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CHARACTERISATION OF $\text{Sr}_2\text{FeEuO}_6$ BY MÖSSBAUER SPECTRA OF $^{57}\text{Fe}$

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The crystallographic structure of the new ternary compound $\text{Sr}_2\text{FeEuO}_6$ /1/ belongs to the extended group of alkaline earth pentaoxometalates /2/ where the isolated $\text{FeO}_4$ tetrahedra are arranged in the (001) plane (Fig. 1). These tetrahedra are flattened along the crystallographic x and y axes. The oxygen ion, which is not a part of the coordination tetrahedra, is octahedrally coordinated by Sr and Eu ions which are statistically distributed over the same sites. In the tetragonal unit cell with the space group 14/mcm there are four equivalent iron sites with Fe--O distances of 1.851 Å. This value is among the shortest iron-oxygen distances in ferrites. Therefore, it was of interest to examine this compound by Mössbauer effect of $^{57}\text{Fe}$ in order to obtain additional experimental evidence of its physical and chemical properties.

Fig. 1: Crystal structure of $\text{Sr}_2\text{FeEuO}_6$

The samples of $\text{Sr}_2\text{EuFeO}_6$ prepared by a ceramic technique showed a small amount of impurity phase. Therefore, the absorbers used for Mössbauer measurements were prepared by grinding the single crystals obtained by the high temperature solution method.

In the temperature range above 20 K the spectra of $^{57}\text{Fe}$ in $\text{Sr}_2\text{FeEuO}_6$ show two absorption lines (Fig. 2) consistent with the interaction of the quadrupole moment of the first excited state of the $^{57}\text{Fe}$ nucleus with an electric field gradient. The hyperfine parameters of $^{57}\text{Fe}$ at room temperature are:

$$\delta = 0.13 \pm 0.01 \text{ mm/s}$$

$$\Delta E_Q = 1.01 \pm 0.01 \text{ mm/s}$$

The isomer shift parameter $\delta$ of $^{57}\text{Fe}$ in $\text{Sr}_2\text{FeEuO}_6$ is similar to that in the other tetrahedral $\text{Fe}^{3+}$ ferrites /3-8/ and indicates a strong covalency of the Fe--O bonds. The obtained value supports a trend towards smaller isomer shifts with decreasing Fe--O distances in the $\text{FeO}_4$ groups as can be seen from the Table 1.

Fig. 2: Mössbauer spectrum of $^{57}\text{Fe}$ in $\text{Sr}_2\text{FeEuO}_6$ with the source of $^{57}\text{Co}$ in Pd

Unequal areas of the absorption lines observed for $\text{Sr}_2\text{FeEuO}_6$ above 20 K can be explained by partial
orientation of the crystallites in the sample. In the
absorbers, in which random orientation has been assured by
careful grinding of Sr$_2$FeEuO$_5$ with fine NaF powder, this
asymmetry vanished.

TABLE 1. Comparison of Fe–O distances with isomer shifts
in some FeO$_4$ groups

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Fe–O (Å)</th>
<th>I.S. (mm/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_3$(FeO$_4$)(MoO$_4$)$_2$</td>
<td>1.908</td>
<td>0.28</td>
<td>4</td>
</tr>
<tr>
<td>Ca$_2$Fe$_2$O$_5$</td>
<td>1.879</td>
<td>0.21</td>
<td>5</td>
</tr>
<tr>
<td>YFeO$<em>5$O$</em>{12}$</td>
<td>1.866</td>
<td>0.16</td>
<td>6</td>
</tr>
<tr>
<td>NaFeO$_2$</td>
<td>1.86</td>
<td>0.17</td>
<td>7</td>
</tr>
<tr>
<td>KFeO$_2$</td>
<td>1.85</td>
<td>0.15</td>
<td>8</td>
</tr>
<tr>
<td>Sr$_2$FeEuO$_5$</td>
<td>1.851</td>
<td>0.13</td>
<td>this work</td>
</tr>
</tbody>
</table>

The measured quadrupole splitting parameter
$\Delta E_Q = 1.01 \pm 0.01$ mm/s of $^{57}$Fe in Sr$_2$FeEuO$_5$ is quite
large, indicating a strong angular distortion from an ideal
tetrahedral symmetry of the iron ions.

A simple point charge lattice sum calculation yields an
axially symmetric EFG and a negative quadrupole splitting
parameter: $\Delta E_Q = -0.69$ mm/s. The accuracy of the
obtained value is estimated to be about 30% because the
induced dipole moments and covalency effects were
neglected in the calculations. However, the negative sign of
$\Delta E_Q$ may be reliable. A more detailed molecular–orbital
cluster approach study as has been already applied to iron
oxides /9/, would be of great interest for the determi-
nation of the electronic charge density at the iron nucleus
on the tetrahedral site in Sr$_2$FeEuO$_5$.

The transition from the quadrupole doublet spectra to
the sextet pattern with sharp resonance lines takes place
in a relatively short temperature interval. The magnetic
ordering temperature is estimated to be $20 \pm 1$ K, in good
agreement with the preliminary magnetic susceptibility
measurements. The magnetic structure of Sr$_2$FeEuO$_5$ has
not yet been reported, but structural characteristics give
evidence that superexchange interactions through two
oxygen ions take place in this compound.

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