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Kinetics of optical reorientation in amorphous $GeSe_2$ films

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ABSTRACT

Reorientation cycles of photo-induced anisotropy in an amorphous chalcogenide film have been investigated. The kinetics of the reorientation process show a simple power-law time dependence on short time scale. A model based on bistable defect centres with widely distributed relaxation times is proposed. It is speculated that excitations from or to the band tails might be involved in the reorientation process. Finally the influence of circularly polarized light on the induced anisotropy is discussed. An interesting 'back-shoot' effect is shown which gives further support to the proposed wide distribution of relaxation times.

§1. INTRODUCTION

Photostructural changes in amorphous chalcogenide thin films have been studied extensively in the past (deNeufville 1975, Tanaka 1980, Frumar, Firth and Owen 1984, Elliott 1986). An interesting aspect of these photostructural changes is that illumination with polarized light generates an anisotropic structure. This phenomenon was reported for As_2S_3 (Zhdanov, Kolomiets, Lyubin and Malinovskii 1979, Lyubin and Tikhomirov 1989) and $GeSe_2$ films (Hajtó, Jánossy and Forgács 1982, Jánossy, Jákli and Hajtó 1984). Both dichroism and birefringence (i.e. anisotropy of the absorption coefficient and refractive index respectively) were found to develop in the sample under the influence of polarized radiation. It was established that the optical axes of the anisotropic structure are determined by the direction of polarization of the illuminating light. Reorientation of the structure is possible in any direction by a corresponding rotation of the polarization of the incoming beam. Irradiation by circularly polarized or unpolarized light results in a gradual disappearance of the anisotropy. These observations could be interpreted in terms of localized bistable defect centres (Hajtó *et al.* 1982, Kolobov, Kolomiets, Konstantinov and Lyubin 1981). The concept of bistable defect centres is based on the assumption that certain atomic arrangements exist in the material which have two stable configurations. This idea is well supported by the strong electron–lattice coupling and low coordination of the chalcogen atoms. The bistable feature is often visualized by a double-well potential diagram. Those defect centres which are responsible for the photo-induced effects have a potential barrier large enough to prevent thermal transitions between the stable configurations at room temperature. However, following electronic excitation of the centres by light, the transitions become possible.

Hajtó *et al.* (1982) investigated the kinetics of the formation and reorientation of the anisotropic structure in detail. The experimental data indicated a wide distribution of relaxation times. In particular for large irradiation times, the birefringence changed proportionally to the logarithm of the irradiation time. This observation was explained by assuming that the heights of the energy barriers separating the two equilibrium

configurations of the defect centres have a distribution over an energy range large compared with kT.

In the present paper, further studies are described in connection with the kinetics of the orientation process in amorphous $GeSe_2$ films. We investigated reorientation cycles, that is we exposed the film to a constant input power and switched the polarization periodically between two orthogonal directions. At the beginning of each reorientation cycle (i.e. immediately after switching the polarization) the birefringence varied according to a power of the time. We show that this time dependence implies a power-law distribution for the relaxation times in the limit of short times. In terms of energy barriers, this behaviour corresponds to an exponential distribution of the barrier heights. The width of the energy barrier distribution turned out to be close to the width of the density-of-states distribution for the tail states in the mobility gap. It is suggested therefore that the light-induced transition of a defect centre from one of its configurations to the other involves the excitation of an electron from the tail states into the conduction band (or a similar transition for a hole).

We also carried out experiments with circularly polarized light, which provided additional evidence of the wide distribution of relaxation times. As was shown earlier by Hajtó *et al.* (1982), at a certain stage of the reorientation cycle the structure becomes macroscopically isotropic. With the help of circularly polarized radiation, we demonstrated that this isotropy is a result of the balance between fast-switching centres (which are already reoriented) and slowly reacting defect centres which remained still in their initial state. On the other hand, in the isotropic state induced by prolonged irradiation with circular polarization, both 'fast' and 'slow' defects show isotropic distributions in themselves.

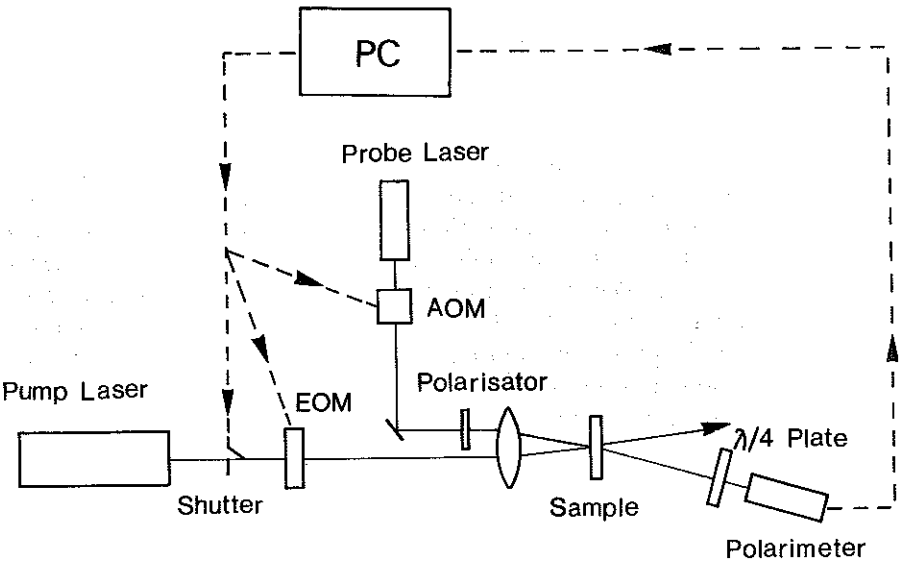
§2. Experimental details

In the experiments, vacuum-evaporated 7 μm thick a-$GeSe_2$ layers on glass substrates were studied. The experimental set-up is shown in fig. 1. A He–Ne laser, capable of 30 mW output power, was used to generate anisotropy in the sample (pump laser). The polarization state of the pump beam was controlled by an electro-optic modulator. Without any applied voltage on the modulator the polarization was vertical; on increasing the voltage the polarization became first circular and, at a higher voltage, horizontal.

The optical anisotropy was measured by a second low-power He–Ne laser (probe laser). The probe beam, polarized by 45° with respect to the vertical direction, was carefully adjusted to intersect the pump beam at the sample. The probe beam produced a significantly smaller spot than the pump beam; hence it was possible to probe the central part of the irradiated area. Thus complications arising from the transverse intensity distribution of the pump beam were avoided.

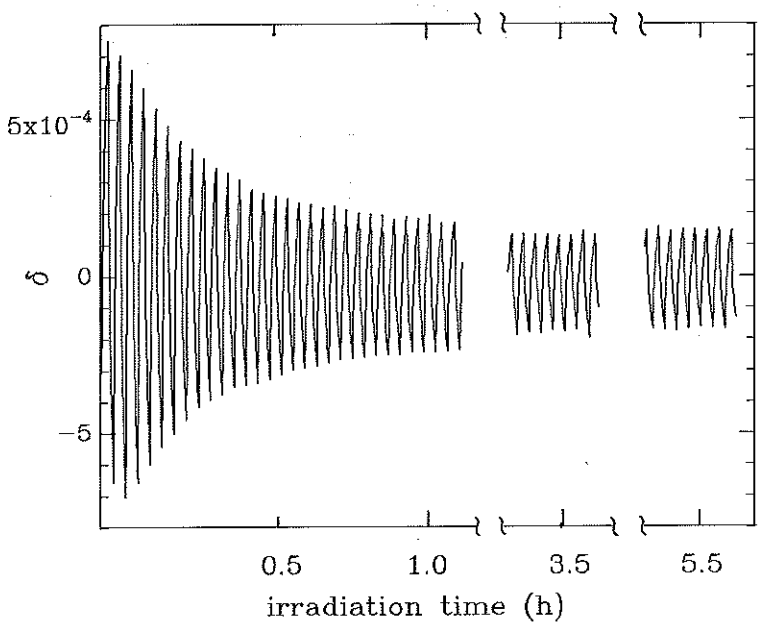
The birefringence was determined with the help of a $\lambda/4$ plate and a polarimeter as described by Hajtó *et al.* (1982). Data were taken at regular time intervals (typically 1 s); a measurement took approximately 20 ms. In order to minimize the effect of the probe beam on the induced anisotropy, an acousto-optic modulator allowed the probe beam to pass through the sample only during the measurements. In some cases (especially in the vicinity of the turning points of the reorientation cycles) the pump beam was blocked during the birefringence measurements. In this way firstly the part of the signal which originated from the scattering of the pump beam was eliminated and secondly it was possible to study the changes induced by short illumination times, comparable with the measuring time.

Fig. 1



Experimental set-up for measuring light-induced optical anisotropy: AOM, acousto-optical modulator; EOM, electro-optical modulator. The data acquisition and the control of the light beams were performed by a PC-XT computer.

Fig. 2



Time dependence of the amplitude of reorientation cycles. The sample is an a-$GeSe_2$ film 7 μm thick, (incident laser intensity, 120 W cm^{-2}). During the first 1–2 h the amplitude decreases drastically but afterwards it remains constant even during many hours of prolonged irradiation.

The set-up described above made it possible to detect changes of about 10^{-4} rad in the optical phase difference between the horizontal and vertical components of the probe beam. For films 7 μm thick this corresponds to a birefringence of $\Delta n \approx 10^{-5}$.

§ 3. Study of reorientation cycles

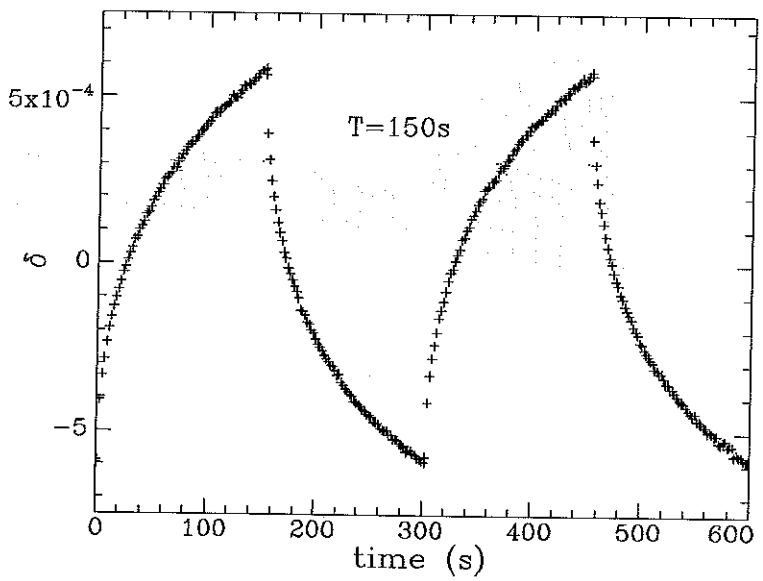
As described earlier, reorientation cycles were generated by illuminating the sample with alternating vertical and horizontal polarizations, keeping the input power constant (typically 7–8 mW, focused to a spot radius of 50 μm). In fig. 2 the variation in the birefringence is shown as a function of the illumination time for an *as-deposited* film. After an initial period, in which the amplitude of the birefringence curve decreased, a steady state was reached. The initial period is connected to light-induced irreversible processes occurring in virgin films (Rajogopalan, Hashavardhan, Malhotra and Chopra 1982). The details of this transient part of the curves were sensitive to the preparation conditions and age of the films and even within one sample it varied from one place to another. On the other hand, the stabilization of the birefringence cycles occurred systematically. Apart from the first period, no change in the amplitude could be detected even after several hours of irradiation that included a few hundred reorientation cycles.

In fig. 3 (*a*), two successive cycles are shown; in fig. 3 (*b*) the data of a half-cycle are presented on log–log and log–linear scales. The curve on the log–linear scale shows a logarithmic time dependence of the signal for large t values, in accordance with the result of Hajtó *et al.* (1982). The curve on a log–log scale indicates that at the beginning of the cycle the birefringence δ varies according to a power law

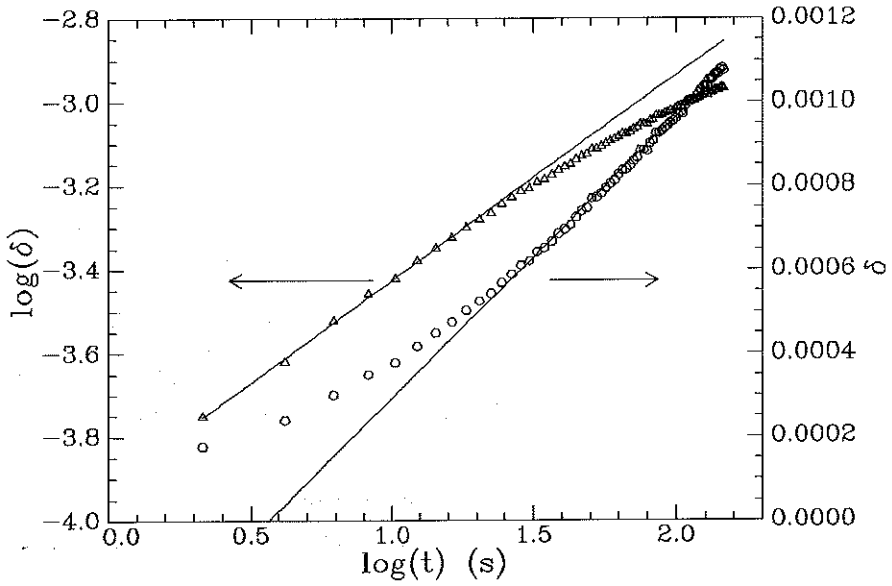
$$\delta(t') = \delta(0) - At'^{r}. \tag{1}$$

Here t' denotes the time counted from the turning point of the curve. For the curve displayed in the figure, r equals 0·46; in different measurements carried out on different

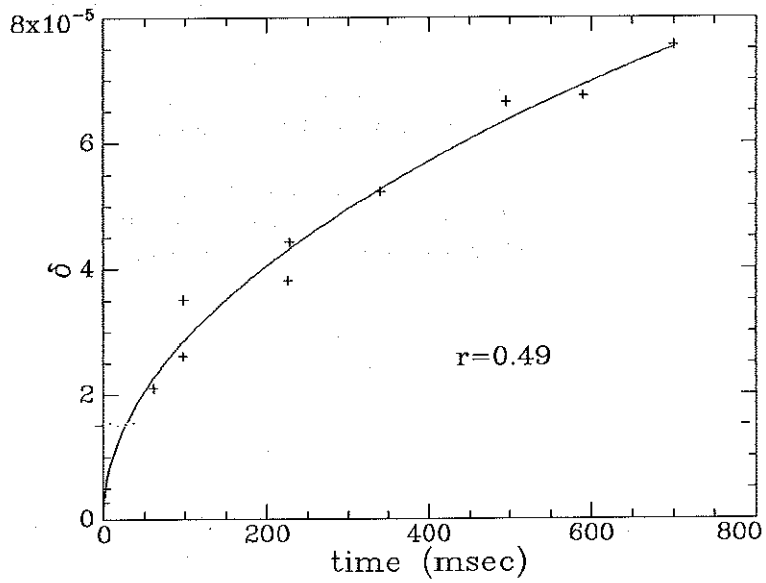
Fig. 3



(*a*)



(*b*)



(*c*)

(*a*) Time dependence of birefringence during reorientation cycles. $T = 150$ s. (*b*) Reorientation of anisotropy with horizontal polarization (first quarter of (*a*)). On a log–linear scale the data show a linear dependence for large t, while on a log–log scale the linear dependence appears for small t. (*c*) Kinetics of reorientation for $t < 1$ s: (——), a power-law fit of the data with an exponent $r = 0{\cdot}49$.

areas of the sample it varied between 0·43 and 0·52. For small values of t' (<1 s) the birefringence change $\delta(t')-\delta(0)$ was measured with the help of the shutter, as described in the previous section. The result is shown in fig. 3 (*c*). The solid curve is a power-law fit to the data. The exponent is 0·49, close to the value obtained for irradiation times one order of magnitude larger. Hence a simple power law fits the experimental data over a wide range of illumination times.

We interpret the above result in the framework of the model presented by Hajtó *et al.* (1982). According to this model, photo-induced anisotropy is a result of the light-induced transformation of certain localized atomic arrangements. It is supposed that each centre has two configurations, namely A and B. These configurations are anisotropic; hence the probability of their excitation depends on the polarization direction of the exciting radiation. We denote by $\gamma+\Delta\gamma$ the probability per unit time of the $A\rightarrow B$ transition and by $\gamma-\Delta\gamma$ that of the reverse transition. For simplicity we suppose that

$$\Delta\gamma=\begin{cases}\varepsilon, & \\ -\varepsilon, & \text{for} \\ 0, & \end{cases}\begin{cases}\text{vertical polarization,}\\ \text{horizontal polarization,}\\ \text{circular polarization.}\end{cases} \tag{2}$$

Following the model of Hajtó *et al.* (1982) we can assume that γ has a distribution; since the effect takes place in an amorphous system where the defect centres are similar to but not identical with each other, this is a reasonable assumption. A further assumption is that, despite the small difference in the structure of different defect centres, their contribution to the birefringence depends only on the difference between the population of the two stable states. On the other hand a small change in the structure of the defect centre results in a significant change in the characteristic transition probability.

First we derive a formula for defect centres with relaxation time between τ and $\tau+\mathrm{d}\tau$. The relaxation time τ is defined as $\tau=1/\gamma$. The number of these centres is $\rho\,\mathrm{d}\tau$.

The distribution of the actual configurations in the A and B states is governed by the rate equations

$$\begin{aligned}\frac{\mathrm{d}\rho_A}{\mathrm{d}t}&=-(\gamma+\Delta\gamma)\rho_A+(\gamma-\Delta\gamma)\rho_B,\\ \frac{\mathrm{d}\rho_B}{\mathrm{d}t}&=(\gamma+\Delta\gamma)\rho_A-(\gamma-\Delta\gamma)\rho_B.\end{aligned} \tag{3}$$

Here ρ_A and ρ_B are the number of centres with relaxation time τ, in the A and B configurations respectively.

Taking into account that the number of sites does not change during the reorientation cycle, one obtains

$$\frac{\mathrm{d}\Delta\rho}{\mathrm{d}t}=\frac{\Delta\rho_{eq}-\Delta\rho}{\tau}, \tag{4}$$

with $\Delta\rho_{eq}=\rho\Delta\gamma/\gamma$ and $\Delta\rho=\rho_A-\rho_B$.

In the experiment the films were exposed to a constant input power; the polarization was switched from horizontal to vertical at $T, 3T, 5T, \ldots$ and from vertical

to horizontal at $2T, 4T, \ldots$. After a certain number of cycles, the response becomes periodic; hence

$$\Delta\rho(t)=\Delta\rho(t-2T).$$

Applying the above condition for $t=lT$ and $t=(l+1)T$ (l integer) yields

$$\Delta\rho(t')=\Delta\rho_{eq}\left(\frac{2\exp(-t'/\tau)}{1+\exp(-T/\tau)}-1\right), \tag{5}$$

where t' is the time elapsed from the last switching (either from horizontal to vertical or inversely).

The measured birefringence signal is the sum of the contributions of defect centres with different τ. The time variance of the birefringence can be written in the following form:

$$\delta(t')-\delta(0)=-B\int_0^\infty 2\Delta\rho_{eq}(\tau)\frac{1-\exp(-t'/\tau)}{1+\exp(-T/\tau)}\mathrm{d}\tau, \tag{6}$$

with

$$\delta(0)=B\int_0^\infty \Delta\rho_{eq}(\tau)\frac{1-\exp(-T/\tau)}{1+\exp(-T/\tau)}\mathrm{d}\tau.$$

The observed power-law time dependence of the birefringence for small t' values suggests that the density of number of sites follows also a power law, at least in the limit of small relaxation times. To obtain an exponent r in the time dependence of $\delta(t')-\delta(0)$ (see eqn. (1)), it has to be assumed that

$$\rho(\tau)=C\tau^{r-1}. \tag{7}$$

Inserting this form of $\rho(\tau)$ into eqn. (6), the integral can be evaluated for $t'/T<1$ as

$$\delta(t')-\delta(0)\propto t'^r\left[1+a_1\left(\frac{t'}{T}\right)^{1-r}+a_2\left(\frac{t'}{T}\right)^{2-r}+\ldots\right]. \tag{8}$$

$a_1, a_2, \ldots$ are constants depending only on the value of r. The above expression converges if $0<r<1$. In the limit $t'/T\ll 1$ it yields $\delta(t')-\delta(0)\propto t'^r$, as required.

In fig. 4, theoretical fits of reorientation half-cycles are presented, which are based on eqn. (8)). In the case of $T=150$ s, excellent agreement is found for the whole cycle (fig. 4 (*a*)) while, for $T=4000$ s, a deviation of the calculated curve from the measured curve is seen for large t' (fig. 4 (*b*)). The latter fact indicates that the form of the density, given in eqn. (7), is valid only for not too large τ values. In the limit of large relaxation times the distribution derived by Hajtó *et al.* (1982) may be more appropriate.

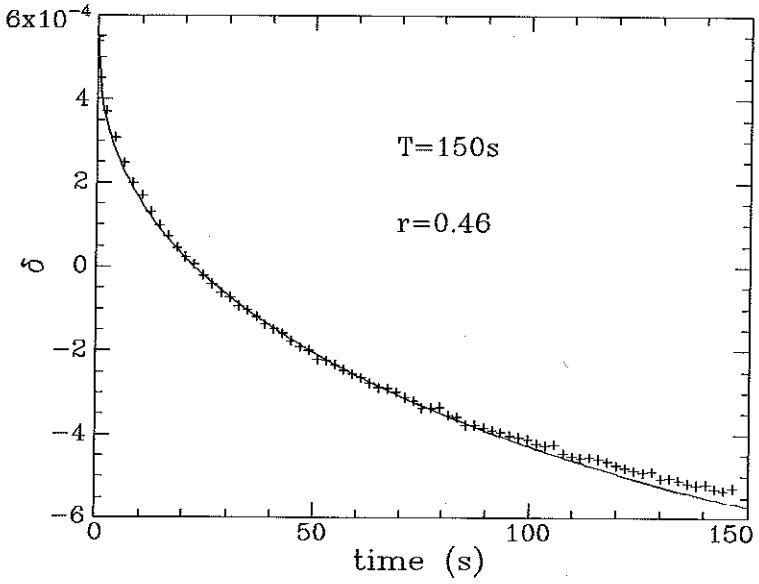
The distribution of relaxation times τ can be converted to a distribution of potential barriers assuming that

$$\tau=\tau_0\exp\left(\frac{U}{kT}\right). \tag{9}$$

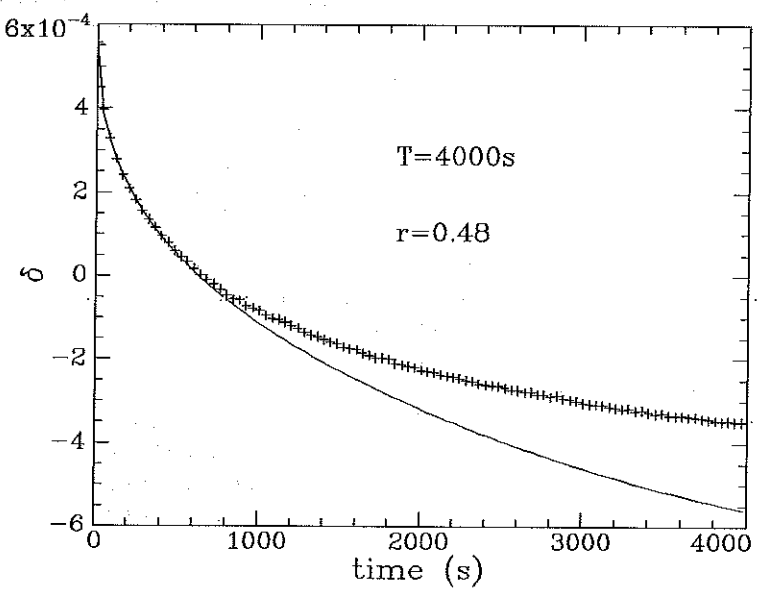
We denote by $g(U)\,\mathrm{d}U$ the number of sites with potential barrier between U and $\mathrm{d}U$ and use the relation

$$g(U)=\rho(\tau)\frac{\mathrm{d}\tau}{\mathrm{d}U}=\frac{\rho(\tau)\tau}{kT}.$$

Fig. 4



(*a*)



(*b*)

(*a*) Theoretical fit for the reorientation half-cycle with $T=150$ s. A slight deviation can be seen between the measured and calculated data for t larger than 100 s. (*b*) Theoretical fit for the reorientation half-cycle with $T=4000$ s. For large t a significant deviation is seen between the calculated and measured curves indicating that the $\rho(\tau)\propto\tau^q$ relation holds for short relaxation times only.

The specific form of $\rho(\tau)$ given in eqn. (7) leads to an exponential distribution of U:

$$g(U) \propto \tau^r \propto g_0 \exp\left(\frac{U}{kT^*}\right) \tag{10}$$

with $T^* = T/r$.

This distribution has similar form to what is normally supposed for the density of states in the mobility gap (near to the valence or conduction band) (Soukoulis and Cohen 1984, Cohen 1985). We note that this kind of distribution of the tail states is assumed for the explanation of the sublinear intensity dependence of the photocurrent in amorphous semiconductors (Rose 1963). A distribution of tail states

$$g_t(U) = g_{0,t} \exp\left(\frac{U}{kT_t^*}\right)$$

leads to a photocurrent proportional to I^σ, where I is the illumination intensity and $\sigma = 1/(1 + T/T_t^*)$. From preliminary measurements of the photocurrent in our sample, we found that $\sigma = 0{\cdot}7$. This value of σ gives $T/T_t^* = 0{\cdot}43$. On the other hand, the experimental value of $r = T/T^*$ is around 0·5. Hence the quantities T^* and T_t^* are close to each other. We speculate therefore that the reorientation of light-induced anisotropy involves excitations to or from the tail states. Because we use subbandgap illumination (photon energy, 1·96 eV; bandgap of a-$GeSe_2$, about 2·1 eV), the probability of such excitations contains an exponential factor similar to that in eqn. (9) (Kolobov *et al.* 1981). Of course, the experimental observations presented here are not sufficient to derive any detail of the underlying microscopic process.

§4. Birefringence induced by circularly polarized light

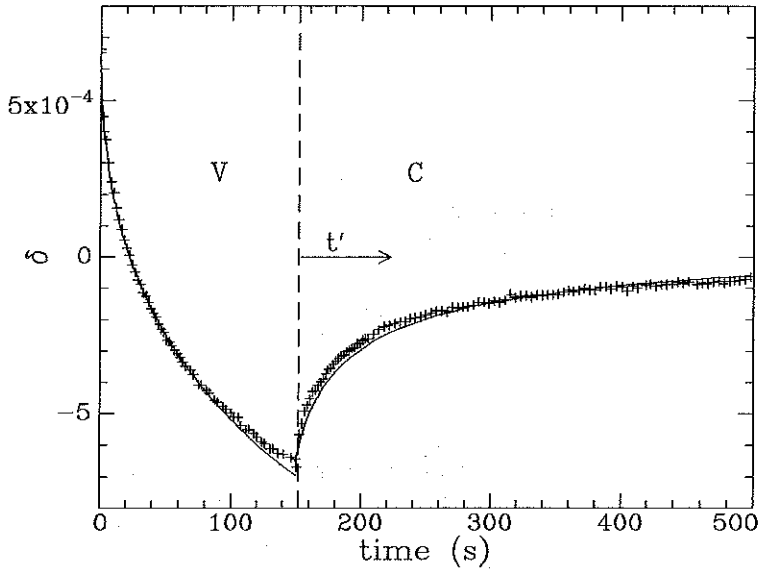
As was mentioned by Hajtó *et al.* (1982) and Lyubin and Tikhomirov (1989), light-induced anisotropy can be erased by illumination with circularly polarized light. This effect is illustrated in fig. 5 (*a*); at $t' = 0$ the polarization was switched from linear to circular and as a result the birefringence gradually disappeared.

In fig. 5 (*b*) we also show the influence of circularly polarized radiation on a spot at which the birefringence was erased by linearly polarized light. The reorientation cycle was interrupted at a moment when the birefringence was zero ($t' = t'_0$). At this stage the irradiated spot was optically isotropic; however, under the influence of further illumination with circular polarization it became birefringent again ('back-shoot' effect). After a certain increase (in the negative direction), the birefringence slowly disappeared. When the same procedure was executed in the other branch of the cycle, the birefringence first became positive and then approached zero from positive values.

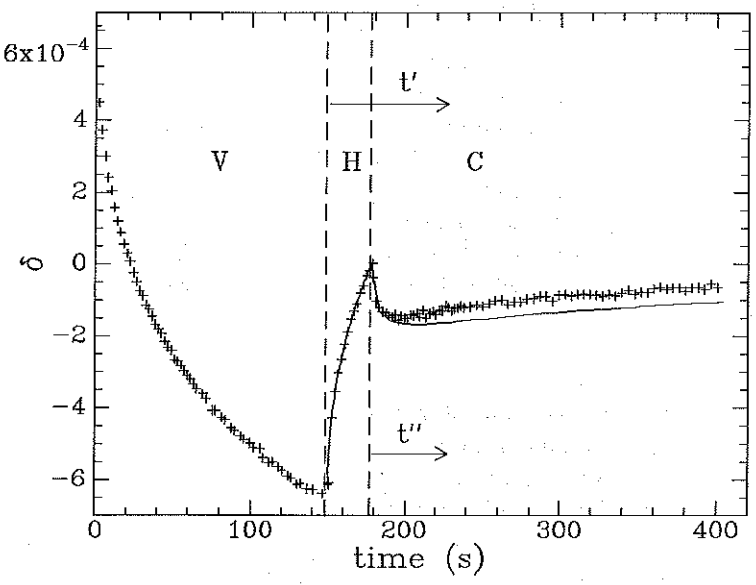
The above observation can be readily explained in terms of a wide distribution of the relaxation times. The zero birefringence, obtained during a reorientation cycle, indicates macroscopic isotropy. Microscopically, however, this isotropy is the resultant of the positive birefringence contribution, coming from the sites with low $\tau (\ll t'_0)$ and the negative contribution of the sites for which τ is much larger than t'_0. At $t' = t'_0$, for the 'fast' sites the distribution of A and B configurations is already in equilibrium with the radiation, while for the 'slow' sites the initial distribution has not yet been affected.

The equilibrium belonging to circularly polarized light is an even distribution of the sites in the states A and B. When the polarization is switched to circular, this equilibrium is first reached by the 'fast' sites. Therefore the balance between the fast and slow bistable centres is destroyed and a signal of birefringence appears. This signal originates from the 'slow' centres; hence its sign is negative, as observed experimentally.

Fig. 5



(*a*)



(*b*)

(*a*) Effect of circularly polarized light on anisotropic structure, (——), theoretical fit. At $t = 150$ s the polarization of the pump beam was switched from vertical to circular. The birefringence gradually disappeared. (*b*) Effect of circularly polarized light on the isotropic structure: (——), theoretical fit. At $t = 174$ s (when the structure became temporarily isotropic) the polarization of the pump beam was switched from horizontal (H) to circular (C). As a result, the birefringence reappeared ('back-shoot') and then slowly disappeared.

The slow decrease in the birefringence at large illumination times reflects the response of the centres with large τ.

The above consideration can be made quantitative with the help of our model. The rate equation for circularly polarized light (considering defect centres with relaxation time between τ and $\tau+\mathrm{d}\tau$ is

$$\frac{\mathrm{d}(\Delta\rho)}{\mathrm{d}t}=-\frac{\Delta\rho}{\tau}. \tag{11}$$

Hence

$$\Delta\rho(t'')=\Delta\rho_0\exp\left(-\frac{t''}{\tau}\right), \tag{12}$$

where t'' is the time counted from the moment of switching to circular polarization. $\Delta\rho_0$ denotes $\Delta\rho$ for $t''=0$.

Now the time evolution of the birefringence is

$$\delta(t'')\propto\int_0^\infty\Delta\rho_0(\tau)\exp\left(-\frac{t''}{\tau}\right)\mathrm{d}\tau. \tag{13}$$

In the case of switching to circular polarization at a turning point of the cycle we have

$$\Delta\rho_0(\tau)=\Delta\rho_{\mathrm{eq}}(\tau)\frac{1-\exp(-T/\tau)}{1+\exp(-T/\tau)}, \tag{14}$$

while the 'isotropic' point of the reorientation curve corresponds to the initial distribution

$$\Delta\rho_0(\tau)=\Delta\rho_{\mathrm{eq}}(\tau)\left(\frac{2\exp(-t_0'/\tau)}{1+\exp(-T/\tau)}-1\right). \tag{15}$$

In fig. 5, curves calculated for the two cases are presented, using the power-law distribution for $\rho(\tau)$. There is good quantitative agreement between theory and experiment, giving further support for the validity of the model presented.

§ 5. Conclusion

In this paper it has been demonstrated that the light-induced anisotropic structure in chalcogenide thin films can be reoriented several hundred times without any sign of a decrease in the effect. The kinetics of the reorientation process involve a wide distribution of relaxation times. We investigated here first of all the short-time response of the structure. It was found that the density of bistable centres with small relaxation times increases as τ^q; the experimental value of $q=r-1$ was around $-0{\cdot}5$.

The present experiments were carried out with relatively low pump intensity levels (about 100 W cm^2). Even so, the birefringence change generated by light illumination of 20 ms could be easily measured. Extrapolation of this result suggests that, with tight focusing ($r_0\approx1\,\mu$m) and using the same input power, a pulse duration of few microseconds should cause detectable changes in the anisotropy. A similar consideration shows that pulsed lasers capable of at least a millijoule per pulse could induce by a single pulse a birefringence signal well above the noise level. Further experiments in this direction are planned in the future.

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