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Optical anisotropies in chalcogenide glasses induced by band-gap light

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A model is proposed that qualitatively explains a variety of experiments on light-induced optical anisotropies in chalcogenide glasses and amorphous films. The model accounts for the sign of the observed anisotropies in thin films and predicts that even unpolarized light will cause these materials to become optically anisotropic. The model probably applies also to oxide glasses and other light-sensitive disordered materials and polymers. Photoinduced anisotropies are produced when one or both of the photocarriers excited by band-gap light remain in the absorbing microvolume and cause local changes in atomic bond configurations while recombining nonradiatively.

I. INTRODUCTION

Exposure to band-gap light produces major changes in the properties of nonoxide glasses that contain as major constituents chalcogen elements such as sulphur and selenium. Among these are irreversible as well as reversible changes in structure which result in changes in the optical, electrical, and mechanical characteristics. These photostructural phenomena have been described in several recent reviews.[1-12] Their origin appears to be related to changes in atomic bond configurations and positions which occur during nonradiative recombination of photoexcited electron-hole pairs.[13]

Exposure to linearly or circularly polarized light produces in addition an anisotropy of the dielectric tensor which results in linear or circular dichroism and birefringence, respectively.[14-21] These optical anisotropies induced by exposure to polarized light are observed not only in annealed glasses but also, and essentially undiminished, in glasses photodarkened by light exposure. The photoinduced anisotropies can be reversibly reproduced after annealing, and the axes defining the optical anisotropy can be turned by turning the polarization direction of the exposing light. These anisotropic phenomena differ from the isotropic photostructural changes in their induction and anneal kinetics as well as their dependence on temperature and photon energy.

In this paper we discuss some optical anisotropies which one should expect to find in chalcogenide glasses after exposure to polarized band-gap light. We compare these predictions with the experimental results. We also discuss some experimental conditions that yield results which can differ appreciably from the predictions of our model.

II. FEATURES OF PHOTOINDUCED ANISOTROPIES

An example of the photoinduced anisotropy is shown in Fig. 1 which is taken from the work of Lyubin and Tikhomirov.[22] They used a 2.4-μm-thick evaporated film of $As_{50}Se_{50}$ and measured the intensity changes of a directly transmitted probing beam as a function of exposure time to a strong inducing light beam. A He-Ne laser supplied both beams, the probing beam with 50 mW/cm^2 and the inducing beam with 350 mW/cm^2 incident power. The sawtooth curves of Figs. 1(a) and 1(b) belong to the right-hand scale. They show the change of the photoinduced dichroism by the parameter

$$D=\frac{I_{\parallel}-I_{\perp}}{(I_{\parallel}+I_{\perp})/2} \tag{1}$$

as the sample is exposed to inducing light of different states of polarization. The symbols ↕ and ↔ mark linear polarization parallel and perpendicular to an arbitrary direction in the sample plane, ○ marks circularly polarized and ✥ unpolarized inducing light. The polarizations of the transmitted probe light intensities $I_{\parallel}$ and $I_{\perp}$ refer to the same arbitrary direction.

The left-hand scale and the monotonically decreasing curves represent the decreasing transmitted light intensities as the film gradually photodarkens. This photodarkening is an isotropic effect and results from a redshift of the optical absorption edge due to reversible photostructural changes.[1-13]

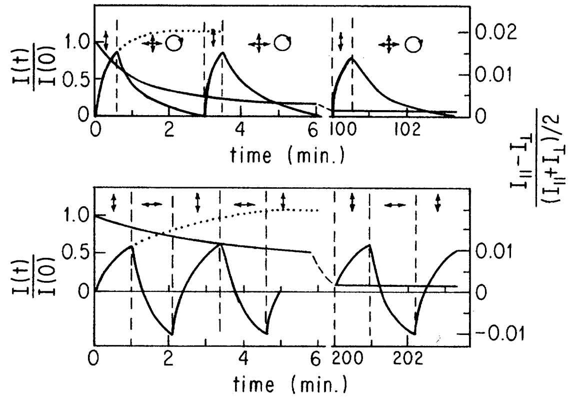

FIG. 1. Monotonically decaying curves are relative transmission $I(t)/I(O)$, and sawtooth-shaped curves are photoinduced dichroism D (right-hand scale) of an AsSe film as a function of exposure (upper panel) to linearly polarized light alternating with unpolarized or circularly polarized light of a He-Ne laser with 350 mW/cm^2 intensity and (lower panel) to linearly polarized He-Ne laser light alternating its polarization direction by $\pi/2$. After Ref. 22.

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The observations of Lyubin and Tikhomirov are summarized as follows.

- (i) The dichroism parameter D increases for parallel inducing light. This means that the absorption of light linearly polarized along the polarization of the inducing light becomes less than the absorption of light polarized perpendicular to the inducing light or $\alpha_{\parallel}<\alpha_{\perp}$.
- (ii) The induced dichroism can be erased with either unpolarized or circularly polarized light, see Fig. 1(a).
- (iii) The optical anisotropy can be induced and erased repeatedly.
- (iv) The optical axis of the anisotropy can be reoriented repeatedly by changing the polarization direction of the inducing light, see Fig. 1(b).
- (v) The induced dichroism $\alpha_{\parallel}<\alpha_{\perp}$ is accompanied by an induced birefringence $n_{\parallel}<n_{\perp}$.
- (vi) The magnitude and the kinetics of the anisotropy, and its erasure and reorientation of the optical axis do not depend on the extent of photodarkening. In Fig. 1 the first two cycles were measured at the beginning of photodarkening and the last one near the end; notice the break in the time scale.
- (vii) Photoinduced optical anisotropies also occur in materials which have no photodarkening effect.

III. THE MODEL

A. Linearly polarized light

On the molecular scale, the structure of chalcogenide glasses is strongly anisotropic. Even without specifying the larger anisotropic structural units, such as rings, chains, platelets, or pyramids, which may define the local structure or medium range order of a particular glass composition, it is clear that one needs a volume containing a considerable number of atoms to find the optical isotropy of a macroscopic sample. The minimum isotropic volume will grow with the size of the anisotropic structural units. This minimum volume is optically isotropic only because of the spatial averaging over smaller anisotropic volume elements it contains. Let us choose these smaller anisotropic microvolumes such that they can be grouped into three categories having, respectively, the largest projection of their dielectric tensor and hence a large absorption cross section for light polarizations in the x, y, or z directions. If we sum over those microvolumes belonging to each category separately (e.g., v_{ix} for strong absorption of the x polarization), we obtain three absorption contributions:

$$\bar{\alpha}_x \approx \sum_{i=1}^{N_x} \frac{\alpha_{ix} v_{ix}}{V_{\text{tot}}},$$

$$\bar{\alpha}_y \approx \sum_{j=1}^{N_y} \frac{\alpha_{jy} v_{jy}}{V_{\text{tot}}}, \tag{2}$$

$$\bar{\alpha}_z \approx \sum_{k=1}^{N_z} \frac{\alpha_{kz} v_{kz}}{V_{\text{tot}}}.$$

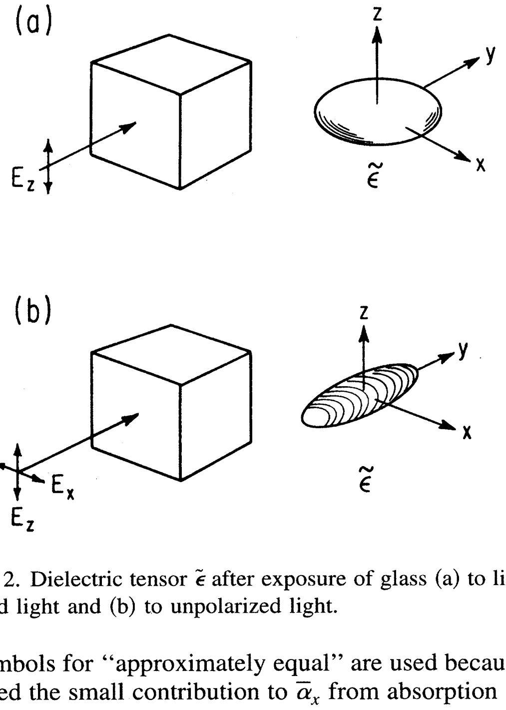

FIG. 2. Dielectric tensor $\tilde{\epsilon}$ after exposure of glass (a) to linearly polarized light and (b) to unpolarized light.

The symbols for "approximately equal" are used because we neglected the small contribution to $\bar{\alpha}_x$ from absorption in the v_{iy} and v_{iz} elements. V_{tot} is the total volume.

Isotropy of the macroscopic sample demands that

$$\bar{\alpha}_x \approx \bar{\alpha}_y \approx \bar{\alpha}_z . \tag{3}$$

There are many ways of choosing anisotropic microvolumes. It is reasonable to choose small sizes in order to obtain strong anisotropies. The choice will depend on photon energy, which we select to be equal to the band gap at present. Among the many possible choices there will always be one for which

$$N_x = N_y = N_z = \tfrac{1}{3} N, \tag{4}$$

where N is the total number of anisotropic microvolumes. This we choose for convenience to simplify the following discussion. The choice of small volumes makes Eqs. (2) and (3) more exact.

In order to proceed with our argument we accept at this point that the recombination process of a photoexcited electron-hole pair is capable of changing the local bonding configuration and with it the optical properties. How this can happen will be explained in a later section. Following absorption of electron-hole pair producing light the resultant changes in optical properties can be grouped in the following categories: (A) redistribution: $\Delta N_x + \Delta N_y + \Delta N_z = 0$; (B) bleaching: $\Delta N < 0$; (C) creation: $\Delta N > 0$; (D) electron and hole diffusion.

Let us assume absorption of light polarized in the z direction as sketched in Fig. 2(a). A particular absorption process will then take place preferably in one of the volume elements v_{kz}. The local structural change possibly caused by the recombination will either change the anisotropy of this microvolume or leave it intact. In the latter case nothing has happened, but when a change does take place that particular absorption element is lost for the z polarization. Either bleaching occurred or the altered anisotropy is such that it now absorbs x or y polarized light. The latter case leads to a redistribution

$$-\Delta N_z = \Delta N_x + \Delta N_y\,. \tag{5}$$

Alternately, the oscillator strength which is lost in the bleaching process at the photon energy of the z-polarized inducing light is shifted to a different energy and will be counted there as a creation process. This situation illustrates that the choice of small anisotropic microvolumes depends on the photon energy. The creation and bleaching processes change the total number N of anisotropic microvolumes that have an absorption cross section for the chosen photon energy range; hence there must be microvolumes that do not absorb in this photon energy range.

Before we return to the redistribution processes, which can yield light-induced anisotropies in chalcogenide glasses, we should briefly discuss the last category electron and hole diffusion. When electrons and holes diffuse over distances larger than the scale of the anisotropic microvolumes before recombining then any resulting local structural changes will occur not in the original absorbing microvolume but in more distant microvolumes that have different orientations from the original one. Such recombinations will not produce a net anisotropy because the anisotropies of the more distant microvolumes are not correlated with that in which the absorption occurred or with the polarization of the inducing light. Diffusive recombination can however produce a net anisotropy when only one member of the carrier pair diffuses away, let us say the electron, while the hole remains in the microvolume of the first absorption event. If this hole later recombines with an electron that was photoexcited by a second absorption event in a different microvolume, the polarization memory is preserved because the first as well as the second absorption occurs preferentially in microvolumes of the polarization of the inducing light. The cumulative effect of redistribution events will reduce the absorption for the polarization direction of the inducing light and enhance equally the absorption in the two perpendicular directions. For inducing light polarized in the z direction one therefore obtains

$$-\Delta\alpha_z = \Delta\alpha_x + \Delta\alpha_y\,. \tag{6}$$

As a consequence, the dielectric tensor becomes an ellipsoid of revolution with the optical axis in the z direction with absorption coefficients $\alpha_z < \alpha_x = \alpha_y$ and refractive indices $n_z < n_x = n_y$; see Fig. 2(a). The induced anisotropy is optically reversible when bleaching and creation processes are negligible. The optical axis will change with the polarization direction of the inducing light.

This model leads to the following interesting prediction: illumination even with unpolarized light produces an optical anisotropy in glasses. This is a consequence of redistribution. Unpolarized light traveling in the y direction is only absorbed by microvolumes responding to x and z polarizations. Recombination, local structure changes, and redistribution must then yield a decrease in absorption for x and z polarizations and an increase in absorption for the y polarization:

$$-\Delta\alpha_x - \Delta\alpha_z = \Delta\alpha_y\,. \tag{7}$$

The dielectric tensor is then an ellipsoid of revolution with the axis in the direction of propagation; $\alpha_x = \alpha_z < \alpha_y$ and $n_x = n_z < n_y$. The glass appears isotropic for light propagating in the y direction as one would expect, but the true anisotropy can be observed with polarized light traveling in one of the perpendicular directions x or z. This situation is illustrated in Fig. 2(b).

B. Circularly polarized light

The model can be extended to circularly polarized light. The small average coordination number of chalcogenide glasses and particularly the presence of chalcogenes provides a local molecular structure with sizable helicity. It is only the spatial averaging over a macroscopic volume which gives the glass its isotropy. We again proceed by subdividing the glass into small anisotropic microvolume with strong helicity character or strongly preferred absorption in the chosen wavelength range of right- or left-handed polarized light propagating in either the x, y, or z direction. We allow for the possibility that there will be many microvolumes which cannot be classified in this manner. If we sum up the absorption contributions in each category separately, one finds that the average absorptions of the six categories are equal because the annealed glass is isotropic.

Extended exposure to one kind of circularly polarized light will lead to recombination events and structural changes in the microvolumes of that particular category. These structural changes may or may not result in changes in the local optical anisotropy. If they do, then the associated absorption contribution is shifted out of the wavelength range of the probing and inducing light (bleaching) or into one of the other categories (redistribution). When one observes optical reversibility, then redistribution is the more likely occurrence. For linearly polarized light the oscillator strength will be redistributed from say the z direction with equal probability to the x and y directions. In the case of circularly polarized light the redistribution from the absorbing one to the other five helicities will probably not occur with the same probability. Helicities that are structurally similar to the one which is absorbing the inducing light are favored over those that are dissimilar. Hence not all categories will obtain an equal share of the redistribution. This situation is more complicated than the one of linearly polarized light because at least four neighboring atoms are needed to define a helicity. Nevertheless, when the glass is exposed to say right-handed polarized light we expect the absorption of the right-handed light to decrease and the absorption for left-handed light to increase.

C. Mechanism for change in local structure

We now examine our assumption that the recombination of photoexcited electron-hole pairs can change the local bonding configuration and hence the local optical anisotropy. We also wish to explain why these phenomena are generally observed in almost all chalcogenide glasses but not in their corresponding crystalline modification.

It is well known that electron-hole recombination processes produce photostructural changes in chalcogenide glasses that lead to a variety of phenomena such as irreversible photodarkening and bleaching, photopolymerization and

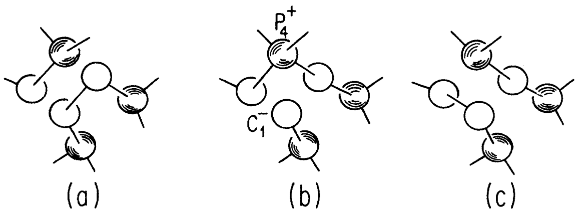

FIG. 3. (a) Normal coordination of pnictogen and chalcogen atoms in chalcogenide glass; (b) intimate valence alternation pair as self-trapped exciton; (c) altered bonding configuration produced after the decay of the transient self-trapped exciton.

photodensification, photocrystallization, and photodoping, as well as photodarkening which can be reversed by annealing.[1–13]

At the heart of these phenomena are elemental electron-hole recombination processes that change the local bonding configurations and also promote the movement of atoms. As discussed earlier[13] such recombination-induced local bond changes and diffusion steps can cumulatively produce the observed macroscopic changes. These changes are usually reversible only when the initial state is in the annealed state. Photostructural changes are favored in chalcogenide glasses and amorphous films because of the rapid localization of photoexcited carriers, the low energy of valence alternation defect pairs[23,24] and steric freedom of low coordination atoms to change their positions and bond configurations.[25]

We begin with a brief description of the recombination processes that produce changes in local bond configuration and then address issues that are specific to the light-induced optical anisotropies. These concern the observation that the anisotropies can be changed and optically cycled even after photodarkening has saturated and even in films that do not exhibit a photodarkening effect or other photostructural changes.

Electron-hole pairs recombine via a number of radiative and nonradiative processes. The fast nonradiative recombination rate observed in chalcogenide glasses may be understood, according to Street,[26] when the electron-hole pair forms a transient local bonding arrangement, which consists of a closely spaced coordination defect pair, which constitutes a self-trapped exciton. This transient coordination defect pair may be pictured as an intimate pair of valence alternation defects[24,25] as illustrated in Fig. 3(b). The positive site is over- or undercoordinated while the negative one is usually undercoordinated relative to the normal coordination of the atoms. The configuration of the transient bonding arrangement can return either to its original state or to other bonding configurations that differ from the original one. An example of a change in local bonding induced by an electron-hole recombination process is shown by sequence (a) to (b) to (c) in Fig. 3. The directions of two bonds are rotated by nearly 90° in this example; as a consequence the local optical anisotropy is changed. These processes are very similar to those proposed earlier by Grigorovici, Vancu, and Ghita[16] except that these authors envisioned a two-photon process. A second electron-hole pair photoexcited and recombining in the same region may lead to another and perhaps a more stable configuration that is energetically separated from the original one by a larger barrier, but two photons are not needed in principle.

As explained earlier,[13] an accumulation of photostructural events tends to produce a so-called light-saturated state that is characterized by having less medium-range order than the annealed state. Once this more disordered state is established, the changes in macroscopic properties such as density, hardness, and optical absorption come to saturation. To explain continuing changes in optical anisotropy it is important to realize that recombination-induced bond rearrangements continue as long as the material is exposed to electron-hole pair producing light. In the light-saturated state recombination processes continue to produce local bonding changes during illumination and these in turn compete with local thermal relaxation processes to establish a dynamic equilibrium or steady state. Most measured properties are macroscopic averages over local configurations and thus are insensitive to these local changes which continue to occur during illumination even in the steady state.

The dynamic nature of the steady state during illumination is revealed by several experiments such as photoenhanced annealing of the photodarkened state[27] and reversible changes in optical density in response to changes in photon energy or light intensity.[28,29]

Since the local bonding configuration defines a local optical anisotropy which is sensitive to the polarization of light, the dynamic nature of the illuminated state is clearly revealed by the photo-induced optical anisotropies and the possibility of reorienting the optical axis by changing the polarization direction of the inducing light. They provide an effective method for studying the kinetics of the recombination-induced local bonding changes.

The fact that nonradiative recombination of electron-hole pairs can produce local bonding changes in chalcogenide glasses and amorphous films appears to be the common cause for a variety of reversible and irreversible phenomena. It therefore seems surprising or contradictory that the light-induced optical anisotropies are observed regardless of the state of photodarkening and even in compositions that show no photodarkening effect.[22] The answer may be the following. Reversible photodarkening occurs when the recombination-induced configuration changes produce a more disordered structure which has a smaller optical gap than the annealed one. The decrease in optical gap may be the consequence of enhanced lone pair interactions. The degree or magnitude of photodarkening depends essentially on the structural difference between the annealed and light-saturated state. The local bonding changes however occur under illumination in either state and are relatively independent of the magnitude of the difference in structure between the annealed and light-saturated state. It is therefore possible that optical anisotropies can be induced in materials that exhibit very little or no photodarkening. On the other hand, if the structures are very different before and after extended illumination as for example in the case of freshly deposited films which undergo irreversible structural changes, then one should find that those changes affect the magnitude of the light-induced optical anisotropies.

IV. EXPERIMENTAL CONSTRAINTS

Both the reversible and irreversible photostructural effects produce changes in the density of the material. It is reasonable to expect that uniaxial as well as volume strains result from illumination with polarized light. If the sample under investigation is a film deposited on a substrate or if illumination is restricted to a narrow light beam, then the illuminated material will be subjected to relatively large shear stresses. These in turn will give rise to an optical anisotropy which is superposed on that expected in a stress free sample, i.e., a sample without boundary constraints that is illuminated uniformly with inducing light. Additional stresses may result from heating effects and thermal gradients when high light intensities are being used.[21]

The stress-optical coefficients of a number of chalcogenide glasses have been determined by Linke and Eberhardt.[30,31] The coefficient C_0 defined by the relation

$$n_{\perp} - n_{\parallel} = C_0 \chi \tag{8}$$

typically varies between +20 and −40 TPa^{-1}. The perpendicular and parallel directions are those of the electric vector relative to the uniaxial compression χ.

Scattering effects may also affect the experimental results if the changes in transmitted light intensity are to be interpreted as changes in absorption.[32] The annealed state and the final anisotropic state, produced after long exposure to polarized light, should be optically quite homogeneous. The partially exposed states of glass however are expected to be relatively more heterogeneous for two reasons. For an incomplete redistribution of anisotropic microvolumes, see Eq. (5), one expects to find statistical variations in their spatial distribution. The corresponding differences in refractive index produce an enhanced scattering that depends on the polarization of the probing light. The enhanced scattering will also affect the inducing light, producing in the material an inducing light pattern that is fanning out and thus more complicated than the uniform inducing beam that exists in front of the sample.

Another cause for light-induced heterogeneities may be the following. A region of the sample that is beginning to photodarken is more likely to darken further because of its increased absorption. These heterogeneities tend to disappear as photodarkening approaches saturation. Since $\alpha_{\parallel} < \alpha_{\perp}$ this effect is less important for light-induced optical anisotropies, on the other hand internal strains around optically altered regions can enhance the local absorption via the stress-optical constants and provide a positive feedback that produces heterogeneities.

V. COMPARISON WITH EXPERIMENTS

Many experimental results on the photoinduced optical anisotropies agree qualitatively with the predictions of our model, but a few observations suggest that the model may still be incomplete. As we discuss some of the successes and failures in the following, it is convenient to refer to reversible photostructural changes, such as photodarkening, as the scalar effect and to photoinduced optical anisotropies as the vector effect.[16]

There have been a number of assertions that the mechanisms leading to the scalar and vector effects are substantially different.[17,22,33] These are based on the following observations.

(a) The vector effect occurs regardless of whether the scalar effect is just beginning or is saturated, and it occurs even in materials that do not have a scalar effect.
(b) The vector effect decreases with photon energy above the gap energy E_g whereas the scalar effect does not.
(c) The vector effects peaks near 300 K while the scalar effect increases monotonically with decreasing temperature.
(d) The vector effect anneals at 50–100 °C below the glass transition temperature T_g while the scalar effect anneals near T_g.

The lack of correlation between the vector and scalar effects is caused in our model mainly by two factors. First, the two effects measure different consequences of recombination-induced changes in bond configurations. Regardless of whether these changes lead to a decrease in medium range order, a change in density or an increase in lone-pair orbital interactions (scalar effects),[13] the bond changes may lead to alterations of the optical anisotropy in the microvolumes (vector effect). As mentioned above, the magnitude of the reversible scalar effect depends on the structural difference between the light-saturated and the annealed state while optical anisotropies can be induced in either state. This explains observation (a). Second, while essentially all nonradiative intrinsic recombination processes contribute to scalar effects, only a certain subset of these processes produce vector effects. In order to retain the correlation between the polarization of the inducing light and the resultant changes in the local anisotropies by redistribution, only those recombination events which occur in the same microvolumes in which the electron-hole pairs were excited, can produce the vector effect. Carrier diffusion and subsequent recombinations in microvolumes having polarizations different from that of the absorption processes destroy this correlation. In brief, optical anisotropies can arise only when one or both of the photocarriers remain in the absorbing microvolume and recombine nonradiatively. The recombination is called geminate when both carriers remain and recombine in the absorbing microvolume.[34]

The additional restriction to nonradiative recombination in the absorbing microvolumes might explain points (b) and (c) of the above list: excitations $h\nu > E_g$ enhance the probability that both the electron and the hole drift out of their absorbing microvolume. Regarding point (c) we do not know enough about the temperature dependence of geminate recombination to make a firm judgment but the probability may indeed decrease with decreasing temperature because of the increasing steady-state concentration of trapped photoexcited carriers.[35,36] The temperature dependence of the vector effect[17,37] may be governed by the dependence on temperature of the fraction of recombination processes which fulfill the requirements stated above for producing anisotropies: either one or both photocarriers must remain in the absorbing microvolume. The difference in annealing temperatures, observation (d), might reflect the difference in structural changes that are associated with the two effects. A change in density or medium-range order appears to require an anneal temperature close to T_g whereas local bond changes affecting the anisotropy, which continue to occur under illumination even in the steady state, do not need larger structural changes and atomic motions and thus anneal at somewhat lower temperatures.

The striking optical reversibility of the direction of the optical axis, shown in Fig. 1, indicates that the distribution process dominates over processes involving bleaching and creation. Our model explains the observation that once the sample has been exposed to polarized light, the induced anisotropy cannot be truly erased by changing the polarization of the inducing light by 90° or by exposure to circularly polarized light.[14,16,21] Instead one passes through a pseudoisotropic state $\alpha_{\|}=\alpha_{\perp}$, that is not identical with the truly isotropic one. In the pseudoisotropic state the dielectric tensor is an ellipsoid of revolution with its axis pointing in the propagation direction of the inducing light. The prediction of our model, that illumination even with unpolarized light produces an optical anisotropy, was confirmed recently by Tikhomirov *et al.*[38] and by Tanaka *et al.*[37]

Remarkably pronounced scattering of the probing light beam after exposure to a polarized excitation beam was observed by Lyubin and Thikomirov.[18,20] Such enhanced scattering is not unexpected as mentioned earlier, more studies are needed however before one can tell whether the observations agree with the present model.

We expect a positive value for D in Eq. (1) because our model predicts $\alpha_{\|}<\alpha_{\perp}$ as absorbing microvolumes characterized by the polarization of the inducing light change their structure and add their oscillator strength to the other polarizations. The observations made on thin films largely agree with our expectation. However, recent studies on bulk samples which were a few mm thick showed negative D values or changes from positive to negative D with increasing inducing time.[39,40] We believe that these observations do not invalidate our model because of the following considerations.

Experiments with thick samples require that one uses subband-gap light for which the absorption coefficient is $\alpha \approx 1$ cm^{-1}. Because of the smallness of the absorption coefficient, the value of D is mainly affected by photoinduced scattering which is also anisotropic and by changes in the shape of the transmitted laser beam. When the laser beam is focused near the front surface of a thick sample, optically anisotropic diffraction patterns appear in the transmitted beam and the value of D depends on the location and size of the detector. Moreover, absorption near $\alpha \approx 1$ cm^{-1}, is largely associated with defects while the structural anisotropy of the microvolumes and their photoinduced changes were in our model not linked to defects.

There are however several exceptional cases where negative D values were observed in thin-film samples exposed to band-gap light. Some of these exceptions could be traced to complicating factors such as interference effects in thin film samples,[41] i.e., changes in transmission unrelated with changes in $\alpha_{\|}<\alpha_{\perp}$, or heating by an intense laser beam.[42,43] Quite surprisingly and as yet unexplained is the observation by Lee and Paesler[33] and Lee, Pfeiffer, Paesler, Sayers, and Fontaine[44] that the sign of the induced dichroism parameter D can change with the intensity of the exciting light. These authors used 4–6 μm thick films of amorphous As_2S_3, a material widely used by other workers. The films were evaporated and subsequently annealed. The inducing light was an Ar-ion laser whose wavelength was chosen near the bandgap where $\alpha \approx 10^3$ cm^{-1}. The small intensity probe beam obtained from the same laser traversed the sample at normal incidence while the inducing beam crossed the same spot at 10° from the normal. The experimental conditions are not significantly different from those used in other laboratories.

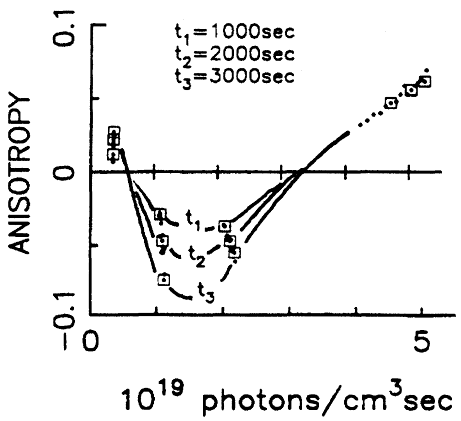

FIG. 4. Change of the sign and kinetics of the optical anisotropy of thin AsS_3 film with inducing light intensity at 300 K. Curves for three exposure times are shown. After Lee *et al.* (Ref. 44).

One of their interesting and puzzling results is shown in Fig. 4 where we have changed the sign of their anisotropy factor such that the ordinate is proportional to the factor D of Eq. (1). D is positive as expected for small as well as for large inducing intensities, but D is negative for a small range of intermediate intensities. The abscissa of Fig. 4 shows the volume generation rate of electron-hole pairs in the sample assuming a quantum efficiency of unity. A generation rate of 5×10^{19} cm^{-3} s^{-1} corresponds to an inducing intensity of about 6 mW/cm^2. Figure 5 shows the transmitted light fraction for the two-probe polarizations as a function of inducing time as the intensity of the inducing light is switched between an intermediate value which yields a negative D and a high value which produces a positive D. For the parallel polarization one observes an essentially monotonic decrease of I/I_0 which essentially is the scalar effect of photodarkening. The perpendicular component of I/I_0, in contrast, changes drastically whenever the inducing light intensity is changed causing the reversal in the sign of the anisotropy factor D. Lee[45] also observed that the magnitude of the negative D effect diminishes after repeated or extended exposure to a light intensity which gives the normal positive D. Moreover, the kinetics is different for the positive and negative anisotropy as illustrated in Fig. 4 by the different dependencies on exposure time.

Although we cannot give a complete explanation of the dependence of the sign of the dichroism on inducing light intensity we like to remark the following. The dynamic state which is approached under illumination is a competion between light-induced creation and annealing as well as thermal annealing.[13] This accounts for the fact that photodarkening depends on the inducing light intensity and can be diminished or partially annealed by reducing the light intensity.[28,29] This essentially is happening to I/I_0 of the per-

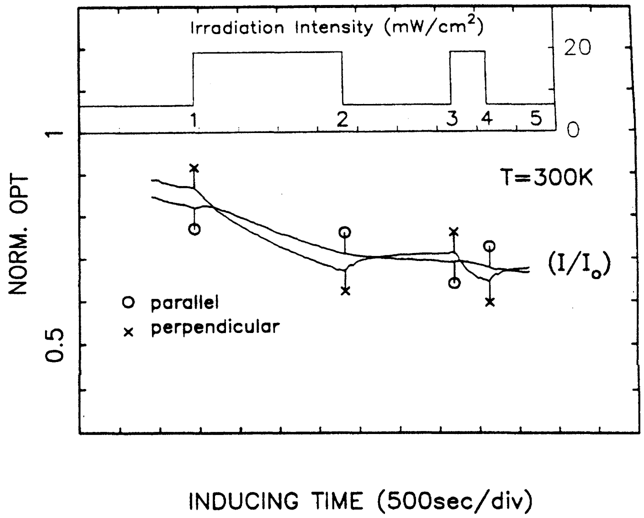

FIG. 5. Change of the relative optical transmission I/I_0 of parallel and perpendicularly polarized probing light through an AsS_3 film as the inducing intensity is changed as shown in the upper panel. After Lee *et al.* (Ref. 44).

pendicular component in Fig. 5, the fraction of transmitted probing light increases as soon as the inducing light intensity is decreased. Such light-induced annealing is not noticeable for the parallel component which decreases monotonically. This asymmetry in the response of the dynamic state leads to the anomalous sign D. Why this is so requires further detailed studies. Unfortunately, no other laboratory has studied the dependence of the sign of the anisotropy factor D on light intensity. Another process which depends on the intensity of the inducing light is the recombination process of the photocarriers. Since only those recombination processes, in which at least one of the carriers remains in the absorbing microvolume, qualify for producing anisotropies while all recombination processes participate in photoinduced creation and annealing of structural changes, it is possible that their relative fraction depends on the light intensity. All nonradiative recombination processes produce photodarkening and photoinduced annealing of the photostructural changes and hence determine the specific dynamic steady state which depends on light intensity.

VI. SUMMARY AND CONCLUSIONS

We have proposed a model to explain the light-induced optical anisotropies (vector effects) in thin chalcogenide films. This model has common features with the one proposed to explain the reversible and irreversible photostructural changes (scalar effects) in chalcogenide glasses.[13] Common to both are changes in atomic bond configurations that result from nonradiative recombinations via transient self-trapped excitons. A major difference between the mechanisms leading to the vector and the scalar effects is that in order to give rise to the vector effect at least one member of the photoexcited carrier pairs must remain and recombine in absorbing microvolume. This additional condition imposed on the recombination events effective for producing optical anisotropies is one reason for the lack of correlation between the vector and scalar effects. Another reason is the different manifestations of the two effects. The reversible scalar effect is most commonly detected as a shift of the optical absorption edge which presumably is associated with a structural change that results in an change in the lone-pair orbital interactions. The reversible vector effect is a change in the local optical anisotropies which may, but need not be, accompanied by a scalar effect.

The model accounts for the generality of these effects in noncrystalline chalcogenides without invoking defects or special centers. The present discussion deals with the general class of glassy and amorphous chalcogenide materials. The magnitude of the light-induced optical anisotropies, however, will depend on material parameters, such as the covalent connectivity, the openness of the structure or its bond free volume. The magnitude of the reversible photodarkening effect was found to depend on the chalcogen element, being largest for sulphur containing glasses and smallest for tellurium glasses.[46] No such trends have been explored yet for the anisotropy effects. It will also be interesting to see whether small additions of metal impurities quench the vector effects as efficiently as they quench the scalar effects.[47] We expect that they do because certain metal impurities provide an alternative nonradiative recombination channel that does not lead to photostructural changes.[13]

We focused our attention on chalcogenide materials because of the wealth of experimental data on the induced anisotropies in these materials. It is likely that these effects also occur in oxide glasses[48] and in photosensitive polymers. Photostructural changes and photopolymerization have been known since antiquity. Bitumen of Judea has been used for example to caulk vessels and to set jewelry. Exposure to sunlight was known to be an essential processing step. Related materials were also used in early photography to fix the image. The photostructural changes, albeit irreversible occurring in those materials should also reveal interesting anisotropy effects under polarized light.

The new model accounts qualitatively for a large number of observations. It explains the sign of the induced anisotropies in thin films in which the dichroism is governed by absorption. The model makes the interesting prediction that even unpolarized light is able to induce an optical anisotropy. This prediction has recently been verified.

Bulk samples which are a few mm thick show interesting anisotropy effects after exposure to polarized subgap light.[18,20,32,40,49,50] These phenomena are not considered here. They might be associated with defects which are responsible for light absorption at subgap photon energies where the absorption coefficients is $\alpha \approx 1\ \mathrm{cm}^{-1}$ and the transmitted light intensities are strongly affected or even governed by scattering.

The dependence of the sign of the dichroism in thin films of As_2S_3 on the intensity of the inducing light, observed in one laboratory,[33,44,45] cannot be explained by this model. This anomalous effect as well as other photoinduced anisotropies in light scattering[18,20,32,40,49,50] and photoinduced dissolution of metals[51] suggest that our understanding of the photoinduced anisotropies is still incomplete.

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