

Temperature dependence of the photoinduced anisotropy in chalcogenide glasses: Activation energies and their interpretation

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Three distinct regions have been observed in the measured temperature dependence of photoinduced anisotropy in chalcogenide glasses (Se and AsSe). At high temperatures the relaxation of the induced anisotropy is governed by an Arrhenius law with a change of activation energy at the glass-transition temperature T_g (thus suggesting a method for detection of T_g in glasses). Conversely, the low-temperature relaxation is not thermally activated. These observations are explained by introducing a triple-well configurational diagram for the valence-alternation pairs (VAP's) and their environments, which are believed to be responsible. A transient neutral state connects two (initial and final) charged states of the VAP's. A symmetry reversal of the pyramid centered at an overcoordinated chalcogen atom is suggested as a microscopic mechanism for the photoinduced anisotropy. [S0163-1829(97)51302-6]

Metastable photoinduced anisotropy (PAN) is a property of all chalcogenide glasses when excited with linearly polarized light.¹ A microscopic mechanism of PAN has been proposed which is based on light-induced orientation of intrinsic anisotropic structural elements of these glasses,^{1,2} i.e., valence-alternation pairs (VAPs)³ and their environments. As electronic states and structural elements that are characteristic of the glassy state are involved in PAN, information on their origin can be elucidated, together with the nature of PAN. Metastable anisotropy is not restricted to the chalcogenide glasses; it has in fact also been observed in oxide glasses and polymeric films.¹ Applications of the effect (specifically photoinduced birefringence) in telecommunications are promising.¹

In this paper we present data on the temperature dependence of photoinduced dichroism and its activation energies. We observe a trimodal distribution of these activation energies in *g*-Se and *g*-AsSe with changes in behavior at the glass-transition temperature T_g on the one hand, and some ~ 100 K below T_g on the other hand. The results allow us to develop a microscopic model of PAN based on reorientation of the VAPs. The model is probably general for all amorphous materials possessing lone-pair electrons. Observed activation energies can be modeled by a triple-well configurational potential of the VAPs which will be altered at the glass-transition temperature T_g . This suggested change in configuration may provide a new method of detecting T_g , based on measurements of activation energies of PAN below and above the glass-transition temperature. Low-temperature relaxation of PAN is suggested to be due to tunneling of atomic groups centered at VAPs.

The samples studied were glassy films of Se as well as AsSe alloys. The films were irradiated by a strongly absorbed ($\alpha \sim 5 \times 10^3 - 10^4 \text{ cm}^{-1}$), linearly polarized He-Ne laser beam ($\lambda = 633 \text{ nm}$, $P = 60 \text{ mW/cm}^2$). The film thickness h was chosen to avoid problems with optical interference due to reflected light, i.e., such that $\alpha h \sim 3$. (We emphasize this

circumstance since in As-Se glasses the refractive index in the region of the absorption edge is unusually large $n \sim 3$). Measurements of photoinduced dichroism were carried out at discrete time intervals with a probe beam, as described in Ref. 4, by modulating the polarization of the probe beam between two mutually orthogonal states and detecting the differential signal by means of a lock-in amplifier. The measurement periods were short enough ($< 1 \text{ sec}$) so as not to reduce the dichroism during the measurements. The kinetics of the quantity $2(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) = (\alpha_{\perp} - \alpha_{\parallel})h$ correspond to the kinetics of the photoinduced dichroism. $I_{\parallel, \perp}$ and $\alpha_{\parallel, \perp}$ represent the transmitted intensities and absorption coefficients for the polarization of the probe beam respectively parallel and perpendicular to the electric vector of the inducing light, and $\alpha_{\perp} - \alpha_{\parallel}$ is the linear photoinduced dichroism. The temperature of the sample was controlled by means of a nitrogen-flow cryostat, and induction and measurements of PAN were carried out at the same temperature.

Figure 1(a) shows, for *g*-Se at several different temperatures, the kinetics of the appearance of photoinduced dichroism characterized by the value of $A = 2(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$. It is seen that saturation values A_s of the photoinduced dichroism (as well as the times to reach saturation) rapidly decrease when the temperature approaches the glass-transition temperature of Se [$T_g = 40 \text{ }^\circ\text{C}$ (Ref. 5)].

The photoinduced dichroism, i.e., the curves of Fig. 1(a), and similar ones for AsSe films, can be fitted with a stretched exponential function $A(t) = A_s(1 - \exp(-t/\tau)^\gamma)$. We observed that γ reached a minimum ($\gamma \sim 0.5$) at temperatures where the saturation value of PAN, A_s , was maximum ($\sim 230 \text{ K}$ for Se), being almost temperature independent at lower temperatures and approaching its maximum value ($\gamma = 1$) at temperatures close to T_g .

Figures 1(b) and 1(c) show the dependencies of $\ln A_s$ vs $1/T$ for *g*-Se in a temperature range near to T_g (b) and in the whole temperature range measured below T_g (c), respec-

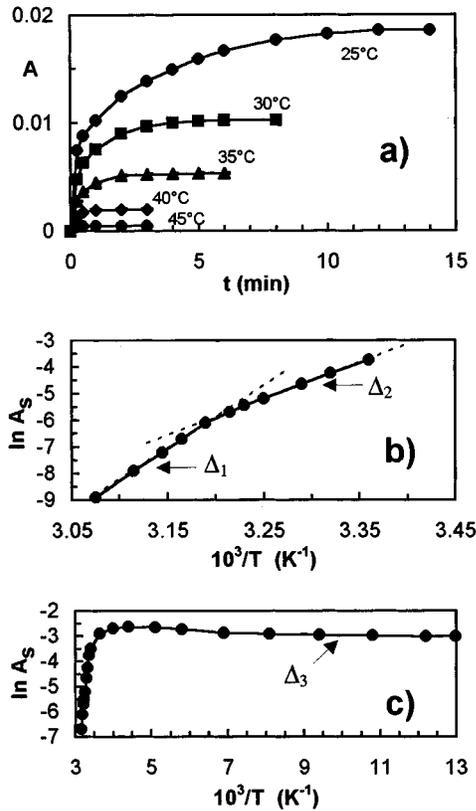
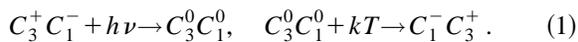


FIG. 1. Kinetics of photoinduced dichroism $A=2(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$ in g -Se at different temperatures (a), and the natural logarithm of saturation values of the dichroism, A_s , vs $1/T$ close to T_g (b), and between T_g and liquid-nitrogen temperatures (c).

tively. Two activation energies $\Delta_1=1.9$ eV and $\Delta_2=0.7$ eV are seen in Fig. 1(b) with a break point close to the literature value for T_g of Se. A rather broad maximum of photoinduced dichroism in Se is observed at ~ 230 K in Fig. 1(c), where a low-temperature activation energy $\Delta_3=-10$ meV is also found. The observed break in slope of the temperature dependence of A_s in Fig. 1(b) near T_g means that the glass-transition temperature in materials possessing PAN may be detectable by means of such a feature. This method was applied to g -AsSe films where we registered $T_g=162$ °C, in good agreement with the value of 165 °C reported in Ref. 5. However, the PAN becomes very small just 5 °C above T_g , which makes it difficult to determine the high-temperature slope precisely. The following activation energies were measured in g -AsSe films: $\Delta_1\sim 1.6$ eV, $\Delta_2=0.3$ eV, and $\Delta_3=-20$ meV.

It was argued in Refs. 1 and 2 that the reactions which will play a major role in causing the PAN can be written as



Here notations of Ref. 3 are used and C stands for a chalcogen atom (e.g., Se), the subscript is the coordination number, and the superscript is the charge on the chalcogen. The intimate valence-alternation pair (IVAP) $C_3^+ C_1^-$ possesses a pronounced anisotropy of electric and magnetic dipole moments, essential to produce PAN. IVAP's always exist in glassy chalcogenides, their estimated concentration deduced from experimental data for the structural elements

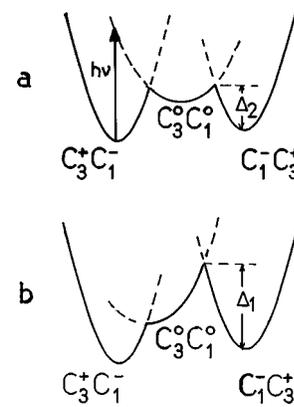


FIG. 2. Configurational-coordinate potential-energy diagram of various states of IVAP's below (a) and around (b) T_g . The energies Δ_1 and Δ_2 refer to the activation energies of the thermal-annealing process of the PAN defect configurations.

responsible for PAN^{1,6} being in good agreement with the concentration of intrinsic diamagnetic defects deduced from light-induced spin resonance.^{7,8} Thus no special impurities appear to be involved in PAN. Another reason for choosing IVAP's to model PAN is that they strongly affect the surrounding atoms which adjust their positions around the C_3^+ center to compensate for the Coloumbic repulsion of electrons on the C_1^- atom.^{3,9,10} Thus motion of charge inside an IVAP will strongly influence the structure in its vicinity, extending microstructural changes of IVAP's to medium-range structural changes in their environments.

To illustrate reactions (1) one may consider a triple-well potential as shown in Fig. 2(a) with the wells corresponding to $C_3^+ C_1^-$, $C_3^0 C_1^0$, and $C_1^- C_3^+$ configurations of the IVAP and its surroundings. Light excitation will produce unstable neutral IVAP's (unstable since no equilibrium spin resonance is observed in glassy chalcogenides^{3,7-9}) which decay, either back to the initial $C_3^+ C_1^-$ or to a new $C_1^- C_3^+$ configuration. In the latter case the orientation of electric and magnetic dipoles (associated with the lone-pair chalcogen orbitals) of the IVAP is changed and the original isotropic distribution of IVAP orientations is disturbed. The above reaction will occur to a different extent in different VAP's, depending on whether their lone-pair electrons (contributing to the tail of the valence band¹¹) are or are not orthogonal to the electric vector of the inducing light. Due to the strong interaction of C_3^+ centers with their environment, the positions of surrounding atoms also will be changed (as well as the orientation of their lone-pair electrons, which creates macroanisotropy for the light absorption), thus extending the changes inside the IVAP itself to structural changes in medium-range order.

Examining the temperature dependence of the saturation value of the anisotropy, as shown in Fig. 1(c), in the light of the configuration-coordinate diagrams of Fig. 2, the relative constancy of A_s at low temperatures is noteworthy. Since the anisotropy at that point is on the order of 1%, it could mean that most available dipoles are aligned, and that inducing and relaxing processes balance each other. The relaxation could be an essentially temperature-independent tunnelling from the $C_1^- C_3^+$ into $C_3^+ C_1^-$ configuration, as will be discussed

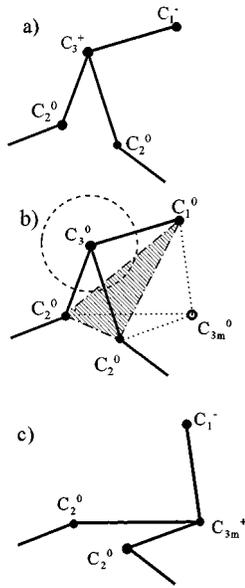


FIG. 3. The flip of the pyramid involving an IVAP centered at a C_3^+ atom proposed to be responsible for photoinduced anisotropy in g -Se. (a) The IVAP configuration before optical excitation. (b) The transient configuration after optical excitation, in which the electron excited from a lone-pair orbital of the C_1^- atom is trapped in an antibonding orbital (represented by the dashed circle) localized at the C_3^0 atom. The C_3^0 atom has the possibility to tunnel through the plane, shown hatched, to the mirror-image position represented by the dotted bonds. (c) The final metastable IVAP configuration, after the pyramid flip, proposed to be responsible for photoinduced anisotropy.

later in conjunction with Fig. 3, while the slight temperature dependence (Δ_3) could be caused by a decreased optical absorption in a slightly widening optical gap, or due to some temperature-assisted change of the lattice parameters and consequently to an enhancement of wave functions overlap between the $C_1^- C_3^+$ and $C_3^+ C_1^-$ state. At high temperatures (below T_g), an activated behavior of A_s with energy Δ_2 is observed. Thermal relaxation over a barrier of height Δ_2 is a likely cause. The activation energy then abruptly increases at T_g to the value Δ_1 ; a change of the barrier height at the glass transition due to a change of the overall configuration is suggested in Fig. 2(b). It may be noted that, for Se, the activation energy $\Delta_1 \sim 2$ eV corresponds approximately to the activation energy of the viscosity in the neighborhood of T_g . A higher flexibility of the Se lattice and easier relaxation of the induced anisotropy would naturally occur in parallel.

The temperature dependence of the stretched-exponential parameter γ for the time dependence of the photoinduced dichroism, as described earlier, is in accord with the above model. Its constant value near $\gamma=0.5$ at low temperatures agrees with a fixed distribution of tunnelling systems, and its gradual shift to monorelaxation behavior ($\gamma=1$) at high temperatures reflects the progressive lattice softening near T_g .

A model for the structural change in g -Se corresponding to reactions (1) is shown in Fig. 3. The key element here is the pyramid $C_3^+ C_1^- C_2^0 C_2^0$ [Fig. 3(a)] consisting of a C_3^+ atom and its three neighbors, one of which is the C_1^- of the same IVAP. Another reason for considering such a 4-atom unit is that photoinduced circular dichroism and birefringence (op-

tical activity) are also observed in g -Se (Ref. 12) and it is known from the general theory of optical activity¹³ that asymmetric pyramids must be taken into consideration.

Excitation of an electron from C_1^- and its trapping by C_3^+ produces a $C_3^0 C_1^0$ pair with an antibonding electron localized near to the C_3^0 atom [schematically shown in Fig. 3(b) by the dashed circle]. It is seen that the pyramid $C_3^0 C_1^0 C_2^0 C_2^0$ is rather flexible now, since (i) the antibonding electron weakens the bonds of the C_3^0 atom, (ii) the C_1^0 atom has only one (weakened) bond and no electrostatic forces like in the $C_3^+ C_1^-$ case, and (iii) a void should exist near to the C_1^- atom before excitation to accord with its singlefold coordination.⁹ This means that the C_3^0 atom can tunnel into a position C_{3m}^0 (where its bonds will be the same) which is its mirror image with respect to the plane defined by $C_1^0 C_2^0 C_2^0$ [shown by the dash-dot lines in Fig. 3(b)], from where its antibonding electron can return to the C_1^0 atom, thus restoring the IVAP as the metastable configuration $C_{3m}^+ C_1^-$ [Fig. 3(c)] (the symbol “ m ” means mirror image). Reactions (1) can thus be seen as a simple flip of the pyramid $C_3^+ C_1^- C_2^0 C_2^0$ centered around the C_3^+ atom, where no thermal activation energy is needed for the low-temperature tunnelling process. The flip of this asymmetric pyramid is accompanied by a change of its anisotropy and chirality, producing linear or circular dichroism, respectively (as was explained in Ref. 2).

As an alternative to the scenario shown in Fig. 3, one could consider another possibility where, in the intermediate configuration [Fig. 3(b)], the C_1^0 attracts an electron from one of the surrounding normally coordinated C_2^0 atoms and forms a new IVAP via bond switching and transfer of an antibonding electron. However, such an IVAP would be oriented randomly relative to the initial IVAP due to the random position of this C_2^0 atom relative to the C_1^0 . It was argued in Ref. 1 that such a random process cannot produce a high optical reversibility of PAN (multiple reorientation of the photoinduced optical axis when changing the polarization of the inducing light), since after several repeat reexcitations the final IVAP will be oriented absolutely randomly relative to the initial one, in contrast to the case shown in Fig. 3 where optical reversibility is complete. In reality, both processes may coexist, giving only partial reversibility of the PAN, but the first one (Fig. 3) will dominate since the optical reversibility of PAN in chalcogenide glasses is excellent.

Since a tunnelling of atoms between configurations with opposite chiralities, but the same vibrational energies, is involved in the model of Fig. 3, it is of interest to look for a relationship between these configurations and the well-known two-level systems in glasses.

Similar considerations (as in Fig. 3) can be easily applied to other chalcogenide glasses (e.g., As_2Se_3 or $GeSe_2$) by exchanging some of the atoms in the base of the pyramid centered at C_3^+ by an element of group V or IV. This model may also be valid for oxide glasses (i.e., flip of a pyramid centered at an O_3^+ atom), where PAN is also observed,¹⁴ since oxygen atoms also possess lone-pair electrons. However, the concentration of VAP's in oxide glasses may be two orders of magnitude lower than in chalcogenide glasses, since the PAN is two orders of magnitude smaller as well.⁶

In conclusion, it has been shown that the temperature dependence of the photoinduced anisotropy in Se and AsSe glasses can be understood in terms of a triple-well configurational diagram with two stable, but differently polarized

states of nearly equal energy, and a metastable excited state above it. The intrinsic IVAP's of the chalcogenide glasses can provide a microscopic model for such a triple-well potential.

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