ORIENTATION OF THE MAGNETIC IONS IN MONOVALENT AND
DIVALENT DOPED Sr-Zn W-TYPE HEXAGONAL FERRITES

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Abstract—A knowledge of the distribution of divalent metallic (Me$^{2+}$) and trivalent iron (Fe$^{3+}$) cations among seven different sublattice sites of an hexagonal ferrite with W-type structure is interesting and essential in understanding and arriving at the orientation of the magnetic ions as well as non-magnetic ions. Cation distribution in turn is very useful in understanding the variation of various magnetic and electrical properties with varying dopant's concentration. Therefore, the orientation of the magnetic ions of two hexagonal ferrite systems viz., Sr-Zn-Co and Sr-Zn-Li has been arrived at using saturation magnetization values.

I. INTRODUCTION

The hexagonal ferrites with W-type of structure are materials of recent interest because of their potential applications in microwave devices and also as permanent magnets. In recent years, considerable amount of work has been carried out on W-type of ferrites [1,2] as they are expected to yield 20% higher (BH)$_{\text{max}}$ value than those of Ba-M ferrites. Using the Gorter scheme [3], the orientation of both monovalent lithium and divalent cobalt doped Sr W-type hexagonal ferrites has been undertaken and results of such a study are presented in this paper.

II. EXPERIMENTAL

Two ferrite systems having compositional formulae

\[
\text{SrZn}_{2x}\text{Co}_x\text{Fe}_{16}\text{O}_{27} \quad (\text{Sr-Zn-Co})
\]

and

\[
\text{Sr}[\text{Zn}_{2(1-y)}(\text{LiFe})_y]\text{Fe}_{16}\text{O}_{27} \quad (\text{Sr-Zn-Li})
\]

where $x = 0$ to 2 and $y = 0$ to 1 were prepared by the well known solid state reaction method using SrCO$_3$, ZnO, CoO, LiCo$_3$ and Fe$_2$O$_3$ in stoichiometric proportions. The first set of samples were sintered at 1230°C for 6 hours while those of the second one were fired at 1300°C for 4 hours followed by quenching to room temperature. Other details of preparation and characterization of these materials are given elsewhere [4]. The saturation magnetization ($\sigma_s$) measurements were carried out using a Vibrating Sample Magneto meter (Model No.PAR 155).

III. RESULTS AND DISCUSSION

The experimental values of $\sigma_s$ of both the groups of ferrites under investigation are given in Table I. It can be seen from the table that $\sigma_s$ values after increasing continuously with increasing cobalt content, exhibiting a maximum value for the sample SrZnCo-5, are found to decrease later. Similarly, in the case of SrZnLi-ferrite system also, one can observe that $\sigma_s$ values are found to increase continuously with the incorporation of lithium reaching a maximum value of 82 emu/g for the material SrZnLi-5. The observed variation of $\sigma_s$ of both the groups of materials can be explained on the basis of orientation of magnetic ions as follows.

The crystal structure and chemistry of W-type hexagonal ferrites are closely related to M-type (magneto plumbite) ferrite. In fact, the structure of both these ferrites can be described as an alternating stacking of spinel (S) and hexagonal (R) blocks in the direction of the hexagonal C-axis. As the content of S-block is Fe$_6$O$_{12}$ and that of R-block is BaFe$_6$O$_{11}$, the composition of a unit cell of W-type ferrites is 4S+2R, which works out to be equal to two formula...
units. The elementary cell contains 92 atoms and belongs to the P6/mmc group. The distribution of divalent Me\textsuperscript{2+} and trivalent Fe\textsuperscript{3+} cations among five different sublattice sites of M-type ferrites, along with their spin orientations are useful in understanding and arriving at the orientation of the magnetic ions of W-type ferrites using the Gorter scheme. By understanding the distribution of magnetic ions at various sublattice sites of W-type ferrites in general, one can obtained the cationic distribution of Sr-Zn-Co and Sr-Zn-Li ferrites of the present investigation adopting the procedure outlined below.

It is known that Zn\textsuperscript{2+} ions prefer tetrahedral sites, while Co\textsuperscript{3+} ion chooses the octahedral sites [5]. Further, whenever cobalt occupies the octahedral sites of the hexagonal (R) block, it is supposed to replace Fe\textsuperscript{3+} ions, which in turn move over to the tetrahedral sites of the same block. But the tetrahedral site of the hexagonal block, is having only one ion, and hence, it can not accommodate the two Fe\textsuperscript{3+} ions displaced from the octahedral site. As such, the question of Co\textsuperscript{3+} ions occupying the octahedral site of the hexagonal block does not arise. However, if both the substituted cobalt ions occupy the octahedral sites of the spinel (S-S) block replacing the Fe\textsuperscript{3+} ions there, they can in turn move over to the two tetrahedral sites of the same block. As such, it is logical to conclude that the non-magnetic Zn\textsuperscript{2+} ions on tetrahedral sites of the spinel block are progressively replaced by the substituted Co\textsuperscript{3+} ions. Further as it has been observed that the $\sigma$ values after showing an initial increase up to 1.0 mole of cobalt, are found to decrease continuously thereafter, it can be tentatively concluded that when cobalt is added, it may initially occupy the spin-up position of the octahedral sites of the spinel block up to 1.0 mole of cobalt and later the spin-down position of the same site. Similarly, Li\textsuperscript{1+} ions also prefer octahedral sites and hence, explanation for the orientation of various magnetic ions for Sr-Zn-Li ferrites may also logically assumed to be same as Sr-Zn-Co ferrites. Based on these arguments, the orientation of various magnetic ions for each composition of Sr-Zn-Co and Sr-Zn-Li ferrites have been worked out and are given in Table II.

After cancelling the equivalent and opposite spin orientations, the net magnetic moments for each composition in Bohr magnetons ($\mu_B$) have been evaluated and are given in Table I. The experimental values of magnetic moments for each composition are included in the Table for the purposes of comparison. It is clear from the table that the analytically obtained values of the magnetic moments to a large extent are in agreement with those of the experimental ones, thereby indicating the correctness of the approach adopted in arriving at the distribution of magnetic ions at various crystallographic sites of Sr-Zn-Co and Sr-Zn-Li ferrites.

**ACKNOWLEDGEMENTS**

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**REFERENCES**

### TABLE I Experimental data on Sr-Zn-Co & Sr-Zn-Li ferrites

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Composition</th>
<th>$\sigma_s$ (emu/gr)</th>
<th>Net magnetic spins</th>
<th>Magn. moment ($\mu_B$)</th>
<th>Expt.</th>
<th>Cal.</th>
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<tbody>
<tr>
<td>SrZnCo-1</td>
<td>SrZn$<em>{2}$Fe$</em>{16}$O$_{27}$</td>
<td>66.7</td>
<td>Fe$_8$↑</td>
<td>18.43</td>
<td>17.75</td>
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<td>SrZnCo-2</td>
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<td>73.4</td>
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<td>20.25</td>
<td>18.44</td>
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<td>20.38</td>
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<td>18.09</td>
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<td>Fe$_8$↑</td>
<td>21.25</td>
<td>19.97</td>
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### TABLE II Orientations of magnetic ions in Sr-Zn-Co & Sr-Zn-Li ferrites

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<tr>
<th>Ferrite</th>
<th>S-Block (Octa)</th>
<th>S-Block (Tetra)</th>
<th>S-S Block (Octa)</th>
<th>R-S Block (Octa)</th>
<th>R-Block (Tetra)</th>
<th>R-Block (Octa)</th>
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<td>SrZnCo-1</td>
<td>[Fe$_2$↓] (Fe$_2$↓Zn$_2$)</td>
<td>[Fe$_3$↑]</td>
<td>[Fe$_6$↑]</td>
<td>(Fe↑)</td>
<td>[Fe$_2$↓]</td>
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<tr>
<td>SrZnCo-2</td>
<td>[Fe$<em>2$↓] (Fe$<em>2$↓Zn$</em>{1.6}$Fe$</em>{0.4}$↑)</td>
<td>[Fe$<em>{2.6}$↑Co$</em>{0.4}$↑]</td>
<td>[Fe$_6$↑]</td>
<td>(Fe↑)</td>
<td>[Fe$_2$↓]</td>
<td></td>
</tr>
<tr>
<td>SrZnCo-3</td>
<td>[Fe$<em>2$↓] (Fe$<em>2$↓Zn$</em>{1.2}$Fe$</em>{0.8}$↑)</td>
<td>[Fe$<em>{2.2}$↑Co$</em>{0.8}$↑]</td>
<td>[Fe$_6$↑]</td>
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<td>[Fe$_2$↓]</td>
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<tr>
<td>SrZnCo-4</td>
<td>[Fe$<em>2$↓] (Fe$<em>2$↓Zn$</em>{1.0}$Fe$</em>{1.0}$↑)</td>
<td>[Fe$<em>{2.0}$↑Co$</em>{1.0}$↑]</td>
<td>[Fe$_6$↑]</td>
<td>(Fe↑)</td>
<td>[Fe$_2$↓]</td>
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<td>SrZnCo-5</td>
<td>[Fe$<em>2$↓] (Fe$<em>2$↓Zn$</em>{0.8}$Fe$</em>{1.2}$↑)</td>
<td>[Fe$<em>{1.8}$↑Co$</em>{1.0}$↑Co$_{0.2}$↑]</td>
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<td>(Fe↑)</td>
<td>[Fe$_2$↓]</td>
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<tr>
<td>SrZnCo-8</td>
<td>[Fe$_2$↓] (Fe$<em>2$↓Fe$</em>{2}$↑)</td>
<td>[Fe$<em>{1.0}$↑Co$</em>{1.0}$↑Co$_{1.0}$↑]</td>
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<td>[Fe$_3$↑]</td>
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<td>[Fe$_2$↓]</td>
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