PECULIARITIES OF THE SPIN STATE AND THE DISTRIBUTION OF Fe3+ IN SODIUM BORATE GLASSES

V. Imshennik, I. Suzdalev, Yu. Maksimov, F. Litterst

To cite this version:

HAL Id: jpa-00219785
https://hal.archives-ouvertes.fr/jpa-00219785
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
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 $\Delta E$=1.1±0.1 mm/s IS=0.46±0.03 mm/s (relat. $\approx$−Fe) and the magnetic hyperfine structure (HFS) with $H_H$=52.0±0.5 T, IS=0.36±0.03 mm/s (relat. $\approx$−Fe). At small concentration of iron (x=0.1,1%) the HFS is predominant in spectra (fig.1), the ESR signals with $g$=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 $g$=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 $(S_{2}^{\frac{5}{2}}\pm \frac{3}{2}, \pm \frac{1}{2})$ [1] according to the Hamiltonian (I).

$H=D(S_2^{2}-\frac{1}{3} S(S-I)) + \lambda (I_x^{2}-\frac{1}{3})$ (I).

by using the program given in [2]. This computer fit gives $\lambda$=0.22±0.02 for

\[\gamma = 10\% \quad \gamma = 5\% \quad \gamma = 1\% \quad \gamma = 0.1\%\]
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.

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.

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.

Increasing 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 $\mu = 5/2 \mu_0$ the relative amount of iron atoms in dimers ($Z_2$) with $\mu = 0$ and trimers ($Z_3$) with $\mu = 1/2 \mu_0$ [3] we can get from the follow equations, assuming $Z_1 + 2Z_2 + 3Z_3 = I$. $S_d/S_t = Z_2 + Z_3$. $M = Z_1 \mu (\mu \mu_0/kT)Z_1 + Z_3 \mu (\mu \mu_0/kT)Z_3$ where $B$-Brillouin function, $S_d$ and $S_t$ are the areas of doublet and total one in mosehauer spectra for thin absorber at T=4.2 K. The results of numerical calculations are given in the Table.

<table>
<thead>
<tr>
<th>Concentr. %</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_1$</td>
<td>0.9</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>$Z_2$</td>
<td>0.1</td>
<td>0.25</td>
<td>0.7</td>
</tr>
<tr>
<td>$Z_3$</td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>

It should be mentioned that due to a Boltzmann population of high levels $I = Z_1 < 2Z_2$ 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$_2$O$_3$ and BO$_4$ units with bridging and non-bridging oxygen atoms. The existence of both types of oxygen atoms as nearest neighbors 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: