JOURNAL OF MATERIALS SCIENCE 23 (1988) 3357–3361

On the substitution of calcium in cobalt ferrite

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X-ray, magnetization, susceptibility and Mössbauer spectroscopic measurements have been performed on the Co–Ca ferrite system, $Ca_xCo_{1-x}Fe_2O_4$. The measurements show that a solid solution is possible only for $x < 0.2$. Thereafter the system shows a mixture of two phases. The variations in lattice constant and Néel temperature are explained on the basis of calcium substitution. The decrease in magnetization in the mixed phases is due to an increase of paramagnetic phase and decrease of ferrimagnetic phase with concentration. The Mössbauer spectra at 300 and 77 K support the concept of mixed phases.

1. Introduction

In previous work [1, 2] we have studied the $Ca_xCo_{1-x}Fe_2O_4$ system for $x \leqslant 0.4$, by means of Mössbauer spectroscopic measurements at room temperature (300 K), magnetization measurements at 300 and 77 K and susceptibility measurements from room temperature to the Néel temperature (T_N). From the above measurements it was concluded that the only 15% calcium can be substituted in cobalt ferrite without altering the cubic structure. At $x = 0.2$ an additional phase appears and it grows in intensity as the concentration increases. X-ray and Mössbauer measurements show that the newly appearing phase is orthorhombic and paramagnetic in nature. The ion distribution found ($x \leqslant 0.15$) from the Mössbauer spectroscopic and X-ray measurements is given elsewhere [1]. The Ca^{2+} ions occupy A sites. To estimate the Néel temperatures theoretically the ion distribution previously found [1] was used.

It is interesting to prepare the calcium-rich phase of this mixed ferrite system to see how much percentage of cobalt can be substituted in calcium ferrite and to observe the structural change if any occurs. This paper deals with X-ray diffraction, susceptibility, magnetization and Mössbauer spectroscopic measurements. The X-ray analysis was performed to characterize the samples. The magnetization measurements were undertaken to investigate the variation of saturation magnetization (σ_s) with calcium concentration. The variation of low-field a.c. susceptibility (χ) with temperature (T) was studied to determine the Néel temperatures and to see the χ–T behaviour. The Mössbauer studies of the Co–Ca ferrite system were performed to investigate the magnetic properties of this ferrite system for varying calcium concentration at 300 and 77 K.

2. Experimental procedure

Samples were prepared by the usual ceramic method. Reagent-grade oxides Fe_2O_3, CaO and CoO were mixed in the proper proportions to yield the desired composition, pelletized and fired at 900° C for 48 h and slowly cooled down to room temperature. The powder X-ray diffraction patterns were recorded on a Philips diffractometer using Fe$K\alpha$ radiation to characterize the samples. The a.c. susceptibility measurements of powdered samples with temperature were performed using a double coil set-up [3] operating at a frequency of 263 Hz and r.m.s. field of 0.5 Oe. Magnetization measurements were carried out using the high-field hysteresis loop techniques described elsewhere [4]. Room-temperature and low-temperature Mössbauer spectra were obtained with a constant acceleration transducer and a 512 multichannel analyser operating in the time mode. A gamma source of ^{57}Co(Rh) of 10 mCi was used. All the spectra were obtained in the transmission geometry and 14.4 keV gamma rays were detected with a xenon–methane-filled proportional detector. The spectrometer was calibrated using iron metal foil. The absorbers were made of thickness between 20 and 30 mg cm^{-2}. The low-temperature Mössbauer spectra were obtained with the same spectrometer used with a liquid nitrogen cryostat.

3. Results and discussion

X-ray analysis of the Co–Ca ferrite system shows a single phase (cubic) for $x \leqslant 0.15$ and a mixture of two phases (cubic and orthorhombic) for $x = 0.2$ to 0.9. A plot of the lattice constant (a) of the cubic phase against x is shown in Fig. 1. It is clear from Fig. 1 that the lattice constant initially increases up to $x = 0.2$, then it decreases as the concentration is increased further; it remains constant for $x = 0.5$ to 0.9. The increase in lattice constant for the cubic phase can be explained by similar arguments to those used for the Cu–Zn ferrite system [5]. The Ca^{2+} ions, having the larger ionic radius (0.099 nm), when substituted for the divalent metal ions in the lattice, replace the smaller Fe^{3+} (0.060 nm) and Co^{2+} (0.074 nm) ions on the A sites. The reverse is also true for the decrease in lattice constant, so the decrease in lattice constant at $x = 0.25$ can be attributed to the reduction of Ca^{2+} ions on the A sites. The continuous decrease of lattice constant till $x = 0.5$ suggests that there is a continuous reduction of Ca^{2+} ions on the A sites of the

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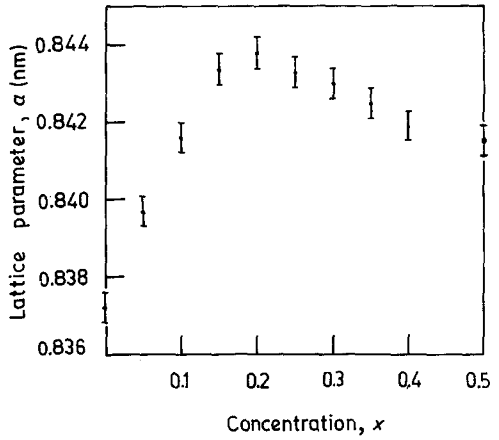

Figure 1 Variation of the lattice constant (cubic phase) of the $Ca_xCo_{1-x}Fe_2O_4$ system as a function of concentration (x), for $x \leqslant 0.5$.

cubic lattice. It remains constant for $x \geqslant 0.5$, suggesting constancy in the ion distribution of the cubic phase. The maximum lattice constant obtained at $x = 0.2$ does not mean that the substitution is 20% because the rise in lattice constant from $x = 0.15$ to 0.2 is very small compared to that for $x = 0.1$ to 0.15. The decrease in magnetization and the appearance of paramagnetic doublet in the Mössbauer spectrum and an additional phase in the X-ray data at $x = 0.2$ confirm that the substitution of Ca^{2+} ions is less than 20% but is greater than 15%. From the behaviour of the lattice constant one can approximately estimate it to be 16%. The X-ray lines become broader for $x > 0.2$; this may be due to a distribution of calcium substitution.

The appearance of an additional phase (orthorhombic) at $x = 0.2$ grows in intensity with x. The observed lattice constants for this phase remain constant and are exactly the same as those of pure calcium ferrite. The intensities of the X-ray lines of this phase increase with x while those of the cubic phase decrease. This suggests that the second phase observed at $x = 0.2$ may be due to pure calcium ferrite. The continuous increase in the intensites of X-ray lines of the orthorhombic phase up to $x = 1.0$ suggests that the concentration of this phase increases with x.

The saturation magnetizations (σ_s) at 300 K of all the samples have been estimated within an accuracy of 5% and are listed in Table I. σ_s shows a linear increase with x for $x \leqslant 0.15$; thereafter it slowly falls to zero at $x = 1.0$. The decrease in magnetization is due to the presence of orthorhombic phase in the sample, because this phase is paramagnetic at room temperature (Mössbauer data). In addition to this, the reduction of calcium substitution with x also decreases the magnetization. The observed decrease in magnetization in the sample is due to the combined effect of the above two factors. As in our discussion of the X-ray results, for $x > 0.2$ the calcium substitution reaches less than 16% in the cubic phase and the remaining phase appears as calcium ferrite; therefore more and more calcium ferrite develops in the sample and the cubic phase proportionately decreases constantly with x and so does the magnetization.

Fig. 2 displays typical plots of the relative a.c. susceptibility χ/χ_{RT} (RT = room temperature) against temperature (T) in an r.m.s. field of 0.5 Oe for $x = 0.05$, 0.2, 0.3, 0.6 and 0.8. The explanation for the observed peaking effect near T_N and the broad peak around 530 K in χ–T plots is given in our earlier work [2]. The same χ–T curve was observed for $x = 0.5$ to 0.9 samples (Fig. 2). This suggests an identical magnetic phase for $x = 0.5$ to 0.9. The Néel temperatures have been obtained and are given in Table I. The observed Néel temperatures for $x \geqslant 0.2$ correspond to the cubic phase in the mixture of two phases because, as mentioned earlier, the second phase is paramagnetic at room temperature. The decrease in Néel temperature up to $x = 0.2$ (Table I and Fig. 2) is due to the substitution of non-magnetic Ca^{2+} ions on the A sites of cobalt ferrite. The increase in Néel temperature at $x = 0.25$ indicates a reduction of Ca^{2+} ions on the A sites, that is a decrease in calcium substitution at $x = 0.25$. The further decrease in Néel temperature from $x = 0.3$ to 0.5 shows a continuous reduction of the Ca^{2+} ions on the A sites of the cubic phase. The Néel temperature remains constant for $x = 0.5$ to 0.9. A tailing effect (not shown in Fig. 2) in the χ–T behaviour is observed for $x > 0.2$ and may be due to a distribution of calcium substitution. These results are in confirmity with our X-ray results.

TABLE I Magnetization measurements of Co–Ca ferrite system at 300 K

x	σ_s (e.m.u. g^{-1})	T_N (K)*	
		Observed	Calculated
0.00	79	808	–
0.05	86	790	785
0.10	97	765	761
0.15	105	740	736
0.20	84	738	
0.25	66	748	
0.30	59	768	
0.35	47	793	
0.40	42	793	
0.50	32	798	
0.60	23	798	
0.70	17	798	
0.80	11	798	
0.90	5	798	

* T_N within the accuracy of ±5 K.

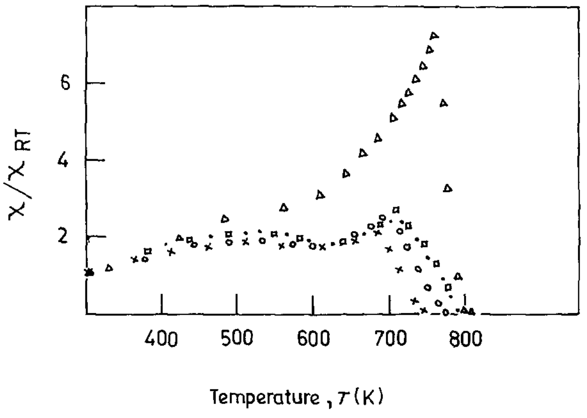

Figure 2 The temperature dependence of relative a.c. susceptibility (χ/χ_{RT}) at low field for the $Ca_xCo_{1-x}Fe_2O_4$ system for x = (△) 0.05, (x) 0.2, (○) 0.3, (●) 0.6 and (□) 0.8.

The Néel temperatures are also estimated theoretically for $x = 0.05$ to 0.15, applying molecular field theory and using the ion distribution found from X-ray and Mössbauer measurements. The Néel temperature depends upon the active magnetic linkages per magnetic ion per formula unit. The substitution of non-magnetic ions on A sites reduces the active magnetic linkages and therefore the Néel temperature. Theoretical calculations to estimate Néel temperatures for substituted spinel ferrites are given by Gilleo and Geller [6, 7] using a statistical model, and give

$$T_N(k_0, k_t) = \frac{3n(k_0, k_t)T_N(0, 0)}{24N(k_0, k_t)}$$

Here 24/3 is the number of interactions per magnetic ion per formula unit. $T_N(0, 0)$ is the Néel temperature of unsubstituted ferrite. $n(k_0, k_t)$ denotes the active magnetic interactions per formula unit and is given by

$$n(k_0, k_t) = 24(1 - k_0)[1 - E_0(k_t)](1 - k_t) \times [1 - E_t(k_0)]$$

where k_0 and k_t are the fractions of non-magnetic ions substituted on octahedral and tetrahedral sites, respectively. $E_0(k_t)$ and $E_t(k_0)$ are the probabilities of octahedral and tetrahedral sites being substituted by none or one magnetic ion, respectively. $N(k_0, k_t)$ denotes the number of magnetic ions actively participating in the ferrimagnetism and is given by

$$N(k_0, k_t) = 2(1 - k_0)[1 - E_0(k_t)] + (1 - k_t)[1 - E_t(k_0)]$$

In the equation for estimating T_N the factor 3/24 is considered assuming three magnetic ions per formula unit for an unsubstituted ferrite. This is not true in most of the mixed ferrites like $MgFe_2O_4$-$ZnFe_2O_4$ [8] and $MgFe_2O_4$-$CdFe_2O_4$ [9]. There are only two magnetic ions per formula unit. In the case of the $CoFe_2O_4$-$ZnFe_2O_4$ system [10, 11] there are three magnetic ions for an unsubstituted ferrite ($CoFe_2O_4$). Under these circumstances there are varying numbers of (Fe^{3+})-O^{2-}-$[Fe^{3+}]$ and (Fe^{3+})-O^{2-}-$[Co^{2+}]$ linkages of different strength which must be taken into account in determining the Néel temperatures.

Considering the above factors, the Néel temperature $T_N(x)$ for a substituted ferrite can be expressed in terms of an unsubstituted ferrite, $T_N(x = 0)$, by

$$T_N(x) = \frac{M(x = 0)T_N(x = 0)n(x)}{n(x = 0)M(x)}$$

Here $M(x)$ is the relative weighted total magnetic ions per formula unit, calculated by considering the weighting of magnetic ion M′ to that of iron ion as $\mu_{M'}/\mu_{Fe}$ where $\mu_{M'}$ and μ_{Fe} are the magnetic moments of M′ and iron ions, respectively. $M(x)$ can be expressed as

$$M(x) = 2 + (1 - x)\frac{\mu_{M'}}{\mu_{Fe}}$$

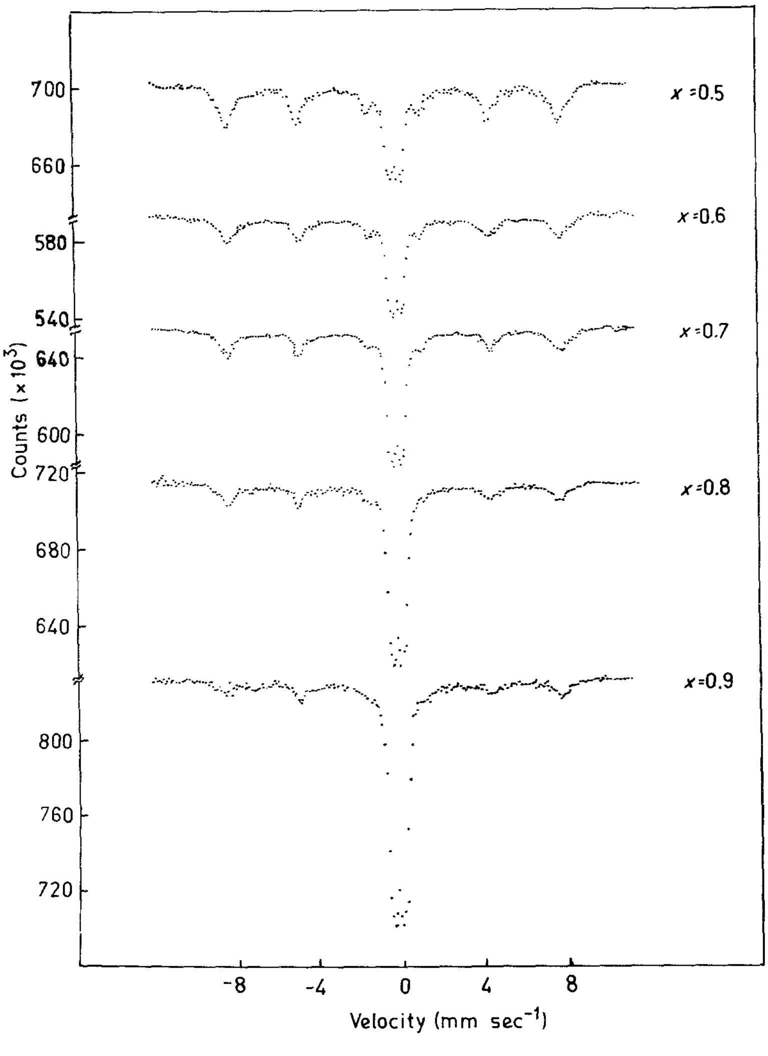

Figure 3 Room-temperature (300 K) Mössbauer spectra of the $Ca_xCo_{1-x}Fe_2O_4$ system for $x = 0.5$, 0.6, 0.7, 0.8 and 0.9.

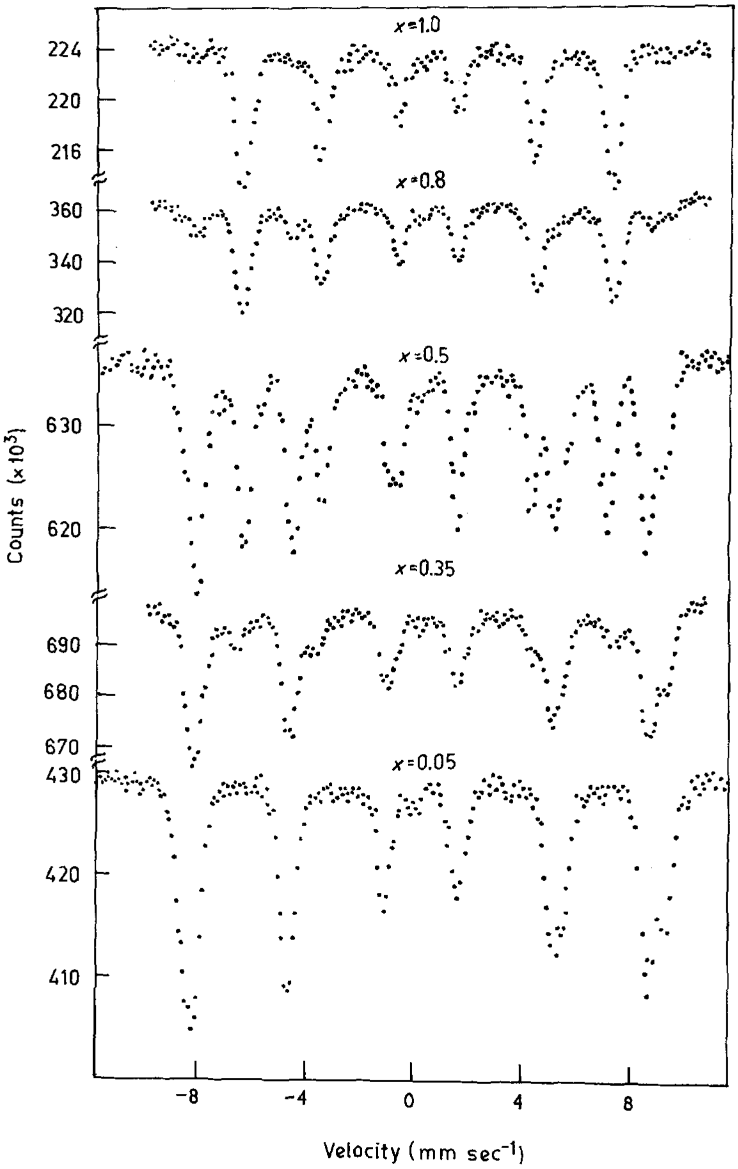

Figure 4 Mössbauer spectra of the $Ca_xCo_{1-x}Fe_2O_4$ system at 77 K for $x = 0.05, 0.35, 0.5, 0.8$ and 1.0.

where x is the non-magnetic substitution. $n(x)$ is the number of relative weighted magnetic interactions per formula unit, calculated considering the weighting of A–O–B magnetic interaction to that of Fe–O–Fe as $\mu_i\mu_j/\mu_{Fe}^2$, where μ_i and μ_j are the magnetic moments of corresponding magnetic ions; $n(x)$ is given by

$$n(x) = \frac{24}{25}\sum_{i,j=1}^{2} A_i B_j \mu_i \mu_j$$

where A_i and B_j are the fractions of magnetic ions on the tetrahedral and octahedral sites, respectively. Here $i, j = 1$ stands for magnetic ions M′ and $i, j = 2$ for that of iron. The Néel temperatures estimated using the above equation for $x \leqslant 0.15$ are in very good agreement with experimentally observed Néel temperatures and are given in Table I. Néel tempertures of the Mg–Zn ferrite system [8] were estimated using the above equation and are in very good agreement with experimentally observed Néel temperatures.

Fig. 3 displays the room-temperature Mössbauer spectra for $x = 0.5$ to 0.9. A doublet superimposed on a six-line pattern was observed. The six-line pattern corresponds to the cubic phase and the doublet corresponds to the orthorhombic phase. There is no change in the position of the inner doublet with concentration. The only change is in the intensity. The intensity increases with x and is maximum at $x = 1.0$, while that of six-line pattern decreases. This is in very good agreement with our X-ray data. The presence of a six-line pattern in the Mössbauer spectrum and the observation of a cubic phase in the X-ray data for $x = 0.9$ indicates non-substitution of cobalt in calcium ferrite. It is concluded from the above observations that the other phase seen in the mixed ferrites is pure calcium ferrite. Typical Mössbauer spectra for $x = 0.05, 0.35, 0.5, 0.8$ and 1.0 at 77 K are shown in Fig. 4. The spectra for $x = 0.05$ and 1.0 are only due to pure cubic and orthorhombic phases, respectively, whereas the spectra for $x = 0.35$, 0.5 and 0.8 can be clearly attributed to two mixed phases (cubic and orthorhombic). The orthorhombic phase has a Néel temperature between 300 and 77 K, and gives a six-line pattern at 77 K (Figs 3 and 4). Therefore the Mössbauer spectra taken at 77 K (Fig. 4) show a composite of two six-line patterns corresponding to both phases.

4. Conclusion

The system $Ca_xCo_{1-x}Fe_2O_4$ has been studied in detail by means of X-ray diffraction, magnetization, susceptibility and Mössbauer spectroscopic measurements. It has been found from the above measurements that a solid solution is possible up to $x \sim 16\%$. An additional phase observed for $x > 0.15$ is due to pure $CaFe_2O_4$. The variations in Néel temperature and saturation magnetization with x can be explained on the basis of calcium substitution. The theoretically estimated Néel temperatures for $x \leqslant 0.15$ agree very well with the experimentally observed values.

Acknowledgements

The authors are thankful to RSIC, IIT, Bombay for providing X-ray diffractometric charts. One of the authors (G.J.B.) wishes to thank the Council of Scientific and Industrial Research, New Delhi for providing financial support in the form of a Senior Research Fellowship.

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Received 5 October 1987
and accepted 29 January 1988