New spinels of scandium have been synthesized in the system 
\( \text{ZnFe}_2_x\text{Sc}_x\text{O}_4 \) \((x = 0.2, 0.4, 0.6, 0.8 \text{ and } 1.0)\). The Vegard's rule is not 
obeyed for the series. The compounds are semiconductors in the 
temperature range 300-650 K. Slight changes in oxygen content of the 
 lattice have been suggested on the basis of electrical behaviour and 
DTA and TG studies.

In our earlier publication\(^1\) we have reported the crystal 
structure of \( \text{ZnSc}_2\text{O}_4 \) as a distorted spinel. In con-
tinuation of this work we have prepared a series of 
compounds with chemical formula \( \text{ZnFe}_2_x\text{Sc}_x\text{O}_4 \) \((x = 0, 0.2, 0.4, 0.6, 0.8 \text{ and } 1.0)\), with a view to further 
investigating the phenomenon of electrical conduction 
in spinel structure, as these compounds may be 
considered as solid solutions of \( \text{ZnFe}_2\text{O}_4 \) and \( \text{ZnSc}_2\text{O}_4 \) 
spinel.

These compounds were prepared by first intimately 
mixing (under acetone) \( \text{ZnO}, \text{Fe}_2\text{O}_3 \) and \( \text{Sc}_2\text{O}_3 \) in the 
required molar ratios for getting the desired stoi-
chiometry. The mixture was dried in air. It was heated at 
1200°C in a platinum boat for 120 hr. The X-ray 
diffraction patterns of the powder samples were ob-
tained using filtered Co K\(_\alpha\) radiation. All the X-ray 
diffraction patterns showed a single phase.

For the determination of dc-resistivity, pellets of 
1 cm diameter and 0.4 cm thickness were prepared 
under a pressure of one tonne in a hydraulic press. 
Silver paste\(^1\) was used as the electrical contact ma-
terial. The measurements were carried out in the 
temperature range 300-650 K by applying a steady 
potential of 5 V across the pellet. An LCR bridge 
(Radart 1203) was used for measurement of the 
resistivity.

Thermoanalytical studies of the compounds 
\( \text{ZnFe}_2\text{O}_4 \) and \( \text{ZnFeScO}_4 \) were carried out on an 
automatic derivatograph\(^2\) which recorded TG, DTG 
and DTA curves. The derivatograms of the 
compounds were taken in static air at the heating rate\(^3\) of 
10 K/min using \( \alpha\)-\( \text{Al}_2\text{O}_3 \) as the reference material. The 
sample was ground to 325 mesh (44 microns) to allow 
retention of the crystallinity. About 1 g of the 
compound was used to record derivatogram.

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### Table 1—Crystallographic Results of the Series \( \text{ZnFe}_2-x\text{Sc}_x\text{O}_4 \)

<table>
<thead>
<tr>
<th>Composition ((x))</th>
<th>Density ((\text{g}/\text{cm}^3))</th>
<th>Lattice constant (a) ((\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.34</td>
<td>8.43</td>
</tr>
<tr>
<td>0.2</td>
<td>5.22</td>
<td>8.47</td>
</tr>
<tr>
<td>0.4</td>
<td>5.14</td>
<td>8.49</td>
</tr>
<tr>
<td>0.6</td>
<td>5.04</td>
<td>8.52</td>
</tr>
<tr>
<td>0.8</td>
<td>4.95</td>
<td>8.54</td>
</tr>
<tr>
<td>1.0</td>
<td>4.91</td>
<td>8.54</td>
</tr>
</tbody>
</table>

### Table 2—Resistivity Data for the System \( \text{ZnFe}_2-x\text{Sc}_x\text{O}_4 \)

<table>
<thead>
<tr>
<th>Composition ((x))</th>
<th>Resistivity ((\Omega\cdot\text{cm})) at 393 K</th>
<th>Temp. range ((\text{K}))</th>
<th>(\Delta E) ((\text{eV}))</th>
<th>Temp. range ((\text{K}))</th>
<th>(\Delta E) ((\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>(2.4 \times 10^7)</td>
<td>301-562</td>
<td>0.82</td>
<td>632-680</td>
<td>0.36</td>
</tr>
<tr>
<td>0.2</td>
<td>(7.6 \times 10^3)</td>
<td>301-485</td>
<td>0.52</td>
<td>520-655</td>
<td>0.35</td>
</tr>
<tr>
<td>0.4</td>
<td>(7.4 \times 10^4)</td>
<td>301-510</td>
<td>0.62</td>
<td>510-655</td>
<td>0.65</td>
</tr>
<tr>
<td>0.6</td>
<td>(8.0 \times 10^4)</td>
<td>301-515</td>
<td>0.42</td>
<td>515-655</td>
<td>0.69</td>
</tr>
<tr>
<td>0.8</td>
<td>(5.4 \times 10^4)</td>
<td>301-537</td>
<td>0.59</td>
<td>537-653</td>
<td>0.45</td>
</tr>
<tr>
<td>1.0</td>
<td>(2.4 \times 10^6)</td>
<td>301-450</td>
<td>0.55</td>
<td>521-655</td>
<td>0.53</td>
</tr>
</tbody>
</table>

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Fig. 1—Plot of lattice parameter versus composition of 
\( \text{ZnFe}_2\text{Sc}_4\text{O}_4 \).

X-ray crystallographic results are listed in Table 1. 
The results show that all the compounds crystallize in a 
spinel structure. The variation of lattice constant \(a\) 
versus composition \(x\) is shown in Fig. 1 which shows 
that lattice constant increases from \(x = 0\) to \(x = 0.8\).

The variation of resistivity with \(1/T\) is shown for 
\( \text{ZnFe}_2\text{O}_4 \) in Fig. 2 and for other compounds in Fig. 3 
\((x = 0.2 \text{ to } 1.0)\). The values of activation energy at 
different temperatures are listed in Table 2.

The variations of energy of activation \(\Delta E\) \((301-\) 
450 K) and \(\rho_{RT}\) (r.t.r.) with composition \((x)\) are shown 
in Figs 4 and 5 respectively.

The compounds \( \text{ZnFe}_2\text{O}_4 \) \((x = 0)\) and 
\( \text{ZnFeScO}_4 \) \((x = 1)\) show exotherms at 588 and 653 K.
The usual problem of site and charge distribution does not arise as Zn$^{2+}$ ions have very strong A site preference$^6$ and the valencies of Zn and Sc are definite. Thus the ionic distribution will be Zn$^{2+}$[Fe$^{3+}$Sc$^{3+}$]$\text{O}_4$.

Our results on electrical resistivity show that all the compounds are semi-conductors in the temperature range 300-650 K. The resistivity at room temperature for the compounds ZnFe$_2$O$_4$(x = 0) and ZnFeScO$_4$(x = 1) is comparable and in general it increases from the composition x = 0.2 to x = 1.0.

The study of variation of electrical resistivity with temperature (Fig. 3) shows that for all the compounds the slope of the plot of log$\rho$/vs $1/T$ changes at 500 ± 40 K, and each compound shows two values of $\Delta E$ (Table 2).

For understanding the intricate electrical behaviour of these compounds, DTA and TG curves of two compounds (x = 0 and x = 1) have been studied. The compound ZnFe$_2$O$_4$ shows an exotherm at 588 K while ZnFeScO$_4$ shows it at 653 K with reaction intervals of 498-913 and 493-893 K respectively. Thus, the solid state reaction of the type A (solid)+B (solid)+C (gas) can be suggested in view of the slight oxidative degradation of these compounds in the temperature range 490-900 K.

The broad peaks observed in DTA curves indicate higher value of the order of that observed for reactions involving oxidative degradation as suggested by Kissinger$^7$. Thus, the possibility of slight changes in oxygen content of these compounds can be kept in view with possible structural formula ZnFe$_{2-x}$Sc$_x$O$_{4-x}$ in the temperature range 490-900 K.

The observed derivatographic results can be explained using statistical thermodynamic model$^8$ of condensed metals in order to explain the electrical properties of these compounds. Thus, the changes of
activation energy of these compounds above 500 K are due to evolution of oxygen from the lattice, and may also be due to formation of defects and reduction of metal ions.

References
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6 Miller A J, Appl Phys, 30 (1959) 245.