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ELECTRON-PARAMAGNETIC RESONANCE OF Mn^{2+} IONS IN $\mathrm{Tl_2SeAs_2Se_3}$

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It was reported earlier on the EPR of Mn ions in glassy samples and crystallized glasses of the systems As–Se–Te (1) and As–Se–Ge (2). The present article is devoted to an investigation of EPR in $\mathrm{Tl_2SeAs_2Se_3}$ with an admixture of manganese, introduced in amounts of 0.1-1 wt.% at the expense of $\mathrm{Tl_2SeAs_2Se_3}$.

The samples were synthesized by the usual method (3) under conditions corresponding to the glassy state of $\mathrm{Tl_2SeAs_2Se_3}$. At a temperature of 900°C they were held for 5 h and cooled under the cooling regime of a switched-off furnace. The samples obtained had the conchoidal fracture characteristic of glasses (with the exception of the sample $\mathrm{Tl_2SeAs_2Se_3}$ + 1% Mn, in which the presence of a crystalline phase was noticeable).

EPR was studied on a standard RE-1301 radiospectrometer at temperatures of 300 and 77 K. The sample under study was lowered to the bottom of a small Dewar vessel, the narrow part of which was located at the center of the transmission resonator of the spectrometer, and comparison of the line intensities at 300 and 77 K was carried out by recording spectra first at room temperature and then after filling the Dewar with liquid nitrogen. The line width δH was determined as the distance between the extrema of the first derivative of the absorption curve. Measurements at a temperature of 4.2 K were carried out on a superheterodyne spectroscope of the 3-centimeter range.

Table 1

EPR data for Mn^{2+} in $\mathrm{Tl_2SeAs_2Se_3}$ samples

Sample No.	Mn concentration, wt.%	g-factor	δH, room temp.	δH, nitrogen temp.	g-factor	δH, room temp.	δH, nitrogen temp.
1	0.1	2 ± 0.1	600	–	4.3 ± 0.1	440 ± 40	440 ± 40
2	0.1	2 ± 0.1	450 ± 50	600 ± 50	4.3 ± 0.1	480 ± 80	440 ± 50
3	0.2	1.96 ± 0.2	360 ± 40	500 ± 40	4.3 ± 0.2	440 ± 40	440 ± 40
4	0.5	2 ± 0.1	700	1200 ± 100	4.1 ± 0.1	400 ± 40	~ 400
5	0.7	2 ± 0.1	750 ± 100	1000 ± 100	–	–	–
6	1	2 ± 0.1	750 ± 40	1250 ± 100	~ 4.3	~ 400	~ 400

Experimental results. The measurement results are presented in Table 1 (the Mn concentration is indicated according to the synthesis); some of the observed spectra are shown in Figs. 1 and 2. As is seen from Table 1, in all the samples studied the observed spectrum consisted of two resonance lines: with g-factor ~ 4 and g-factor ~ 2. The exception was sample No. 5 (with 0.7 wt.% Mn according to the synthesis), in which only one EPR line with $g \sim 2$ was observed.

The line with $g \sim 4$ is distinguished by a certain asymmetry, which is especially clearly seen in Fig. 1a (the line on the left), where the EPR spectrum of sample No. 1 is presented; in this sample the line with $g \sim 2$ is very weak and does not overlap with the li-

$g \sim 4$. In samples Nos. 2 and 3 one may note some overlap of the wings of the lines with $g \sim 4$ and with $g \sim 2$; however, both at room temperature and at 77°K the asymmetry of the line with $g \sim 4$ is similar in character to the asymmetry of this line in sample No. 1. In samples Nos. 4 and 6, with a larger amount of manganese, the line with $g \sim 4$ overlapped to a considerable extent with the line at $g \sim 2$, so that determination of its width and shape and of the exact value of the g-factor is difficult. However, if one assumes that the line with $g \sim 2$ is symmetric (at room temperature, when the intensity of the line with $g \sim 4$ is very small, this line is symmetric; see Fig. 2, a) and that its left wing decreases smoothly as the field is reduced, then the width of the line with $g \sim 4$ can also be estimated as the distance between the extrema of the derivative, although it is possible that the overlap of the lines introduces a noticeable error into the estimate of δH_{g_4} (and also of δH_{g_2}). The exact values of the g-factor of the line with $g \sim 4$ in these cases cannot be determined. Apparently, however, the g-factor does not change appreciably, since for these samples the distances of the left and right extrema from the field value corresponding to the DPPH line remain approximately the same as for glasses Nos. 1—3.

In all the samples studied, when the temperature was lowered to 77°K, the intensity of the line with $g \sim 4$ increased by a factor of 4—6, while the intensity of the line with $g \sim 2$ increased by a factor of 1.5—2.3.

In sample No. 5, for which the line with $g \sim 4$ was not observed, and in sample No. 6, where the intensity of the line with $g \sim 4$ at room temperature is small, the shape of the line with $g \sim 2$ is approximately symmetric. The spectrum of sample No. 3 was studied at a temperature of 4.2°K. In this case the width of the line with $g \sim 4$ was no more than 300 Oe. The shape of the line was approximately preserved, and the intensity of the line with $g \sim 4$ was comparable with the intensity of the line with $g \sim 2$, which agrees with the ratio of their intensities at 77°K.

Discussion of results. 1. The EPR line with $g \sim 4$, caused by Mn ions, in $Tl_2SeAs_2Se_3$ samples, in comparison with the analogous line in the As—Se—Ge system and especially As—Se—Te (where the appearance of the line with $g \sim 4$ is fluctuational in character), is distinguished by greater stability of its characteristics and, for equal amounts of Mn, by greater intensity.

Let us consider a possible model of the paramagnetic center responsible for the EPR line with g-factor ~ 4.

In work (4) a model of the structure of $Tl_2SeAs_2Se_3$ is proposed: covalently bonded open chains —Se—As—Se—As—Se—are stabilized by ionized quadrupole nodes

$$\begin{array}{c} -\mathrm{As}-\mathrm{Se}^{\ominus}\ \mathrm{Tl}^{\oplus} \\ \mathrm{Tl}^{\oplus}\ \mathrm{Se}^{\ominus}-\mathrm{As}- \end{array}$$

Compounds of Mn with Tl are not known. An estimate of the bond energies Mn—Se and Mn—As allows one to consider that manganese interacts primarily with selenium and secondarily with arsenic. It therefore seems quite possible that the manganese atom is located in an ionized quadrupole node

$$\begin{array}{ccc} \mathrm{Se}^{2-} & & \mathrm{Tl}^{+} \\ & \mathrm{Mn}^{2+} & \\ \mathrm{Tl}^{+} & & \mathrm{Se}^{2-} \end{array}$$

thereby giving one negative charge to each of the neighboring Se^- ions, which are thereby converted into Se^{2-}, while the charge state of manganese becomes Mn^{2+}. The Mn^{2+} ion is in a strong electric field of four charges: two Se^{2-} ions and two Tl^+ ions.

Fig. 1. EPR spectrum at room temperature of samples No. 1 (a) and No. 3 (b)

Figure 1: Fig. 1. EPR spectrum at room temperature of samples No. 1 (a) and No. 3 (b)

Fig. 2. EPR spectrum of sample No. 6 at room (a) and liquid-nitrogen (b) temperatures

Figure 2: Fig. 2. EPR spectrum of sample No. 6 at room (a) and liquid-nitrogen (b) temperatures

The Mn^{2+} ion is isoelectronic with the Fe^{3+} ion, for which in oxide glasses a line with g-factor ~ 4 was also observed (^{5}). In work (^{5}) it was shown that the appearance of such a line for Fe^{3+} can be explained

in the approximation of a strong crystalline field, when the spin Hamiltonian of the system is written in the form

$$\mathcal{H} = g_0 \beta H + E(S_x^2 - S_y^2). \tag{1}$$

In this case, in a magnetic field the splitting of the pair $W = 0$ is characterized by the value of the g-factor, independent of orientation and equal to 4.286. The experimentally observed values of the g-factor in $Tl_2SeAs_2Se_3$ with an Mn impurity (see Table 1) agree well with this value.

In works (^{5,6}) it was shown that the appearance in the spin Hamiltonian of the term $E(S_x^2 - S_y^2)$ may be due to different arrangements of the electric charges surrounding the paramagnetic ion, possessing rhombic distortions of symmetry.

Fig. 1. EPR spectrum at room temperature of samples No. 1 (*a*) and No. 3 (*b*)

Fig. 2. EPR spectrum of sample No. 6 at room (*a*) and liquid-nitrogen (*b*) temperatures

An example may be a complex of four charges, two of which are not equal to the other two, arranged at the corners of a tetrahedron with the paramagnetic ion at the center (symmetry C_{2v}). As Griffiths showed, for such a complex, in the first approximation, the spin Hamiltonian of the system may be taken to be equal to (1). An analogous situation may occur for the Mn^{2+} ion in the quadruply coordinated site considered. The ions Se^{2-} and Tl^+ may form a spatial complex possessing a field component of rhombic symmetry, which will lead to the appearance of a line with $g \approx 4.3$, in accordance with the spin Hamiltonian (1).

The intense line with $g \approx 4.3$, observed in the samples studied, cannot be associated with Mn ions located in different interstices, where the environment of the paramagnetic ion is sufficiently chaotic. The fact that the shape of the first derivative of the line is approximately the same for all samples, with little overlap of spectra, that the scatter of the *g*-factor is small, that the line is comparatively narrow and its width does not increase with increasing manganese concentration and, within the limits of measurement error, changes hardly at all from sample to sample—all this indicates that the paramagnetic ion is located in the glass network in a definite position possessing a very stable environment, creating a strong electric field. Such a model is also supported by a certain decrease in the line width when the temperature is lowered from 77 to 4.2°K.

2. In samples of $Tl_2SeAs_2Se_3$ with an Mn^{2+} impurity, in contrast to the systems As–Se–Tl + Mn and As–Se–Ge + Mn, the line with $g \sim 2$ did not disappear at a temperature of 77°K, but even increased somewhat in intensity. However, the increase in the line width observed upon lowering the temperature (see Table 1), especially significant for samples Nos. 4-6 with a high Mn concentration, is possibly also associated with the formation in $Tl_2SeAs_2Se_3$ of certain

antiferromagnetic complexes whose Néel point lies below 77° K. Otherwise, the line with $g \sim 2$ may be represented as a superposition of two lines: one due to Mn in antiferromagnetic complexes, which broadens and decreases in intensity when the temperature is lowered to 77° K, and another associated with other paramagnetic centers, whose intensity may increase upon cooling. This assumption is supported by the fact that the line with $g \sim 2$ for sample No. 3 narrows from 440 oersteds at 77° K to 100-150 oersteds at 4.2° K, while its intensity remains of the same order as that of the line with $g \sim 4$.

The large difference, observed at high Mn concentrations, between the values of the *g*-factor corresponding to the center of the line with $g \sim 2$ and to its edges may be due to significant fluctuations in the symmetry of the environment of the paramagnetic centers contributing to the line with $g \sim 2$, and also to the fact that the symmetry axes of the crystal field of the individual centers are arbitrarily oriented with respect to the direction of the external magnetic field H (5).

3. A comparison of the e.p.r. spectra of all the samples studied showed (see Figs. 1 and 2) that, as the percentage content of manganese increases, the number of centers contributing to the line with $g \sim 2$ increases more rapidly than the number of centers responsible for the line with $g \sim 4$. (An accurate estimate of the relative numbers of paramagnetic centers from the intensities of the corresponding resonance lines is in this case hindered by their strong overlap.)

Thus, despite the considerable scatter of the experimental data, which is characteristic of glasses, in $Tl_2SeAs_2Se_3$ in the studied range of Mn content (0.1–1 wt.%) it is possible to trace a certain concentration dependence of the e.p.r. spectrum, i.e., with increasing amount of Mn one observes an increase in the width of the line with $g \sim 2$ and a preferential increase in the intensity of this line compared with the intensity of the line with *g*-factor ≈ 4.3.

The absence of a more stringent dependence of the e.p.r. spectrum on the Mn concentration is apparently due, to a significant extent, also to the fact that in the samples studied charged states of Mn may form which do not give e.p.r. This imposes requirements on the technology of introducing the paramagnetic impurity into chalcogenide glasses.

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