HYPERFINE STRUCTURE OF THE ELECTRON PARAMAGNETIC RESONANCE LINE OF Mn^{2+} WITH A *g*-FACTOR 4.3 IN THE CHALCOGENIDE GLASSES Tl$_{2}$SeAs$_{2}$Se$_{3}$, Tl$_{2}$SAs$_{2}$S$_{3}$, AND Tl$_{2}$TeAs$_{2}$Te$_{3}$

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Figure 1

Figure 1: Figure 1

Abstract

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HYPERFINE STRUCTURE OF THE ELECTRON PARAMAGNETIC RESONANCE LINE OF Mn^{2+} WITH A *g*-FACTOR 4.3 IN THE CHALCOGENIDE GLASSES $Tl_2SeAs_2Se_3$, $Tl_2SAs_2S_3$, AND $Tl_2TeAs_2Te_3$

(Presented by Academician L. A. Artsimovich on 18 VIII 1966)

As reported earlier (1), in the chalcogenide glasses $Tl_2SeAs_2Se_3$ with an Mn impurity (0.1-1 wt. %) two EPR lines of Mn ions were observed: a line with *g*-factor 2 and a line with *g*-factor 4.3. The change in the width and intensity of these lines upon lowering the temperature from room temperature to 77°K, as well as the magnitude of the *g*-factor, made it possible to assign the observed EPR lines to Mn^{2+} ions located in the glass network in different environments. The line with *g*-factor 2 was associated with Mn^{2+} ions entering microcrystalline antiferromagnetic formations with a Néel-point temperature below 77°K, and with Mn^{2+} ions situated in the glass matrix in positions having high symmetry or a small crystal-field magnitude. The line with *g*-factor 4.3 was assigned to an Mn^{2+} ion characterized by a significant bond with the surrounding atoms of the glass matrix, which form a strong crystal field with a rhombic component. A model was proposed (1) for the incorporation of such an Mn ion into a quadruply coordinated site of the glass matrix, in which the Mn atom gives up two electrons to neighboring Se^- ions in Se^-Tl^+ pairs, converting them into Se^{2-}. Thus, the Mn^{2+} ion forms a strong bond with selenium ions. It was also noted (1) that there was great stability of the width of the line with *g*-factor 4.3 both at room temperature and at liquid-nitrogen temperature (on passing from sample to sample). Such stability was explained by the high stability of the symmetry of the ion environment. However, further studies of the spectra at 77°K showed that at this temperature, in samples with 0.1 and 0.2 wt. % Mn impurity (samples Nos. 2 and 3 in (1)), a very weak hyperfine structure (h.f.s.) is resolved on the line with g 4.3 (Fig. 1a).

Fig. 1. Hyperfine structure of the EPR line (first derivative) of Mn^{2+} with g-factor 4.3 at 77°K in $Tl_2SeAs_2Se_3$ + 0.2% Mn samples upon cooling together with the furnace (*a*) and upon quenching in water (*b*). Scale: 100 Oe.

The samples investigated in (1) were held during synthesis at a maximum temperature of 900°C for 5 hours and were then cooled in the cooling regime of the switched-off furnace (2). An attempt was made to improve the resolution of the observed h.f.s. by changing this regime: a) the maximum heating temperature was reduced to 750°, and the holding of the samples at this temperature was increased to 24 hours; b) in addition, in the case of both regimes the temperature was slowly lowered from the maximum and, upon reaching 600 or 550°, the samples were again held at these temperatures for 1–3 hours and then quenched in cold water. Comparison

Comparison of the results obtained on samples of the indicated synthesis regimes convinced us that changing the synthesis does not affect the linewidth with $g \sim 4.3$ and does not lead to an improvement in the resolution of the h.f.s., affecting only the linewidth with $g \sim 2$. At the same time it was found that quenching the samples in cold water, which increases the homogeneity of the glass, improves this resolution (Fig. 1b) both in the case of the regime used previously and in the case of the regimes with the changes described.

The magnitude of the splitting and the number of weakly resolved components $(2I + 1)$ show that the h.f.s. is due to superhyperfine contact interaction with the isotope Mn^{55} $(I = 5/2)$, and the line with $g \sim 4.3$ is a superposition of six $(2I + 1)$ lines of hyperfine structure. The linewidth is determined by the splitting between the outermost h.f.s. lines. To a first approximation the splitting between the individual components may be considered identical. In all the samples studied the first 4 components are resolved more distinctly; the fifth and sixth components are resolved poorly. This may in part be connected with a certain decrease in the intensity of the components, as is seen from Fig. 2, which presents an oscillogram of the line with $g \sim 4.3$ in a sample $Tl_2SeAs_2Se_3+$ 0.2% Mn, cooled in the regime of cooling with the furnace switched off, recorded while observing e.p.r. at liquid-helium temperature.

In all the samples studied the magnitude of the splitting between the h.f.s. lines (A) is 68±2 Oe. This value does not change appreciably under considerable deviations from stoichiometry, as shown by e.p.r. studies in the glasses $AsSe_{35}Tl_{0.5}$, $AsSe_{1.37}Tl_{0.75}$, and $Tl_2Se \cdot 7.2As_2Se_3$.

In some samples the h.f.s. was already weakly resolved at room temperature. The splitting value, within the experimental error, did not change noticeably when the temperature was lowered to 77°K. At 4.2°K, by recording the e.p.r. signal on an oscillograph, the value of A could not be determined accurately*, but an approximate estimate gives a value of A close to that obtained at 77°K. As is known, the value of the constant A makes it possible to draw conclusions concerning the nature of the bond of the paramagnetic ion under study with the ligand atoms surrounding it. In this connection the value of A in the

Fig. 2. Absorption line of the EPR of Mn^{2+} at 4.2° K in a sample $Tl_2SeAs_2Se_3 + 0.2\%$ Mn, cooled together with the furnace.

Figure 2: Fig. 2. Absorption line of the EPR of Mn^{2+} at 4.2° K in a sample $Tl_2SeAs_2Se_3 + 0.2\%$ Mn, cooled together with the furnace.

e.p.r. spectrum of Mn^{2+} decreases on going from more ionic to more covalent compounds (^{3}). Thus, the value of A should decrease in the series of glassy compounds similar in structure, $Tl_2SAs_2S_3$, $Tl_2SeAs_2Se_3$, $Tl_2TeAs_2Te_3$, in which Mn interacts with the elements S, Se, and Te, of decreasing electronegativity ($X_S = 2.5$, $X_{Se} = 2.4$, $X_{Te} = 2.1$). Our e.p.r. measurements at 77°K showed that in the indicated glassy substances with an impurity of 0.2 wt.% Mn such a decrease in the constant of isotropic hyperfine interaction A does in fact occur: $A = 72.5 \pm 2$ Oe in $Tl_2SAs_2S_3$, $A = 68 \pm 2$ Oe in $Tl_2SeAs_2Se_3$, and $A = 61 \pm 2$ Oe in $Tl_2TeAs_2Te_3$**. The larger change in the value of A on going from $Tl_2SeAs_2Se_3$ to $Tl_2TeAsTe_3$ than on going from $Tl_2SeAs_2Se_3$ to Tl_2SAsS_3 is connected with the greater difference of the electronegativities X_{Se} and X_{Te} than X_{Se} and X_S. However, no appreciable change of the h.f.s. constant upon replacement of part of Se by Te was found. Samples $Tl_2Se_{1/2}As_2Se_3 \cdot 0.5As_2Tl_3 + 0.2Mn$ (19% Tl) and $Tl_2SeAs_2Te_3 + 0.2\%Mn$ ($\sim 37\%$ Te) were studied. In the first case no change in A was observed. In the second case the h.f.s. was not resolved because of the low intensity of the line with $g \sim 4.3$.

The values of the constants A in the investigated glasses based on S, Se, and Te agree with the values of A obtained in crystalline sulfides, selenides, and tellurides (^{3}). In (^{3}) an approximate dependence is given of the degree of ionicity of the bond on the magnitude of the constant A. According to this estimate, the degree of ionicity of the bond of the Mn^{2+} ion with the surrounding atoms of the glass matrix in the compounds studied increases approximately from 20 to 35% on going from Te to S.

Thus, the presence of the dependence considered above of the hyperfine isotropic-interaction constant on the type of chalcogen confirms the supposition of a strong, to a considerable degree covalent, bond of Mn with the chalcogen atoms in the proposed model of incorporation of the Mn^{2+} ion into the glass matrix.

Fig. 2. Absorption line of EPR Mn^{2+} at 4.2° K in a sample $Tl_2SeAs_2Se_3 + 0.2\%$ Mn, cooled together with the furnace.

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* E.p.r. observations at 4.2°K on a superheterodyne spectrometer of the 3-centimeter range on samples $Tl_2SeAs_2Se_3 + 0.1\%$ Mn, $Tl_2SeAs_2Se_3 + 0.2\%$ Mn, and $Tl_2Se \cdot 3As_2Se_3 + 0.2\%$ Mn were carried out by N. E. Kask, to whom the authors express their gratitude.

** The linewidths δH at nitrogen temperature are respectively 410 ± 10 Oe, 400 ± 10 Oe, and 360 ± 10 Oe.

The observed difference in the intensities of the individual components of the h.f.s. (Fig. 2) is possibly connected with the superposition on the h.f.s. of Mn^{2+} of a superhyperfine structure caused by interaction with the magnetic isotope Se^{77} ($I = 3/2$, natural abundance $\sim 7\%$) or with As^{74} atoms ($I = 3/2$, natural abundance 100%), which, according to the proposed model, are located in the second coordination sphere. Synthesis of samples from Se with an increased content of Se^{77} would possibly make it possible to answer this question.

The hyperfine structure of the line with $g \sim 4.3$ disappears when the Mn concentration in the samples is increased. For example, the h.f.s. is no longer observed in samples with 0.4 wt.% Mn, whereas the line width does not change. The disappearance of the h.f.s. with increasing Mn content (C_{Mn}) is possibly connected with the fact that, with increasing C_{Mn}, the intensity of the line with $g \sim 2$ increases preferentially, and this line begins to overlap strongly with the line with $g \sim 4.3$. The h.f.s. was not observed on the line with $g \sim 2$ even at a concentration of 0.1% Mn. This is possibly connected with a large spread in the value of the g-factor characterizing this line, which is due to fluctuations in the symmetry of the environment of the paramagnetic ion that are larger than for the line with $g \sim 4.3$.

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REFERENCES

1. L. D. Bogomolova, V. N. Lazukin, I. V. Chepeleva, DAN, **168**, No. 1, 59 (1966).
2. N. A. Goryunova, B. T. Kolomiets, V. P. Shilo, ZhTF, **28** (5), 981 (1958).
3. L. V. Bershev, A. S. Marfunin, DAN, **155**, No. 3, 632 (1964).

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