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Paramagnetic Defects in γ-Irradiated, Pure and Doped (with As, Cl and Br) Selenium

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Abstract

This paper presents results of an EPR spectrum investigation of γ-irradiated (Co^{60} dose 10^7 Rad) glasses Se, $SeCl_x$, $Se_{0.95}As_{0.05}Cl_x$ and $Se_{0.95}As_{0.05}Br_x$ (x=0.001–0.1) at 77 K. An analysis of spectra reveals that two types of paramagnetic radiation-induced defects arise (broken bonds localized on Se and As atoms) from the irradiation of such chalcogenide glasses.

1. Introduction

The problem of defects in glasslike Se, and in chalcogenide glasses based on Se, is one of the fundamental problems in the physics of disordered semiconductors. Closely related and of similar interest is the problem of paramagnetism of chalcogenide glasses containing high concentrations of structural defects ($\sim 10^{17} cm^{-3}$) [1-4].

Unlike a-Si, for example, where these defects are nonparamagnetic, Electronic Paramagnetic Resonance (EPR) is observed in Se and other glasses based on it, in rare cases at liquid helium temperatures and when the concentration of paramagnetic centres is small, $<10^{14} cm^{-3}$.

2. Experimental

An EPR investigation was carried out on γ-irradiated Se, Se Cl_x, $Se_{0.95}As_{0.05}Cl_x$ and $Se_{0.95}As_{0.05}Br_x$ at 77 K (x=0.001-0.1) for study of defect states in pure Se and defect and impurity states in the doped glasslike Se and glasses based on it.

As it has been earlier shown [5], large doses of γ-irradiation at 77 K creates paramagnetic defects in concentrations large enough to allow their study via the EPR method. The problem of stabilizing the perturbations created by the high energy irradiation in the glass is very interesting. Se is normally a two-coordinated neutral atom bonded with two nearest neighbours (D^0 by the Mott-Davis model) [1]. Transformation of two such D^0 into the system consisting of positively charged ion D^+ [1-3] and negatively charged ion D^- requires low energy since the total number of covalent bonds does not change. The energy of pair formation, with alternating valence, is approximately equal to the difference between the ionized potential and electron affinity of the dangling bond D^-. The removal of the electron from D^- leads to D°, which is extremely chemically active, and immediately connects with an atom of the nearest chain. According to Mott's model [1], the reaction $D^- \rightarrow D^\circ + e$ requires more energy than the reaction $D^0 \rightarrow D^+ + e$. Owing to this unique characteristic, the reaction $2D^\circ \rightarrow D^+ + D^-$ is exothermic. The spin of the Se chain end is compensated by the spin of trapped electron (in D^-). Mott, Davis and Street [1] supposed that metastable states of D° may be formed under optical excitation. In fact, one group has revealed the optically induced EPR absorption

spectra in Se [7]. The Se was cooled in a resonator down to 12 K and illuminated by 1.98 eV light, with intensity I = 1 mW/cm^2, inducing an EPR signal with $g \approx 2$ and $\delta H \approx 200$ Gs. This signal disappears when the sample is heated by infrared irradiation. Thus, the two-coordination of the Se atom, the presence of indivisible pairs, the flexibility of local structures, strong electron-phonon interaction and, as a result, the negative effective correlation energy, leading to the pairing of spins (elimination of broken bonds)-impede the stabilization of local structures even at low temperatures [8]. The addition of three-coordinated As, four-coordinated Ge and other atoms and uncontrollable impurities breaking the two-valence of the glass net, promote the stabilization of paramagnetic states D°.

Investigation via EPR of samples both pure and Cl-doped selenium ($SeCl_{0.001}$, $SeCl_{0.01}$, $SeCl_{0.1}$) as well as $Se_{0.95}As_{0.05}Cl_{0.001}$, $Se_{0.95}As_{0.05}Cl_{0.01}$, $Se_{0.95}As_{0.05}Cl_{0.1}$, $Se_{0.95}As_{0.05}Br_{0.1}$, has been carried on a Bruker ESR-200 Model X Band spectrometer at 77 K. Samples were irradiated at 77 K by a Co^{60} source at doses of about 10^7 Rad. Samples were kept at the same temperature at which they were examined by EPR. Paramagnetic defects induced by the irradiation disappeared as sample temperatures rose to room temperature.

3. Results and Discussion

The observed EPR spectra is shown in Figure 1-4. As it can be seen from Figure 1, small changes in $SeCl_x$ sample spectra occur with increase of Cl content. It is necessary to note that the form of spectra is typical for transitions between spin levels with three-axial anisotropy of the g-tensor (g_1,g_2,g_3). The presence of cis- and trans-configuration of broker bonds in selenium, corresponding to the presence of rings and chains in Se, allows one to possit that the spectrum in $SeCl_x$ (both in a-Sulfur and chalcogenide glasses on a base Sulfur at its large concentration) is the superposition of two spectra, belonging to the cis- and trans-configurations of the paramagnetic defects. Large width of individual lines, which are broadened inhomogeneously due to dispersion of spin Hamiltonian parameters, and strong anisotropy of the g-tensor, probably, leads to broadening of the EPR spectrum. Values of g_1 coincide for both configurations of defects (as in case of S) so the distinct narrow extremum is observed in the strong field region near $g \sim 2$. In the region g_2 some blur of the extremum is observed which allows difference between g_2 and g_2^1 for two configurations of the order of 0.02−0.03.

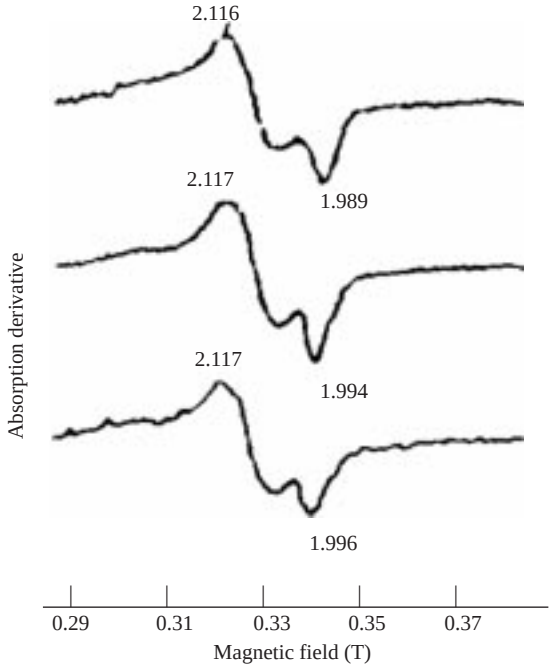

Figure 1. EPR spectra of $SeCl_x$, γ-irradiated at 77 K (Co^{60}, dose 10^7 Rad; 1,2 and 3 at x=0.001; 0.01 and 0.1, respectively).

It is necessary to note that on introducing Cl or Br as impurities into Se and then treating thermally at T $\leq$ 720 K, an EPR absorption with g=2.003 and $\delta H = 6Gs$ has been observed and attributed to donor-acceptor interaction of Se chains (donor) with Cl or Br (acceptor) [9].

More detailed information about g-tensor values for two configurations of radiative defects can be given by computer modelling of the EPR spectrum. However, since only the value of g_1 may be measured, one can trace the influence of Cl and Br impurities on the EPR spectrum in Se. It is necessary to note that small impurities did not cause a visible increase of the unpaired spin concentration in most cases. Growth of the paramagnetic centre concentrations have occured only in $Se_{0.95}As_{0.05}Cl_{0.1}$ samples in comparison with $Se_{0.95}As_{0.05}Cl_{0.01}$ samples (see Figure 2).

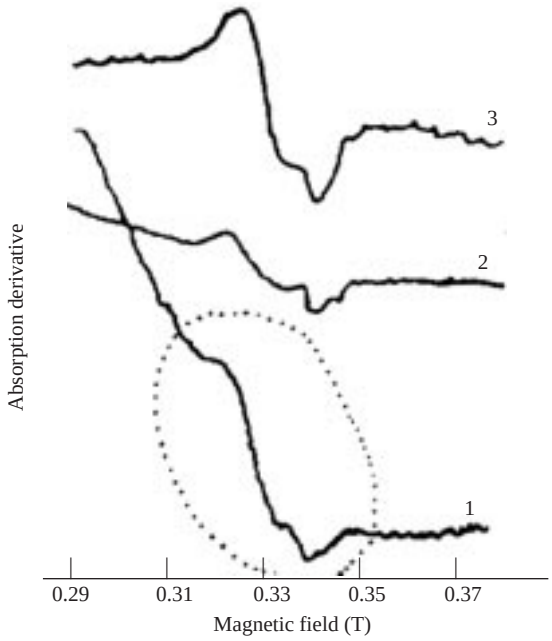

Figure 2. EPR spectra of Se (1), $Se_{0.95}As_{0.05}Cl_{0.01}$ (2) and $Se_{0.95}As_{0.05}Cl_{0.1}$ (3), γ- irradiated at 77 K (Co^{60}, dose 10^7 Rad).

EPR spectrum of the broken bond of Se in $Se_{0.95}As_{0.05}Cl_{0.1}$ (Figure 3) is considerably more rarefied than the spectra of other samples. It suggests that the coordination spheres of the defect are more ordered in Br glass. As it can be seen in the Table, the shift of g_1 in $Se_{0.95}As_{0.05}Br_{0.1}$ with respect to g_1 for Se is more than the shift observed in those samples with Cl. Results show that additions of Cl or Br cause a small reconstruction of structure near the defect leading to a change in g_1. The simultaneous apperance of several kinds of radiation-induced defects have been observed in $Se_{0.95}As_{0.05}Br_{0.1}$ glasses. As it is seen from the Table, the value of g_1 decreases with the rise of Cl content. Addition of Br causes more decrease of g_1.

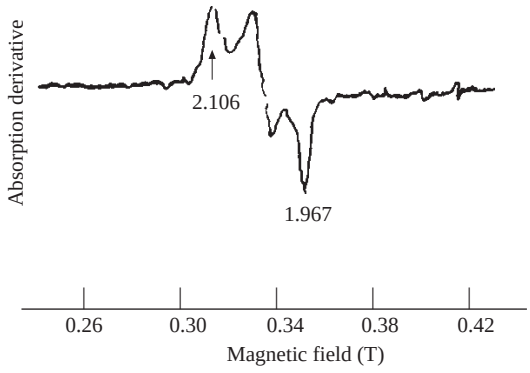

Figure 3. EPR spectrum of $Se_{0.95}As_{0.05}Br_{0.1}$, γ-irradiated at 77 K (Co^{60}, dose 10^7 Rad).

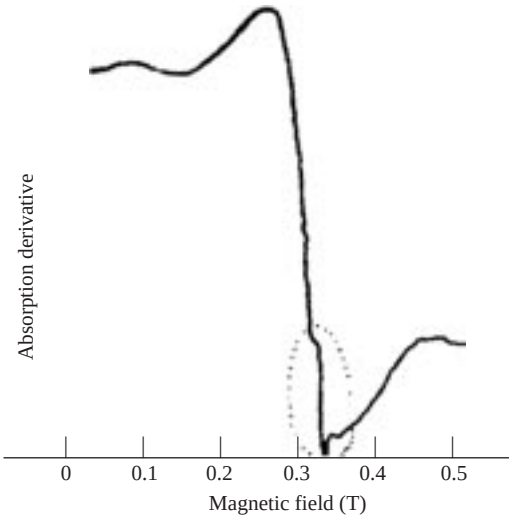

Figure 4. EPR spectrum of $Se_{0.95}As_{0.05}Cl_{0.001}$, γ-irradiated at 77 K (Co^{60}, dose 10^7 Rad).

Table. Values of $g_1$in the EPR spectra of Se glasses considered.

Samples	g_1 ($\pm$0.002)
Se	1.996
$SeCl_{0.001}$	1.995
$SeCl_{0.01}$	1.994
$SeCl_{0.1}$	1.989
$Se_{0.95}As_{0.05}Br_{0.1}$	1.967

In none of the investigated samples did we observe signals from NO_2 paramagnetic molecules appearing due to γ-irradiation an observation that would be due to uncontroled N and O impurities.

4. Conclusion

Thus, with the help of the EPR method it was shown that, under γ-irradiation, glasses, Se, $SeCl_x$, $Se_{0.95}As_{0.05}Cl_x$ and $Se_{0.95}As_{0.05}Br_x$ (x=0.001-0.1) exhibit, in general, the development of two types of radiation defects: broken bonds localized on Se and As atoms.

References

[1] N.F. Mott, E.A. Davis and R.A. Street, *Philos. Mag.*, **32**, (1975), 961.

[2] M. Kastner, D. Adler and H. Fritsche, *Phys. Rev. Lett.*, **37**, (1976), 1504.

[3] H. Fritsche and M. Kastner, *Philos. Mag.* **B37**, (1978), 285.

[4] L.P. Kazakova, F.A. Lebedev, N.B. Zakharova, J.J. Yatlinko, A.I. Isayev, S.I. Mekhtieva, *J. of Non-Crust. Solids*, **167**, (1994), 65.

[5] I.V. Chepeleva, *J. of Non-Crust. Solids,* **97**, (1987), 1179.

[6] M. Kastner, Amorph. Hig. Semicond. Proc. Int. Conf. 7^{th} 504, (1977).

[7] S.G. Bishop, U. Strom and P.C. Taylor, *Phys. Rev. Lett.*, **34**, (1975), 1346.

[8] S.R. Ovshinsky, *J. of Non-Crust. Solids*, **32**, (1979), 17.

[9] G.B. Abdullayev, N.I. Ibragimov, Sh.V. Mamedov, *Phys. Selenium and Tellurium, Perg. Press,* **321**, (1969).