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Magnetic properties for metastable negative-*U* defects in amorphous semiconductors

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Abstract

Optically induced metastable centers are studied in As_2S_3 chalcogenide glasses using the magnetic susceptibility technique for $3.5 \leq T \leq 300$ K. The temperature dependencies of the magnetic susceptibility (χ) exhibit spin instability of both a hole center localized at a nonbonding lone pair chalcogen orbital and an electron center formed by an As p-orbital. The χ fatigue at low temperatures is shown to result from the negative-*U* dissociation of paramagnetic states $2D^0 \rightarrow D^- + D^+$ that causes also the absence of an ESR signal before illumination. Irradiation with light whose energy corresponds to the Urbach tail of the absorption edge is found to result in a growing χ signal that is due to optically induced paramagnetic states revealed also by the EPR signals: $D^- + D^+ + h\nu \rightarrow 2D^0$, whereas subsequent irradiation with infrared light in the mid-gap bleaches both the optically induced magnetic susceptibility and ESR signal to its cold dark efficiency. Metastable properties for paramagnetic states located in the gap of As_2S_3 are discussed in the framework of the negative-*U* reaction that is accompanied by the restoration of the PL and the fatigue of the ESR signals and the magnetic susceptibility value.

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1. Introduction

The models proposed to describe the localized states in the forbidden gap of chalcogenide glasses are still far to be applied in the interpretation of the photoluminescence, optical absorption and ESR studies carried out on the amorphous semiconductors [1–9]. The principal disagreement in experimental results obtained using the ESR [5,10–12] and AC conductivity technique [3,4] is the number of unpaired spins that is rather lower ($<10^{14}$ cm^{-3}) than the value expected on the basis of the density of localized states at the Fermi energy [1,2]. A weak Curie paramagnetism at low temperatures is evidence of the diamagnetism of pure chalcogenide glasses and pinning the Fermi energy that is able to suppress the presence of unpaired spins. The goal of this work is to demonstrate the advantage of the magnetic susceptibility technique to identify the negative-*U* properties for the intrinsic defects found in chalcogenide glasses by the ESR measurements under optical pumping.

2. Methods

Samples of glassy As_2S_3 were prepared from 99.999% pure elemental constituents in sealed quartz ampoules by standard rocking furnace techniques followed by an air quench. Some ESR signals were exhibited in cold dark before illumination, which have been due to the presence of residual iron-related centers [12]. The ESR signal near the free-electron *g* value that can be related to the paramagnetic states of dangling bonds has not been observed before bandgap illumination. Temperature dependencies of magnetic susceptibility were measured in the range 3.5–300 K with the magnetic balance spectrometer MGD312FG. High sensitivity, 10^{-9}–10^{-10} CGS, should

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be noted to be provided by the $B\,dB/dx$ stability using this installation. Pure InP samples characterized by temperature stable magnetic susceptibility, $\chi = 313.10^{-9}$ cm^3/g, was used to calibrate the $B\,dB/dx$ values. The ESR spectra were obtained at 4.2 K in a helium gas flow variable temperature Dewar system with a standard Brucker-Physik AG X-band (9 GHz) spectrometer, and an optical access cavity. Paramagnetic component of magnetic susceptibility, the ESR spectra and the red shift of a band edge absorption coefficient are found to be optically induced by irradiation with the 0.53 μm laser diode (4H-SiC) at low temperatures whose energy corresponds to the Urbach tail of the absorption edge. Subsequent quenching of magnetic susceptibility and ESR spectra as well as the restoration of initial spectral dependence of a band edge absorption coefficient is provided by the illumination with the 1.55 μm laser diode (InGaAsP–InP). Besides, the subsequence of cooling operations

$300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5\ \mathrm{K} \rightarrow \cdots$

under 0.53 light illumination was used to study long time photostructural transformations in glassy As_2S_3.

3. Results and discussion

The temperature dependence of magnetic susceptibility shown in Fig. 1a demonstrates the Curie paramagnetism in As_2S_3 only at high temperatures, whereas at low temperatures its reduction is revealed by two peaks that are evidence of the spin instability from two different paramagnetic centers. The effect found is rather similar to spin pairing in magnetic sublattices [13] and seems to be due to the formation of the pairs of the singlet dangling bonds that belong to the S- and As-related centers. Therefore, such a behavior of χ at low temperatures is described by the following relationship taking account of both the Curie paramagnetism of residual dangling bonds in the first term and the Van Fleck paramagnetism of their singlet pairs in the second term

$$\chi = \frac{\mu_B^2 g^2 |S(S+1)|^2}{3kT} N_{P_b} + \frac{\mu_B^2 g^2 N_{\mathrm{pair}}}{3kT} \frac{\sum_S S(S+1)\exp\left(-\alpha \frac{S(S+1)}{2kT}\right)}{\sum_S \exp\left(-\alpha \frac{S(S+1)}{2kT}\right)} \qquad (1)$$

where α is the exchange constant.

The concentrations of residual dangling bonds and their pairs are found to be dependent on cooling rate that is revealed by a following hysteresis in the χ temperature dependence. The dangling bond pairing causes also the absence of some ESR signals at low temperatures, while at high temperatures the ESR from dangling bonds cannot be measured because of fast electron spin–lattice relaxation. The χ fatigue at low temperatures confirms the mechanism

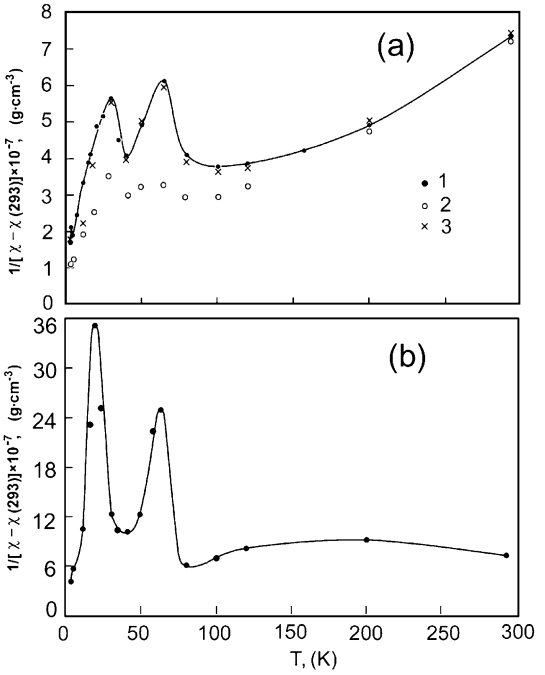

Fig. 1. (a) The temperature dependence of the magnetic susceptibility due to a hole center localized at a nonbonding lone pair chalcogen orbital and an electron center formed by an As p-orbital in As_2S_3: (1) cooling without light illumination; (2) after 0.53 μm light illumination at 3.5 K; (3) subsequent 1.55 μm light illumination at 3.5 K. (b) The temperature dependence of the magnetic susceptibility due to a hole center localized at a nonbonding lone pair chalcogen orbital and an electron center formed by an As p-orbital in As_2S_3 after subsequence of cooling operations $300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5\ \mathrm{K} \rightarrow \cdots$ under the 0.53 μm light illumination.

of the ESR absence in the chalcogenide glasses without previous illumination that has been suggested on the basis of the negative-U conception [6–9]. In the framework of this mechanism, the paramagnetic one-electron states of dangling bonds dissociate spontaneously into empty and

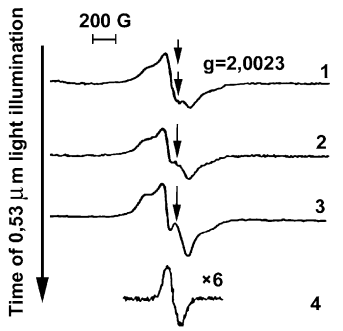

Fig. 2. Optically induced ESR spectra obtained by 0.53 μm light illumination at 3.5 K in glassy As_2S_3.

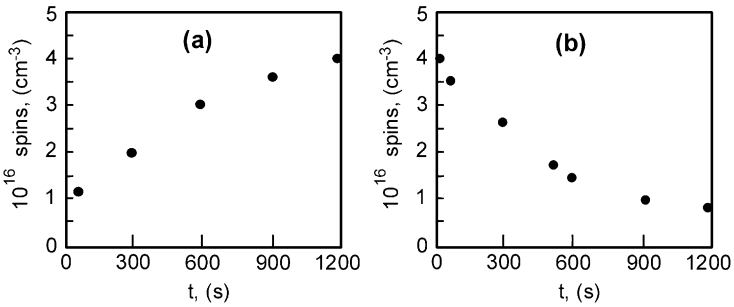

Fig. 3. (a) Growth curves of the optically induced magnetic susceptibility for glassy As_2S_3 as a function of time under continuous 0.53 μm light illumination at 3.5 K (a). (b) Subsequent reduction of optically induced magnetic susceptibility for glassy As_2S_3 as a function of time continuous 1.55 μm light illumination at 3.5 K.

two-electron states, $2D^0 \rightarrow D^+ + D^-$. Therefore, optically induced ESR signal growth (Fig. 1a) results from opposite reaction: $D^+ + D^+ + h\nu \rightarrow 2D^0$ [12]. As a result of such procedure, the χ temperature dependence seems to be described by the Curie law (Fig. 1a). The kinetics of the χ quenching (Fig. 3a) is rather similar to the time-dependent ESR growth [10–12]. Besides, the one-electron paramagnetic states that create deep levels in bandgap gives rise to corresponding red shift in the spectral dependence of the absorption coefficient (Fig. 4a) which has been found, for the first time, by Bishop et al. [12].

The analysis of the EPR spectra as well as the magnetic susceptibility data shows that the broad low field ESR line and low temperature peak in the $1/\chi$ temperature dependence result from the processes due to spin instability of an electron center formed by an As p-orbital, whereas the narrow high field ESR line and high temperature peak in the $1/\chi$ temperature dependence are attributable to a hole center localized at a nonbonding lone pair chalcogen orbital. The models of these negative-U centers that are responsible for the self-compensation in As_2S_3 seems to be suggested using the following Anderson's Hamiltonian [6,7,14]

$$H = P^2/2M + æQ^2/2 + E_0(n\uparrow + n\downarrow) + Un\uparrow n\downarrow - FQ;$$

$$F = (F_0 + \delta F)\beta_0 + F_1\beta_1 + (F_2 - \delta F)\beta_2; \qquad \beta_n^2 = \beta_n;$$

$$n = 0, 1, 2; \qquad \beta_0 = (1 - n\uparrow)(1 - n\downarrow);$$

$$\beta_1 = n\uparrow n\downarrow - 2n\uparrow n\downarrow; \qquad \delta F = e\mathbf{E}\cos\theta; \qquad (2)$$

here P and Q are the canonical pulse and the center's coordinate; M and $æ$ are the center's mass and the force constant; E_0 and U_0 are the seeding electron energy and the singlet-like electron–electron interaction at the center, F_n and β_n are the EVI constants and the projection operators for the charge states of a center with a full number of electrons $n = 0, 1, 2$; the quantity δF is the extent to which the charged states perturbed when a center is located in electric field $\mathbf{E}$ and θ is an angle between the direction of the field $\mathbf{E}$ and the coordinate Q. After diagonalization of the Hamiltonian by the charged states of an amphoteric center, the adiabatic terms $E_n(Q)$ are obtained (Fig. 5a)

$$E_0(Q) = æ(Q - Q_0 - \delta Q)^2/2 \Leftrightarrow \text{the } D^+\text{-center};$$

$$E_1(Q) = -I_1(\mathbf{E}) + æ(Q - Q_1)^2/2 \Leftrightarrow \text{the } D^0\text{-center};$$

$$E_2(Q) = -I_2(\mathbf{E}) + æ(Q - Q_2 + \delta Q)^2/2 \Leftrightarrow \text{the } D^-\text{-center};$$

where the potentials of one $I_1(\mathbf{E})$ and two $I_2(\mathbf{E})$ electron ionization of a dot indicate the change of the $U(\mathbf{E})$-energy in the process of the capture of the phone and correlated electrons $D^+ \rightarrow D^0 \rightarrow D^-$ (Fig. 5a)

$$I_1(\mathbf{E}) = I_1 - F_0\delta F/æ; \qquad I_1 = -[E_0 + (F_0^2 - F_1^2)/2æ];$$

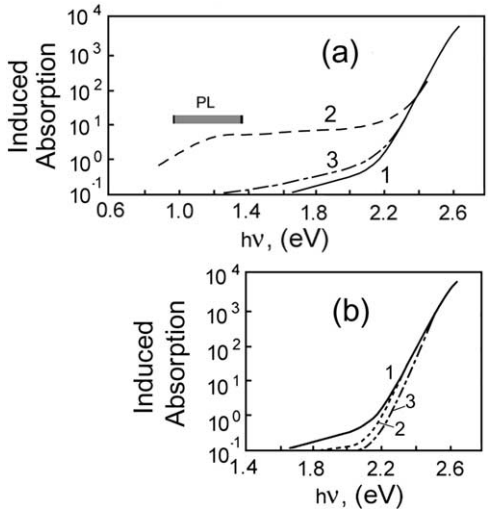

Fig. 4. Optically induced absorption spectra obtained at 3.5 K for glassy As_2S_3. (a) (1) after dark cooling at 3.5 K; (2) after 0.53 μm light illumination at 3.5 K; (3) after subsequent 1.55 μm light illumination at 3.5 K. (b) (1) after dark cooling at 3.5 K; (2) after two subsequent cooling operations $300 \rightarrow 3.5 \rightarrow 300$ K under the 0.53 μm light illumination; (3) after three subsequent cooling operations $300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5$ K under the 0.53 μm light illumination.

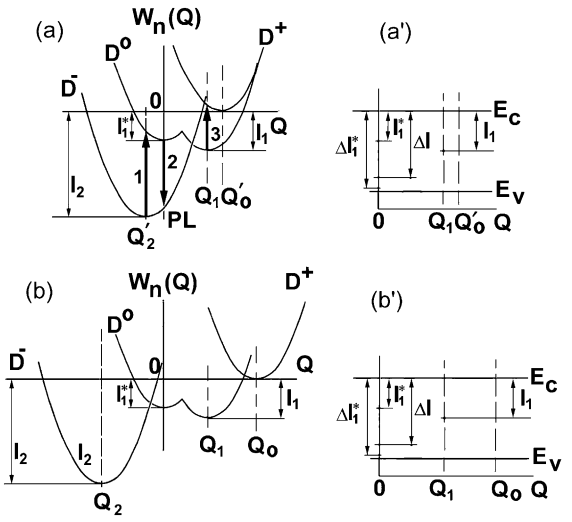

Fig. 5. Adiabatic potentials and equivalent one-electron band scheme two-electron centers in chalcogenide glasses in metastable state (a, a′) characterized by an internal electric field that is induced by the dipole centers and in stable state after subsequence of cooling operations 300 → 3.5 → 300 → 3.5 → 300 → 3.5 → 300 → 3.5 K → ⋯ under 0.53 μm light illumination (b, b′) that reduces an internal electric field.

$$I_2(\mathbf{E}) = I_2 - F_0\delta F/æ;$$

$$I_2 = -[2E_0 + U_0 + (F_0^2 - F_1^2)/2æ];$$

$$U(\mathbf{E}) = 2I_1(\mathbf{E}) - I_2(\mathbf{E}) = U - [E_0\delta F + (\delta F)^2]U = 2I_1 - I_2$$

$$= U_0 + (2F_1^2 - F_2^2 - F_0^2)/2æ.$$

Thus, the change of the local effective correlation energy for the D^0 and D^- position is subject to the polaron shift $W_1 = (F_1^2 - F_2^2)/2æ$. Therefore, the energy of the photoionization ($D^- \rightarrow D^0$) and the kinetics of the capture on the neutral paramagnetic centers ($D^0 \rightarrow D^-$) are dependent on both internal and external electric field (Fig. 5a and b).

The negative-U dissociation of one-electron states at low temperatures is explained in the frameworks of the two-electron adiabatic potentials (Fig. 5a and b) and equivalent one-electron band schemes (Fig. 5a′ and b′), whereas the metastability of the negative-U dangling bonds that is defined by a barrier between two-electron and one-electron states is revealed by the Curie dependence at high temperatures which is evidence of the thermally excited D^0-states (Fig. 1a). The metastable properties for the negative-U dangling bonds are also revealed by a stabilization of one-electron paramagnetic state after the 0.53 μm light illumination at low temperatures, which is created by the photoionization of the D^--state: $D^+ + D^- + h\nu \rightarrow D^+ + D^0 + e \rightarrow 2D^0$. The verification of the deep level position in bandgap that belongs to the D^0 paramagnetic state is demonstrated by subsequent 1.55 μm light illumination which results in optically induced quenching of both the magnetic susceptibility (Figs. 1a and 3b) and ESR signals (Fig. 2) as well as bleaches initial band edge absorption coefficient and PL spectrum in As_2S_3 [12]. The same kinetics of the quenching found by studying the χ value (Fig. 3b) and the ESR signals [12] should be noted to define the concentration of the paramagnetic dangling bonds.

The results obtained seem to be due to the As_2S_3 samples that contain the As- and S-related negative-U centers which cause the electric dipoles (Fig. 6a). Optical generation of the one-electron paramagnetic states is accompanied by the disappearance of the dipole centers (Fig. 6b). These electric dipoles seem to create the strong internal electric field ($\sim 10^7$–10^8 V cm^{-1}) that defines the metastable properties for the dangling bonds (Fig. 5a and b) and the Urbach tail of the absorption coefficient in chalcogenide glasses (Fig. 4a and b) [15].

The metastable properties for dangling bonds in As_2S_3 are

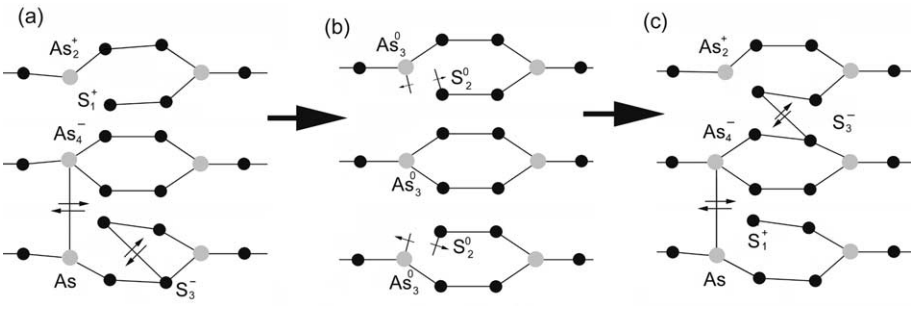

Fig. 6. The As_2S_3 chain that reveals the different versions of the negative-U centers such as a hole center localized at a nonbonding lone pair chalcogen orbital and an electron center formed by an As p-orbital. (a) The As_2^+–As_4^- and S_1^+–S_3^- negative-U dipole centers that create internal electric fields in glassy As_2S_3 after its preparation accompanied by an air quench. (b) The paramagnetic As_3^0 and S_2^0 centers that are optically induced by the 0.53 μm light illumination at 3.5 K. (c) Opposing As_2^+–As_4^- and S_1^+–S_3^- negative-U dipole centers that are not capable of creating internal electric fields after subsequence of cooling operations 300 → 3.5 → 300 → 3.5 → 300 → 3.5 → 300 → 3.5 K → ⋯ under the 0.53 μm light illumination.

found to be suppressed by the subsequence of cooling operations $300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5 \rightarrow 300 \rightarrow 3.5\ \mathrm{K} \rightarrow \cdots$ under the 0.53 light illumination (Fig. 1b). The analysis of the dependence shown in Fig. 1b exhibits a stabilization of singlet two-electron states (D^-) that is revealed by the Van Fleck paramagnetism in the χ temperature behavior. The effect found appears to be caused by self-compensation of electric dipoles (Fig. 6c) that gives rise to reduction of the internal electric field (Fig. 5b) and corresponding long time photostructural transformations in glassy As_2S_3 (Fig. 4b).

4. Summary

The magnetic susceptibility and ESR techniques have been used, for the first time, to identify the metastable properties for the negative-U intrinsic defects in glassy As_2S_3. The electric dipole centers formed by negative-U dangling bonds have been shown to define the Urbach tail of the absorption coefficient spectra as well as to be responsible for long time photostructural transformations in chalcogenide glasses.

References

[1] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon, Oxford, 1971 p. 268.
[2] H. Fritzsche, J. Phys. Soc. Jpn 49 (Suppl. A) (1980) 39.
[3] A.E. Owen, J.W. Robertson, J. Non-Cryst. Solids 2 (1970) 40.
[4] W.E. Spear, P.V. LeComber, J. Non-Cryst. Solids 8–10 (1972) 727.
[5] S.C. Agarwal, Phys. Rev. B 7 (1973) 685.
[6] P.W. Anderson, Phys. Rev. Lett. 34 (1975) 953.
[7] P.W. Anderson, J. Phys. (Paris) C-4 (1976) 339.
[8] R.A. Street, N.F. Mott, Phys. Rev. Lett. 35 (1975) 1293.
[9] M. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. 37 (1976) 1504.
[10] S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. Lett. 34 (1975) 1346.
[11] S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. Lett. 36 (1976) 543.
[12] S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. B 15 (1977) 2278.
[13] V.A. Grazhulis, V.V. Kveder, Yu.A. Osipyan, Phys. Status Solidi (b) 103 (1981) 519.
[14] N.T. Bagraev, V.A. Mashkov, Solid State Commun. 51 (1984) 515.
[15] A.V. Kolobov, S.R. Elliot, Adv. Phys. 40 (1991) 625.