LASER INDUCED OPTICAL ANISOTROPY
IN SELF SUPPORTING AMORPHOUS GeSe$_2$ FILMS

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1. INTRODUCTION

A variety of photo induced changes have been observed in amorphous chalcogenide films (deNeufville 1976). The best known of these effects are photodarkening and photobleaching which were intensively studied.

There are also observations that linearly polarised laser beam can produce optical anisotropy in chalcogenide glasses and chalcogenid evaporated films (Zhdanov et al. 1979, Hajtó and Ewen 1979). However the experimental results reported up to now are not sufficient to understand the underlying mechanism which produces the observed optical anisotropy. In this paper we report a comprehensive study of the laser induced optical anisotropy in self supporting amorphous $GeSe_2$ films.

The vacuum evaporated $GeSe_2$ films exhibit interesting non linear optical effects e.g. light induced oscillations of the transmission. These properties were reviewed in a recent paper (Hajtó 1980).

The experiments described here were carried out at the incident laser power density range from $3W/cm^2$ to $50 W/cm^2$. In this relatively low intensity range no oscillation of the optical properties occurs, however a non linear behaviour of the optical absorption already appears (the absorption increases with the increase of the laser power density at a fixed wavelength).

The paper is organized as follows: in Sec.2. we describe the experimental method; the results are presented in Sec.3. A model for the development of optical anisotropy is presented in Sec.4. The comparison of the model and the experimental results is given in Sec.5. Section 6 contains some final conclusions.

2. EXPERIMENTAL ARRANGEMENT

The a-GeSe$_2$ films were preapred by vacuum evaporation from Ta boat at P = 2x10^{-6} Torr (2.7x10^{-4} Pasc) onto glass substrates, using polycrystalline GeSe$_2$ ingots as evaporation source. The deposition rates were about 20 $\overset{o}{A}$/sec in all cases and the thickness during the evaporation was measured by a quartz crystal monitor. For the measurements the films were removed from the glass substrates using ultrasonic bath in order to reduce the effects of multiple light reflections and of the mechanical stresses occuring in the GeSe$_2$- substrate interface.
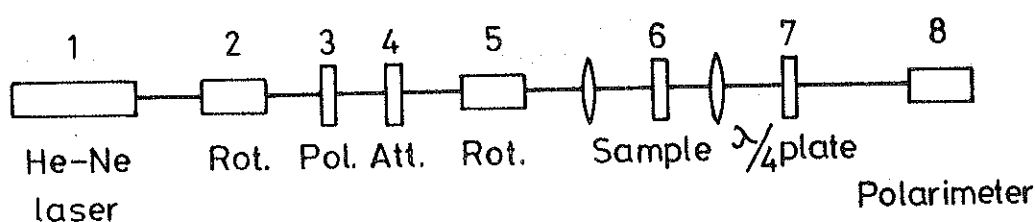
Fig. 1. *Experimental arrangement for the measurements of light induced optical anisotropy*

For illumination we used a linearly polarised c.w. He-He laser beam (λ = 6328 $\overset{o}{A}$) which was focused to a Gaussian optical spot, 100-200 μm in diameter. The intensity and the direction of the polarisation of the incident laser beam were regulated with Spectra-Physics polarisation rotators (Model 310-21, no.2 and 5 in Fig. 1).

The optical anisotropy was measured with the same laser beam as used for producing the anisotropy but attenuated by a filter (4 in Fig. 1). The optical characteristics of the outcoming beam were determined by using a polarimeter (8 in Fig. 1) designed in our institute (Nagy 1978). The polarimeter consists of a Wollaston prism which separates the components of the laser beam polarised parallel and perpendicular to the optical axis of the prism. It measures the intensity ratio of these components. Carrying out measurements with and without a λ/4 plate (7 in Fig. 1) and at different directions of polarisation of the incident measuring light beam, the different characteristics of the optical anisotropy of the sample like rotatory power, birefringence, dichroism and the direction of the principal axes of the index ellipsoid can be determined. All of the experiments were performed at room temperature.

3. RESULTS

3.1 Laser induced dichroism and birefringence in self supporting GeSe$_2$ films

In the as deposited films usually no sign of anisotropy was observed. As a result of laser irradiation both birefringence and dichoism were found systematically. The direction of the principal axes of the index ellipsoid coincided with the direction of the indicent beam polarisation, consequently, no optical activity was induced. The typical curves showing the increase of the laser induced dichroism and the simultaneous decrease of the absorption coefficient (photobleaching) as a function of time of illumination at a given laser power density are presented in Fig. 2. As a measure of dichroism we take $\Delta\alpha = \alpha_x - \alpha_y$ where α_x is the absorption coefficient in the X direction (direction of the incident beam polarisation), α_y is the absorption coefficient in the y direction (perpendicular to X). The dichroism is positive if
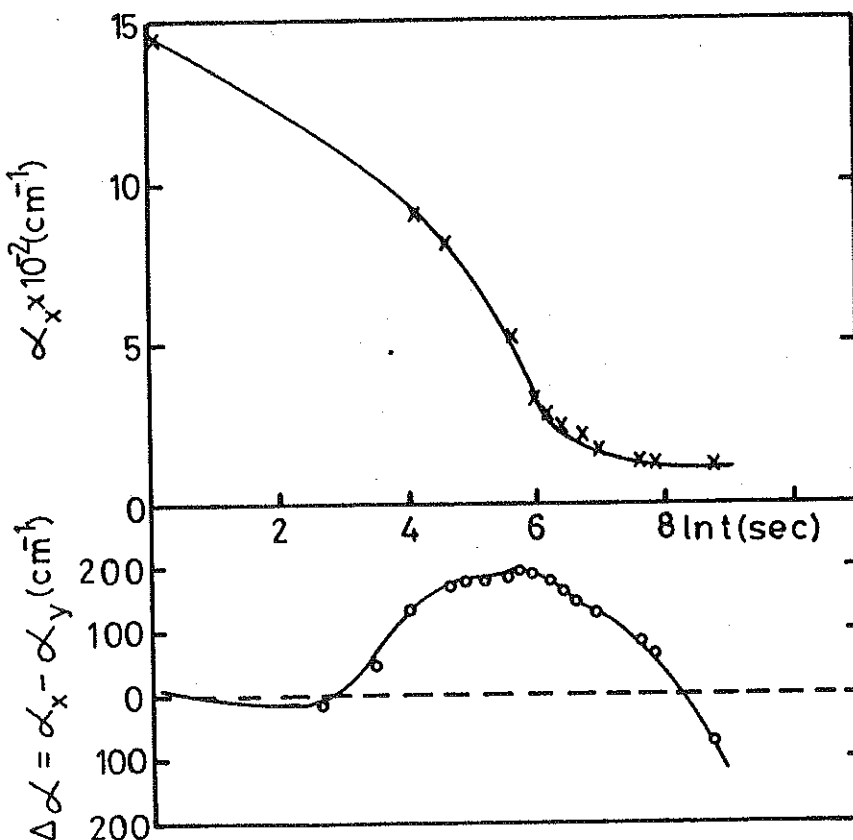

Fig. 2. _Time dependence of the dichroism and absorption coefficient in a-GeSe$_2$ film, thickness of the film = 6 μm, incident laser intensity 50 W/cm^2_

the absorption coefficient is higher in the direction of incident beam polarisation. As shown in Fig. 2, the dichroism is essentially positive for the first period of illumination. This observation, is in accordance with the observation of Zhdanov et al. (1979) where a positive laser induced dichroism was found in As-Se films. However continuing the laser irradiation for a sufficiently long time we observed that the dichroism reaches a maximum and afterwards decreases again approaching the final equilibrium value which is *negative*. The time dependence of laser induced dichroism strongly suggests that at least to distinct processes, affecting the absorption should be involved during the illumination.

As shown in Fig. 2, during the photobleaching α_x (measured at $\lambda = 6328$Å) decreases by one order of magnitude. Note that the final equilibrium value of the absorption coefficient is comparable with the laser induced anisotropy $\Delta\alpha$ indicating a very high dichroism.

The details of these processes will be discussed in a following paper. From now on we concentrate only on the laser induced birefringence.

The observed birefringence Δn defined as $n_x - n_y$ (the difference in refractive indices measured in the direction of laser polarisation X and perpendicular to it) varies linearly with the logarithm of time of the illumination through several orders of magnitude (see Fig. 3). No change of its sign could be observed in contrary to the case of dichroism. The logarithmic dependence of birefringence renders difficult to determine its saturation value. The highest values of the laser induced birefringence in self supporting $GeSe_2$ films observed by us were $\Delta n \approx 6 \times 10^{-3}$.

It is worth mentioning that the laser induced anisotropic structure in the amorphous network is stable, at least at room temperature (memory state). No sign of relaxation to the isotropic state was observed keeping the sample in dark for a few days.

A remarkable feature of the laser induced anisotropy is that its principal axis can be reoriented into any direction by changing the direction of incident beam polarisation (see Fig. 4).
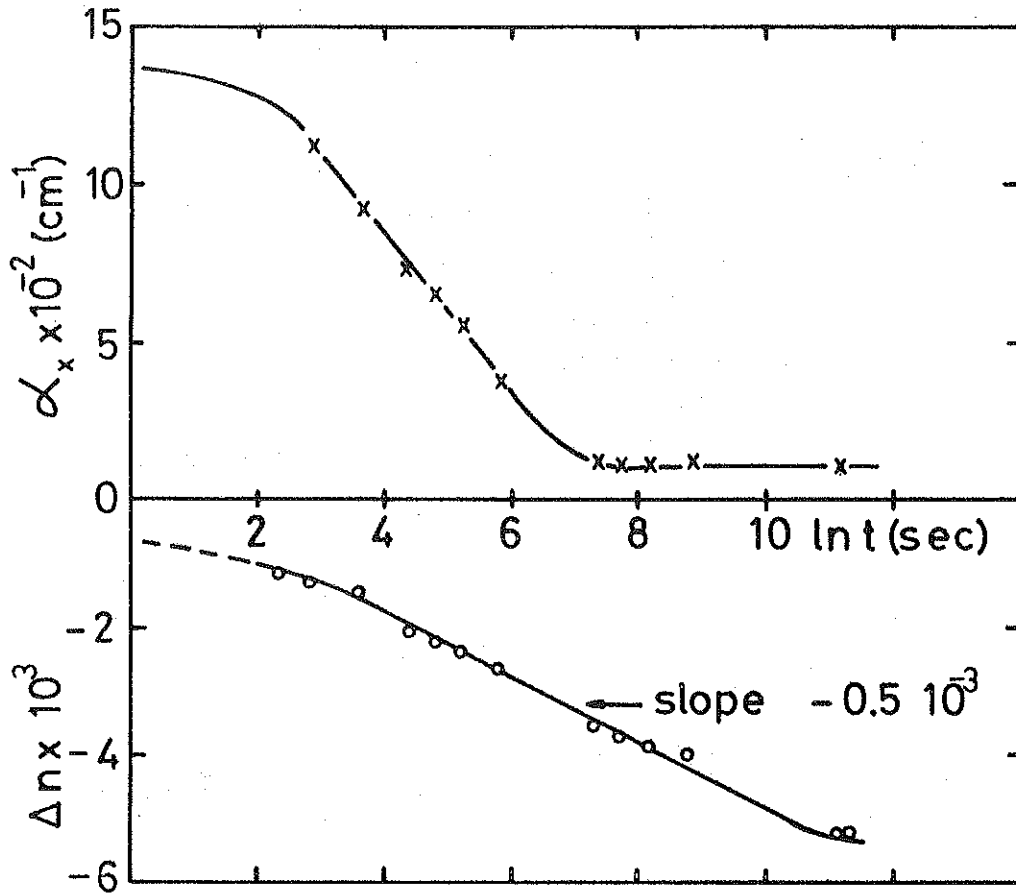
Fig. 3. Time dependence of the laser induced birefringence and absorption coefficient at the same experimental conditions as given at Fig. 2

3.2 Kinetics of reorientation of the laser induced birefringence

Most of the reorientation experiments were performed by orienting first the structure in a given direction of polarisation (say y direction) and then rotating the incident beam by 90° (to x direction).

We investigated how does the direction of the principal axes of the index ellipsoid and the absolute value of the anisotropy of the principal refractive indices vary during the reorientation.

For the two orthogonal principal axes ξ and η (see insert in Fig. 5) we have:

$$E_\xi^{out} = E_\xi^{in} \; e^{i \frac{2\pi}{\lambda} n_1 d} \tag{1}$$

$$E_\xi^{out} = E_\xi^{in} \; e^{i \frac{2\pi}{\lambda} n_2 d} \tag{2}$$

where E^{in} and E^{out} are the electric field vectors of the incoming and out-going light beams, d is the thickness of the sample, n_1 and n_2 are the principal refractive indices. To be definite, we consider ξ as the direction to which the smaller principal refractive index belongs ("fast axis") (Hartshorne and Stuart 1970). The birefringence of the sample can be completely described by giving the angle Ψ between ξ and x and the value of n_2-n_1. Note that by definition n_2-n_1 is always positive.
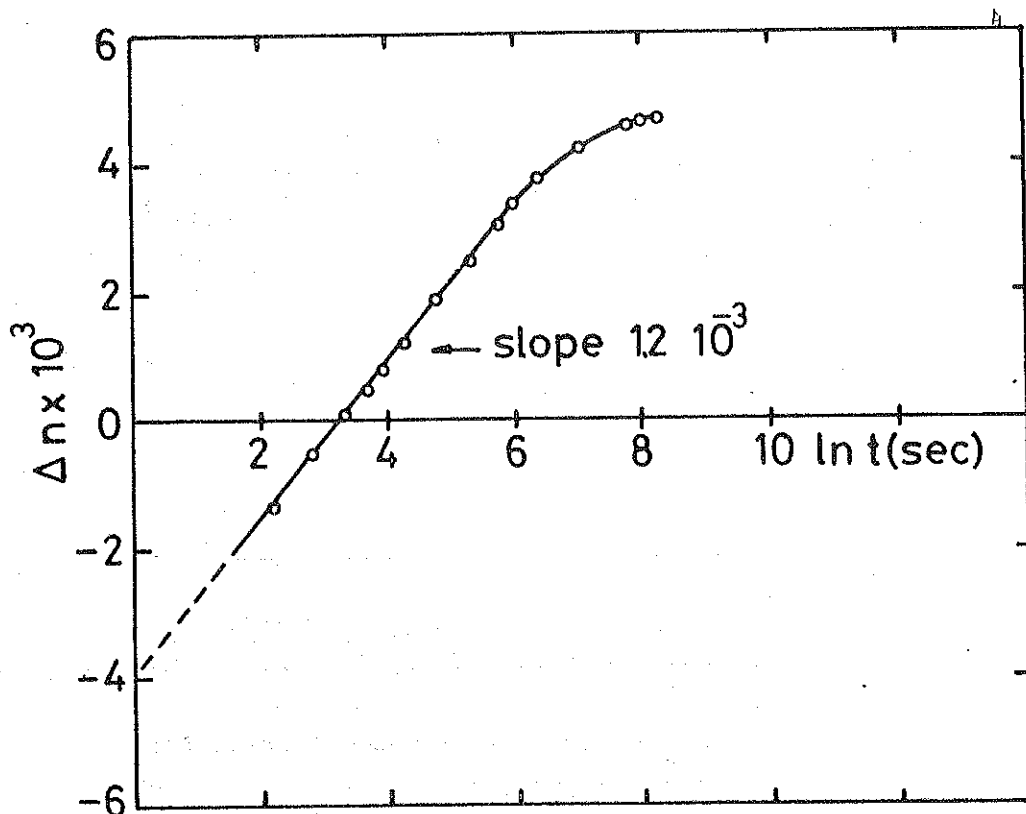

Fig. 4. *Reorientation of the anisotropy from x to y direction on the same spot as used for the measurements in Fig. 3 by the same experimental conditions*

The results are shown in Fig. 5. As it can be seen, first Ψ remains almost constant during the illumination, while n_2-n_1 decreases. At a given time n_2-n_1 becomes practically zero i.e. the material becomes *isotropic*. Continuing the irradiation the sample becomes again anisotropic ($n_2-n_1 > 0$) but now Ψ is changed by 90°.

It is interesting to note that this type of reorientation which passes through an isotropic state is contrary to the laser induced orientation observed in liquid crystals (Csillag et al. 1982).
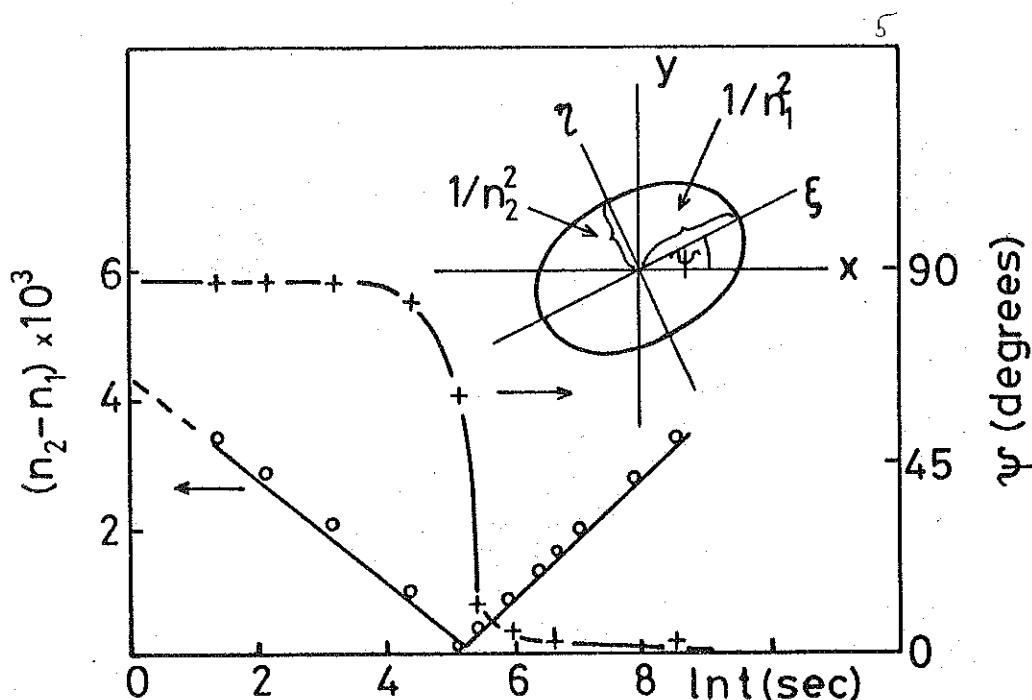
Fig. 5. Variation of the "fast axis" and the difference of the principal refractive indices during the reorientation. The insert shows the index ellipsoid.

In this latter case $n_2 - n_1$ remains almost constant while ψ is changing continuously during the reorientation. The difference arises from the fact that in the case of liquid crystals the reorientation consists of the collective rotation of molecules while in the present case the reorientation takes place through independent atomic events.

As we have seen the x and y axes remain the principal axes during the reorientation process, consequently it is sufficient to use the quantity $\Delta n = n_x - n_y$ for describing the kinetics. $(n_x - n_y)$ can be both positive or negative depending on the orientation of the "fast axis".

The time dependence of $(n_x - n_y)$ in a well defined time interval showed definite logarithmic behaviour (see Fig. 6) which can be described by the equation

$$n_x - n_y = -A \ln t / t_o \qquad (3)$$

We found this relation empirically in all cases and the slope was independent from the incident laser power density (see Fig. 7). This fact indicates that A is determined only by the structure of the amorphous network in $GeSe_2$. However the time at which the sample becomes isotropic (t_o) depends
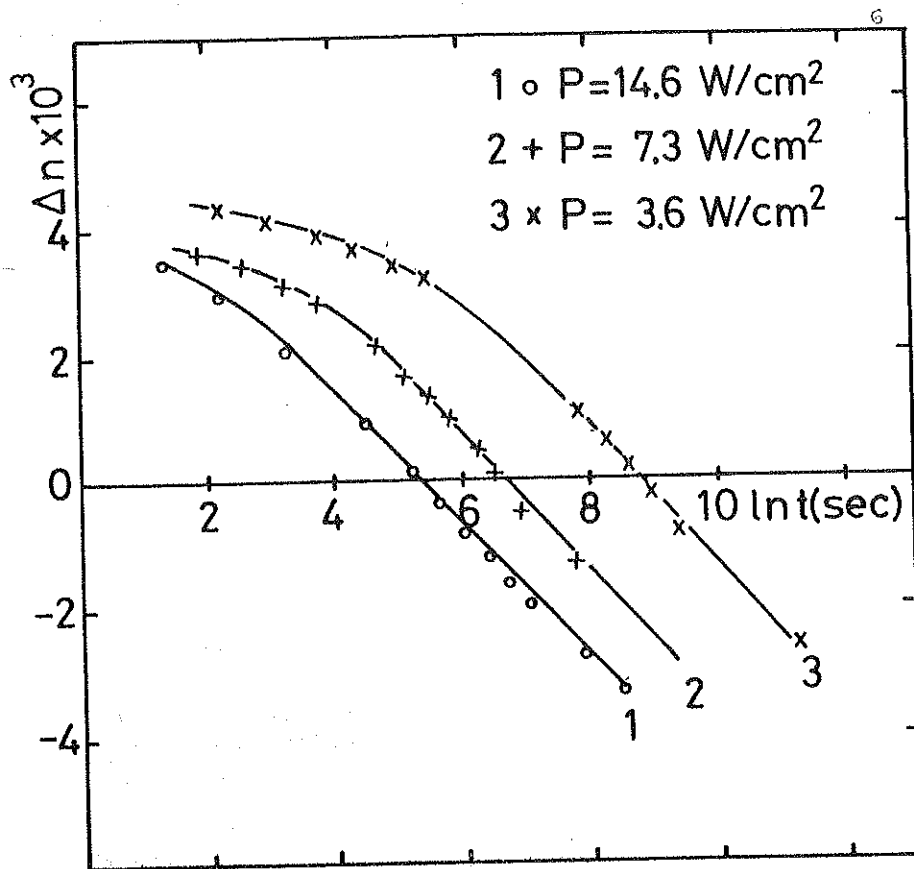
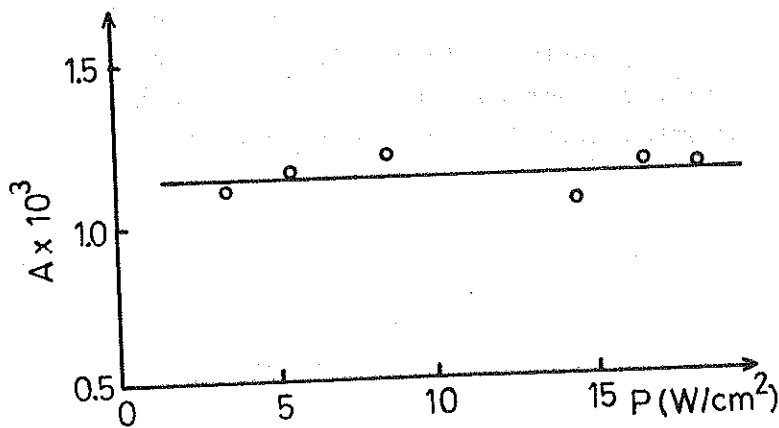_Fig. 6._ Kinetics of reorientation at different laser intensities

Fig. 7. The slope (A) as a function of laser intensity

primarly on the incident laser intensity. t_o can be written in the form

$$t_o \sim P^{-s} \tag{4}$$

where P is the laser power density and s gives the number of photons involved in an elementary process. Plotting ln t_o against the logarithm of laser power density P as seen in Fig. 8 the actual value of the slope s is between 2 and 3 indicating that two or more photon reactions play an important role during the reorientation process.
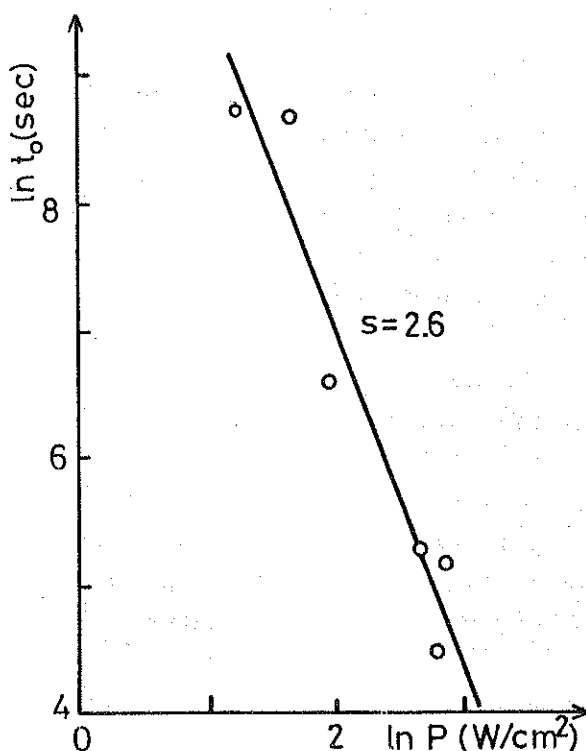

Fig. 8. ln t_o vr. ln P

4. THEORETICAL CONSIDERATIONS

4.1 Considerations about the nature of light induced anisotropy

Our experimental results showed that optical anisotropy can be induced by a polarised laser beam although the structure of $GeSe_2$ remained amorphous; no sign of microcrystallites was observed by simultaneous electron diffraction measurements (Hajtó et al. 1981). This fact indicates that the phenomenon of optical anisotropy is principally connected to the peculiar structure of the amorphous $GeSe_2$.

It was shown by Phillips et al. (1980) that the molecular structure of chalcogenide glasses is not an isotropic one on a scale of medium range (30-1000 atoms). There is evidence from X-ray and Raman data (Phillips 1981) that the amorphous $GeSe_2$ is built up of large, structurally anisotropic units, so called "outrigger rafts" polymerized along one direction. Without any applied external field the direction of polymerized rafts are distributed randomly on a macroscopic scale thus the sample is optically isotropic.

We propose a mechanism by which the plane polarised light can produce optical anisotropy on a macroscopical scale. This model is analogous to some extent to the model proposed by Zhdanov et al. (1979) for the light induced anisotropy in amorphous As-Se films.

It is assumed theoretically (Mott and Davis 1979) that light can create electron-hole pairs by bond excitation and during the electron-hole recombination an atomic displacement may occur in the amorphous system. As a consequence, a new atomic configuration might be established. We suggest that the "outrigger rafts" in $GeSe_2$ can continuously rearrange under the influence of laser irradiation in this manner. To understand the development of the optical anisotropy we assume that the cross section for producing an electron-hole pair depends strongly on the angle between the incident beam polarisation and the excited bond. Thus the stability of a given raft depends on its relative orientation with respect to the direction of incident beam polarisation. As a final result of the laser irradiation we obtain an amorphous structure in which there are more polymerized rafts oriented into the more stable direction (determined by the direction of the laser field, see Fig. 9). This could be the origin of the observed optical anisotropy.

At the present time it is not clear whether the rafts are oriented perpendicular to $\vec{E}$ (where $\vec{E}$ is the electric field of the light) as we assumed in Fig. 9, or oriented parallel to it. Polarised Raman spectroscopy experiments could help in solving this problem.

The whole process should not be necessarily a one photon reaction. Grigorovici and Vancu (1981) have shown the possibility of two photon reaction for the light induced polimerisation (photodarkening) in amorphous As-Se films. Our experimental results also suggest (see Sec. 3.2) that at least two photon reactions are involved in the displacement of an atom.
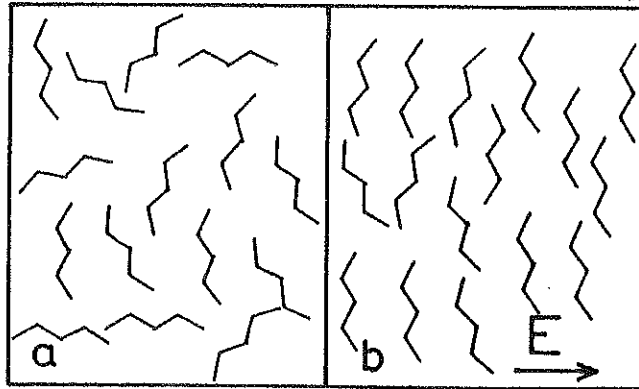
Fig. 9. *Polymerized rafts in the a-GeSe$_2$. a) as deposited state; b) laser oriented state*

4.2 Model for the light induced anisotropy

In the following we make more quantiative the considerations, given in the previous section.

Let us assume that in the amorphous network there are N sites per unit volume where atoms can displace as a result of laser irradiation. We suppose that in the environment of these sites there are two equilibrium atomic configurations. These configurations will be represented simply by a double well potential, whose two minima correspond to the two equilibrium positions of the atoms (Fig. 10). Such a double well potential model has been originally presented for the linear temperature dependence of the specific heat in an amorphous system (Anderson et al. 1971) and applied by Tanaka (1980) for the photostructural changes in chalcogenide glasses. Here we consider for simplicity symmetric wells.

The two equilibrium configurations correspond to two different contributions to the anisotropy of the refractive indices. We denote by index 1 the minima which correspond to a positive contribution to $\Delta n = n_x - n_y$ (see Fig. 10). The observed anisotropy according to this model is due to the fact, that the atoms are unequally distributed in the two minima. It may be assumed that Δn is proportional to $N_1 - N_2$ where N_1 and N_2 denote the number of atoms per unit volume in the 1-st and 2-nd minima resp. $(N_1 + N_2 = N)$.
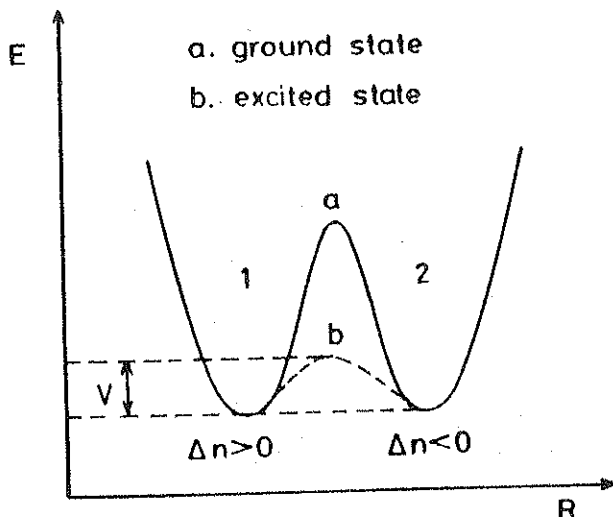
Fig. 10. *Double well potential applied to our model*

In the ground state the two wells are separated by a barrier whose height is large enough to prevent transitions between the two minima (no thermal relaxation was observed when the sample was kept in dark, see Sec. 3.1). We assume that the laser beam can replace atoms from one of the minima to the other one in the following way. First the light creates for example a metastable electron-hole pair; in this excited state the barrier height is reduced to V (see Fig. 10) and the displacement of the atoms becomes possible. The probability per unit time of the excitation can be written in the form $\gamma_1 f(P)$ and $\gamma_2 f(P)$ for the 1-st and 2-nd minima resp. P is the laser power density, γ_1 and γ_2 are chosen such, that $\gamma_1 + \gamma_2 = 1$. The difference, $\gamma_2 - \gamma_1$ reflects the fact that the polarised light beam excites the two configurations with different probabilities. The probability per unit time of a transition between the two minima in the excited state is connected to the barrier height V as $\frac{1}{\tau_o} e^{-V/kT}$ (Gilroy and Phillips 1981).

If the barrier height V and the other parameters involved were the same for all sites, the time development of $\Delta N = N_1 - N_2$ would be governed by the simple relaxation equation

$$\tau \frac{d\Delta N(t)}{dt} + \Delta N(t) = \Delta Neq \qquad (5)$$

with $\Delta Neq = (\gamma_2 - \gamma_1)N$, $\tau = \frac{\tau_o}{f(P)} e^{V/kT}$

the solution of which is

$$\Delta N(t) = \Delta N(0) + (\Delta Neq - \Delta N(0))(1 - e^{-t/\tau}) \qquad (6)$$

However as the effect takes place in an amorphous system it is reasonable to assume that V has a probability distribution (Anderson et al. 1971). Hence Eq.(6) should be replaced by

$$\Delta N(t) = \int \{\Delta c_o(V) + (\Delta c_{eq}(V) - \Delta c_o(V))(1-e^{-t/\tau(V)})\} \, dV \tag{7}$$

with $\Delta c_{eq} = c(V) \cdot (\gamma_2 - \gamma_1)$

Here $c(V)dV$ gives the number of sites per unit volume with barrier height between V and $V + dV$; $\Delta c_o(V)dV$ is the difference of the number of atoms in the 1-st and 2-nd minima in these sites at $t = 0$.

As the sites are not too different from each other, we may imagine that $c(V)$ has a rather sharp maximum at some V_o and its value is only significant between the energies V_1 and V_2. Let us take for $c(V)$ the simplest possible form which reflects this property:

$$c(V) = \begin{cases} \dfrac{N}{V_2-V_1} & \text{if} \quad V_1 < V < V_2 \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

In an as deposited film we have $\Delta c_o \equiv 0$. In this case, differentiating Eq.(7) with respect to t, performing the integral over V using the form of $c(V)$ given above, we get

$$\frac{d\Delta N}{dt} = \Delta N_{eq} \frac{kT}{V_2-V_1} \frac{e^{-t/\tau_2} - e^{-t/\tau_1}}{t} \tag{9}$$

with $\tau_1 = \tau(V_1)$ and $\tau_2 = \tau(V_2)$

The observed logarithmic time dependence of the birefringence can be explained by assuming that $V_2 - V_1 \gg kT$. In this case a long time interval exists where the inequalities

$$\tau_1 \ll t \ll \tau_2 \tag{10}$$

are satisfied. In this interval $e^{-t/\tau_1} \approx 0$, $e^{-t/\tau_2} \approx 1$, and the solution of Eq.(9) is

$$\Delta N(t) \approx \Delta N_{eq} \frac{kT}{V_2-V_1} \ln t + C \tag{11}$$

For the birefringence we have for this time interval

$$\Delta n(t) = -A \ln t/t_o \tag{12}$$

with $A = -g\Delta N_{eq} \frac{kT}{V_2-V_1}$, $\ln t_o = g \frac{C}{A}$

where g is the factor connecting ΔN and Δn.

The reorientation process can be treated similarly. In this case the initial condition can be written as $\Delta c_0 = -\Delta c_{eq}$ (provided that saturation has been reached by the irradiation with y-polarised light beam). By similar considerations as before we get

$$\Delta N(t) \approx 2\Delta N_{eq} \frac{kT}{V_2 - V_1} \ln t + C \quad \text{for } \tau_1 \ll t \ll \tau_2 \tag{13}$$

$\Delta n(t)$ has the same form as given in Eq.(12), but A is now

$$A = -2g\Delta N_{eq} \frac{kT}{V_2 - V_1} \tag{14}$$

Our model allows also to treat the influence of an unpolarised or circularly polarised light beam on an area where previously anisotropy had been induced. For unpolarised light beam $\gamma_1 = \gamma_2$. As it can be seen from Eq.(5), in this case ΔN decreases in time and its equilibrium value is 0. In other words the unpolarised light beam erases the anisotropy.

5. COMPARISON OF THE MODEL WITH THE EXPERIMENTS

The model presented in the previous section gives the following results.

a.) The saturation value of the induced birefringence should be independent of the intensity of the light beam. As mentioned, it was hard to determine precise saturation values in our experiments. Nevertheless we found that the increase of the birefringence (measured on a logarithmic time scale) slowed down at $\Delta n = 4-5 \times 10^{-3}$. This slowing down was observed at somewhat different values of Δn in different measurements, but no definite correlation was found between this value and the laser intensity. The uncertainty in the n values at the slowing down might be explained by the assumption that the number of sites per unit volume, N, varies within the sample.

b.) The model provides an explanation for the observed logarithmic time dependence (see Eqs.(11) and (12)). The conditions for this kind of dependence can be written as $\tau_1 \ll t \ll \tau_2$. We note that τ_1 and τ_2 can be estimated also from the experiments by regarding the deviations from the logarithmic dependence (see for example cure 3 in Fig. 6 and the curve in Fig. 4). This allows us to estimate the value of $V_2 - V_1$, i.e. the spread of the barrier height in the excited state. For this estimation see point e.) below.

c.) According to Eqs.(12) and (14) the slope A of $\Delta n(t)$, plotted on a logarithmic time scale, should be independent of the light intensity. The

experimental verification of this prediction for the reorientation process is given in Fig. 7.

d.) The comparison of Eq.(12) and Eq.(14) shows that the slope A should be twice as large for the reorientation process as for the orientation process in an as deposited area. This prediction is in a rather good agreement with the experimental results (see Figs 3 and 4). We emphasize that the kinetics presented in Figs 3 and 4 were measured subsequently on the same spot using the same laser intensity.

e.) The constant C, or equivalently t_o in Eq.(12) depend on the form of the function f(P). Assuming that $f(P) \sim P^s$ (s-photon reaction) the model predicts

$$t_o \sim P^{-s}$$

This relation was verified experimentally in Sec. 3.2, the actual value of s was found to be 2.6.

Using this form of f(P) we have

$$\tau_1 \sim P^{-s} e^{V_1/kT}, \qquad \tau_2 \sim P^{-s} e^{V_2/kT} \tag{15}$$

Estimating for example τ_1 from curve 3 in Fig. 5, τ_2 from Fig. 4, we get with the help of Eq.(15) that V_2-V_1 is in the order of magnitude of 0.1 eV.

f.) It is evident that anisotropy cannot be induced using unpolarised light. Our model predicts in addition that circularly polarised light should erase the previously induced anisotropy. This was found indeed in the experiments.

6. CONCLUSION

In the present paper we presented a comprehensive study of the light induced anisotropy in $GeSe_2$ films. As shown, both birefringence and dichroism is induced by linearly polarised laser beam. The direction of the principal axis is determined by the direction of the laser polarisation. By changing this latter direction, the previously induced anisotropic structure can be reoriented.

The development of the anisotropic structure can be explained by assuming that anisotropic units, which exist already before the laser irradia-

tion (the "outrigger rafts" in Phillips' model), become oriented under the influence of the polarised light beam. Our studies showed clearly that this orientation process cannot consist of collective rotation of these units; it takes place through independent atomic events as a result of which the rafts rearrange. The rather unusual logarithmic time dependence of the orientation and reorientation processes can be explained by the plausible assumption that the heights of the barriers, hindering the atomic displacements have an energy distribution whose spread is much larger than kT.

We emphasize once more that these studies were carried out at relatively low power densities (~ 10 W/cm^2). Studies at higher power densities, where strongly nonlinear optical phenomena occur are under way.

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