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Model for photoinduced anisotropy and its dark relaxation in chalcogenide glasses

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The relaxation kinetics of photoinduced anisotropy (PA) in chalcogenide glasses in the dark, subjected to repeated switching on and off of the linearly polarized inducing light, can be approximated by a simple exponential in the initial stages only and by a stretched exponential (Kohlrausch law) at later stages. The parameters of these decays are changed only weakly for simple exponential decay, but strongly for stretched exponential decay, after repeated switching on and off of the inducing light. A model is put forward to account for the PA effect, as well as the changes in its dark-relaxation kinetics, based on structural changes of intimate valence-alternation pairs and their environments, resulting in changes of their microanisotropy and chirality in accordance with the polarization of the inducing light.

It is known that metastable photoinduced anisotropy (PA) is a property of chalcogenide glasses (bulk and films) when excited with either interband- or subgap-polarized,[1–5] and even unpolarized,[3,4] light. This effect is rather intriguing, since the chemical compositions of chalcogenide glasses are rather simple [e.g., Se;Ge(Sb,As)-S(Se)] and one may obviously imagine that their structure should be isotropic on a macroscopic scale. Nevertheless, extended x-ray-absorption fine structure[6,7] and x-ray-scattering[8] studies have revealed that a change in the structure of chalcogenide glasses occurs after prolonged irradiation, suggesting that PA is caused by a photoinduced change of the structure. Preliminary results showed that a nonexponential relaxation (decrease) of PA occurs when the inducing light is switched off.[9] As the origin of PA is presumably due to a photoinduced change of the glass structure, we suggest that the dark relaxation of PA is due to structural relaxation of the glass from an anisotropic to an isotropic state.

In this paper, we present data on the changes in the kinetics of the appearance and the relaxation in the dark of metastable PA following repeated switching on and off of the inducing light. A model is proposed to explain these data, and the PA effect itself, based on structural changes of intimate valence-alternation pairs (IVAP's) and their local environments. These pairs, as well as nonintimate valence-alternation pairs, were postulated earlier as D^+D^- (Ref. 10) or $C_3^+C_1^-$ (Ref. 11) pairs to account for the coexistence of diamagnetism and pinning of the Fermi level in the gap of chalcogenide glasses. The structural changes proposed here are due to photoinduced charge transfer between negatively and positively charged atoms of IVAP's resulting in changes of their microanisotropy (and that of their environment) and chirality in accordance with the polarization of the inducing light. The model is also able to explain photoinduced gyrotropy (circular dichroism and birefringence) when chalcogenide glasses are illuminated with circularly polarized light.[2,12] Due to the lack of translational symmetry, the structural origin of metastable macroscopic PA in glasses is different from the anisotropy of crystals and is more similar to the structural anisotropy of liquid crystals.

The samples studied were amorphous films of the composition AsSe prepared by the methods of thermal evaporation and high-frequency sputtering, and films of composition Ge_2PbS_3 prepared by flash evaporation.

The films were irradiated by the strongly absorbed ($\alpha \sim 10^4$ cm^{-1}) linearly polarized beam of a He-Ne laser. The measurements of photoinduced dichroism, which is a manifestation of PA, were carried out at discrete intervals with a probe beam as described in Ref. 2, modulating the polarization of the probe beam between two mutually orthogonal states. The measurements were taken rapidly enough (~ 1 sec) so as not to reduce the dichroism during the measurements. The kinetics of the quantity $2(I_\parallel - I_\perp)/(I_\parallel + I_\perp) = (\alpha_\perp - \alpha_\parallel)h$ (where $I_{\parallel,\perp}$ and $\alpha_{\parallel,\perp}$ are the intensities and absorption coefficients for probe beams polarized parallel and perpendicular to the electric vector of the inducing light, respectively, h is the sample thickness, and $\alpha_\parallel - \alpha_\perp$ is the linear photoinduced dichroism) correspond to the kinetics of the photoinduced dichroism. The thicknesses of the films were chosen to have approximately the same value of transmittance of the He-Ne laser beam, i.e., the same amounts of absorbed light energy. Interference effects were avoided due to the high absorption.

Figure 1 shows the kinetics of the appearance (solid curves) and dark relaxation (dashed curves) of the photoinduced dichroism characterized by the quantity $2(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ following several cycles of switching on and off of the inducing light.

The general features of Figs. 1(a)–1(c) are as follows: (i) a monotonic increase and decrease of dichroism when the inducing light is switched on and off, respectively; (ii) the increase of the dichroism from the value A_2 to A_1 in subse-

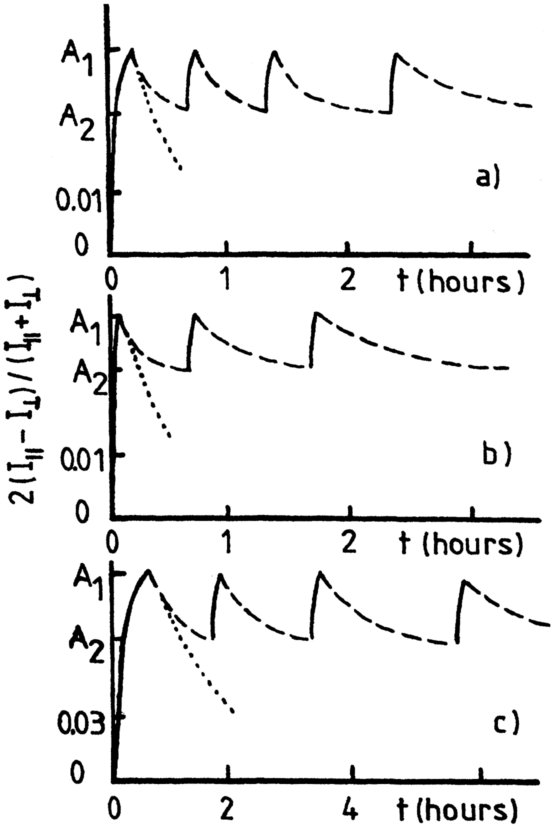

FIG. 1. Kinetics of the appearance (solid lines) and dark relaxation (dashed lines) of photoinduced dichroism when switching on and off, respectively, the linearly polarized inducing light of a He-Ne laser ($\lambda = 633$ nm, P is the laser-power density) in films of chalcogenide glasses (thickness d) of composition AsSe prepared by (a) high-frequency sputtering, $d = 2$ μm, $P = 0.1$ W/cm^2, (b) vacuum evaporation, $d = 3$ μm, $P = 0.1$ W/cm^2, and (c) of composition Ge_2PbS_3 prepared by flash evaporation, $d = 2.5$ μm, $P = 20$ W/cm^2. Lines are drawn to guide the eye. Dotted curves are the fits to the dashed curves using a simple exponential.

quent cycles after repeated switching on and off of the inducing light is accelerated [solid lines in Fig. 1(a)]; (iii) a slowing down of the dark relaxation of the dichroism from the value A_1 to A_2 is observed in subsequent cycles [dashed lines in Fig. 1(a)].

A simple analysis shows that neither the kinetics of the appearance nor of the dark relaxation of the dichroism can be approximated by a simple exponential law. It is easier to analyze the curves of dark relaxation because it is difficult to reach saturation in the growth of the dichroism. Only the initial part of the relaxation curves can be described by a simple exponential $A(t) = A_0 \exp(-t/\tau_D)$, where A_0 and $A(t)$ are the values of the dichroism at the beginning and at time t of the relaxation process, respectively, and τ_D is a time constant. Fitting of the initial parts of the dashed curves of Fig. 1 by this function gives the values of τ_D listed in Table I. The dotted curves in Fig. 1 are the fits to the experimental dashed curves using a simple exponential. The rest of the relaxation curves can be fitted by a stretched exponential (Kohlrausch law) $A(t) = A_0 \exp(-t/\tau_C)^\gamma$, where τ_C is a time constant and the exponent γ lies in the range $0 < \gamma < 1$. Corresponding values of τ_C and γ are also listed in the table. The blanks in the table correspond to the cases when the fitting error is very high due to a relatively short period of observation.

It can be seen from the table that the kinetics of the appearance and dark relaxation of dichroism in AsSe films prepared by different methods are more or less similar, although a trend is seen that all the kinetics are slower in films prepared by high-frequency sputtering compared to those made by thermal evaporation. Note that a pronounced photodarkening effect, i.e., a scalar increase of the absorption coefficient,[1] is observed in the latter films but not in the former ones. In contrast, the kinetics are much slower in Ge_2PbS_3 films, where the maximum photoinduced dichroism and the laser-light intensities used were much higher.

To understand the microscopic origin of PA in chalcogenide glasses, it is reasonable to look for strongly anisotropic structural elements, sensitive to the polarization state of light, which are intrinsic features of these materials. In this regard, a model of intrinsic (native) valence-alternation pairs (VAP's) in glassy chalcogenides was suggested.[10,11] After Ref. 11, these are denoted $C_3^+ C_1^-$ pairs, where C stands for a chalcogen atom, the subscript is the coordination number, and the superscript is the charge on the chalcogen. Obviously, VAP's are anisotropic structural elements due to their electric-dipole moment.

To develop the model of Ref. 11 we recall that the only structural elements of chalcogenide glasses known for certain are the $As(Sb)Se_3(S_3)$ pyramids in As(Sb)-Se(S) systems, or the $GeSe_4(S_4)$ tetrahedra in glasses of Ge-Se(S) systems, where the subscripts stand for the coordination number of the central cation. This fact has been well established by Raman, IR-absorption, x-ray-absorption, and scattering studies. In addition, it was observed in Refs. 2 and 12 that, when exposed to circularly polarized light, photoin-

TABLE I. Values of time constants τ_D, τ_C, and exponent γ obtained from fits to the dashed curves of Fig. 1 for successive dark-relaxation decays of the photoinduced dichroism with simple exponential (τ_D) and Kohlraush (τ_C and γ) laws in amorphous films of composition AsSe prepared by high-frequency sputtering (AsSe hf), or by thermal evaporation (AsSe te), and films of composition Ge_2PbS_3.

Cycle		τ_D (min)			τ_C (h)			γ	
	AsSe hf	AsSe te	Ge_2PbS_3	AsSe hf	AsSe te	Ge_2PbS_3	AsSe hf	AsSe te	Ge_2PbS_3
1	25	25	90	6	20	370	0.40	0.35	0.19
2	45	60	150	10	100		0.35	0.28	
3	50		180	57			0.28		
4	60			900			0.19		

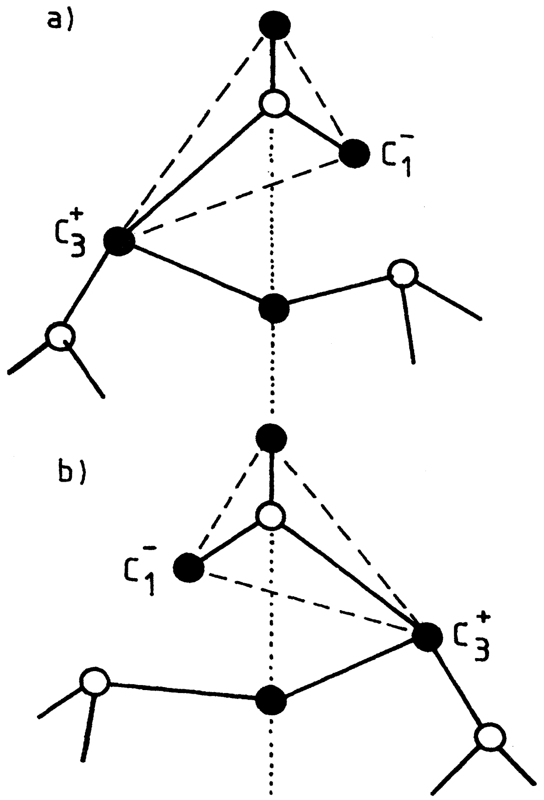

FIG. 2. Schematic illustration of the center responsible for the photoinduced anisotropy and gyrotropy effect in pnictogen-chalcogen systems (e.g., As-Se) before (a) and after (b) optical excitation. Open and solid circles are pnictogens and chalcogens, respectively, solid lines are bonds, and dashed lines delineate the PC_3 pyramids. Centers (a) and (b) are mirror images of one another in the plane shown by the dotted line.

duced gyrotropy (circular dichroism and birefringence/optical activity) appears in As-Se(S) glassy systems; i.e., the active centers responsible for this effect must consist of at least four atoms to be able to yield some degree of chirality.

Consider here the most simple case of a PC_3 pyramid (Fig. 2), where P stands for a pnictogen atom (e.g. As,Sb) and C stands for a chalcogen atom (e.g., Se,S), and the particular example of a pyramid containing an IVAP, meaning that positive and negative charges are located at two corners of the pyramid. We place the IVAP's on C sites since the vectoral effects of PA and photoinduced gyrotropy depend only very weakly on the concentration of pnictogen atoms;[1,12] i.e., chalcogen atoms must play the principal role in vectoral effects. It was pointed out[11] that structural distortions occur around C_3^+ sites (responsible for the negative-U character of the centers), and we suggest that the chemical bond P-C_3^+ is longer than the P-C_1^- bond. More detailed considerations, including the cases of Ge-containing glasses, a-Se, and more complex configurations, will be given elsewhere.

Our preliminary results on the intensity dependence of PA indicate that mostly one-photon processes are involved with only a small contribution from two-photon processes. The one-photon reaction $C_1^-C_3^+ + h\nu = C_1^0C_3^0$, a charge-transfer process, results in unstable singly and threefold-coordinated neutral centers that, in a second step, should thermally decay either back to $C_1^-C_3^+$ [Fig. 2(a)] or to $C_3^+C_1^-$ [Fig. 2(b)] stable charged centers. The one-photon reaction $2C_2^0 + h\nu = C_1^-C_3^+$ probably also takes place, increasing the number of IVAP's. Data on photoinduced spin resonance (Ref. 13 and references therein) confirm the existence of the latter reaction, since an acceleration of the kinetics of the appearance of photoinduced spin resonance was observed (this spin resonance was explained as a result of reactions such as $C_1^-C_3^+ + h\nu = C_1^0C_3^+$ or similar ones[13]) in samples that were light soaked at room temperature prior to measurements of the photoinduced spin resonance being taken at low temperatures. Our data on the acceleration of the kinetics of the appearance of photoinduced dichroism in subsequent cycles (Fig. 1) may be understood when taking into account that the number of IVAP's participating in subsequent cycles is increased.

In Ref. 3, only geminate recombination was considered to yield PA. We also accept this suggestion since, in the case of nongeminate recombination, electrons excited from a C_1^- center will be removed from the pyramid under consideration in Fig. 2 and trapped by a C_3^+ center of some different randomly placed pyramid, not causing the structural change considered here and not depending on the polarization state of the inducing light, and thus not producing PA. In this respect, subgap excitation should be more efficacious than above-gap excitation, in accordance with experiment.[2] Note that a difference in the shapes of photoinduced spin resonances has been observed for such different conditions of excitation.[14]

Before irradiation, IVAP's are located randomly with respect to each other, since glass is generally isotropic overall. Linearly polarized light excites most effectively those centers where the lone pair (more strictly speaking the plane defined by two p-type lone-pair orbitals of a C_1^- atom, normal to the P-C_1^- bond) is parallel to the electric vector of the inducing light, but not those centers where the lone pairs are orthogonal to the electric vector. As a result, a macroscopic anisotropic structure is formed in the glass after prolonged irradiation by linearly polarized light with the presumed orientation of IVAP lone pairs being orthogonal (and, as seen from Fig. 2, with the presumed orientation of the $C_3^+C_1^-$ electric dipoles being parallel) to the electric vector of the light. Note that estimations[15] of the concentration of IVAP's needed to cause macroscopic anisotropy give a surprisingly small value ($\sim 5\times10^{17}$ cm^{-3}). We suggest that this is due to the very strong interaction of IVAP's with their environment in glassy chalcogenides, which is supported by the very low values of the parameter γ ($\sim$0.2–0.4) of the Kohlrausch law reported in this paper, the very high cubic susceptibility $\chi^{(3)}$ (Ref. 16) (two orders of magnitude higher than in oxide glasses), and probably the very large Stokes shift in the luminescence.[17]

Obviously, when changing the polarization of the linearly polarized inducing light by 90°, a repeated exchange of charges inside IVAP's and reorientation of the optical axis to an orthogonal direction can take place, thus permitting the high degree of optical reversibility of PA observed experimentally.[1,2]

A very interesting aspect of the particular suggested structural change shown in Fig. 2 is that it is accompanied by a change of chirality of the PC_3 pyramid and its environment. The chirality itself is due to the pronounced asymmetry of this pyramid caused by different coordinations of C_3^+ and C_1^- sites. The structural change suggested here is also able (uniquely it seems) to account for the observed photoinduced gyrotropy (circular dichroism and optical activity) when a pnictogen chalcogenide glass is illuminated by circularly polarized light,[2] since pyramids of opposite chirality have different magnetic-optical dipole moments for optical transitions. In particular, prolonged irradiation by right-hand circularly polarized light will produce an excess of left-hand pyramids by means of charge transfer inside the IVAP shown in Fig. 2 due to the higher probability of excitation of right-hand pyramids by right-hand polarized light. [Right- and left-hand pyramids are defined to be those which have magnetic dipole moments for optical transitions parallel and antiparallel, respectively, to the light wave vector (Ref. 18 and references therein).] Interestingly, the effect of photoinduced gyrotropy (optical activity) in amorphous semiconductors was predicted theoretically in Ref.18 as a nonlinear optical effect. It was noted in Ref. 18 that the time scale for decay of photoinduced optical activity should be related to the time required for carriers to diffuse from the place of excitation (called domains of right- or left-hand chirality), this time being dependent on the size of these domains.

Dark relaxation of PA can be explained either as a thermally activated transfer or as a tunneling of lone-pair electrons. The former case will occur if the thermal energy kT_{room} is comparable with the height of the barrier separating the states in Figs. 2(a) and 2(b) with opposite chirality. In a more sophisticated approach, multiphonon-assisted decay can occur when the collective interaction of localized optical phonons takes the system above the barrier.[19]

The structural relaxation of the environment around IVAP's was considered in Refs. 10 and 11 as an important aspect in their formation. The slowing down of the decay kinetics in subsequent cycles observed in Fig. 1 certainly shows that the configurations of relaxing centers are different on average at the beginning of each subsequent cycle; in particular, the depth of the well corresponding to the metastable anisotropic state is higher in each subsequent cycle. The slowing down of the PA decay observed in amorphous chalcogenides is reminiscent of the same behavior observed for the annealing of photoinduced defects in *a*-Si:H.[20] There, too, stretched-exponential decay is observed with the annealing time increasing with increasing degradation (illumination) time. Crandall[20] accounts for this behavior in terms of defect relaxation occurring via thermal excitation over the barrier in a double-well potential and there being an exponential distribution of such barrier heights. Obviously, the same model can also apply to the case of PA decay in amorphous chalcogenides.

Obviously, the environment of relaxing centers is oriented in accordance with the electric-dipole moments of IVAP's due to their Coulombic interaction, the size of the environments (called domains in Ref. 18) being quite large due to the very high value of $\chi^{(3)}$. In principle, these domains may interact with one another. After *many* repeated switchings on and off of the linearly polarized inducing light, one may reach a more or less stable macroscopically anisotropic glass with domains aligned with respect to one another. This seems to be in contradiction with the generally accepted idea of isotropy of disordered solids, but nevertheless may be reasonable if one recalls that stable anisotropy (different from the anisotropy of usual crystals due to the lack of translation symmetry) can be a property even of liquids (e.g., liquid crystals) due to the self-consistent interaction of anisotropic molecules carrying electric-dipole and -multipole moments.

Finally, it should be recalled that ordered chirality is a property of crystalline analogues of chalcogenide and oxide glasses (e.g., spirals in c-As_2Se_3 and c-As_2S_3, or right- and left-hand modifications of c-SiO_2) in contrast to the disordered chirality in glasses considered above, which can be, nevertheless, ordered by irradiation with polarized light.

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