ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} AND Gd^{3+} IONS IN THE CHALCOGENIDE GLASSES TlAsSe$_2$ AND TlAsS$_2$ IN THE 2 AND 0.8 cm BANDS

I. V. Chepeleva

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ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} AND Gd^{3+} IONS IN THE CHALCOGENIDE GLASSES $TlAsSe_2$ AND $TlAsS_2$ IN THE 2 AND 0.8 cm BANDS

I. V. Chepeleva

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The study of the EPR spectra of Mn^{2+}, Gd^{3+}, and other ions in the ground S-state is of considerable interest because the nature of the splitting of the levels of these ions by the crystalline field is still not entirely clear. In most cases, S-ions give EPR lines with a g-factor close to 2. For Fe^{3+}, Mn^{2+}, and Gd^{3+} ions in oxide ([1]), borate and sulfur-oxygen glasses ([2]), in chalcogenide glasses ([3–5]), and in solutions ([6], [7]), EPR lines with a g-factor significantly exceeding the usual value 2 have recently been observed. The appearance of such lines in a number of cases was formally explained by assuming that these ions are in an environment with a strong low-symmetry component of the crystalline field. In the glasses studied, of the arsenic—chalcogen—thallium system $TlAsS_2$, $TlAsSe_2$, for Mn^{2+} ions in the 3 cm band, in addition to the line with g-factor ≈ 2, an intense line with g-factor ≈ 4.3 was observed. These lines were assigned to different Mn^{2+} centers ([3]); thus, depending on the synthesis conditions and the Mn concentration, one can obtain samples giving either only the line with $g \approx 4.3$, or only the line with $g \approx 2$. For Gd^{3+} ions in the 3 cm band, a complex spectrum was observed, representing a superposition of lines of different widths and intensities and corresponding to effective g-factor values of the order of 2; 2.8; 5.9; 8, etc. The positions of the lines of this Gd^{3+} spectrum cannot be explained within the framework of either of the two approximations used earlier ([1], [2], [8]): a strong rhombic field or a strong axial field. In order to clarify the reasons for the complex character of the spectra and for the appearance, in the 3 cm band, of lines with a g-factor considerably exceeding 2 for Mn^{2+} and Gd^{3+} ions in glasses of the arsenic—chalcogen—thallium system, observations of the EPR of these ions were carried out in the 2 and 0.8 cm bands, since the use of higher frequencies may, generally speaking, lead to a violation of the condition of a strong crystalline field. EPR measurements in the 2 cm band were carried out on a spectrometer with double modulation manufactured by Japan Electron Optics Lab, model FES-3B, at room temperature and at 77° K; in the 0.8 cm band, on a highly sensitive spectrometer with double modulation at room temperature.

Fig. 1. EPR spectrum of Mn^{2+} ions in $TlAsS_2 + 0.1$ wt.% Mn: a—$\lambda \sim 3.2$ cm, $T = 77$°K; b—$\lambda \sim 2$ cm, $T = 77$°K; c—$\lambda \sim 0.8$ cm, $T \sim 290$°K.

Figure 1: Fig. 1. EPR spectrum of Mn^{2+} ions in $TlAsS_2 + 0.1$ wt.% Mn: a—$\lambda \sim 3.2$ cm, $T = 77$°K; b—$\lambda \sim 2$ cm, $T = 77$°K; c—$\lambda \sim 0.8$ cm, $T \sim 290$°K.

The changes in the Mn^{2+} spectra in $TlAsSe_2$ and in $TlAsS_2$ that occur on going from the 3 cm band to the 2 and 0.8 cm bands are seen from Table 1 and Fig. 1. At 2 cm the line with $g \approx 4.3$ broadens, and its intensity relative to the line with $g \approx 2$ decreases by several times. The h.f.s. due to Mn^{55} is much less resolved in the $TlAsSe_2$ sample and is practically not resolved at all in $TlAsS_2$, for which the resolution of the h.f.s. is poorer even at 3 cm. At 0.8 cm the line with $g \approx 4.3$ disappears completely, and the Mn^{2+} EPR spectrum consists only of one symmetric line with $g \approx 2$. These facts can be interpreted with the aid of the previously proposed assumption (^{3}) that the line with $g \approx 4.3$ is due to Mn^{2+} ions situated in an environment that gives a strong crystalline field of rhombic symmetry ($|E| \gg g_0 \beta H$). Then it may be assumed that the condition $|E| \gg g_0 \beta H$ is fulfilled less well at 2 cm, as a result of which the line with $g \approx 4.3$ broadens, its intens—

decreases, while the h.f.s. is smeared out. It should be noted that the degree to which the condition $|E| \gg g_0 \beta H$ is fulfilled may be different for the different ions contributing to the line with $g \approx 4.3$, since in the disordered glass network there may be a substantial spread of values of the crystal-field parameters. In the 0.8-cm range $|E|$ will be smaller than $h\nu$; as a result, the Mn^{2+} ions that at 3 cm produced the line with $g \approx 4.3$ will now contribute to the EPR absorption in the region $g \approx 2$. Using these considerations, as well as the results of calculations (1), one can obtain a rough estimate of the magnitude $|E| \approx 0.27$ cm^{-1}.

In the 3-cm range, depending on the synthesis and cooling conditions of the $TlAsSe_2$ and $TlAsS_2$ glasses, as well as on the concentration of introduced Mn, the EPR spectrum of Mn^{2+} ions giving absorption in the region $g \sim 2$ may either possess an asymmetry, sometimes very considerable, or appear as a symmetric line. Table 1 presents the results for two limiting cases: an exchange-narrowed line in $TlAsSe_2$ and a strongly asymmetric Mn^{2+} spectrum in $TlAsS_2$ (Fig. 1a). In the first case the line width does not change substantially in the different ranges. In the sample $TlAsS_2 + 0.1\%$ Mn, however, the asymmetry of the spectrum in the region $g \sim 2$ decreases at shorter wavelengths: at 2 cm the line with $g \approx 2$ already has only a small asymmetry, and at 77 K a weakly resolved h.f.s. is observed for it (Fig. 1b); at 0.8 cm the line with $g \approx 2$ becomes completely symmetric, and a distinct h.f.s. is resolved for it already at room temperature. As in the case of the line with $g \approx 4.3$, the h.f.s. of the line with $g \approx 2$ is non-equidistant: the effective splitting decreases toward lower fields.

Fig. 1. EPR spectrum of Mn^{2+} ions in $TlAsS_2 + 0.1$ wt.% Mn.
a—$\lambda \sim 3.2$ cm, $T = 77$°K;

b–$\lambda \sim 2$ cm, $T = 77$°K;
c–$\lambda \sim 0.8$ cm, $T \sim 290$°K.

This character of the frequency dependence of the line with $g \sim 2$ indicates that its asymmetry at 3 cm cannot be caused by anisotropy of the g-factor, since in that case the asymmetry would have to increase with increasing measurement frequency (9). It may be supposed that the weak line observed in low fields belongs to the same ion that gives the strongly asymmetric spectrum in the region $g \sim 2$, since the line in low fields is observed only in samples with strong asymmetry of the spectrum at $g \sim 2$; this line is no longer observed at 2 cm, where the asymmetry of the spectrum with $g \sim 2$ is greatly reduced; it is also not observed at 0.8 cm. The frequency dependence of the spectrum, where there is a large extent in the region $g \sim 2$ ($\Delta H_{13} \sim 1300$ Oe) and absorption in low fields, indicates that the crystal-field energy for this Mn^{2+} ion is comparable with the Zeeman energy in the 3-cm range. The asymmetric line at $g \approx 2$ and the line in low fields can be interpreted as fine-structure lines, with the total envelope of the derivative of the absorption being determined by the complex angular dependence of the contributions of individual paramagnetic centers and by the probabilities of the corresponding transitions. As the measurement frequency is increased, the interaction with the crystal field becomes less and less significant in comparison with the Zeeman energy, which leads to a more symmetric line shape with $g \approx 2$ and to the disappearance of the line in low fields.

Exact analytical expressions for the positions of the fine-structure lines···

λ, cm	Glass $TlAsSe_2$ + 0.1 wt. %{Mn}	Glass $TlAsS_2$ + 0.1 wt. %{Mn}	Glass $TlAsSe_2$ + 0.2 wt. %{Cr}
	$g \simeq 2$	$g \simeq 4.3$	$g \sim 2$	$g \simeq 4.3$	$g \sim 2$	$g = 5.85 \pm 0.08$
3.2	$\delta H^k = 175 \pm 15$ $\delta H^a = 300 \pm 20$	$\delta H^k = 370 \pm 15$ $\delta H^a = 364 \pm 10$ $A^a = 62.5 \pm 3$ $r^k \sim 20$; $r^a \sim 4$	$\delta H_1^{k,a} = 230 \pm 10$ $\Delta H_{13}^{k,a} = 1250 \pm 100$	$\delta H^k = 390 \pm 20$ $\delta H^a = 385 \pm 10$ $r^k \sim 2.2$; $r^a \sim 1.5$	$\delta H_1^k \sim 120$ $\delta H_1^a \sim 130$	$\delta H^k = 95 \pm 10$ $\delta H^a = 98 \pm 10$ $r^k \sim 1.6$; $r^a \sim 1.4$

λ, cm	Glass $TlAsSe_2$ + 0.1 wt. % Mn	Glass $TlAsS_2$ + 0.1 wt. % Mn	Glass $TlAsSe_2$ + 0.2 wt. % Gd
2	$\delta H^{k} = 180 \pm 20 \delta H^{a} = 320 \pm 20$	$\delta H^{k} = 520 \pm 20 \delta H^{a} = 460 \pm 20 A^{a} = 63 \pm 5 r^{a} \sim 11$	$\delta H^{k} = 460 \pm 30 \delta H^{a} = 430 \pm 20 A^{a} = 65 \pm 5$	$\delta H^{a} = 420 \pm 20 r^{k} \sim 9;\ r^{a} \sim 6.5$	$g \sim 1.98 \delta H^{k} \sim 120$	$g = 5.85 \pm 0.05 \delta H^{k} = 90 \pm 5 \delta H^{a} = 80 \pm 5$
0.8	$\delta H^{k} = 160 \pm 10$		$\delta H^{k} = 395 \pm 10 A^{k} = 66 \pm 3$		$g = 1.98 \pm 0.005 \delta H^{k} = 78 \pm 5$	$n^{k} \sim 17$

* The indices k and a refer, respectively, to room and nitrogen temperatures; r is the ratio of the amplitudes of the line with $g \sim 2$ to the amplitude of this line; δH_1 is the line width; ΔH_{13} is the distance between the upper and lower extrema of the derivative absorption line for $g \sim 2$ (Fig. 1a); A is the mean effective value of the hyperfine-structure constants; δH and A are given in oersteds.

temperatures in the case when the effects of interaction with the crystalline field are comparable with the Zeeman energy and perturbation theory is inapplicable, cannot be obtained because of the large value of the spin $S = 5/2$ and the complicated angular dependence. In addition, the asymmetric spectrum at $g \sim 2$ cannot be interpreted in the strong- or weak-field approximation of axial symmetry. Thus, the absence of the possibility of comparison with theoretical calculations does not allow one to establish the type of symmetry of the crystalline field responsible, at 3 cm, for the asymmetry of the line with $g \sim 2$ and for the line in small fields, nor to identify the transitions.

The changes in the spectrum of Gd^{3+} ions in $TlAsSe_2$ + 0.2% Gd, occurring when e.p.r. is observed in different ranges, are seen from Fig. 2 and Table 1. At 2 cm the spectrum consists of only two lines: a strongly asymmetric line with $g \approx 1.98$ and a line with $g \approx 5.85$; in this case the amplitude of the second line, compared with the amplitude of the first, decreases, but its shape, width, and g factor practically do not change. The stability of these characteristics with increasing frequency indicates that the line with $g \approx 5.85$ is due to a transition with an isotropic g factor. In the $TlAsS_2$ + 0.2% Gd sample, in which at 3 cm the relative amplitudes of the lines with $g > 2$ are smaller (for example, $r^{k} \sim 8.6$ for the lines with $g \approx 5.8$), in the 2 cm range only one line was observed with $g \approx 1.98$, $\delta H^{k} \sim 100$ Oe.

The single asymmetric line with $g \approx 1.98$ for Gd^{3+} in $TlAsSe_2$ and $TlAsS_2$ in the 0.8 cm range narrows in comparison with the 2 cm range.

Fig. 2. EPR spectrum of Gd^{3+} ions in $TlAsSe_2 + 0.2$ wt.% Gd at $T \sim 290$°K. a–$\lambda \sim 3.2$ cm; b–$\lambda \sim 2$ cm; c–$\lambda \sim 0.8$ cm

Figure 2: Fig. 2. EPR spectrum of Gd^{3+} ions in $TlAsSe_2 + 0.2$ wt.% Gd at $T \sim 290$°K. a–$\lambda \sim 3.2$ cm; b–$\lambda \sim 2$ cm; c–$\lambda \sim 0.8$ cm

As in the case of Mn^{2+} ions, the frequency dependence of the Gd^{3+} spectrum can be explained by the incorporation of Gd^{3+} ions into the glass network in surroundings with a strong crystal field, whose symmetry, however, is not clear. The disappearance of the Gd^{3+} spectral lines at 2 cm indicates that the splitting of the corresponding levels by the crystal field becomes smaller than the splitting of the levels by the magnetic field. For the line with $g \approx 5.85$, the crystal-field effects are more substantial, since the line disappears at shorter wavelengths. At 0.8 cm the Zeeman energy becomes greater than the crystal-field energy, and EPR absorption is observed only at $g \sim 2$. The question remains open as to whether all spectral lines with an effective factor $g > 2$ are caused by a single type of Gd^{3+} center in a strong crystal field.

Fig. 2. EPR spectrum of Gd^{3+} ions in $TlAsSe_2 + 0.2$ wt.% Gd at $T \sim 290$°K. a–$\lambda \sim 3.2$ cm; b–$\lambda \sim 2$ cm; c–$\lambda \sim 0.8$ cm

The great similarity of the structure of the Gd^{3+} spectrum at 3 cm in our glasses to the structure of the Gd^{3+} spectrum in solutions of gadolinium chloride and rhodanide (7) rather indicates that the entire spectrum is due to one type of Gd^{3+} center. In the 3-cm range, the relative amplitudes of the lines with $g > 2$, as compared with the amplitude of the lines with $g \approx 2$, increase when the temperature is lowered from room temperature to 77°K, and the degree of increase grows toward lower fields. This could occur if all the lines were due to different fine-structure transitions of one and the same ion, and the corresponding levels giving lines in lower fields lay lower than the levels giving lines with $g \sim 2$. On the other hand, the microinhomogeneity of the structure of the glasses studied (covalent chains, ionic dipoles, etc.) fully permits the possibility of incorporation of Gd^{3+} ions into different surroundings with different magnitudes and symmetries of the crystal field. This is also indicated by the fact that in $TlAsSe_2$ the line with $g \approx 5.85$ disappears at higher frequencies than the rest of the spectral structure. In any case, identification of the symmetry and parameters of the crystal field is complicated by the large value of the spin ($S = 7/2$ for Gd^{3+}), by the superposition of lines, and by the complex angular dependence of the EPR spectrum in glasses.

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