Magnetic properties of Cd and Al substituted cobalt ferrite

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The crystal structure and magnetic properties of simultaneously substituted cadmium and aluminium spinel series 
\( \text{Co}_{1-x}\text{Cd}_{x}\text{Fe}_{2-x}\text{Al}_{x}\text{O}_4 \) with \( x=0.0, 0.1, 0.2, 0.3, 0.4 \) and 0.5, are studied by X-ray diffraction and saturation magnetization measurements. The single phase fcc spinel structure of all the samples was confirmed by X-ray diffraction. X-ray analysis showed that the lattice parameter \( a' \), increases with increasing \( x \). The apparent density and X-ray density exhibit similar behaviour. The Bragg peaks of XRD patterns were used to determine the possible cation distribution among the tetrahedral (A) and octahedral [B] sites. X-ray intensity calculations indicate that \( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \) ions occupy tetrahedral (A) and octahedral [B] sites respectively, while \( \text{Fe}^{3+} \) ions occupy both tetrahedral (A) and octahedral [B] sites.

The saturation magnetization \( \chi_s \) and magneton number \( n_0 \) (the saturation magnetization per formula unit) measured at 300 K using high field hysteresis loop technique decrease with increasing \( x \), suggesting decrease in ferrimagnetic behaviour. Neel’s two sublattice model is applicable up to \( x \leq 0.2 \) while Y-K three sublattice model is applicable for \( x \geq 0.2 \). The cation distribution obtained from magnetization data is in good agreement with the cation distribution estimated from X-ray intensity calculations. The Neel temperature \( T_N \) deduced from a.c. susceptibility data decreases with \( x \), suggesting a decrease in ferrimagnetic behaviour.

Oxides having the general formula \( \text{AB}_2\text{O}_4 \) (A and B are transition metal ions) and crystallizing with spinel like structure (Fd \( 3m-O_h^3 \)) have been gaining attention in recent years. The interest in these oxides emerges from their versatile applicability in the radio to microwave frequency regions. The cobalt ferrite \( \text{CoFe}_2\text{O}_4 \) possesses an inverse spinel structure and the observed degree of inversion depends upon the heat treatment\(^1\). The interesting physical and chemical properties of spinel ferrites arise from the ability to distribute the cations among the available tetrahedral (A) (Interstices with four nearest neighbours) and octahedral [B] (Interstices with six nearest neighbours) sites\(^2\). It is well known that when ferrites are sufficiently diluted with non-magnetic atoms they can show a wide spectrum of magnetic structures; ferrimagnetic order, cluster spin glass, etc.\(^3\)

Most of the Zn substituted mixed ferrites like Ni-Zn\(^4\), Cu-Zn\(^5\) and Co-Zn\(^6\) show canted spin arrangement on the octahedral site. Zinc substituted spinel ferrites show good magnetic properties for technical applications. As Zn and Cd are both divalent, it would be interesting to investigate similar effects in Cd substituted ferrites. The magnetic properties of \( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \) substituted\(^2,9\) \( \text{CoFe}_2\text{O}_4 \) have been studied separately. Practically, no information about the magnetic properties of the \( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \) substituted \( \text{CoFe}_2\text{O}_4 \) ferrite system exists in the literature. The aim of the present study is to prepare and investigate the structural and magnetic properties of simultaneously diluted cobalt ferrite by \( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \) non-magnetic substituents at tetrahedral and octahedral sites.

**Experimental Procedure**

The samples of \( \text{Cd}^{2+} \) and \( \text{Al}^{3+} \) co-substituted cobalt ferrite \( \text{Co}_{1-x}\text{Cd}_{x}\text{Fe}_{2-x}\text{Al}_{x}\text{O}_4 \) with \( x=0.0 \) to 0.5 in steps of 0.1 were prepared by usual double sintering ceramic method in which a molar ratio of analar \( \text{CoO}, \text{CdO}, \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) (all 99.9% pure supplied by E. Merck) were mixed and then ground to a very fine powder by using agate mortar for about two hours. Pre-sintering was carried out at 990\(^\circ\)C and the final sintering was done at 1050\(^\circ\)C for compressed pellet form of diameter 10 mm and thickness of about 3 mm.

The phase purity of the samples was analyzed using X-ray powder diffractometer (XRD; Model PW 1710, Philips, Netherlands). Data collection was carried out using a Cu target at 25 kV and 20 mA in the range 20-70\(^\circ\). A step scan with step size of 0.02\(^\circ\) and 0.5 s count was used. The magnetization measurements of all the samples were carried out...
using high field hysteresis loop technique\textsuperscript{10} at 300 K. The a.c. susceptibility measurements on powdered samples were made in the temperature range 300–800 K using a double coil set up\textsuperscript{11} operating at a frequency of 263 Hz and in r.m.s. field of 7 Oe.

\textbf{Results and Discussion}

The single phase formation of the composition of the ferrites has been confirmed from X-ray diffraction pattern. Fig. 1 depicts typical X-ray diffraction patterns for $x=0.1 \& 0.5$ of $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$ ferrite. The $d$ spacing for the recorded peaks are calculated according to Bragg's law. The lattice constant $a_{\text{exp}}$ with an accuracy of $\pm 0.002 \text{ Å}$ is calculated using the least square fit programme. The lattice parameter $a'$ as a function of composition is given in Table 1. The applicability of Vegard's law\textsuperscript{12}, which refers to linear variation of lattice parameter with change in composition in a solid solution, has also been tested. Fig. 2 shows linear Vegard's plots for the series $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$. It is evident from Fig. 2 that the lattice parameter $a'$ increases with composition $x$, because $\text{Cd}^{2+}$ ions with larger ionic radius (1.03 Å) replace $\text{Co}^{2+}$ (0.72 Å) which have smaller ionic radii on the tetrahedral [A] site. The X-ray density (theoretical) $d_\text{X}$ was calculated as follows:

$$d_\text{X} = \frac{M \times N}{\chi^3} \text{ g cm}^{-3}$$  \hspace{1cm} (1)

where $M$ is molecular weight and $N$ is the Avogadro's number. The values of X-ray density are summarized in Table 1. It is evident from Table 1 that X-ray density decreases with $x$ which is consistent with linear increase in $a'$ with $x$. The average particle size for all the compositions is estimated from full width at half maximum of X-ray diffraction line by using Scherrer formula\textsuperscript{12} as summarized in Table 1.

The saturation magnetization $\sigma_\text{s}$ and the magnetization number $n_B$ (the saturation magnetization per formula unit in Bohr magneton) at 300 K obtained from the hysteresis loop technique\textsuperscript{10} for $x=0.1$ to 0.5 are summarized.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
$X$ & Lattice parameter & X-ray density & Particle size \\
\hline
$0.1$ & $8.381$ & $5.350$ & $333$ \\
$0.2$ & $8.415$ & $5.339$ & $292$ \\
$0.3$ & $8.445$ & $5.337$ & $333$ \\
$0.4$ & $8.464$ & $5.356$ & $292$ \\
$0.5$ & $8.514$ & $5.315$ & $166$ \\
\hline
\end{tabular}
\caption{Lattice parameter, X-ray density for $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$ system}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$X$ & $\sigma_\text{s}$ (emu/g) & $n_B$ ($\mu_B$) & Curie Temperature (K) \\
\hline
$0.1$ & $68.07$ & $2.890$ & $3.20$ & $740$ \\
$0.2$ & $71.27$ & $3.058$ & $3.40$ & $665$ \\
$0.3$ & $64.17$ & $2.781$ & $3.60$ & $620$ \\
$0.4$ & $49.92$ & $2.186$ & $3.80$ & $580$ \\
$0.5$ & $26.37$ & $1.166$ & $4.00$ & $510$ \\
\hline
\end{tabular}
\caption{$\sigma_\text{s}$, $n_B$, Curie temperature for $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$ system}
\end{table}

\begin{figure}
\centering
\begin{subfigure}{0.45\textwidth}
\includegraphics[width=\textwidth]{fig1.png}
\caption{Typical XRD pattern for $x=0.1$ and $x=0.5$}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\includegraphics[width=\textwidth]{fig2.png}
\caption{Variation of lattice parameter $a'$ with $x$}
\end{subfigure}
\end{figure}
are summarized in Table 2. From field dependence of magnetization and observed magnetic moments (Table 2), it is clear that the samples with $x=0.1$ to $0.5$ show ferrimagnetic behaviour which decreases with increasing $x$ values. From the observed magnetic moment and $n_B$ values, it is clear that $n_B$ increases with $x$ up to $x<0.2$ and thereafter it decreases.

It is evident from Table 2 and Fig. 4 ($n_B$ versus $x$) that the $n_B$ gradually increases on increasing $x$ values attains a maximum at $x \sim 0.2$ and then decreases with further increase in $x$.

The cation distribution depends on many factors such as temperature, pressure and compositions$^{13,14}$ and also, on the method of preparation of the compounds$^{13,16}$. In the present method, based on X-ray diffractogram, the ratio of intensities due to the reflection (220) and (440) has been chosen as a criterion to determine the cation distribution. The calculated intensity ratios were then compared with the observed intensity ratios. A similar procedure was adopted by Datta and Roy$^{14}$. The absorption and temperature factors are not taken into account in our calculations because these do not affect the relative intensity calculations for spinels at room temperature$^{17}$. It has been reported$^{18,19}$ that the cations, Cd$^{2+}$ and Al$^{3+}$, have marked preference for tetrahedral (A) and octahedral [B] sites respectively.

The basic equation used to calculate the intensity of the reflection due to the plane (hkl) is,

$$I_{hkL}=I_{hkL}^{\mu}P\left(1+\cos^2\upsilon\right)/\sin^2\upsilon \cos \upsilon$$  \hspace{1cm} (2)

where $I_{hkL}$ is the intensity of the plane (hkl), $P$ the multiplicity factor for the plane (hkl), and $(1+\cos^2\upsilon/\sin^2\upsilon \cos \upsilon)$ is the Lorentz polarization factor. The structure factor $F$ is a function of oxygen parameter $\upsilon$ as well as distribution parameter $y$. The formulae for the structure factors for the planes (hkl) are taken from those reported by Furahashi et al.$^{20}$ The multiplicity factor and Lorentz polarization factor are taken from literature$^{12}$. The ionic scattering factors$^{21}$ are used for the calculation of the structure factor $F$.

Calculations of intensity for the planes (220) and (440) are made for various values of distribution parameter $y$ using a computer programme. The value of the distribution parameter $y$ is reached by comparison of theoretical and experimental intensity ratios of (220) and (440) planes. The value of $y$ for which the theoretical and experimental intensity ratios agree close, taken to be the correct and the value of $y$ computed as described above. Fig. 3 shows the calculated and observed intensity ratios for the plane (220) and (440) for all the compositions. The analysis of X-ray intensity data suggests the following general cation distribution, for $x=0.1$ to $0.5$.

$$(\text{Cd}^{2+}_{x} \text{Fe}^{3+}_{1-x})(\text{Co}^{2+}_{x} \text{Al}^{3+}_{x} \text{Fe}^{3+}_{x})\text{O}_4 \quad \text{(3)}$$

According to Neel’s$^{22}$ two sublattice model of ferrimagnetism, the magnetic moment per formula unit in $\mu_B$, $n_B^N$, is expressed as:

$$n_B^N(x)=M_B(x)-M_A(x) \quad \text{(4)}$$

where, $M_B$ and $M_A$ are the B and A sublattice magnetic moment in $\mu_B$. The calculated $n_B^N(\mu_B)$ values for $x=0.1$ to $0.5$ have been calculated using Eqs (3)-(4), and also the ionic magnetic moments of Fe$^{3+}$

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**Fig. 3** — Intensity ratio $I_{220} / I_{440}$ versus $x$

**Fig. 4** — Variation of $n_B$ with $x$
MAGNETIC PROPERTIES OF Cd AND Al SUBSTITUTED COBLAT FERRITE

Fig. 5—Plots of normalized a.c. susceptibility versus temperature (for x=0.1 to 0.3)

The calculated \( n_B^{N} \) (\( \mu_B \)) values for x=0.1 to 0.5 using Eqs (3)-(4) are shown in Fig. 4. The calculated \( n_B^{N} \) values for x=0.1 & 0.2 agree very well with the observed \( n_B \) values, confirming the collinear spin ordering. The calculated \( n_B^{N} \) values for x=0.3 to 0.5 clearly differ from the observed values (Fig. 4) indicating that significant canting exists on B-site suggesting magnetic structure to be non-collinear. Thus, the change of spin ordering from collinear to non-collinear display a strong influence on the variation of saturation magnetic moment per molecule as observed in magnetization (Fig. 4) with chemical composition.

The lattice constants, which depend on the assumption about the cation distribution, were also obtained theoretically by the following relation 21:

\[
a_0 = \frac{8}{3}\sqrt{\frac{1}{2}} (r_A + r_B) + \frac{5}{3}\sqrt{\frac{1}{2}} (r_B - r_A)
\]

where, \( r_A \) is the radius of the oxygen ion (1.32 Å), \( r_A \) and \( r_B \) are the ionic radii of tetrahedral [A sites] and octahedral [B sites], respectively. In order to calculate \( r_A \) and \( r_B \), it is necessary to know the cation distribution. The ionic radius for each site is calculated by formulae given by Mazan et al. 24 considering ionic radius of Cd\(^{2+}\), Al\(^{3+}\), Co\(^{2+}\) and Fe\(^{3+}\) as 1.03, 0.51, 0.72, 0.64 Å, respectively and assuming the cation distribution given by Eq. (3). The values of \( r_A \) and \( r_B \) are tabulated in Table 3.

The theoretical values of the lattice constant \( (a_0) \) as a function of concentration x are also shown in Fig. 2. It is clear from Fig. 2 that the experimental and theoretical values of lattice constant are in good agreement up to x=0.2 and thereafter they differ from each other. This suggests that the assumed cation distribution is in good agreement with real distribution in that range.

Table 3 — \( r_A \), \( r_B \), Cation distribution, Intensity ratio for Co\(_{1-x}\)Cd\(_{x}\)Fe\(_{2-x}\)Al\(_x\)O\(_4\) system

<table>
<thead>
<tr>
<th>x</th>
<th>Cation distribution</th>
<th>( r_A (Å) )</th>
<th>( r_B (Å) )</th>
<th>( I_{220}/I_{440} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(Co(<em>{0.10})Fe(</em>{0.90})) (^A)</td>
<td>0.679</td>
<td>0.6695</td>
<td>1.16</td>
</tr>
<tr>
<td>0.2</td>
<td>(Co(<em>{0.20})Fe(</em>{0.80})) (^A)</td>
<td>0.718</td>
<td>0.6590</td>
<td>1.54</td>
</tr>
<tr>
<td>0.3</td>
<td>(Co(<em>{0.30})Fe(</em>{0.70})) (^A)</td>
<td>0.757</td>
<td>0.6485</td>
<td>2.28</td>
</tr>
<tr>
<td>0.4</td>
<td>(Co(<em>{0.40})Fe(</em>{0.60})) (^A)</td>
<td>0.796</td>
<td>0.6380</td>
<td>2.32</td>
</tr>
<tr>
<td>0.5</td>
<td>(Co(<em>{0.50})Fe(</em>{0.50})) (^A)</td>
<td>0.835</td>
<td>0.6275</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Fig. 5 shows plots of normalized low field a.c. susceptibility \((X_{ac}/X_{RT})\) against temperature for x=0.1 to 0.3. For x=0.1, the \( X_{ac}(T) \) data display two peaks, one sharp near the Curie temperature \((T_c)\) and another broad peak at much lower temperature, while for the rest of the samples (x=0.2 to 0.5), only a broad maximum is observed. This nature can be explained on the basis of magnetic ordering in the system. A number of investigators 10,11,23,26,27 have studied the temperature dependence of a.c. susceptibility for CoFe\(_2\)O\(_4\) and they have observed two peaks, one near \( T_c \) (763 K) and a second at 533 K. The second peak at 533 K observed in pure CoFe\(_2\)O\(_4\) is referred to as the isotropic peak 28, which could be seen clearly for a magnetic material in a multidomain state if the material has a temperature at which magneto-crystalline anisotropy is zero 29. According to Bean 30, the susceptibility is inversely proportional to the coercive force. Therefore, the increase in susceptibility after the isotropic peak is attributed to a
decrease in coercive force. The existence of a coercive force clearly indicates that the samples contain spin clusters of different size and each spin cluster should be large since a very high blocking temperature is observed. The addition of Cd and Al (to pure CoFe₂O₄) reduces the coercive force and as a result, the peak value of susceptibility decreases, and also it changes the shape of the $X_{\text{RT}}/X_{\text{RT}}$ curve for $x>0.1$ exhibiting a broad maximum near $T_c$, and complete suppression of the isotropic peak (Fig. 5).

Therefore, it can be said that samples of this system contain multidomain and spin clusters. The Curie temperatures determined from susceptibility data are listed in Table 2 for all the samples. It is evident from Table 2 that $T_c$ decreases with increase in composition $x$. The decrease in $T_c$ is attributed to the fact that the net reduction of Fe$^{3+}$ ions reduces the number of active magnetic linkages.

Conclusions

Structural, magnetization and a.c. susceptibility measurements on the spinel system, Co$_{1-x}$Cd$_x$Fe$_{2-x}$Al$_x$O$_4$ show that the system for $x>0.2$ exhibit non-collinear magnetic structure indicating strong A-B coupling. The simultaneous site dilution causes frustration and disorder more rapidly in the system as compared to the system with single site dilution.

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References