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PECULIARITIES OF THE SPIN STATE AND THE DISTRIBUTION OF Fe$^{3+}$ IN SODIUM BORATE GLASSES

V.K. Imshennik, I.P. Suzdalev, Yu.V. Maksimov and F.J. Litterst

Institute of Chemical Physics, Moscow, USSR.

+ Physics Department E-15 der Technischen Universität, München, BRD.

Mossbauer spectroscopy, ESR, and magnetic susceptibility measurements were used to investigate the spin state and the distribution of Fe$^{3+}$ in sodium borate glasses (Na$_2$O. 3B$_2$O$_3$. xFe$_2$O$_3$ where x=0.1, 1.5, 10 at %).

Mossbauer spectra at 4.2 K<T<300 K consist of the doublet with $\Delta E_q$=1.1±0.1 mm/s IS=0.40±0.03 mm/s (related to Fe) and the magnetic hyperfine structure (HFS) with H$_\mu$=52.0±0.5 T, IS=0.36±0.03 mm/s (related to Fe). At small concentration of iron (x<1 at %) the HFS is predominant in spectra (fig.1), the ESR signals with $g\approx 4.3$ is observed and the magnetization data (fig.3) correspond to S=5/2 paramagnetic state. When the concentration of iron increases the doublet becomes more intensive than the HFS structure and strong signal ESR with $g\approx 2$ occurs at 4.2 K<T<300 K but the saturation magnetization decreases (fig.3). It is obvious that the HFS spectra appear due to slow relaxation rate of isolated Fe$^{3+}$ ions homogeneously distributed in glassy matrix.

Application of a small external magnetic field breaks the bond between the electronic and nuclear spins and the HFS spectra become more resolved.

The HFS spectra of fig 2 obtained under $H_{ext}=0.065$ T were fitted with the model of 3 sextuplets (S$_{z}^2=5/2,3/2,1/2$) [1] according to the Hamiltonian (I).

$$H=\delta S_{z}^2-1/3 S(S+1)+\lambda(S_{x}^2-S_{y}^2)$$

(I)

by using the program given in [21]. This computer fit gives $\lambda=0.22\pm0.02$ for
Fig. 3. The magnetization per Fe$^{3+}$ ion for different \( x \) as a function of applied magnetic field at \( T=4.2 \) K. --- The simple Brillouin function. --- The Brillouin function corrected for anisotropic values.

\[
x=1\%, \lambda=0.24\pm0.03 \text{ for } x=0.1\% \text{ and } \Delta S_9=0.12\pm0.04 \text{ mm/s for both samples.}
\]

The fact of description the hf spectra with one value of \( \lambda \) which is about equal for \( x=1\% \) and \( x=0.1\% \) indicates the similarity of distorted octahedral environment of Fe$^{3+}$ ions, and therefore the similarity of structural units in glassy matrix where Fe$^{3+}$ ions place as modifier.

It should be noticed that the correct value of quadrupole splitting of the hf spectra mentioned above can be obtained only from \( S_9=5/2 \) Kramers doublet. The doublet yield anisotropic \( g \) values at any \( \lambda \) [1] and therefore electronic and nuclear spins are directed along \( z \) axis of the Hamiltonian(I), which is collinear or has the constant angle with the main axes of the \( s \) gradient. It is necessary to note that the computer fitted magnetization curves (fig. 3) were corrected for anisotropic \( g \) values too. The difference of quadrupole splitting of doublet and hf structure shows, that the doublet doesn't arise from fast relaxation process and most probably has another nature.

Decreasing of magnetization with the increased concentration of iron prove the existence of an antiferromagnetic interaction between Fe$^{3+}$ ions. But antiferromagnetically coupled dimers and superparamagnetic clusters of Fe$^{3+}$ ions don't produce low temperature ESR signal due to singlet ground level. Only trimers yield such signal. According to magnetization data we suggest the existence of both the antiferromagnetically coupled dimers and trimers of Fe$^{3+}$ ions.

The relative amount of isolated ions \((Z_1)\) with the magnetic moment \( \mu=\gamma\mu_0 \) the relative amount of iron atoms in dimers \((Z_2)\) with \( \mu=0 \) and trimers \((Z_3)\) with \( \mu=1/\mu_0 \) [3] we can get from follow equations, assuming \( Z_1+Z_2+Z_3=1 \).

\[
S_d/S_t=Z_2+Z_3
\]

\[
M=M_1B(\mu_1H/kT)\cdot Z_1+M_2 B(\mu_2H/kT) \cdot Z_2
\]

where B-Brillouin function, \( S_d \) and \( S_t \) are the areas of doublet and total one in mcm. The results of numerical calculations are given in the table.

<table>
<thead>
<tr>
<th>Concentr.</th>
<th>0.1</th>
<th>I</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_1 )</td>
<td>I</td>
<td>0.92</td>
<td>0.25</td>
</tr>
<tr>
<td>( Z_2 )</td>
<td>I</td>
<td>0.14</td>
<td>0.23</td>
</tr>
<tr>
<td>( Z_3 )</td>
<td>I</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

It should be mentioned that due to a Boltzmann population of high levels \( I/\mu<2/\mu \) and therefore the values of table are obtained with error of 10-20%.

Thus we can make the conclusion that in the case of sodium borate glasses there are non-equivalents positions of Fe$^{3+}$ ions in glassy matrix. These positions can be connected with the five crystalline structural groups found in [4] and containing \( B_2O_3 \) and \( B_2O_4 \) units with bridging and non-bridging oxygen atoms. The existence of both types of oxygen atoms as nearest neighbours distort the local environment of Fe$^{3+}$ and produce \( \lambda=0.23 \) for isolated ions and supply antiferromagnetic exchange for dimers and trimers. The peculiarities of distribution are that the sites of isolated ions are occupied first of all and than those of dimers and trimers.

References.