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ELECTRON PARAMAGNETIC RESONANCE OF MANGANESE IONS IN THE GLASSY As–Se–Ge SYSTEM

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The spectra of electron paramagnetic resonance (EPR) in glasses make it possible to judge the nature of the nearest environment of the paramagnetic ion and its changes during heat treatment and in the process of crystallization of glasses. Transition metals are not included in the composition of the most thoroughly studied systems of chalcogenide glasses–such as As–Se, As–Se–Tl, As–Se–Ge, etc.–from the standpoint of electrical conductivity and other physical properties. Therefore, EPR observation in them is possible only upon introduction of a paramagnetic impurity.

In work (^{1}) the observation of the EPR of manganese in some chalcogenide glasses was reported. A difference was found between the EPR spectrum in a glassy sample of the As–Se–Ge system and the spectra of the As–Se–Te system, expressed in the appearance of an absorption line with $g \simeq 4$. Therefore, the aim of the present work was to study the EPR of manganese in glasses of the As–Se–Ge system with a high germanium content (12.5-40 at.%). The compositions of the glasses are given in Table 1.

Table 1

Data from the study of the EPR of manganese in the glassy As–Se–Ge system

Sample No.	Composition, at.% by synthesis	Composition, at.% by synthesis	Composition, at.% by synthesis	Composition, at.% by synthesis	g-factor	δH_1, Oe, 293°K	δH_1, Oe, 77°K	g-factor	δH_2, Oe, 293°K	δH_2, Oe, 77°K	g-factor	δH_3, Oe, 77°K
	As	Se	Ge	Mn								

Sample No.	Composition, at.% by synthesis	Composition, at.% by synthesis	Composition, at.% by synthesis	Composition, at.% by synthesis	g-factor	δH_1, Oe, 293°K	δH_1, Oe, 77°K	g-factor	δH_2, Oe, 293°K	δH_2, Oe, 77°K	g-factor	δH_3, Oe, 77°K
1	24	62.5	12.5	1	2	350±25	1300±200	4.1±0.1	535±25	380±35	–	–
2	28	57	14	1	2	300±20	1170±90	4.1±0.1	630±30	435±25	–	–
3	29	50	20	1	2	400±35	920±85	4.2±0.05	610±40	465±25	–	–
4	28	44	27	1	2	380±25	890±50	4.23±0.03	600±50	430±50	~10	540±50
5	29	30	40	1	2	440±15	580±40	4.35±0.1	460±25	425±25	–	–

The samples were synthesized from materials of increased purity (B-4, B-5) by melting in evacuated (10^{-5} mm Hg) quartz ampoules. The synthesis was carried out for 10 hours; during this time the furnace temperature was raised in steps of 300–500–700° to 850°C. At this temperature the sample was kept for 2 hours, after which it was slowly cooled with the furnace switched off.

The EPR was studied on a standard RE-1301 radiospectrometer at temperatures of 293 and 77°K. Curves of the dependence of the line width on temperature in the range 293-77°K were recorded on the video radiospectrometer described in work ([1]).

I. Experimental results

The form of the EPR spectra of Mn for several samples at 293 and 77°K is reproduced in Fig. 1, and the spectral parameters for all the compositions studied are given in Table 1.

1. In all the investigated samples of the As–Se–Ge system at 293°K

an absorption line with $g = 2$ is observed, which broadens as the temperature is lowered to that of liquid nitrogen; its intensity drops sharply (by a factor of 10-30) in the temperature interval 100-120° K; with further lowering of the temperature to 77° K, the width and intensity of the line do not change. Figure 2 shows the dependence of the line width on temperature in the range 293-77° K for three samples with different germanium contents.

Fig. 1. EPR spectra of Mn for three samples of the As–Se–Ge system. *I* –composition No. 1, *II* –composition No. 4, *III* –composition No. 5; *a* –at 293°K, *b* –at 77°K.

Fig. 1. EPR spectra of Mn for three samples of the As—Se—Ge system. I —composition No. 1, II —composition No. 4, III —composition No. 5; a —at 293°K, b —at 77°K

Figure 1: Fig. 1. EPR spectra of Mn for three samples of the As—Se—Ge system. I —composition No. 1, II —composition No. 4, III —composition No. 5; a —at 293°K, b —at 77°K

Fig. 2. Dependence of the width of the EPR absorption line of Mn with g = 2 on temperature for 3 samples of the As—Se—Ge system. I —composition No. 3, II —composition No. 4, III —composition No. 5

Figure 2: Fig. 2. Dependence of the width of the EPR absorption line of Mn with g = 2 on temperature for 3 samples of the As—Se—Ge system. I —composition No. 3, II —composition No. 4, III —composition No. 5

The line width at 293°K and the temperature at which its intensity drops sharply (T_1) vary only slightly from sample to sample; however, no connection with the germanium content has been established.

Fig. 2. Dependence of the width of the EPR absorption line of Mn with $g = 2$ on temperature for 3 samples of the As—Se—Ge system. I —composition No. 3, II —composition No. 4, III —composition No. 5.

At 77°K, δH_1 increases by a factor of 2-3 in comparison with room temperature, except for composition No. 5, for which the dependence of the line width and intensity on temperature is weaker.

2. In all samples of the As—Se—Ge system, a line with $g \simeq 4$ was also observed. At room temperature it has weak intensity and is clearly visible only in the spectrum of composition No. 5. The intensity of the line increases as the temperature is lowered and as the germanium concentration increases. Its width (δH_2) varies only slightly from sample to sample and decreases in all samples as the temperature is lowered. Thus, for composition No. 4, when the temperature is changed from 293 to 4.2°K, δH_2 decreases from 600 to 215 Oe.

3. In samples of composition No. 4 at 77°K, a line with $g \sim 10$ is observed, the intensity of which depends on the heat treatment of the glass. With un-

under certain conditions of heat treatment this line reveals a complex structure. This line can be judged in more detail in connection with consideration of the question of the influence of heat treatment of chalcogenide glasses on their EPR spectrum.

II. Discussion of Results

1. It is known that the glassy state is associated with the presence of covalent bonds between atoms linked into a spatial network system. According to work (^{2}), in the system As—Se—Ge under study there should be two main types of structural units: trigonal [$AsSe_{3/2}$] and tetrahedral [$GeSe_{4/2}$].

In (^{2}) an estimate is made of the content in glasses of the As—Se—Ge system of various chemical structural units. In the calculation it was assumed that selenium preferentially interacts with germanium and, secondarily, with arsenic.

If one uses the system of estimates proposed in (^{2}), then it can be shown that upon introducing manganese into chalcogenide glasses, selenium will interact primarily with Mn. In this case, owing to the large difference in the electronegativities of manganese and selenium, the fraction of the ionic component of the Mn—Se bond is large, i.e., there is a very considerable probability of the formation of ionic pairs Mn^{2+}—Se^{2-}. However, part of the MnSe molecules may prove to be linked into the glass network. Table 2 gives the values, calculated in accordance with (^{2}), of the concentrations of structural units of the initial glasses before manganese was introduced into them (1 at.% Mn was introduced into these compositions at the expense of 1 at.% As).

Table 2

Concentration of structural units in the As—Se—Ge system

Nos. of glasses	Composition, at. % by synthesis	Composition, at. % by synthesis	Composition, at. % by synthesis	Content in the glass of structural units, mol/cm^3 · 10^2	Content in the glass of structural units, mol/cm^3 · 10^2	Content in the glass of structural units, mol/cm^3 · 10^2	Content in the glass of structural units, mol/cm^3 · 10^2	Content in the glass of structural units, mol/cm^3 · 10^2
	As	Se	Ge	[$GeSe_{4/2}$]	[$AsSe_{3/2}$]	[$AsSe_{2/2}$]	[$AsAs_{3/3}$]	[$GeGe_{4/4}$]
1	25	62.5	12.5	0.73	1.46	–	–	–
2	29	57	14	0.95	–	0.98	–	–
3	30	50	20	1.15	–	0.59	0.58	–
4	29	44	27	1.30	–	–	0.86	0.1
5	30	30	40	0.91	–	–	0.91	0.75

2. An EPR absorption line with $g = 2$, strongly broadening when the temperature is lowered, was observed in almost all chalcogenide glasses of the As—Se—Te system when manganese was introduced into them, and is associated with the appearance of antiferromagnetic crystalline inclusions of

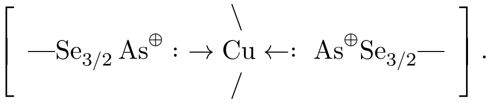
MnSe (¹). Similar formations may also occur in the As–Se–Ge system. The small scatter of the line width (δH_1) at 293° K and of the temperature of the sharp decrease in its intensity (T_1) in different samples of this system is associated with imperfection of the MnSe crystalline phase.

The absence of lines on the Debyegrams of the samples studied and the absence of foreign inclusions that could have been detected with an MIM-8 microscope indicate that such inclusions are small in size, while the complete identity of the EPR spectra recorded for several samples cleaved from one ingot indicates sufficient dispersion of such inclusions.

3. The "residual" line with $g = 2$ at 77° K was observed in all samples and was especially intense for composition No. 5. This line, apparently, is due to manganese that has entered the glass framework.
4. A line with $g \simeq 4.3$ has been observed experimentally in iron-containing silicate glasses (³, ⁴). In work (³) it was shown theoretically that it may be caused by the Fe^{3+} ion located in the strong electric field of a tetrahedron with rhombic distortions.

As noted above, the As–Se–Ge system is characterized by the presence of tetrahedral units [$\mathrm{GeSe}_{4/2}$]. From the data in Table 2 it is seen that, as the composition number increases, the concentration of these units increases (the exception is the transition from sample No. 4 to sample No. 5; however, it should be noted that in composition No. 5 there are many tetrahedral units [$\mathrm{GeGe}_{4/4}$]). In the same order the intensity of the line with $g \simeq 4$ increases. The following mechanism for the appearance of the line with $g \simeq 4$ seems possible to us.

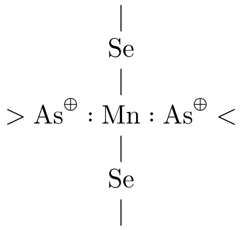
As the number of tetrahedral structural units in the As–Se–Ge system increases, the tendency of the spatial distribution of atoms to preserve tetrahedral coordination increases. The presence of manganese, which, being an element of the iron transition group, can form complex compounds with coordination-valence bonds, and of arsenic, which tends to form tetrahedral sp^3-hybrid orbitals with coordination-valence attachment, may promote an increase in the content of tetrahedral structural units in the system. In Ref. (⁵) the possibility of forming complex compounds of copper with arsenic selenide was considered. As a structural unit the following unit was proposed



$$\left[\ -\mathrm{Se}_{3/2}\,\mathrm{As}^{\oplus} : \rightarrow \overset{\backslash}{\underset{/}{\mathrm{Cu}}} \leftarrow : \ \mathrm{As}^{\oplus}\mathrm{Se}_{3/2}-\ \right].$$

Similar units may also be formed when manganese is introduced into the As–Se–Ge system.

In accordance with (³), the following model for the incorporation of Mn into the glass network proves possible:



$$\begin{array}{c} | \\ \mathrm{Se} \\ | \\ >\mathrm{As}^{\oplus} : \mathrm{Mn} : \mathrm{As}^{\oplus}< \\ | \\ \mathrm{Se} \\ | \end{array}$$

In this case manganese forms semipolar bonds with arsenic and ordinary covalent bonds with selenium; the $3d$ shell of manganese is not changed ($3d^5$, ^6S), and the arguments relating to the Fe^{3+} ion in a rhombically distorted electric field of a tetrahedron are valid.

It should be noted that Mn can enter glasses of the As—Se system in a similar way. Indeed, a weak line with $g \simeq 4$ is observed in some samples of this system, but its appearance is fluctuational in character.

5. In conclusion it is necessary to point out one feature of the observation of EPR of transition-metal ions in chalcogenide glasses. The property of manganese, noted above, of forming ionic bonds with selenium leads to the appearance of ion-polar groups and crystalline inclusions not characteristic of the initial glass. The fraction of manganese entering directly into the glass network is small, and interpretation of the spectrum associated with such manganese is difficult because of the low intensity of the lines. Therefore, an essential point for the successful application of the EPR method to the study of the structure of chalcogenide glasses is the investigation of the synthesis conditions under which transition-metal ions are bound into the glass network in the best possible way.

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