STUDY OF GALLIUM GLASSES BY THE E.P.R. METHOD

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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF GALLIUM GLASSES BY THE E.P.R. METHOD

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Until now the effect of γ-radiation on gallium glasses has not been studied, and no models have been proposed for the color centers in them. In the present work, on a 3-centimeter radiospectrometer RÉ-1301, gallium glasses subjected to preliminary γ-irradiation from a Co^60 source with a dose of 10^6 r were studied. E.p.r. spectra are presented for glasses of two compositions (in mol. %) No. 1 $-16\%\mathrm{Li_2O}\cdot 12\%\mathrm{Ga_2O_3}\cdot 72\%\mathrm{SiO_2}$, and No. 2 $-16\%\mathrm{Li_2O}\cdot 21\%\mathrm{Ga_2O_3}\cdot 63\%\mathrm{SiO_2}$, which lie on different sides of the section $\mathrm{Ga_2O_3/Li_2O} = 1$.

In the region of the induced e.p.r. spectra, before irradiation no resonance lines were observed. After γ-irradiation, in the spectrum of glass of composition No. 1 an asymmetric resonance line with $g = 2.01 \pm 0.004$ was observed, while in glass No. 2 there were several resolved peaks (Fig. 1). Analysis of the latter spectrum makes it possible to distinguish four peaks equidistant from one another, with the value $g = 2.006 \pm 0.004$ for the central point between them.

The spin of the nuclei $\mathrm{Ga}^{69,71}$ is $I = 3/2$, and the magnetic moments of its isotopes are sufficiently close to one another: $\mu(\mathrm{Ga}) = (2.01 + 2.55)/2 \approx 2.3$; therefore the four lines in the e.p.r. spectrum may be regarded as lines of hyperfine structure (h.f.s.) that appeared because of the interaction with the gallium nucleus of the unpaired spin of the paramagnetic trap which formed after γ-irradiation of the glasses. Because of the different magnetic characteristics of the nuclei of gallium isotopes, the h.f.s. lines are broadened, but no additional resolution of the spectrum is observed.

Fig. 1. E.p.r. spectra of glasses of compositions No. 1 $-16\%\mathrm{Li_2O}\cdot 12\%\mathrm{Ga_2O_3}\cdot 72\%\mathrm{SiO_2}$ and No. 2 $-16\%\mathrm{Li_2O}\cdot 21\%\mathrm{Ga_2O_3}\cdot 68\%\mathrm{SiO_2}$, irradiated with a dose of 10^6 r from a Co^60 γ-source

Fig. 2. Bonding scheme in the octahedral complex GaO_6^{9-}.

Figure 2: Fig. 2. Bonding scheme in the octahedral complex GaO_6^{9-}.

Hyperfine structure in e.p.r. spectra was observed by us earlier in aluminum (^{1,2}), phosphate (^{3}), and borate (^{4}) glasses, in which the nuclei of the atoms forming the lattice have spin different from zero. The magnitude of the h.f. splitting A in gallium glasses is (25 ± 5) oersted, while in aluminum glasses of analogous composition it is

is equal to 8 Oe. If only the differences in the ratios I/μ for gallium and aluminum nuclei are taken into account ($\mu(\mathrm{Al}) = 3.6$; $I(\mathrm{Al}) = 5/2$), the following equality should hold:

$$\frac{A(\mathrm{Ga})}{A(\mathrm{Al})} = \frac{\mu(\mathrm{Ga})}{I(\mathrm{Ga})} : \frac{\mu(\mathrm{Al})}{I(\mathrm{Al})} \simeq 1.1.$$

On the basis of the fact that the experimental value of the h.f. splitting for trivalent gallium is approximately 3 times greater than for aluminum, it may be considered that in gallium-oxygen complexes the degree of covalency of the bonds is higher than in alumino-oxygen complexes. This conclusion is consistent with the conclusions of N. S. Garifyanov that $4d$-orbitals form more covalent bonds with ligands than $3d$-orbitals (^{5}). The presence of more rigid covalent bonds in gallium glasses improves the resolution of h.f.s. in their EPR spectra, probably owing to a more regular position of gallium than aluminum in the structural sites.

Fig. 2. Scheme of bonds in the octahedral complex GaO_6^{9-}. a—energy levels of the central gallium atom, b—energy levels of the combined orbitals of gallium and the ligands, c—energy levels of the ligands.

The resonance line with $g = 2.01$, present in the spectrum of glass No. 1, is characteristic of all alkali-silicate glasses in which the formation of microregions of bisilicate is possible (^{6}). It is associated with the trapping of a hole at the upper valence level of the π-bond in the silicon-oxygen tetrahedron, for which the presence of at least one nonbridging oxygen atom is characteristic (^{7}). In glass No. 1, lying in the composition region $Ga_2O_3/Li_2O < 1$, the probability of existence of (GaO_6) units in comparison with (GaO_4) units is small (^{8}). As is seen from Fig. 1, a resolved spectrum with h.f.s. is absent in this glass, i.e., it may be asserted that silicon-oxygen tetrahedra are more effective hole traps than (GaO_4) units.

In glass No. 2, lying in the composition region $Ga_2O_3/Li_2O > 1$, octahedral complexes GaO_6^{9-} are realized, in which the upper filled level is, evidently, the $4d$—$2p$ π-bond level. This level is located sufficiently high in energy; therefore traps associated with (GaO_6) units effectively capture holes. The scheme of energy levels corresponding to the GaO_6^{9-} complex is given in Fig. 2. In octahedral complexes, the formation of 7 bonding molecular orbitals $\sigma(a_{1g})$, $\sigma(e_g)$, $\sigma(t_{1u})$, $\pi(t_{1u})$, $\pi(t_{1g})$, $\pi(t_{2u})$, $\pi(t_{2g})$ is possible when the central atoms and ligands possess orbitals that transform according to identical representations (^{9}). If the corresponding orbitals are absent, then the levels remain nonbonding. There are no electrons on the antibonding levels in the complexes GaO_6^{9-}; therefore they are not considered in the scheme. The upper filled level is the triply degenerate π-bond level (t_{2g}), to which corresponds a wave function formed by a linear combination of the wave function of the central atom $\Psi(\mathrm{Ga})$ for the states $4d_{xy}$, $4d_{yz}$, $4d_{zx}$.

and of the ligand wave function $\Psi(O_x)$, which transforms according to the representation t_{2g} (9). The complete wave function has the form

$$\Psi(t_{2g}) = d\Psi(\mathrm{Ga}) + \sqrt{1-\alpha^2}\,\Psi(O_x),$$

where α is a parameter characterizing the degree of covalency of the bond. The assumption that the hole is trapped at the level of a π-bond is consistent with the small value of the hyperfine splitting in the EPR spectra of the glasses. The spin Hamiltonian corresponding to the paramagnetic trap under consideration may be written in the form

$$H = g\beta\vec{H}\vec{S} + \alpha^2 A\vec{I}\vec{S},$$

where the spin $S = 1/2$ (formation of a paramagnetic trap with $S > 1/2$ is unlikely); $I(\mathrm{Ga}) = 3/2$; the effective value of the g-factor, taking into account the covalent character of the bonds, is $g = 2.006$, and $\alpha^2 A/g\beta = 25$ Oe.

It follows from the data presented that the degree of covalency of the bonds in the (GaO_6) nodes is approximately $\sqrt{3}$ times greater than that for the (AlO_6) nodes, and that the value of the g-factor must be greater than its value for a free electron. The latter follows from the fact that admixture of lower-lying energy states to the wave function of the hole state is possible (transition of the hole to lower-lying energy levels causes an increase in the total energy of the system).

The absence in the EPR spectra of resonance lines from electron traps is probably explained by the fact that the alkali modifier ions, having trapped electrons, form nonparamagnetic microparticles.

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