Anomalous effect of weak magnetic fields on diamagnetic glassy semiconductors

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(Submitted 3 August 1984; resubmitted 17 December 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 2, 74–76 (25 January 1985)

A manyfold change in the viscosity of glassy selenium has been observed in weak alternating magnetic fields when the field frequency and the sample temperature satisfy a certain relationship.

The glassy chalcogenide semiconductors are diamagnetic and generally do not have a significant ($\gtrsim 10^{17}$ spins/cm^3) density of unpaired electrons, but this density does reach a significant level during low-temperature photoexcitation at the optical absorption edge. In an effort to explain this behavior, Anderson[1] hypothesized a negative correlation energy for the pairing of electrons with opposite spins; his suggestion was quickly followed by the appearance of corresponding models of defects,[2–4] diamagnetic in their ground state and paramagnetic in an excited state, which were used to interpret the various specific properties of glassy chalcogenide semiconductors: electrical, magnetic, and optical. Nevertheless, to the best of our knowledge, there has been no attempt to alter the properties of the semiconductor itself by applying a magnetic field to the defects (in those few studies of the effect of a magnetic field on the properties of glassy chalcogenide semiconductors which have been reported, the effects were weak, and the authors have declined to offer a definite theoretical interpretation). The probable reason is the "theoretical impossibility" of this effect: In a field ~ 1 kOe at room temperature, the field energy of a magnetic moment $\sim\mu_B$ is three or four orders of magnitude smaller than the thermal energy kT; i.e., the thermal motion should completely erase any strong effect of a field on a defect. However, reviewing the history of the effect of weak magnetic fields on the kinetics of chemical reactions, which has received a nontrivial theoretical explanation (see, e.g., Ref. 5), we began by consciously ignoring this "thermal rule" and carried out an experiment on the effect of a magnetic field on the viscosity of glassy selenium, a typical basic member of the group of glassy chalcogenide semiconductors. The viscosity was studied on the basis of the assumption that the switching of covalent bonds from some atoms to others in the

 0021-3640/85/020088-04$01.00

course of the viscous flow involved defects, which may be magnetically active. This experiment[6] revealed that a static magnetic field (or electric field) did indeed have an effect on the viscosity of glassy selenium, and the effect reached saturation in a very weak field, $H \lesssim 200$ Oe ($E \lesssim 500$ V/cm). The change in the viscosity was real but comparatively small: 20–30% in comparison with a measurement error up to 10%. In the present letter we describe a sharp intensification of the effect when we switched from a static to an alternating magnetic field.

The samples were made of commercial SVCh-2 selenium, 99.992% pure in terms of controllable impurities. The samples were cut in the form of cylinders 20 mm in diameter and 10 mm high. The ends of the cylinder, which were used for the measurements, were polished. The viscosity was determined by a standard method[1)] on the basis of the rate at which a cylindrical indenter was steadily forced into the sample, held at a constant $T \gtrsim 304$ K (the glass transition temperature or the temperature at which glassy selenium begins to soften). The brass indenter was 1 mm in diameter; the depth of the indentation ranged up to 1 mm. The temperature, measured with a chromel-alumel thermocouple, was held constant within 0.1 K during an experiment. It should be noted, however, that under the actual heat-transfer conditions in this system, which was open on the indenter side, the temperature at the point of indentation may have deviated from the temperature measured by the thermocouple. On the other hand, the deviation could not have exceeded 1 K (Fig. 1). Here is the sequence of steps during an experiment: The system was brought to a stable temperature (in 1–2 h), measurements were taken at this temperature in a field and without a field (each measurement and also the pause between measurements lasted several minutes), the temperature of the heating liquid was changed, a new, stable temperature was

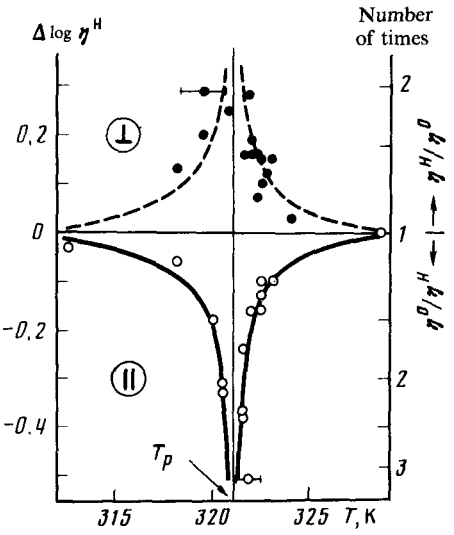

FIG. 1. Effect of a magnetic field with a strength of 240 Oe and a frequency of 50 Hz on the viscosity of glassy selenium as the sample temperature is varied. The dashed lines at the top are a mirror image of the lower lines. The accuracy with which the temperature was held constant is shown here; this accuracy was poorer in an apparatus with an electromagnetic field (a perpendicular field) than in an apparatus with a solenoid (parallel field).

achieved (30 min), measurements were taken, and the cycle was repeated. The field $H = 240$ Oe, of frequency $f = 50$ Hz, was directed either perpendicular ($\perp$) or parallel ($\parallel$) to the indentation direction. The magnitude of the effect was estimated from the difference between the logarithms of the viscosity:

$$\Delta \log \eta^H(T) = \log \eta^H(T) - \log \eta^0(T) = \log [\eta^H/\eta^0]_T ,$$

where η^0 is the viscosity in the absence of a field at the given temperature T, and η^H is the viscosity at the same temperature when a field is applied. It can be seen from Fig. 1 that the effect arises and intensifies sharply near a certain $T_p = 321$ K; the change in the viscosity reaches a factor of two or three. In this regard, the alternating magnetic field differs from a static field, for which (at a given field intensity) the effect is much weaker and essentially independent of the temperature.[6] A similar effect—an intensification of an effect when the field frequency and the sample temperature are related in a certain way (the field frequency was varied at a fixed temperature)—was observed in an alternating electric field in Ref. 7 and called a "viscosity resonance" there. Interestingly, the resonant frequencies f_r shift upward in this case as the temperature is raised. Identifying the electromagnetic nature of the effect will evidently require similar measurements in a magnetic field of variable frequency (such measurements have not yet been carried out).

This experimental result is unusual in that a very weak magnetic field not only can cause a change in a diamagnetic material but also, under certain (resonant) conditions, can change one of its macroscopic properties—its viscosity—by a factor of several units. In our opinion, these results imply that (1) the effect of the field is *not* a brute-force effect, (2) the field acts not on the host material but on deviations from the principal state (defects), and (3) the defects may determine the macroscopic properties of the material, in particular, the viscosity, thought of as a transport of atoms throughout the material which is mediated by defects. The field is apparently capable of determining the direction of such processes involving defects, as is implied by the anisotropy of the effect (Fig. 1). The unresolved question is the particular mechanism for the orienting effect of magnetic field on the defects in a system in which thermal motion would have a disordering effect.

Studies have recently appeared on the effect of weak, static magnetic fields on the electrical conductivity of a selenium melt[8] and of amorphous polyacetylene films.[9] Bilinov *et al.*[8] explained the effect in terms of a magnetization of selenium chains by the field. In order to lift the "thermal prohibition," however, the length of these chains would have to be at least 10^6 atoms, but such macromolecules do not exist in the low-molecular selenium melt. Frankevich *et al.*[9] offer an explanation on the basis of defects (solitons) and corresponding spin effects. This explanation seems more likely, but it could hardly apply in our case, since the behavior of the effect is different from that which we observed in selenium: the magnitude of the effect in Ref. 9 was one or two orders of magnitude lower than in our experiments, and the effect depended on the temperature, while in a static magnetic field we observe no well-defined temperature dependence.[6] The effect in selenium has thus not been given a satisfactory theoretical explanation, and the mechanism for the effect of a magnetic field on the electrical conductivity of polyacetylene[9] may be different from that in our case of the viscosity of

glassy selenium. The question is probably not so much one of studies of different properties as of a fundamental difference between the defects characteristic of organic polymers and those characteristic of glass-forming materials.[2-4]

We note in conclusion that we have also carried out experiments on melts of another glassy chalcogenide semiconductor, As_2S_3, in a static magnetic field $H = 240$ Oe. The results reveal a pronounced shift of the absorption edge toward longer wavelengths by the field. The effect of a magnetic field (and of an electric field) on the viscosity of glassy selenium which we have found is thus apparently a reflection of a more general effect of weak magnetic and electric fields on the properties of glasses. This effect holds promise both experimentally and theoretically. In order to prove this suggestion, we will of course need specific theoretical models and experimental tests. When such experiments are being planned, it should be borne in mind that the presence and magnitude of the effect depend on the specific conditions, such as the particular material, its history (including impurities), the particular property being studied, the sample temperature, and the strength and frequency of the field.

[1)]The viscosity of glass near and above the temperature at which glass is made can be measured from the rate at which a cylindrical indenter penetrates the glass. This measuring method was discussed in a review article by N. G. Nemilov [N. G. Nemilov, Fiz. i khim. stekla (Physics and Chemistry of Glass) **3**, 148 (1977)].

[1]P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[2]R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).
[3]M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).
[4]N. A. Popov, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 437 (1980) [JETP Lett. **31**, 409 (1980)].
[5]A. L. Buchachenko, R. Z. Sagdeev, and K. M. Salikhov, Magnitnye i spinovye effekt v khimicheskikh reaktsiyakh (Magnetic and Spin Effects in Chemical Reactions), Nauka, Novosibirsk, 1978.
[6]S. A. Dembovsky, S. A. Kozuykhin, E. A. Chechetkina, Mater. Res. Bull. **17**, 801 (1982).
[7]S. A. Dembovsky, E. A. Chechetkina, and S. A. Kozuykhin, Solid State Commun. **44**, 1561 (1982).
[8]L. N. Blinov, G. Yushka, K. Arlauskas, and M. S. Gutenev, Fiz. Khim. Stekla **9**, 748 (1983).
[9]E. L. Frankevich, I. A. Sokolik, D. I. Kadyrov, and A. M. Kobryanskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 401 (1982) [JETP Lett. **36**, 486 (1982)].

Translated by Dave Parsons
Edited by S. J. Amoretty