X-ray, SEM, far IR characterization and bulk magnetic properties of Zn$^{2+}$ substituted copper ferrite synthesized by co-precipitation technique

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The alternating current (ac) low field susceptibility vs temperature and magnetization measurements are reported for the spinel solid solution series $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$) synthesized by a wet-chemical method before and after high temperature annealing. The low values of lattice constant, magneton number and Neel temperature for wet-samples (W) as compared to annealed wet (AW) samples are explained on the basis of fine particle nature of wet samples. The high temperature annealing changes the wet-prepared ferrites into ordered magnetic structure of ceramic ferrites. The Neel temperature calculated theoretically are in good agreement to those deduced experimentally. Scanning electron micrographs are used to see the grain growth and homogeneity of the samples while infrared spectra are used to determine water and sulphate content and to confirm ordered spinel ferrite structure.

1 Introduction
As wet chemically prepared ferrites normally consist of fine particles, they exhibit unusual magnetic properties. The spinel oxide materials synthesized by the two different methods exhibit differences in their magnetic properties$^{1-2}$ has generated a considerable interest in the comparative study of structural and magnetic properties of spinel ferrites. It has motivated us to synthesize the mixed spinel solid solution series $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ by co-precipitation technique (wet-chemical method) at lower temperature ($55^\circ\text{C}$) and also to examine the effect of non-magnetic Zn$^{2+}$ substitution for magnetic Cu$^{2+}$ in CuFe$_2$O$_4$ on the magnetic structural properties.

With the exception of a few cases$^{13-15}$, wet-prepared ferrites have, however, not been extensively studied. Recently, the study of magnetic properties of wet-chemically prepared $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ (Ref. 4), $\text{Mg}_x\text{Cu}_{1-x}\text{Al}_2\text{O}_4$ (Ref. 5), $\text{CoFeAlO}_4$ $^{16}$, $\text{CuFe}_2\text{O}_4$ (Ref. 7) have been reported. The Cu-Zn ferrites with the chemical formula $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ have been prepared by conventional ceramic method and extensively studied by a number of workers$^{18-19}$. Materials of the same composition can be prepared by co-precipitation technique over a wide range of composition between copper and zinc ferrites. No attempt has been made so far to study $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system synthesized by co-precipitation method. No information exists in the literature on structural, Infrared (IR), (SEM) and bulk magnetic properties of wet-chemically prepared $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ system.

The aim of the present work is to look into the effect of the preparation condition on the structural and magnetic properties of $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system by means of X-ray diffraction, low field a.c. susceptibility, and magnetization measurements. SEMs are used to see the grain growth and homogeneity of the samples while IR spectra are used to determined water and sulphate content and to confirm ordered spinel ferrite structure.

2 Experimental Procedure
The detailed experimental procedure for the synthesis of the samples and information regarding experimental techniques such as magnetization, susceptibility and X-ray diffraction are given elsewhere$^5$. For recording IR spectra, powders were mixed with Kbr in the ratio 1 : 200 by weight to ensure uniform dispersion in the Kbr pellet. The mixed powders were then pressed in a cylindrical die to obtain clean discs. The IR spectra in the range from $400 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$ were recorded at room temperature on Perkin-Elmer made infrared spectrometer. The scanning electron micrographs have been obtained using Cambridge (England) scanning electron microscope (Sterescan 250 Mk III).
3 Results and Discussion

The X-ray powder diffractograms for all the samples showed the presence of spinel structure with no extra reflection corresponding to any other phase. Fig. 1 shows typical X-ray diffraction patterns for wet (W) and annealed wet (AW) samples with x = 0.2 and 0.4. The X-ray lines for the AW samples were sharp which makes the detection of any impurity phase easy.

The X-ray lines for the wet samples were slightly broader as compared to the AW samples due to the particle size effect. The average particle size for all the wet samples determined through full width at half maximum (FWHM) of the diffraction lines was within the range 30-50 nm, which is much lower than the average particle size found for AW or ceramically prepared samples (≈ 100 nm). The values of lattice constant were determined with an accuracy of ± 0.0002 nm. The variation of lattice constant as a function of zinc concentration (x) is depicted in Fig. 2. The lattice constant gradually increases with increasing Zn$^{2+}$ substitution this obeying the Vegard's law. Usually in a solid solution of spinels within miscibility range, a linear variation in the lattice constant with the concentration of the components is observed. The linear increase in lattice constant is due to the replacement of smaller Cu$^{2+}$ ions (0.069 nm) by larger Zn$^{2+}$ ions (0.074 nm) in the system Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$. The X-ray densities of both the sets of samples have been calculated from molecular weight and volume of unit cell and values are given in Table 1. The values of X-ray densities of both sets of samples are found to decrease with increase in Zn-content (x), which is in consistent with increase in a with increasing concentration (x).

The wet samples of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ system are characterized by smaller values of lattice constant than that of the AW samples (Fig. 2). After temperature annealing the lattice constant of wet samples are found to increase. The smaller values of lattice constants of wet samples can not be explained solely on the basis of rearrangement of cations in the spinel lattice, due to different formation conditions. It may also be due to different degrees of crystallinity of wet and AW samples resulting from the differences in the temperature of crystallinity. The X-ray diffraction lines of AW samples were sharp which indicates that the high temperature sintering at 1100°C of wet samples has increased the crystallite size up to the order of ceramic ferrites.

The scanning electron micrographs (SEM) of the wet and annealed -wet (AW) samples with x = 0.2 are shown in Fig. 3. It is seen that the crystallite size increases due to high temperature sintering and the samples are crack free with well defined grain boundaries. The ‘duplex structure’ wherein very big grain grows at the expense

<table>
<thead>
<tr>
<th>Zn-Content</th>
<th>dx (gm/Cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x)</td>
<td>W</td>
</tr>
<tr>
<td>0.2</td>
<td>5.54</td>
</tr>
<tr>
<td>0.4</td>
<td>5.48</td>
</tr>
<tr>
<td>0.5</td>
<td>5.46</td>
</tr>
<tr>
<td>0.6</td>
<td>5.43</td>
</tr>
<tr>
<td>0.8</td>
<td>5.34</td>
</tr>
</tbody>
</table>
of some small grains in the same structure is not observed. The aim of SEM characterization is not to study the effect of grain structure on magnetic properties but to see the grain growth and homogeneity of the samples.

The magnetic properties of ferrites are decisively dependent on the precise configuration of the atoms or ions in the structure. Therefore, the nondestructive method of characterization such as infrared (IR) spectroscopy is especially suited for such investigations.

The room temperature IR spectra of the composition with $x = 0.2, 0.4, 0.6$ and 0.8 are shown in Figs. 4 and 5. The spectra are recorded in the range of 400 cm$^{-1}$ to 4000 cm$^{-1}$. The far infrared absorption bands in the frequency range of 400 cm$^{-1}$ to 600 cm$^{-1}$ are the characteristic bands of spinel structure$^{12}$. The band positions are presented in Table 2. The high frequency band $v_1$ is in the range of 565 cm$^{-1}$ to 600 cm$^{-1}$ and lower frequency band $v_2$ is in the range of 395 cm$^{-1}$ to 425 cm$^{-1}$. Due to difference in the Fe$^{3+}$ - O$^{2-}$ distances for the octahedral (0.199 nm) and tetrahedral (0.189 nm) complexes, the small changes in the band positions for the two ferrites is observed (Table 2).

Around 600 cm$^{-1}$, a small band with low intensity appeared for certain concentrations of zinc in Cu-Zn ferrites. For the lowest concentration of zinc ($x = 0.2$) the band is not seen clearly. But the broadness and the shape of the spectrum suggests the possibility of its presence. The intensity of this band $v_1'$ is increasing with the concentration of zinc ($x \geq 0.4$), the $v_1$ band is becoming narrower and the $v_1'$ band is becoming more intense. It is well established that the band $v_1$ is due to the tetrahedral complexes, so the small band $v_1'$ may be coming from tetrahedral complexes. Besides Fe$^{3+}$ions in tetrahedral sites Zn$^{2+}$ions are also present in tetrahedral sites. The increase of zinc concentration causes the increase of Zn$^{2+}$ - O$^{2-}$ complexes and hence an increase in the intensity of the $v_1'$ band is expected and is confirmed by the results. In other words, this band $v_1'$ can be assigned to the divalent metal ion-oxygen complexes in the tetrahedral sites.

The IR absorption bands at 3400 cm$^{-1}$ and 16 cm$^{-1}$ are assigned to absorbed water and 1100 cm$^{-1}$ to sulphate ions (Figs. 4 and 5). For the sake of comparison IR spectra of AW-sample with $x = 0.5$ is also shown in

![Fig. 4 — Infrared spectra for ($x = 0.2, 0.8$) wet (W) ($x = 0.5$) annealed-wet (AW) samples](image)

<table>
<thead>
<tr>
<th>Zn-Content ($x$)</th>
<th>Sample</th>
<th>A-site $v_1$ (cm$^{-1}$)</th>
<th>B-site $v_2$ (cm$^{-1}$)</th>
<th>$k_1$ (10$^3$ dyne cm$^{-1}$)</th>
<th>$k_0$ (10$^3$ dyne cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>W</td>
<td>570</td>
<td>415</td>
<td>1.95</td>
<td>1.35</td>
</tr>
<tr>
<td>0.4</td>
<td>W</td>
<td>565</td>
<td>395</td>
<td>1.71</td>
<td>1.39</td>
</tr>
<tr>
<td>0.5</td>
<td>AW</td>
<td>580</td>
<td>425</td>
<td>1.56</td>
<td>1.42</td>
</tr>
<tr>
<td>0.6</td>
<td>W</td>
<td>575</td>
<td>410</td>
<td>1.42</td>
<td>1.47</td>
</tr>
<tr>
<td>0.8</td>
<td>W</td>
<td>600</td>
<td>400</td>
<td>1.16</td>
<td>1.49</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>555*</td>
<td>393*</td>
<td>0.92</td>
<td>1.42</td>
</tr>
</tbody>
</table>

W, wet sample; AW, annealed wet sample; and * Ref. 12
Fig. 4. It is seen that for AW sample the bands corresponding to water and sulphate ions are disappeared which is due to the effect of high temperature (1100°C) sintering process for AW samples.

The force constants determined by Waldran's method are listed in Table 2.

The magnetization measurements were performed at 80 K and 300 K for wet and AW sets of samples. The values of saturation magnetization for all the samples have been estimated to within an accuracy of about 5% and are listed in Table 3.

The values of saturation magnetization ($\sigma_s$) for wet samples are found to be lower as compared to annealed wet samples (Table 3). This is due to the presence of water content and hydroxyl ions in the wet samples are reflected in IR spectras (Figs. 4 and 5), which reduces the magnetization per formula unit. Moreover the fine particle preparation (wet-chemical method) and the substitution of non-magnetic $\text{Zn}^{2+}$ ions in $\text{CuFe}_2\text{O}_4$ leads to the paramagnetic centers which also decreases the magnetization per formula units. According to Upadhyay et al., one possibility of low $\sigma_s$ or $n_B$ (saturation magnetization per formula unit in $\mu_B$) for wet samples as compared to AW samples may be due to decrease in particle size. As the particle size decreases, the percentage of the atoms on the surface of the particle increases, as a result of this there are large number of spins which are uncoupled on the surface, i.e., spin pinning effect. Hence $\sigma_s$ or $n_B$ decreases. As expected, the $\sigma_s$ increases for wet and AW samples at 80K. This is due to lower $T/T_N$ ratio ($T_N = \text{Neel temperature}$) at 80K.

It is seen from Fig. 6 that $\sigma_s$ and thus $n_B$ at 300K and 80K initially increases and then decreases at $x$ is increased (Table 3). The cation distribution determined from X-ray diffraction intensity calculations as:

$$ (\text{Zn}^{2+}_{x} \text{Fe}^{3+}_{1-x})^4 [\text{Cu}^{2+}_{x} \text{Fe}^{3+}_{1-x}]^6 \text{O}_4^2 \tag{1} $$

which is in conformity with the distribution previously obtain through Mossbauer spectroscopic results for ceramic samples.

According to Neel's two sublattice model of ferromagnetism, the Neel's magnetic moment per formula unit in is expressed as,

$$ n_B^N = M_B(x) - M_A(x) \tag{2} $$

where $M_B$ and $M_A$ and $B$ and $A$-site magnetic moments, respectively in $\mu_B$. The calculated values of using the cation distribution [Eq. (1)] and Neel's equation [Eq. (2)] is shown as a solid line in Fig. 7. It is well known that for $\text{CuFe}_2\text{O}_4$ ($x = 0.0$), the value of magneton number $n_B = 1 \mu_B$ while for the $\text{ZnFe}_2\text{O}_4$ ($x = 1.0$) it is $10 \mu_B$. This means that according to Neel's model, saturation moment should increase linearly with zinc content ($x$) up to $10 \mu_B$ per molecule for $\text{ZnFe}_2\text{O}_4$. It is seen from Fig. 7 that a few tenths of zinc substitution per formula unit in $\text{CuFe}_2\text{O}_4$ causes significant departures from the Neel's collinear model. The Neel's theory

<table>
<thead>
<tr>
<th>Zn-content</th>
<th>$\sigma_s$ (emu/gm)</th>
<th>300 K</th>
<th>$n_B$ (µ)</th>
<th>80 K</th>
<th>$\sigma_s$ (emu/gm)</th>
<th>$n_B$ (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>20</td>
<td>27</td>
<td>25</td>
<td>0.86</td>
<td>1.16</td>
<td>1.07</td>
</tr>
<tr>
<td>0.2</td>
<td>29</td>
<td>57</td>
<td>50</td>
<td>1.24</td>
<td>2.45</td>
<td>2.15</td>
</tr>
<tr>
<td>0.4</td>
<td>26</td>
<td>61</td>
<td>52</td>
<td>1.12</td>
<td>2.61</td>
<td>2.23</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>54</td>
<td>48</td>
<td>0.43</td>
<td>2.32</td>
<td>2.06</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>44</td>
<td>23</td>
<td>-</td>
<td>1.89</td>
<td>0.99</td>
</tr>
<tr>
<td>0.8</td>
<td>-</td>
<td>24</td>
<td>03</td>
<td>-</td>
<td>1.04</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*Ref. 10
successfully explains the observed initial rise in the \( n_B \) with \( x \) but it fails to account for the decrease in \( n_B \) after \( x = 0.4 \) (Fig. 7). The discrepancy between the prediction of Neel’s theory and the experimental observations indicates the magnetic structure to be non-collinear.

Similar variation of saturation magnetic moment \( (n_B) \) in other zinc substituted ferrites\(^{16-19} \) has been attributed to the presence of Yafet-Kittel (YK) angles in the spin system on octahedral (B) sites. On account of similarities between Cu-Zn and other zinc substituted ferrites, it is reasonable to assume that YK angles are also present in the former system. The decrease in \( n_B \) after \( x = 0.4 \) can be explained in terms of a uniform YK triangular type magnetic ordering of spin on B-sublattice.

The condition for Yafet-Kittel (YK) angles \( \alpha_{YK} \) to occur in Zn\(^{2+} \) substituted NiFe\(_2\)O\(_4\) has been investigated in the molecular field approximation by Satya Murthy et al\(^{20} \), using a non-collinear three sublattice model. On similar basis we can write the interaction energy involving the YK angles for Cu-Zn ferrite system as:

\[
E(YK) = \frac{5}{4} (1-x)^2 \alpha + 25 (1-x^2) \beta \cos \alpha_{YK} - 25 (1+x)^2 \gamma + 25 (1+x^2) \delta + 10 (1-x^2) \varepsilon \cos 2\alpha_{YK}
\]

The terms \( \alpha, \beta, \gamma, \delta \) and \( \varepsilon \) are the molecular field constants related to the following exchange interactions:

\[
\begin{align*}
\alpha &: A(Fe^{3+}) - B(Fe^{3+}) \\
\beta &: A(Fe^{3+}) - B(Fe^{3+}) \\
\gamma &: A(Cu^{2+}) - B(Cu^{2+}) \\
\delta &: B(Cu^{2+}) - B(Fe^{3+}) \\
\varepsilon &: B(Fe^{3+}) - B(Cu^{2+})
\end{align*}
\]

where, \( i, j = 1, 2 \)

The energy is minimum for:

(a) \( \sin \alpha_{YK} = 0 \),

which corresponds to the Neel’s configuration or for

(b) \( \cos \alpha_{YK} = \frac{5 \{ (1-x)^2 \alpha + 25 (1-x^2) \beta \} \cos \alpha_{YK} - 25 (1+x)^2 \gamma + 25 (1+x^2) \delta + 10 (1-x^2) \varepsilon \cos 2\alpha_{YK} + 5 \{ (1-x)^2 \alpha + 25 (1-x^2) \beta \} \cos \alpha_{YK} - 25 (1+x)^2 \gamma + 25 (1+x^2) \delta + 10 (1-x^2) \varepsilon \cos 2\alpha_{YK} + 5 \{ (1-x)^2 \alpha + 25 (1-x^2) \beta \} \cos \alpha_{YK} - 25 (1+x)^2 \gamma + 25 (1+x^2) \delta + 10 (1-x^2) \varepsilon \cos 2\alpha_{YK}}{(1-x)^2 \gamma + 25 (1+x)^2 \delta + 10 (1+x^2) \varepsilon} \]

which explains the situation where the YK ordering is feasible.

Here for example,

\[
\alpha = \frac{2 ZAa a_B (Fe^{3+} - Cu^{2+})}{n_B gA gB \mu_B}
\]

where \( \alpha_a \) is the interaction between \( A(Fe^{3+}) \) and \( B(Fe^{3+}) \). \( Z_Aa \) is the A nearest neighbours to A, \( N_B \) is the number of B ions per unit volume. \( \mu_B \) is the Bohr magneton, \( g \) denotes the Landé's splitting factor.

The molecular field constants can be estimated from the observed variation of the saturation magnetization per formula unit \( (n_B) \) with zinc concentration \( (x) \). The exchange constants obtained should be consistent with the existing data on similar ferrimagnetic systems. Srivastava et al\(^{19} \) have found \( J_a = -21K \) and \( J_B = -28K \) for Zn\(_x\) Fe\(_{3-x}\)O\(_4\) system. In the case of Zn\(_x\) Fe\(_{3-x}\)O\(_4\), \( J_a \) is the interaction between A (Fe\(^{3+}\)) and Bi (Fe\(^{3+}\)), while in the present case it corresponds to the interaction between A (Fe\(^{3+}\)) and Bi (Cu\(^{2+}\)). Assuming \( J_a \) is approximately equal to the product of the moments of the ions, one gets for:

\[
J_a (Fe^{3+} - Fe^{3+}) \approx -20K
\]

and

\[
J_a (Fe^{3+} - Cu^{2+}) \approx -5K
\]

The value \( J_a = 20K \) compares reasonably well with the \( J_a = -21K \) values of Srivastava et al\(^{19} \), for Zn\(_x\) Fe\(_{3-x}\)O\(_4\) spinel system. Therefore, \( J_a = -5.25K \) and \( J_B = -14.8K \) values are accepted for Zn\(_{0.25}\)Cu\(_{0.25}\)Fe\(_{2}\)O\(_4\). Finally, the values of \( J_a, J_r \) and \( J_a \) are estimated from the best fit to

![Fig. 6 — Variation of saturation magnetization as function of Zn-content (x)](image)

![Fig. 7 — Variation of magneton number with Zn-content (x)](image)
for the variation of saturation magnetization with zinc concentration, by using relation:
\[ n_B = 2(2x + 3) \cos \alpha_{YK} - 5(1 - x) \] ... (4)
where \( n_B \) has been expressed in units of Bohr magneton. It is found that,
\[ J_b = -6.66 K, J_A = -165 K, J_{AB} = -4.53 K \]
As \( J_{AB}^2 = J_A J_{B1} \) it is assumed that the primed values are the same as the unprimed values.

From these values of exchange constants the Yafet-Kittel (YK) angles are calculated using Eq. (3) and these \( \alpha_{YK} \) values are listed in Table 4. The experimental values \( \alpha_{YK} \) have been obtained from the observed variation of \( n_B \) with \( x \) using Eq. (4). These values have also been given in the same Table 4. The variation \( n_B \) determined using theoretical values of \( \alpha_{YK} \) with the help of Eq. (4) is shown in Fig. 7. It is seen that there is a slight discrepancy between the \( n_B \) observed and \( n_B \) calculated.

Thus, the decrease in \( n_B \) after \( x = 0.4 \) can be explained in terms of a uniform Yafet-Kittel triangular type magnetic ordering of spins. It is clear from Table 5 that there is a large disagreement between the \( n_B \) observed and \( n_B \) calculated in case of previous work on \( \text{YK} \) model for ceramic samples of \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \). This has happened because the approximated equation for \( n_B \) value determination and the exchange constants were used by the earlier workers. This work has been an attempt to determine the best fit for the variation of \( n_B \) with \( \text{Zn-concentration (x)} \) with the help of \( \text{YK} \) model and more accurate values of exchange constants.

For a chemically disordered system such as \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \), it is quite possible that the canting is not uniform but instead is locally dependent upon the statistical distribution of non-magnetic neighbouring \( \text{Zn}^2+ \) ions. Therefore, the \( n_B \) values can also be calculated using the localised canting approach.

Using the procedure of Patton and Liu, the local canting \( \theta_l \) for the present system in zero applied field can be written as:
\[ \cos \theta_l = \frac{q_A n_{AB1} + q_{BI} n_{B12}}{q_{BI} n_{B12}} \]
where \( q_A \) and \( q_{BI} \) are the number of magnetic ions on A and B1 sites, respectively. \( n_B \) is the number B1 nearest neighbour to A etc. \( |J_{AB1}| \) and \( |J_{B12}| \) are the exchange integrals. The average canting angle for the present system will be,
\[ \cos \theta_{L-AW} = (1 - x) \frac{|J_{AB1}|}{|J_{B12}|} \]

The magnetization is then calculated from:
\[ n_B = M_0 \cos \theta_{L-AW} - M_A \]

Table 4 — Yafet-Kittel angle (\( \alpha_{YK} \)) and localized canting angle (\( \theta_{L-AW} \)) for annealed-wet (AW) samples of \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) system

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \alpha_{YK} )</th>
<th>( \theta_{L-AW} )</th>
<th>( \theta_{obs} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2</td>
<td>16°56'</td>
<td>16°56'</td>
<td>16°56'</td>
</tr>
<tr>
<td>0.4</td>
<td>40°55'</td>
<td>44°26'</td>
<td>42°26'</td>
</tr>
<tr>
<td>0.5</td>
<td>50°50'</td>
<td>53°29'</td>
<td>52°57'</td>
</tr>
<tr>
<td>0.6</td>
<td>59°59'</td>
<td>61°34'</td>
<td>61°43'</td>
</tr>
<tr>
<td>0.8</td>
<td>76°11'</td>
<td>76°14'</td>
<td>77°11'</td>
</tr>
</tbody>
</table>

Table 5 — Magneton number (\( n_B \)) (\( \mu_B \)) for annealed-wet (AW) and ceramic (C) samples of \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) system

<table>
<thead>
<tr>
<th>( x )</th>
<th>AW</th>
<th>Theo</th>
<th>Theo</th>
<th>Obs*</th>
<th>Theo*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.45</td>
<td>2.51</td>
<td>2.47</td>
<td>2.15</td>
<td>0.09</td>
</tr>
<tr>
<td>0.4</td>
<td>2.61</td>
<td>2.74</td>
<td>2.43</td>
<td>2.23</td>
<td>0.64</td>
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<tr>
<td>0.5</td>
<td>2.32</td>
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<td>2.26</td>
<td>2.06</td>
<td>0.78</td>
</tr>
<tr>
<td>0.6</td>
<td>1.89</td>
<td>2.20</td>
<td>1.98</td>
<td>0.99</td>
<td>0.77</td>
</tr>
<tr>
<td>0.8</td>
<td>1.04</td>
<td>1.20</td>
<td>1.15</td>
<td>0.12</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Yafet-Kittel model; LCS, localised canting of spin theory; and * Ref. 10

The thermal variation of normalized ac susceptibility \( \chi / \chi_{RT} \) vs \( T \) \( [\chi(T)] \) for wet and annealed-wet samples is shown in Figs. 8 and 9. The ‘hump’ or ‘cusp’ in the \( [\chi(T)] \) curves near the magnetic transition is a characteristic of single domain to superparamagnetic transition or cluster spin glass. Mainly due to size of ferro or ferrimagnetic particles, a special magnetic behaviour can arise when thermal energy becomes comparable with the magnetic energy of the particles. When the particle is small enough, the moment will fluctuate between the easy axis as in the case of a paramagnet. The probability of direction reversal by thermal activation is proportional to \( \exp (E/kT) \), where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Since these fluctuating moments are much larger in magnitude than those of a paramagnet but with similar behaviour, it is named as superparamagnetism. Thus observed hump or cusp in \( [\chi(T)] \) curves indicate the presence of single-domain (SD) particles (spin clusters).
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with different "blocking temperature". The increase in susceptibility with temperature for wet samples (Fig. 8) is due to the response of fine SD particles of various sizes as they undergo single-domain to superparamagnetic transition and this happens at \( T = T_b \) = blocking temperature were thermal energy becomes equal to magnetic energy. It is seen from Fig. 9 that the rise in susceptibility with temperature in case of AW samples is not much significant. Moreover the \( [\chi(T)] \) curve of a wet-sample \((x = 0.2)\) approaches to the \([\chi(T)]\) curve of AW samples on cooling the wet sample from its Neel temperature down to room temperature. This happens because after heating cycle the crystallite size of wet-samples increases up to the order of AW sample.

The Neel temperatures are also estimated theoretically applying modified molecular field theory developed by Baldha and Upadhyay\textsuperscript{22} and using the cation distribution [Eq. (1)] found from X-ray diffraction. The Neel temperature \( T_N(x) \) for a substituted ferrite can be expressed in terms of Neel temperature of an un-substituted ferrite. \( T_N(x = 0.0) \) i.e. CuFe\textsubscript{2}O\textsubscript{4} by equation:

\[
T_N(x) = \frac{M(x = 0.0) T_N(x = 0.0)}{n(x)}
\]

where \( M(x) \) is the relative weighted total magnetic ions per formula unit, calculated by considering the weighting of magnetic ion \( M \) to that of ion as \( \mu_M / \mu_{Fe} \), where \( \mu_M \) and \( \mu_{Fe} \) are the magnetic moments of \( M \) (hence Cu\textsuperscript{2+}) and iron ions, respectively. \( M(x) \) can be expressed for \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) as:

\[
M(x) = 2 + (1 - x) \frac{\mu_M}{\mu_{Fe}}
\]

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

\[
n(x) = 24 \sum_{i=1}^{2} A_i B_i \mu_i \mu_j
\]

Table 6 — Neel temperature \((T_N)\) values for \( \text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 \) system

<table>
<thead>
<tr>
<th>Zn-content ((x))</th>
<th>Neel temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>( x )</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>690\textsuperscript{5}</td>
</tr>
<tr>
<td>0.2</td>
<td>625</td>
</tr>
<tr>
<td>0.4</td>
<td>525</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
</tr>
</tbody>
</table>

W = wet; AW = annealed-wet; C = ceramic, * Ref. 10; and 5 Ref. 7

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**Fig. 8** — Thermal variation of ac susceptibility for wet samples with \( x = 0.2 \) and 0.4 (Broken line shows data while cooling the samples).

**Fig. 9** — Thermal variation of ac susceptibility for annealed wet (AW) samples with \( x = 0.2, 0.4, 0.5 \) and 0.6.
where $A_i$ and $B_j$ are the fraction of magnetic ions on tetrahedral and octahedral sites, respectively. Here $i, j = 1$ stands for magnetic ions $M$ and $i, j = 2$ for that of iron.

The Neel temperatures estimated using the above equation are in good agreement with experimentally observed Neel temperature and are listed in Table 6.

4 Conclusion

(i) Fine particle play an important role on controlling the magnetic properties of ferrites (ii) combine study of X-ray, SEM and IR spectra, confirm ordered spinel ferrite structure (iii) there exists a non-collinear spin arrangement for $x \geq 0.2$, and can be explained on the basis of local spin canting model (iv) the observed nature of $\chi \rightarrow T$ curves for wet samples is due to the SD $\rightarrow$ SP transition, and high temperature annealing of the wet prepared ferrites transforms them into the order magnetic structure of ceramic ferrites.

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References