

# Relaxation of a photoinduced anisotropy in chalcogenide glasses

V. K. Tikhomirov

*A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences,  
194021 St. Petersburg, Russia*

(Submitted 27 May 1993)

Pis'ma Zh. Eksp. Teor. Fiz. **57**, No. 12, 806–809 (25 June 1993)

The dark relaxation of the photoinduced anisotropy in chalcogenide glasses is described by a fractional-exponential Kohlrausch law  $\exp(-t/\tau)^\gamma$  over a wide time interval, except in the initial stage, in which the relaxation is described approximately by a Debye law  $\exp(-t/\tau_D)$ . The values of  $\gamma$  and  $\tau$  depend on the level of photoinduced anisotropy which was reached before the beginning of the relaxation in darkness. The nonexponential nature of the anisotropy relaxation is linked with a hierarchical limitation on the relaxation dynamics, caused by a hierarchy of anisotropic structural elements of the average order.

We have previously reported observing a photoinduced anisotropy in chalcogenide glasses of various chemical compositions. The effect is observed in bulk, film, and filamentary samples (see Ref. 1 and the literature cited there). The effect can be summarized by saying that exposure to linearly polarized light for a sufficiently long time causes the samples to become anisotropic (they acquire a linear dichroism and a linear birefringence). The microscopic mechanism for this effect is of interest since the existence of a photoinduced anisotropy opens up some new structural possibilities for glasses. This effect may find applications in polarized optics, especially in the IR region, since chalcogenide glasses are transparent there. We have recently reported<sup>2</sup> observing a “natural” anisotropy in the glass  $\text{As}_2\text{S}_3\text{In}_{0.05}$ . This very low doping level erased the photoinduced anisotropy. Instead, freshly prepared monolithic samples of this glass exhibited very high values of the linear dichroism and the linear birefringence. When the samples were annealed at a temperature above the softening point  $T_g$ , these properties did not fade away; they in fact intensified.

Our purposes in the present study were to take an experimental look at the relaxation of the photoinduced anisotropy after the inducing light was turned off (i.e., in darkness) and to compare this effect with the stable, “natural” anisotropy in glasses with a low doping level.<sup>2</sup> The results show that the relaxation of the photoinduced anisotropy can be approximated over a broad time interval by a “fractional” exponential function  $\exp(-t/\tau)^\gamma$ , with a power  $\gamma$  and a relaxation constant  $\tau$  determined by the duration of the writing of the anisotropy. The nonexponential nature of the anisotropy relaxation is attributed to a hierarchical limitation on its dynamics due to the hierarchy of anisotropic structural elements of the average order, which have been detected by x-ray diffraction.

The anisotropy of the optical transmission was measured by the method described in Ref. 3. The solid line in Fig. 1a shows the typical kinetics of the increase in the

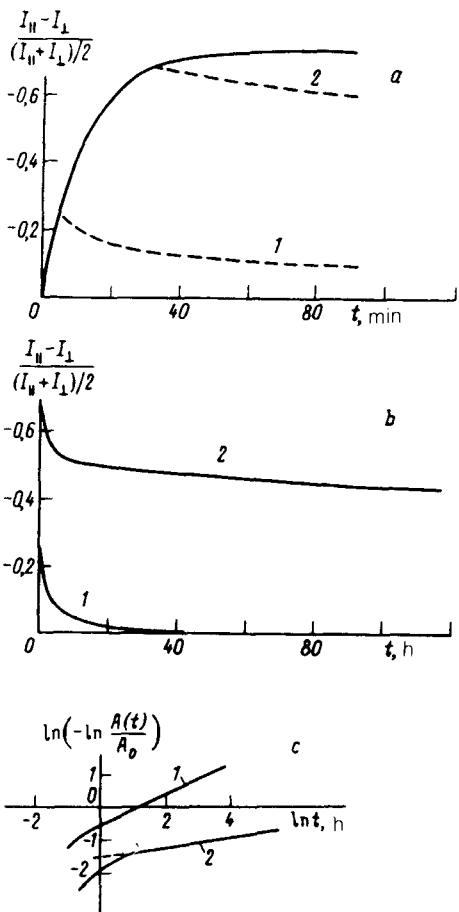


FIG. 1. Kinetics of the relaxation of the photoinduced dichroism in  $As_2S_3I_{0.8}$  samples 1 mm thick at the wavelength of a He-Ne laser ( $\lambda = 633$  nm). The anisotropy was written by a focused beam from a He-Ne laser 1 mm in diameter with a power density  $\sim 1$  W/cm<sup>2</sup>.

linear photoinduced dichroism, characterized by the quantity  $2(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ , where  $I_{\parallel, \perp}$  are the intensities of the trial light beams which were transmitted through the sample after entering it with electric vectors respectively parallel and perpendicular to the electric vector of the light beam which induced the anisotropy. Here we have  $2(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) = \beta h$ , where  $\beta = \alpha_{\perp} - \alpha_{\parallel}$  is the dichroism and  $h$  the thickness of the sample.<sup>1</sup> Curves 1 and 2 show the kinetics of the decrease (relaxation) of the dichroism after the inducing light is cut off (i.e., while the sample was in darkness). These typical curves differ from each other in that their recording started at different times after the beginning of the writing of the anisotropy. In other words, they correspond to relaxation starting from different absolute values of the dichroism. The measurements were taken at discrete times, rapidly enough (in  $\sim 2$  s) that the trial light beam did not reduce the dichroism during the measurement.

Figure 1b shows curves 1 and 2 from Fig. 1a again, in a different time scale. It is easy to see that the relaxation kinetics of the photoinduced anisotropy in darkness depends strongly on the absolute value of the dichroism which was reached before the measurements of the kinetics of the dark relaxation began (in other words, it depends strongly on the duration of the writing of the anisotropy). Quite obviously, the curves

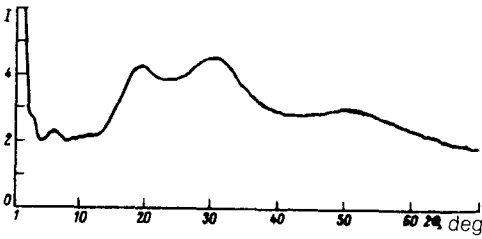


FIG. 2. Diffraction peaks in  $\text{As}_2\text{S}_3\text{I}_{0.8}$  samples recorded on a RIGAKU diffractometer with a high anode brightness. The  $\text{CuK}\alpha$  line ( $\lambda = 1.54 \text{ \AA}$ ) was used in reflection geometry.

in Fig. 1b cannot be approximated by a Debye relaxation law  $A(t) = A_0 \exp(-t/\tau_D)$ , where  $A_0$  and  $A(t)$  are the values of the dichroism before the beginning of the dark relaxation and at the time  $t$ . Let us assume that, in accordance with the ideas of Ref. 4, the relaxation can be described by a Kohlrausch law  $A(t) = A_0 \exp(-t/\tau)^\gamma$ , where  $0 < \gamma < 1$ , and  $\tau$  is a time scale. This law does indeed give a good description of the experimental curves; for curve 1 we have the values  $\gamma = 0.45$  and  $\tau \sim 3 \text{ h}$ , while for curve 2 we have  $\gamma = 0.20$  and  $\tau \sim 1 \text{ month}$ .

Figure 1c shows plots corresponding to curves 1 and 2 in Figs. 1a and b which we used to determine the values of  $\gamma$  and  $\tau$ , from the slopes of the straight lines and their ordinate intercepts. We see that the relaxation is described by a Kohlrausch law over the entire time interval studied. Exceptions to this statement are found at the very earliest times. In particular, for curve 2 the early relaxation law is approximately a Debye relaxation ( $\gamma \sim 1$ ) with a constant  $\tau_D \sim 5 \text{ min}$ .

Moving on to an interpretation of the relaxation curves, we consider the structure of  $\text{As}_2\text{S}_3\text{I}_{0.8}$  glasses. We need to look at the structure since the photoinduced anisotropy is accompanied by a photoinduced structural change in chalcogenide glasses, according to data on x-ray scattering and absorption (see Refs. 5 and 6 and the papers cited there). Figure 2 shows x-ray diffraction data. These results agree with results in the literature.<sup>7</sup> In particular, at  $2\theta = 19^\circ$  we see the "first sharp diffraction peak," which is linked with the existence of an average order in these glasses (see Refs. 8 and 9 and the papers cited there). The characteristic distance  $d$  corresponding to this peak, found from the Bragg condition  $2d \sin \theta = m\lambda$ , is  $4.7 \text{ \AA}$  for  $\text{As}_2\text{S}_3\text{I}_{0.8}$ . At  $2\theta = 11^\circ, 6.5^\circ$ , and  $3^\circ$  (intermediate-angle scattering) we see several diffuse peaks which have not been mentioned previously. The typical dimensions corresponding to them are on the order of 8, 14, and  $30 \text{ \AA}$ . Interestingly, we have  $30:14 \approx 14:8 \approx 8:4.7 \approx 2$  here; i.e., the larger dimension is roughly twice the smaller one. The average order in the glass  $\text{As}_2\text{S}_3\text{I}_{0.8}$  thus propagates to much larger scales than do those corresponding to the first sharp diffraction peak.

A fractional-exponential Kohlrausch law was interpreted in Ref. 4 as resulting from a hierarchical limitation on the dynamics of the glassy relaxation. We would suggest that the hierarchical limitation on the relaxation dynamics of the photoinduced anisotropy stems from a hierarchy of structural moments. Specifically, the structure of the smallest structural elements undergoes a relaxation in the early stages, and this process makes possible the relaxation of progressively larger structural elements. The simplest anisotropic structural element of the average order in the glass  $\text{As}_2\text{S}_3\text{I}_{0.8}$  is evidently a correlated pair of neighboring  $\text{AsS}_3$  or  $\text{AsS}_2\text{I}$  pyramids (Fig.

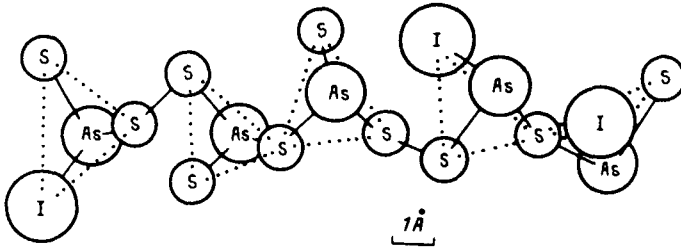


FIG. 3. Structural fragment of the glass  $\text{As}_2\text{S}_3\text{I}_{0.8}$  according to Ref. 7. The dotted lines are the bases of pyramids.

3), which correspond to the peak at  $2\theta = 19^\circ$  and to the value  $d = 4.7 \text{ \AA}$ . A larger structural element consists of two correlated neighboring pairs ( $2\theta = 11^\circ$  and  $d = 8 \text{ \AA}$ ); an even larger element consists of four neighboring pairs ( $2\theta = 6.5^\circ$  and  $d = 14 \text{ \AA}$ ); and so forth. The  $A_0$  dependence of  $\gamma$  and  $\tau$  stems from the different numbers of degrees of freedom which are involved in the formation of the anisotropy in the early stages of the process. In other words, it stems from a difference in the sizes of the structural elements which "have succeeded" in becoming oriented in the selected direction. The relaxation of the smallest structural elements is relatively independent (it ranks highest in the hierarchy) and is approximately a Debye relaxation.

The hierarchical limitation on the relaxation dynamics explains the absence of a relaxation of the "natural" anisotropy in the glass  $\text{As}_2\text{S}_3\text{In}_{0.05}$  (Ref. 2) (which might be called a "glassy crystal" by analogy with liquid crystals). The role played by the In atoms, which constitute  $\sim 1\%$  of the total number of atoms, is basically one of hindering the relaxation of the structural elements which undergo the fastest relaxation; if this relaxation does not occur, there can be no relaxation of the larger structural elements, which determine the macroscopic anisotropy of the glass.

In conclusion we might add that qualitatively the same results were found in a study of the undoped glass  $\text{As}_2\text{S}_3$  and other chalcogenide glasses. The differences were only quantitative: in particular, the value of  $\tau$  in film samples of  $\text{Sb}_2\text{S}_3$  and  $\text{Ge}_{28}\text{Pb}_{16}\text{S}_{56}$  can exceed 1 yr. The x-ray diffraction pattern (Fig. 2) was recorded by N. N. Faleev.

This work was supported by a grant from the Soros Fund awarded by the American Physical Society.

<sup>1)</sup>This relation holds strictly if the dichroism is not too large, i.e., under the condition  $\beta h < 1$  (Ref. 3).

<sup>1</sup>V. M. Lyubin and V. K. Tikhomirov, JETP Lett. **51**, 587 (1990); **52**, 78 (1990).

<sup>2</sup>T. F. Mazets, N. N. Smirnova, E. A. Smorgonskaya, and V. K. Tikhomirov, Pis'ma Zh. Tekh. Fiz. **18**(13), 46 (1992) [Sov. Tech. Phys. Lett. **18**, 419 (1992)]; T. F. Mazets, E. A. Smorgonskaya, V. K. Tikhomirov, and N. N. Faleev, Pis'ma Zh. Tekh. Fiz. **18**(22), 36 (1992) [Sov. Tech. Phys. Lett. **18**, 739 (1992)].

<sup>3</sup>V. K. Tikhomirov, Prib. Tekh. Eksp., No. 5, 201 (1990).

- <sup>4</sup>R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, *Phys. Rev. Lett.* **53**, 958 (1984).
- <sup>5</sup>M. A. Paesler and G. Pfeiffer, *J. Non-Cryst. Solids* **137 & 138**, 967 (1991); J. M. Lee, M. A. Paesler, D. E. Sayers, and A. Fontaine, *J. Non-Cryst. Solids* **123**, 295 (1990).
- <sup>6</sup>W. Zhou, D. E. Sayers, M. A. Paesler, and D. Raoux, *J. Non-Cryst. Solids* **137 & 138**, 127 (1991).
- <sup>7</sup>T. E. Hopkins, R. A. Pasternak, E. S. Gould, and J. R. Herndon, *J. Phys. Chem.* **66**, 733 (1962).
- <sup>8</sup>D. L. Price, S. C. Moss, R. Reijers *et al.*, *J. Phys.* **C21**, L1069 (1988).
- <sup>9</sup>S. R. Elliott, *Phys. Rev. Lett.* **67**, 711 (1991); *Nature* **354**, 445 (1991).

Translated by D. Parsons