^{2+} and Fe^{3+} could be expected like that obtained by Verwey *et al* for Fe_3O_4 [14] and as a result a six line pattern, characteristic to Fe^{2+} , could be observed.

EXPERIMENTAL

Three polycrystalline samples of the ferrites $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ with $X = 0.8, 0.9$ and 1 were prepared, using the usual oxide sintering technique [23]. Carefully weighed amounts of high purity powders of ferric oxide, cobalt oxide and iron (corresponding to the desired compositions) were mixed thoroughly in an agate mortar, pressed into pellets and fired at 1000°C in an evacuated silica tube for three days. After furnace cooling, the materials were ground, repelletized, again fired at 1100°C in air for twenty-four hours and finally slowly cooled to room temperature. The grinding- pressing and firing operations were repeated twice.

The X-ray powder diagrams obviously showed sharp reflection lines in the range of $2\theta = 0$ to 80° , corresponding only to the cubic spinel structure. The samples are therefore crystallographically homogenous. Any super structure line was not observed in the diffraction patterns. The lattice constants were found to agree in general with previous reported data [12, 24]. The chemical analysis for the mixed ferrites samples showed the following chemical formulas:



Mossbauer effect measurements were performed in the temperature range $78 - 850\text{K}$, using a Mossbauer spectrometer with a constant acceleration driving system and coupled to a 512 multichannel analyzer, used in the multiscalar mode.

Metallic iron, stainless steel and $\propto\text{Fe}_2\text{O}_3$ were used for the calibration of both observed velocities and hyperfine magnetic fields. The used source was $50 \text{ mCi } ^{57}\text{Co}$ diffused in Rh matrix and kept at room temperature. All measurements were repeated twice eight hours for each, where the background count rate is reasonable with respect to peak intensities. The solid lines through the data points are the results of least-squares fit. Mossbauer parameters are numerically fitted for all measured spectra and are collected in Table 1.

RESULTS AND DISCUSSION

The obtained Mossbauer spectra (Figures 1 and 2) clearly fall into two different categories:

- That containing Fe^{3+} and showing a magnetic splitting (the compound CoFe_2O_4 , Figure 1 (a)).
- That which appears to contain Fe^{2+} iron, providing a transition from Fe_3O_4 to CoFe_2O_4 (the compositions $\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}^{2-}_4$ Figure 1 (b) and $\text{Co}^{2+}_{0.92} \text{Fe}^{2+}_{0.11} \text{Fe}^{3+}_{1.97} \text{O}^{2-}_4$ Figure 2).

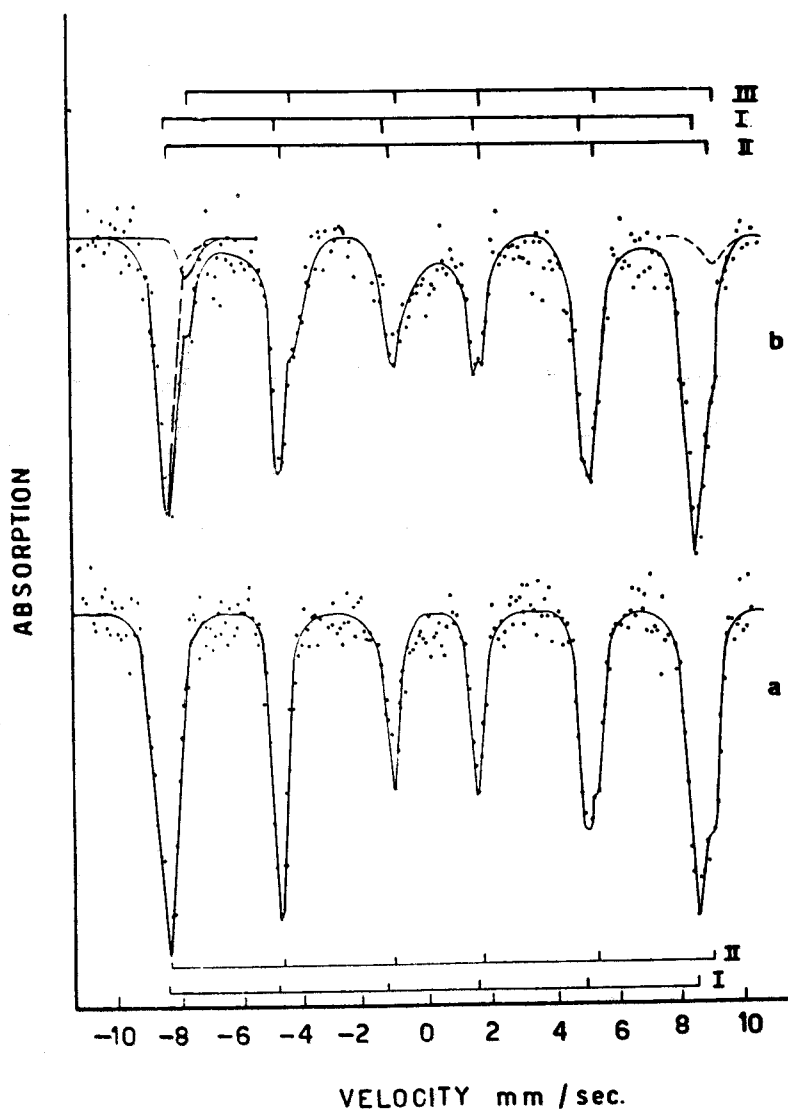


Fig. 1. Mossbauer effect spectra of (a) CoFe_2O_4 (b) $\text{Co}^{2+}_{0.80}\text{Fe}^{2+}_{0.32}\text{Fe}^{3+}_{1.94}\text{O}_4$ at room temperature.

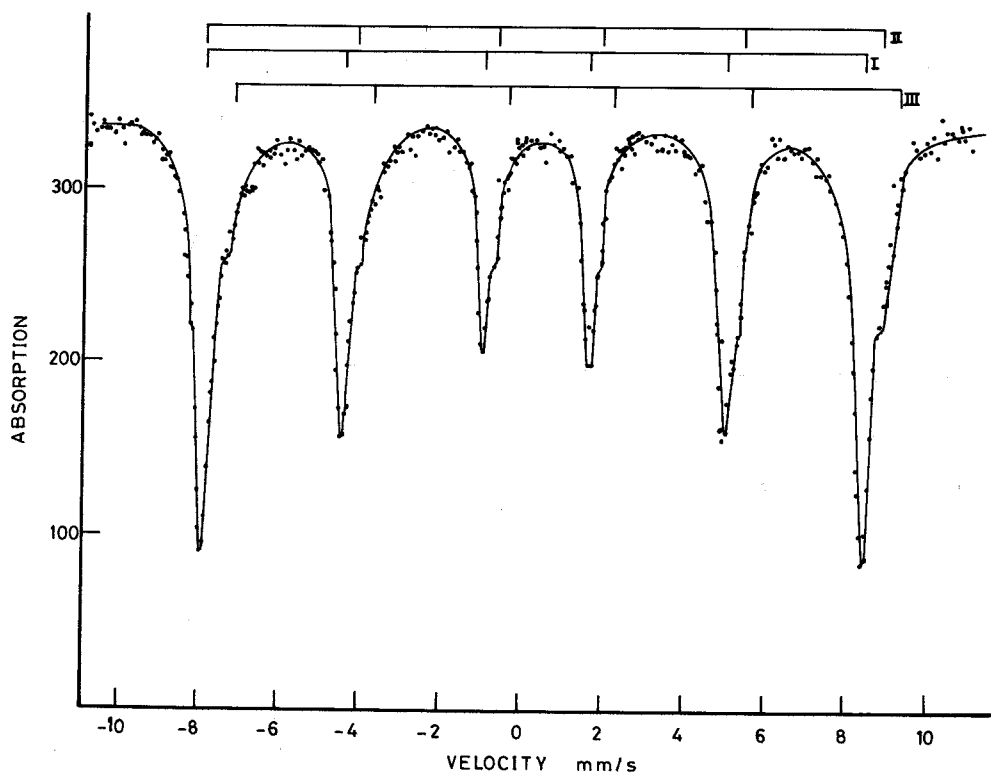


Fig. 2. Mössbauer effect spectrum of $\text{Co}^{2-}_{0.92} \text{Fe}^{2-}_{0.11} \text{Fe}^{3-}_{1.97} \text{O}_4$ at room temperature.

Figure 1 (a) shows the expected Mössbauer spectrum of the stoichiometric compounds with $x = 1$ at room temperature. It consists of two overlapping magnetic hyperfine Zeeman patterns I and II, as indicated in the figure, with peak intensity ratio 1: 1.04, having line widths, similar to those of Fe_2O_3 25

The Mössbauer effect measurements for the mixed ferrites with $x = 0.8$ and 0.9 are given in Figures 1 (b) and 2. They showed, that the average full widths at half maximum for the Mössbauer lines are quite large, compared with those of $\alpha\text{-Fe}_2\text{O}_3$, suggesting the possibility of overlapping sextets. The spectra are successfully analysed into three different six lines pattern I, II and III. The subspectra I and II for each sample have parameters, nearly close to those of CoFe_2O_4 (see Table 1). The obtained spectra at 78 K for the prepared samples did not change dramatically, compared with those at room temperature. It is convenient to develop the discussion under various subheadings, based on the parameters that can be extracted from the Mössbauer effect spectra.

Table 1

Parameters of Mossbauer Subpattern Spectra at 300 K for the $\text{Co}_x^{2+} \text{Fe}^{2+}_{1-x} \text{Fe}_2^{3+} \text{O}_4$ samples.

Compounds	Sub-patterns	Isomer shift relative to metallic iron mm/s	Quadrupole shift mm/s	Hyperfine magnetic field KOe
$\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}^{2-}_4$	I	0.210	0.080	487
	II	0.480	0.040	501
	III	0.817	0.490	484
$\text{Co}^{2+}_{0.92} \text{Fe}^{2+}_{0.11} \text{Fe}^{3+}_{1.97} \text{O}^{2-}_4$	I	0.208	0.080	488
	II	0.480	0.040	500
	III	0.815	0.486	486
$\text{Co}^{2+} \text{Fe}^{3+} \text{O}^{2-}_4$	I	0.204	0.080	490
	II	0.476	0.040	500
Errors		± 0.040	± 0.040	± 2

(i) Isomer Shifts

Table 1 illustrates, how isomer shifts of the iron ions of both tetrahedral and octahedral sites vary with the compositions at room temperature. According to previous data of Goodenough and Loeb [26], pattern I could be identified for A-sites and pattern II for B-sites. We note, that the difference ($\Delta E_I - \Delta E_{II}$) appears to show no significant variation with x, thus indicating that there is a small but definite difference between the two isomer shifts, the for pattern I (i.e. Fe^{3+} ions) being 0.2 mm/sec. less positive than for pattern II ion ions. This difference can be attributed to slight sp^3 covalency, which the tetrahedral ions are known to experience [27]. By using the W.W.J. plot [28], one can show that this tetrahedral covalency is equivalent to 1% of a 4s electron being present on the tetrahedral Fe^{3+} ions. The most interesting feature observed on the measured Mossbauer of a third pattern of six lines (III). The relatively large obtained values of the isomer shift and the quadrupole shift for this pattern indicate the presence of Fe^{2+} ions at octahedral position and in its high spin state [29]. This was proved by the analysis of the relative area for this pattern which was in agreement with chemical analysis for each compound. The area analysis of the outer left high energy peak of the composition $\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}_4$ is given in Figure 3.

(ii) Quadrupole interactions

The electric field gradient (EFG) at a ^{57}Fe nucleus may arise from a non spherical distribution of the 3d electrons of the ion itself and from the charges on neighbouring ions. However, since Fe^{3+} has a half filled 3d-shell, the EFG can arise from the neighbouring ions and thus exists only

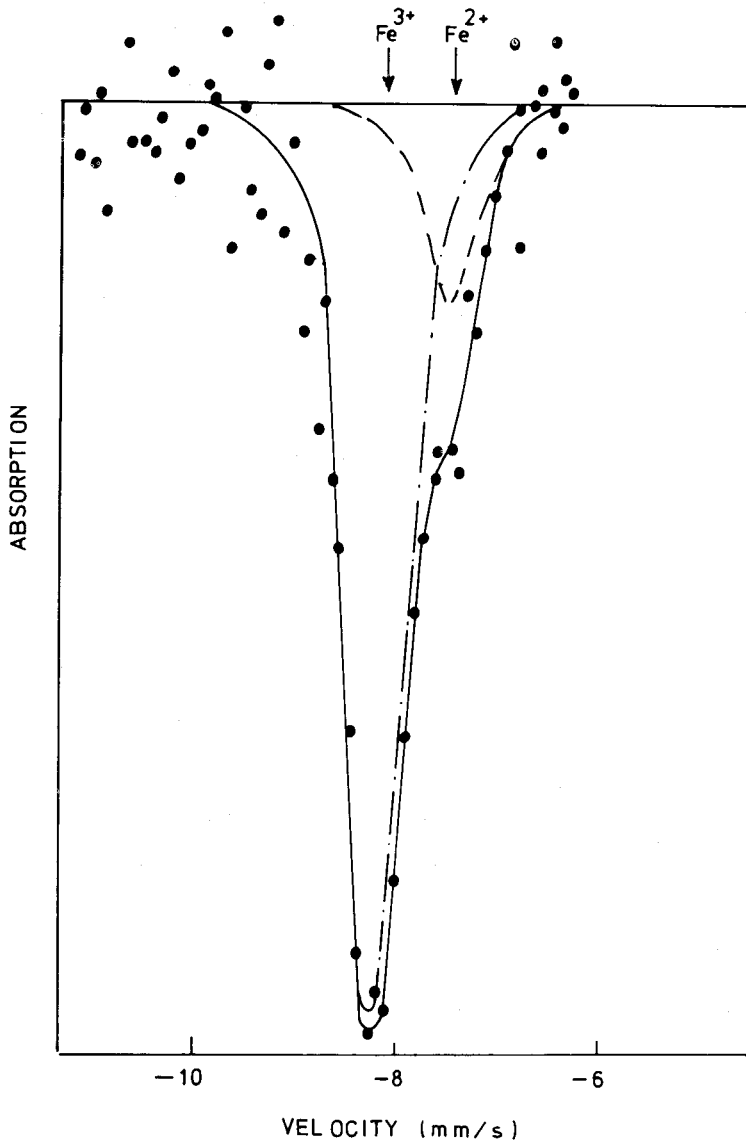


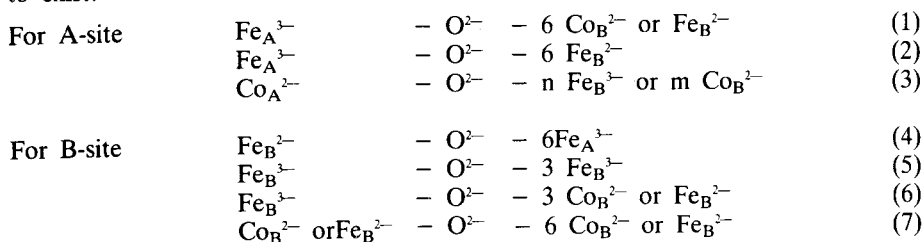
Fig. 3. Analysis of area of the outer left hand line of the $\text{Co}^{2+}_{0.80}\text{Fe}^{2+}_{0.32}\text{Fe}^{3+}_{1.94}\text{O}_4$ Mossbauer spectrum.

at those sites having non-cubic point symmetry. On the other hand, Fe²⁺ has a nonspherical of the 3d electrons, due to the presence of an excess electron, and an EFG is expected. In a system exhibiting chemical disorder, the tetrahedral sites have cubic point symmetry and thus experience no EFG. The octahedral or B-sites, however, have trigonal symmetry and thus an EFG exists with principal axis along [111] direction. The electric field gradient at the octahedral site arises not only from the metal cations, but also the oxygen anions, along the [111] direction. The cubic symmetry of the A-site is maintained, but the octahedron of the oxygen around the B-sites becomes distorted and changes the trigonal component of the octahedral EFG. The oxygen positions are characterized by the oxygen parameter *u* [11] which is equal to 3/8, when there is no distortion. The spinel structure and thus the EFG of the Co^{2-x} Fe^{2-1-x} Fe³⁻² O²⁻⁴ ferrite system is then characterized by the oxygen parameter *u*.

From Table 1 we notice that both tetrahedral and octahedral subsepectra have no remarkable quadrupole shift (in the range of experimental error), indicating the cubic symmetry in both sites. This probably could be due to the replacement of cations, having nearly the same ionic radii [30], which means that the exchange of ions causes no lattice distortion, i.e. no change in the oxygen parameters is expected. Therefore, the relatively large quadrupole shift observed for the pattern III of the mixed compounds with *x* = 0.8 and 0.9 could be explained as indicated above, due to the nonspherical charge distribution of the Fe²⁺ ions [31]. The measurements at higher temperatures up to the Neel point for these samples (Figure 4), showed a gradual decrease of the quadrupole shift to zero, which could be attributed to the quenching of the total angular momentum of the ions.

(iii) Hyperfine magnetic fields

The preceeding analysis of experimental data showed that for the stoichiometric cobalt ferrite, the nuclear magnetic field is considerably smaller for the A-site Fe³⁺ cations than that the B-site iron cations. On the other hand, for the magnetite the situation is the reverse [32]. This is a problem still open to discuss. Since generally in spinel structures each A-site ion is surrounded by twelve nearest B-sites and each B-site ion has six B-sites and six A-sites as nearest neighbours. Then for the inverse Co²⁺ Fe³⁺ O₄ or Fe²⁺ Fe³⁺ O₄, each tetrahedral iron ion will have on the average half of its intersublattice magnetic bonds with Co²⁺ or Fe²⁺ and the other half with Fe³⁺ ions, while every octahedral Fe³⁺ ion will have on the average 3/4 of the magnetic bonds with iron and 1/4 of Co²⁺ or Fe²⁺. The following ferrimagnetic interactions are expected to exist:



The interaction number (3) is a result of the non complete inversion in the compound CoFe₂O₄ [16]. On the other hand, the interaction number (6) may be the most efficient one for the above contradiction between Fe₃O₄ and CoFe₂O₄ data, when considering both the magnetic moment of cations and super exchange interaction integrals between sublattices [33]. Figure 4 shows some resonant absorption spectra of the composition Co²⁺_{0.80} Fe²⁺_{0.32} Fe³⁺_{1.94} O₄ at

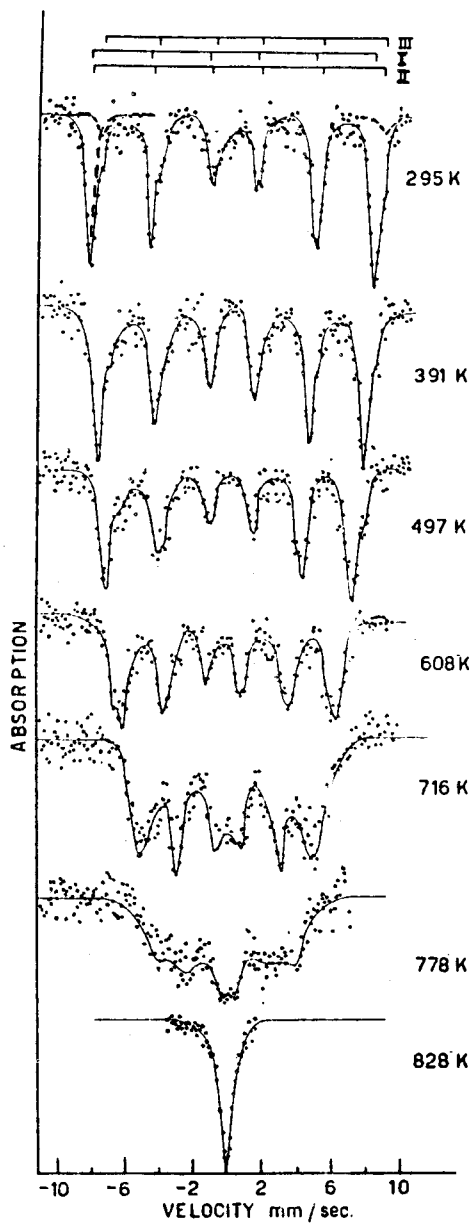


Fig. 4. Mossbauer absorption spectra of Fe^{57} in the composition $Co^{2+}_{0.80} Fe^{2+}_{0.32} Fe^{3+}_{1.94} O_4$ recorded at various temperatures.

different temperatures in its magnetically ordered state. At 300K the spectrum exhibits defined absorption lines and three sites were possible to be resolved. At higher temperatures the absorption lines become very broad and the splitting of the outer lines is no longer visible. However it is still possible to get an acceptable description with a sum of three six lines patterns, but as expected, the quality of the fit decreases with increasing temperature. At 828 K, there is no observed indication for the presence of any magnetic ordering at that temperature and only single peak is observed. Figure 5 shows the temperature dependence of the magnetic hyperfine fields for the $\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}_4$ compound relative to the most observed sextet II, this is because of the complexity of the Mossbauer effect spectrum at high temperatures. The intersection of the curve with the magnetic hyperfine field axes gives $H_{\text{eff}}(0)$ while the intersection with the temperature axes gives Neel transition point $T_N = 814 \pm 10\text{K}$. The relative magnetic hyperfine fields $H(T)/H(0)$ are plotted versus $(1 - T/T_N)$ on a double logarithmic scale, the slope value of the curve is close to 1/3 and verifying the one third power law [34].

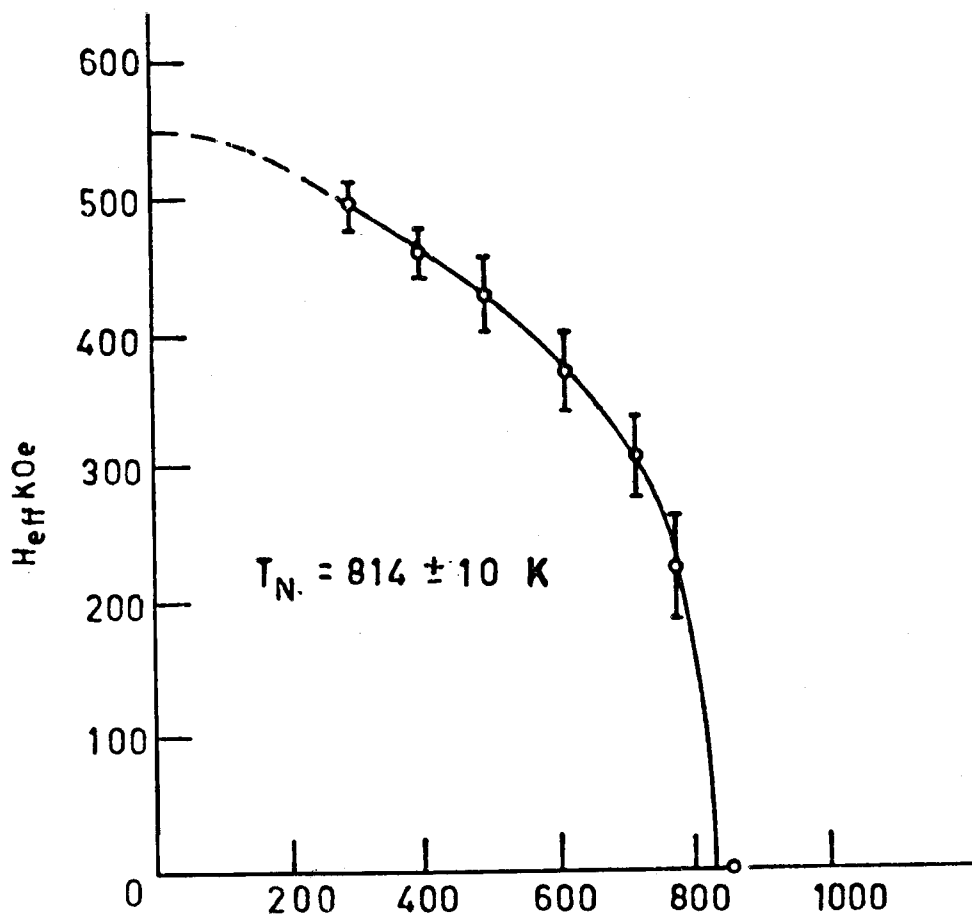


Fig. 5. Magnetic hyperfine field of the octahedral ferric ions versus temperature for the ferrite $\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}_4$.

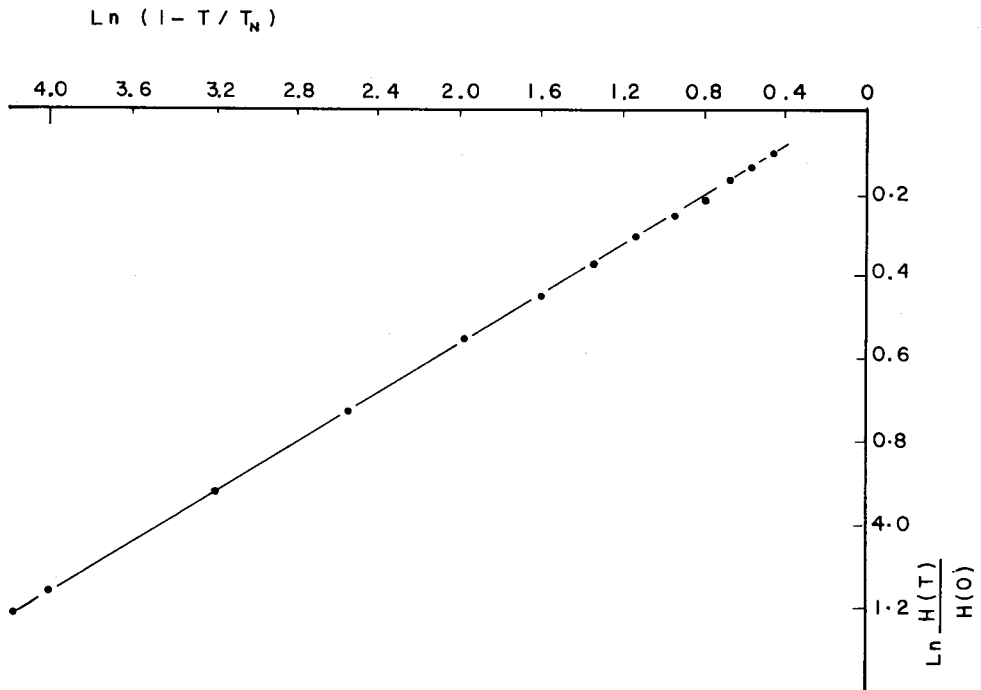


Fig. 6. The one third power law, applied for B-site in the spinel $\text{Co}^{2+}_{0.80} \text{Fe}^{2+}_{0.32} \text{Fe}^{3+}_{1.94} \text{O}_4$.

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«دراسة تأثير موسباور في المجتيتايت المطعم بالكوبالت»

محمد خورشيد فايق

علاء الدين بهجت

لقد تم دراسة تأثير موسباور في مجموعة الحديديات كوس^ح ٣-س^أ (حيث س = ٠,٨ ، ٠,٩ ، ١) ذات التركيب البللورى للاسبنيل في درجات الحرارة (٧٨ - ٨٣٠) درجة مطلقة . وقد ظهر طيف زيمان للعينة ذات قيمة س = ١ وله مجموعتان منطبقتان للتركيب المغناطيسي فوق الدقيق تنتمي إلى الحديد الثلاثي في مواقع رباعية وثمانية الأسطح . وقد تم بنجاح تحليل طيف موسبار للعينات ذات قيم س = ٠,٨ ، ٠,٩ إلى ثلاث مركبات اثنتين منها تنتمي للحديد الثلاثي أما الثالث فينتهي للحديد الثنائي في موقع ثماني الأسطح . وقد تم تعيين درجة حرارة التحول المغناطيسي لهذه العينات وحساب كل بارامترات موسباور لها ومناقشة قيمتها في ظل التفاعلات المغناطيسية الممكنة .