PARAMAGNETIC RESONANCE OF FLUOROBERYLLATE GLASSES WITH COBALT AND NICKEL

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PARAMAGNETIC RESONANCE OF FLUOROBERYLLATE GLASSES WITH COBALT AND NICKEL

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The paramagnetic resonance of fluoroberyllate glasses with cobalt and nickel is associated with the unusual behavior of these elements in glasses and has not been observed up to the present time. The investigation carried out showed that nickel does not enter the glass network and separates out in the form of antiferromagnetic nuclei of $NiFe_2$, while divalent cobalt, being in the glass network in octahedral coordination, gives a paramagnetic-resonance signal at 77°K. The latter fact is of special interest, since many believe that for the Co^{2+} ion in octahedral coordination the EPR effect is absent not only at room temperature but also at nitrogen temperatures ([1]).

We prepared and studied glasses with a constant content of 0.5 mol.% CoF_2, differing in composition (in mol.%): $40BeF_2 \cdot 20AlF_3 \cdot 15CaF_2 \cdot 25KF$; $50BeF_2 \cdot 10AlF_3 \cdot 15CaF_2 \cdot 25KF$; $60BeF_2 \cdot 10AlF_3 \cdot 10CaF_2 \cdot 20KF$; $70BeF_2 \cdot 10AlF_3 \cdot 20KF$, as well as glasses of composition $60BeF_2 \cdot 10AlF_3 \cdot 10CaF_2 \cdot 20KF$ with a variable cobalt concentration and a one-component glass of BeF_2 with 0.05% CoF_2. Study of the optical spectra of these glasses showed that all of them, except glassy beryllium fluoride, have absorption bands (Fig. 1) characteristic of Co^{2+} in octahedral coordination. According to available data ([2], [3]), the band near 7000 cm^{-1} is due to the transition from the ground state $^4T_1(^4F)$ to the level $^4T_2(^4F)$, and the band at 19 000 cm^{-1} is due to the transition to the level $^4T_1(^4P)$. In glasses with contents of 60 and 70 mol.% BeF_2, one more absorption band is observed near 37 000 cm^{-1}, which does not appear in glasses with smaller and larger contents of beryllium fluoride. Earlier, in this region of the optical spectrum, weakly expressed absorption was in some cases observed and was associated with spin-forbidden transitions or transitions of the $\sigma \to d$ type ([3], [4]). The band at 37 000 cm^{-1} observed by us has the same intensity as for spin-allowed transitions; therefore it may be assumed that it is due to the transitions $^2E \to {}^2T$, which are realized for Co^{2+} in strong ligand fields ([2]). However, such a possible interpretation requires verification, which will be carried out by us subsequently.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

The glasses under consideration are red in color, characteristic of glasses colored by Co^{2+} ions in octahedral coordination, whereas glassy beryllium fluoride with cobalt has an intense blue color, typical of tetrahedral Co^{2+} complexes ([6], [7]). The comparatively high (approximately by an order of magnitude) absorption intensity in the latter glass is connected with the fact that in tetrahedral complexes, because of their lower symmetry, some of the prohibitions on transitions between various states, which mix with one another, are lifted ([2]).

Thus, comparing the absorption intensities of blue and red glasses, one can say that in fluoroberyllate glasses with Co^{2+} the coloration is associated with its coordination in the same way as in oxide glasses ([5], [6]).

In octahedral ligand fields, for Co^{2+} (d^7) the ground state is the orbital triplet $^4T_1(^4F)$, which is split into a number of sublevels. It is natural to expect that the greater the splitting of this triplet, the more likely it is to observe paramagnetic resonance of Co^{2+} on the lower spin doublet at higher temperatures. Because of the important role of the internal asymmetry of complexes ([7]), glasses are characterized by larger initial splittings of the ground states than crystals. However, because of the difficulty of interpreting the EPR spectra of glasses, it is not yet possible to estimate these splittings accurately. Nevertheless, the fact that the EPR signal of Co^{2+} is observed at 77°K

Fig. 1

Fig. 2

Fig. 1. Absorption spectra of Co^{2+} in glasses of the following compositions: 1 –60 $BeF_2 \cdot 10\ AlF_3 \cdot 10\ CaF_2 \cdot 20$ KF; 2 –70 $BeF_2 \cdot 10\ AlF_3 \cdot 20$ KF; 3 –80 $BeF_2 \cdot 5\ AlF_3 \cdot 15$ KF. Recorded by the density-plotting method on a Unicam SP-700 spectrophotometer; the spectra are not corrected for sample thickness and the density scales are not superposed. Absorption bands characteristic of Co^{2+} in octahedral coordination are observed ([2]).

Fig. 2. *a* –EPR spectra of glass of composition 60 $BeF_2 \cdot 10\ AlF_3 \cdot 10\ CaF_2 \cdot$ 20 KF with different molar contents of CoF_2, the concentration of which is indicated on the spectrum. *b* –EPR spectrum of glass of composition 70 $BeF_2 \cdot 10$ $AlF_3 \cdot 20$ KF. The rectangle marks the region of the spectrum in which the h.f.s. lines of the Mn^{2+} impurity are resolved. All measurements were performed at 77°K on samples of identical weight and geometry, with the operating conditions of the radiospectrometer unchanged.

agrees with the considerations set forth and confirms them. The resonance line of Co^{2+} is observed in all the fluoroberyllate glasses studied, except for glassy beryllium fluoride (blue glass), near $g = 4.28 \pm 0.01$ for the midpoint between its extrema. At room temperature no paramagnetic resonance is observed.

The recorded spectra were calibrated against signals from DPPH, $g = 2.00$, and from oxygen glass with Fe^{3+} ions in tetrahedral coordination, $g = 4.27$. The measurements were performed on a three-centimeter RÉ-1301 radiospectrometer. A good correlation is observed between the intensity of the line with $g = 4.28$ and the cobalt content in the glass (Fig. 2).

In glasses of the base composition with a higher beryllium content, the EPR spectra of Co^{2+} are more intense, which is possibly connected with an increase in the initial splitting of the ground state of Co^{2+} owing to the stiffening of the ligand fluoroanions by beryllium cations ([8]). To eliminate suspicion that the resonant signal with $g = 4.28$ is associated with contaminating impurities, glasses of the base composition without transition elements and with transition metals of the iron group were prepared. The study of the paramagnetic and spectral properties of these glasses confirmed that, in the glasses with cobalt under investigation, the observed resonance with $g = 4.28$ is caused by Co^{2+}, and made it possible to conclude that the weak signal near $g = 2.00$, which has a characteristic h.f.s. of 6 lines with a splitting between them of about 96 Oe, is due to the Mn^{2+} impurity. The absence of 8 resolved h.f.s. lines from Co^{59} nuclei, which have spin $I = 7/2$, is probably connected with the overlap of these lines at 77°K and with the superhyperfine broadening produced by the surrounding fluorine ions.

Another interesting ion that changes the color of oxide glasses depending on its coordination state is nickel ([5]). However, unlike cobalt, nickel does not color fluoroberyllate glasses, but gives them a smoky color without selective absorption bands. This behavior of nickel is caused by the formation of NiF_2 nuclei. Such nuclei have the properties of antiferromagnets. The corresponding EPR spectrum consists of an almost symmetric resonance line, narrowed by exchange interaction, with $g = 2.33 \pm 0.01$ for the midpoint and a width of about 700 Oe at room temperature. The obtained value of the g-factor coincides with the EPR data for Ni^{2+} in ZnF_2 ([9]) and agrees with the values obtained by other methods for NiF_2 ([10]). Cooling the nickel-containing glasses to 77°K leads to the complete disappearance of the paramagnetic spectrum, since the Néel point of the compound NiF_2 lies in the range 78.5–83°K ([11]).

From the data obtained it may be concluded that the behavior of Co^{2+} and Ni^{2+} ions in fluoroberyllate glasses differs from their behavior in oxide glasses. In fluoroberyllate glasses, nickel forms antiferromagnetic nuclei, while the Co^{2+} ion forms such octahedral complexes that paramagnetic resonance is observed not only at helium temperatures but already at 77°K. Similar phenomena are not observed in oxide glasses.

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Note: Figure translations are in progress. See original paper for figures.