SOVIET PHYSICS JETP VOLUME 36, NUMBER 5 MAY, 1973

NATURE OF THE PHOTOPLASTIC EFFECT

Yu. A. OSIP'YAN and V. F. PETRENKO

Institute of Solid State Physics, USSR Academy of Sciences

Submitted April 7, 1972

Zh. Eksp. Teor. Fiz. **63**, 1735—1744 (November, 1972)

A physical model of the photoplastic effect (PPE) is proposed. The essence of the model is that when a II—VI single crystal is illuminated, the charged dislocations are slowed down by the photo-sensitizing centers which capture the photo-holes. Thermal and infrared quenching of the PPE and also the spectral dependence of the PPE can be described by the model. Results of calculation of photohardening based on the present PPE model are compared with results of an experimental investigation of photoplasticity and photoconductivity.

INTRODUCTION

A new phenomenon, called the photoplastic effect (PPE), was observed in 1967 in an investigation of the plastic deformation of cadmium sulfide. In the PPE, illumination of plastically-deformed cadmium sulfide by visible light produces a high degree of strengthening, and plastic flow continues only at increased stresses. The magnitude of the effect $\Delta\sigma_T/\sigma_T$ can reach 100%. When the light is turned off the strengthening vanishes. The effect can be observed many times in the same sample. The spectral dependence of the PPE has a maximum near the intrinsic absorption edge. The strengthening produced by the light decreases with increasing temperatures.

The existence of PPE was observed subsequently by many investigators in various single crystals of II—VI group[2-4]. This phenomenon is apparently quite general, and we propose that PPE should be observed in all crystals in which the temperature regions of the existence of plastic deformation and of photoconductivity intersect. The PPE is under study at present quite extensively both in the USSR and in other countries. We have recently observed infrared quenching of the PPE in cadmium sulfide[5], and also a dependence of the PPE on the crystallographic orientation of the planes in which the dislocations move[6].

In the present paper, on the basis of an analysis of all the known experimental data on the PPE, we propose for this effect a physical model that lends itself to calculation. The results of the calculations are then compared with results of a simultaneous investigation of the photoconductivity and photoplasticity of cadmium sulfide. It is shown that the calculation results are in good agreement with experiment.

1. PHYSICAL MODEL OF PPE

When a semiconductor is illuminated with light at the intrinsic absorption wavelength, a change takes place in the concentration of the electrons in the conduction band and of holes in the valence band, and also in the charge of the local centers that have captured non-equilibrium carriers. In addition, the non-equilibrium carriers (electrons or holes) can land on broken bonds that lie along the dislocation line, thus altering the charge of the latter. Therefore the possible mechanisms of hardening by illumination reduce to the following: 1) dynamic deceleration of the dislocations by the free photoelectrons, 2) dynamic deceleration of the dislocations by photoholes, 3) an increase of the deceleration of the dislocations by charged point centers or as a result of changes in the charge of the point centers following capture of photocarriers, or else as a result of an increase of the charge of the dislocation line following capture of photocarriers by the broken bonds.

As shown by investigations of the PPE in cadmium sulfide, the magnitude of the photostrengthening is approximately the same in single crystals with dark free-electron concentration from 10^{12} to 10^{18} cm^{-3}, where light adds not more than 10^{13} cm^{-3} of them to the conduction band. Therefore dislocation deceleration by photoelectrons seems not very likely to us. Dislocation deceleration by free photoholes is likewise of low probability, since the photoholes are captured in photosensitive cadmium-sulfide samples by the local centers almost instantaneously (within $10^{-9} = 10^{-8}$ sec)[7].

At the same time, we have a number of facts that confirm the mechanism of the onset of photostrengthening as a result of deceleration of charged dislocations by charged point centers. First, as shown earlier[8], in the wurtzite structure of the investigated CdS and ZnO, the dislocations lying in the (0001) basal plane and having a Burgers-vector edge component differ from all the remaining dislocations in the crystal in the presence of "single-color" broken bonds, i.e., the bonds are broken along the line of the given dislocation either at the Cd atoms (α dislocations) or at the S atoms (β dislocations). The acceptor or donor properties of such broken bonds can lead to the appearance of a charge along the dislocation line. Data on this subject were obtained in experimental studies of Ge[9], InSb[10], and CdS[11]. It turns out that the PPE is observed only when dislocations move in the basal plane and are not observed when the plastic deformation is due to motion of "mixed" dislocations in other slip planes[6,12]. It is thus logical to conclude that the illumination increases the deceleration of only the charged dislocations.

Second, if it is assumed that the dislocations are decelerated by point centers that have captured photoholes, then one should expect a decrease in the photostrength-

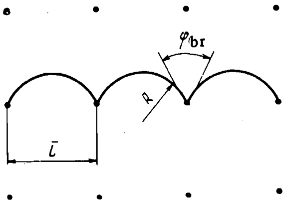

FIG. 1. Motion of dislocations through photo-obstacles.

ening following optical ionization of the holes from these centers. Such a loss of strength, upon additional illumination of the photostrengthened cadmium-sulfide sample with infrared light that transfers a hole from the local center to the valence band, was observed by us earlier[5]. The spectral dependence of the infrared quenching of the photoplastic effect was used to determine the energy position of the decelerating center (1.35 eV above the top of the valence band). This energy corresponds to the so-called photosensitization center, which has been thoroughly investigated in cadmium sulfide[13,14]. The question of the change of the charge of the dislocation line upon illumination, remains open.

Thus, an analysis of the experimental data leads us to the following mechanism of the PPE in cadmium sulfide: strengthening by illumination is due to the interaction of charge dislocations with sensitization centers that have captured photoholes. This model enables us to calculate numerically the crystal photostrengthening due to illumination, and also the dependence of the photostrengthening on the density of the photoelectrons or of the photocurrent.

2. MAGNITUDE OF THE PHOTOSTRENGTHENING

Assume that decelerating centers with density N_{ph} [cm^{-2}] are produced in each slip plane of the charged dislocations as a result of illuminating the crystal. We assume for simplicity that they are located at the points of a quadratic lattice. A dislocation breaks away from the center under the influence of the shear stress τ at a certain break-away angle φ_{br} (Fig. 1). The angle φ_{br} at which the dislocation breaks away from an obstacle characterizes the "force" of the "photo-obstacle." It can be calculated from an analysis of all the concrete mechanisms of the interaction of the dislocation with the sensitization center (Coulomb, elastic, piezoelectric, etc.). We hope to do so in the future. In the present paper, φ_{br} is regarded as a parameter that can be determined experimentally.

The shear stress τ at which the dislocations overcome the pinning centers is given by the formula

$$\tau=\frac{W}{Rb}=\frac{2W}{\bar{L}b}\cos\frac{\varphi_{br}}{2}=\frac{2W}{b}N_{ph}^{1/2}\cos\frac{\varphi_{br}}{2},\qquad(1)$$

where W is the energy per unit dislocation length, b is the Burgers vector, and $\bar{L}$ is the average distance between the pinning centers. Foreman and Makin[15], who considered instead of a quadratic lattice a random disposition of the obstacles, obtained in place of (1) the formula

$$\tau=a(\varphi_{br})N_{ph}^{1/2},\qquad(2)$$

$$a(\varphi_{br})=\frac{2W}{b}\frac{4\pi-\varphi_{br}}{5\pi}\cos^{3/2}\frac{\varphi_{br}}{2}.\qquad(3)$$

At small φ_{br}, the stress τ calculated from formula (2) differs little from the value of τ calculated from formula (1).

It is necessary to add to the flow stress τ_f of the crystal also the stress τ_0 of the dislocation motion in an ideal lattice and the internal-stress field τ_d due to the interaction of the dislocations. But since τ_0 and τ_d are also contained in the flow stress of the illuminated crystal τ_{fph} and in the yield limit τ_{fy} of the non-illuminated crystal, it follows that the value of the photostrengthening is

$$\Delta\tau_f=\tau_{fph}-\tau_{fy}\qquad(4)$$

and does not contain τ_0 or τ_d:

$$\Delta\tau_f=a(\varphi_{br})N_{ph}^{1/2}.\qquad(5)$$

Formula (5) does not take into account the strengthening due to point defects that retain their state upon illumination (conservative centers). One can therefore expect formula (5) to be valid only in those cases when the photostrengthening is much larger than the strengthening by the conservative centers.

We consider now another extreme case, when the photostrengthening is much less than the strengthening by the conservative centers. Let also the angle of break-away of the dislocation from the photo-obstacle not exceed the break-away angles from the conservative centers, i.e., let the photo-obstacle be no less an obstacle to the dislocation than the conservative centers. As will be shown in the experimental part of the paper, this requirement is reasonable. An increase in the density of the conservative obstacles N_c by a small number N_{ph} will lead to a decrease in the average distance between obstacles:

$$1/\bar{L}'\infty(N_c+N_{ph})^{1/2}.\qquad(6)$$

Consequently, the release of the dislocations from the conservative obstacles will occur at stresses

$$\tau\infty 1/\bar{L}'\infty(N_c+N_{ph})^{1/2}.\qquad(7)$$

At such stresses the dislocation begins to overcome the conservative centers, but remains pinned by the photo-obstacles. We consider the case when the strengthening due to the photo-obstacles without conservative centers is much less than the stress that breaks the dislocation from the conservative centers. Therefore, at a stress τ that moves the dislocation freely through the conservative centers, the necessary break-away angle φ_{br} will always be reached on the photo-obstacles. In other words, it suffices to break the dislocation away from all the weak centers to release it also from the strong centers, if the number of strong centers is very small. Then, the photostrengthening produced upon illumination is

$$\Delta\tau_f\infty\frac{1}{\bar{L}'}-\frac{1}{\bar{L}}\infty(N_c+N_{ph})^{1/2}-N_c^{1/2}\approx\frac{1}{2}\frac{N_{ph}}{N_c^{1/2}},\qquad(8)$$

i.e., for small values of the photoplastic effect we have

$$\Delta\tau_f\infty N_{ph}.\qquad(9)$$

For photosensitive cadmium-sulfide crystals we can derive a relation between the number of photoholes on the sensitization centers and the photocurrent I_{ph}. Figure 2 shows a simple model describing the photoconduc-

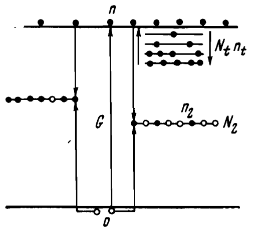

FIG. 2. Band model describing the photoconductivity in CdS.

tivity in cadmium sulfide[13]. Here n is the electron density in the conduction band, p is the hole density in the valence band, N_t is the concentration of the traps for the electrons, N_1 is the concentration of the fast-recombination centers, N_2 is the concentration of the slow-recombination centers, i.e., the sensitization centers (in our model, a sensitization center that has captured a photohole is an obstacle to the dislocation), and G is the rate of photogeneration of electron-hole pairs per unit volume. If the traps are in thermal equilibrium with the conduction band, then

$$n_t = Kn, \tag{10}$$

where K is a coefficient that depends on the temperature and on the distribution of the traps over the band. Assuming that in darkness the centers N_1 and N_2 are filled with electrons, we write down the electron neutrality equation

$$n = p + N_1 - n_1 + N_2 - n_2 + N_t - n_t. \tag{10$'$}$$

For photosensitive cadmium sulfide we can neglect in (8) the value of p, since the lifetime of the free photoholes is very small (~ 10^{-8} sec), as well as the quantity $(N_1 - N_1)$, i.e., the hole density on the fast-recombination centers, since almost all the holes are captured by the slow-recombination centers. Taking into account (10) and the fact that $N_{ph} = d(N_2 - N_2)$, where d is the distance between the slip planes, we obtain

$$n_{ph} = \frac{N_{ph}/d + N_t}{1+K} - \frac{N_t}{1+K} = \frac{N_{ph}}{(1+K)d}, \tag{11}$$

where n_{ph} is the photoelectron density in the conduction band.

Neglecting the change of the mobility μ upon illumination, we have[7]

$$n_{ph} = \frac{I_{ph}L^2}{\mu Vve}, \tag{11$'$}$$

where L is the length of the sample, v is its volume, and V is the applied voltage. Comparing (11) with (11′), we get

$$N_{ph} = \frac{I_{ph}dL^2(K+1)}{\mu Vve}. \tag{12}$$

Substituting (12) in (5), we obtain the dependence of the photo-strengthening Δ_f on the photocurrent I_{ph}, which can be easily measured experimentally.

It is impossible to derive a universal equation for the photostrengthening as a function of the intensity of the incident light, since the dependence of I_{ph} on the light intensity is different for each concrete sample, is connected with a large number of parameters, and has as a rule a complicated form. Nonetheless, the dependence of the photostrengthening on the intensity can be predicted for a concrete sample by first measuring the dependence of I_{ph} on the light intensity and employing formulas (5) and (12). Substituting (12) in (5) and (9) we obtain for the case of weak photostrengthening

$$\Delta\tau_f \propto I_{ph}, \tag{13}$$

For the case of strong photostrengthening

$$\Delta\tau_f = a(\varphi_{br})\left[\frac{I_{ph}dL^2(K+1)}{\mu Vve}\right]^{1/2} \propto I_{ph}^{1/2}. \tag{14}$$

These relations can be easily verified experimentally.

The proposed physical model enables us to predict the qualitative plot of the PPE as a function of the degree of deformation and temperature. With increasing degree of deformation, the density of the conservative obstacles in the slip planes of the charged dislocations increases ("scaffold" dislocations, point defects that multiply when the dislocations intersect, etc.). Against the background of the continuously increasing number of such obstacles, the influence of the photoobstacles on the motion of dislocations will be less and less noticeable, i.e., the PPE will decrease with increasing degree of deformation.

The dependence of the PPE on the temperature within the framework of our model is determined by two factors: by the change of the density of the photo-obstacles N_{ph} and by the change of the conditions under which the dislocations overcome the photo-obstacles with increasing temperature. With increasing temperature, the rate of thermal ionization of the holes from the sensitization centers N_2 will increase. This will lead, first, to a thermal quenching of the photoconductivity[13], and second to a decrease of the PPE as a result of a decrease of N_{ph} (formulas (5) and (9)). But the PPE will decrease also because the dislocations will find it easier to overcome the photo-obstacles with increasing temperature. The latter can cause the thermal quenching of the PPE to be observed at lower temperatures than the thermal quenching of the photoconductivity.

3. EXPERIMENT

The purpose of the experimental part of the paper was an attempt to verify the model described above. To this end, parallel investigations of the PPE, the photoconductivity, and the Hall effect were performed on the same samples. From the results of the latter measurements for each sample, regardless of the PPE, we determined the electronic parameters N_{ph} and μ which enter the formulas for the photostrengthening. The quantities calculated from these formulas were then compared with those determined from the PPE experiments.

A. Procedure. The measurements were performed on hexagonal single crystals of cadmium sulfide grown from the gas phase and from the melt. The dark concentration of the conduction electrons ranged from 10^{12} to 10^{18} cm^{-3} for the different samples. The samples were rectangular parallelepipeds measuring 6 × 3.5 × 3 mm. The large face (6 × 3.5) was a plane of the second kind $(1\bar{2}10)$. The hexagonal axis made an angle of 45° with the longitudinal axis of the samples. The samples were subjected to uniaxial plastic compression along the longitudinal axis at a constant rate that ranged from 5 to 50 μ/min. The deformation temperature ranged from 20 to 300°C. To excite the PPE, the sample was illuminated during the stage of plastic flow with monochromatic light through a special window in the heat-treatment chamber. The source of light was a DKSSh-1000M xenon lamp, the light from which, passing through a SPM-2 prism monochromator, was focused on the sample.

The photocurrents were measured by an identical optical system. For the cadmium sulfide samples we used indium contacts with controllable resistance. The photocurrent was measured by a null method, with the sample connected in one arm of a balanced bridge. The photocurrent signal produced when the bridge became unbalanced was fed to an automatic recorder. The Hall measurements were performed with a standard ZhK 78-07 setup. The photocurrent and the Hall measurements were performed before and after the photoplastic measurements, so as to take into account the influence of the plastic deformation on the electron parameters of the sample.

B. Results. The flow limit of the investigated cadmium-sulfide samples as a function of the degree of doping and heat treatment ranged from 1.5 to 4.5 kg/mm^2. The minimal flow limit 1.5 kg/mm^2 was observed in undoped well-annealed samples. The photostrengthening observed experimentally in these samples was compared with that calculated by formula (14). The volume concentration of the photoobstacles, calculated from measurements of the Hall effect and of the photocurrent, was approximately 5×10^{14} cm^{-3}. Good agreement between the observed PPE and formula (14) was obtained by assuming $\cos \varphi_{br} \approx 1$, i.e., by assuming that the angles of break-away of the dislocations from the photoobstacles are small.

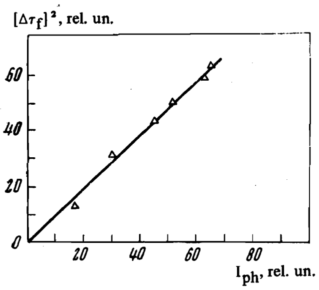

FIG. 3

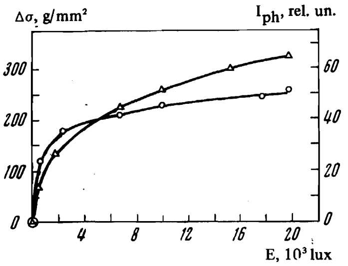

FIG. 4

FIG. 3. Square of the PPE $(\Delta\tau_f)^2$ vs the photocurrent at 100°C, λ = 5600Å, σ_f = 1.5 kg/mm^2.

FIG. 4. Plots of the PPE $\Delta\sigma$ (○) and I_{ph} (△) vs sample illumination at T = 100°C and λ = 5600Å.

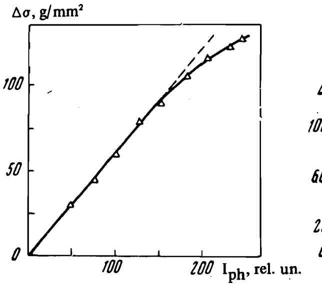

FIG. 5

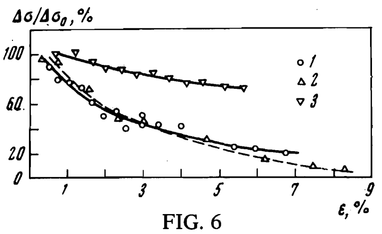

FIG. 6

FIG. 5. Photostrengthening against the photocurrent at T = 100°C, λ = 5600Å, and σ_f = 4.5 kg/mm^2.

FIG. 6. Photostrengthening against the degree of deformation: ○—σ_0 = 2.4, △—σ_0 = 1.5, ▽—σ_0 = 4 kg/mm^2. $\Delta\sigma_0$ is the initial value of the photostrengthening at ϵ_n = 0; T = 150°C.

For the same samples, we verified the relation $\Delta\tau_f \propto I_{ph}^{1/2}$. As seen from Fig. 3, the PPE in these samples satisfies well the relation $\Delta\tau_f \propto I_{ph}^{1/2}$. Figure 4 shows typical plots of the PPE ($\Delta\sigma$) and of the photocurrent I_{ph} against the sample illumination. It turned out that the relation $\Delta\sigma \propto I_{ph}$ (formula (13)) is observed at low values of the PPE ($\Delta\tau_f \leq$ 40–70 g/mm^2) in samples with large flow limits ~ 4.5 kg/mm^2 (Fig. 5). As seen from Fig. 5, a deviation from linearity is observed when the PPE is increased.

Thus, as follows from the model described above, the relation $\Delta\tau_f \propto I_{ph}^{1/2}$ is observed in crystals with a low dark flow limit, and the relation $\Delta\tau_f \propto I_{ph}$ is observed in crystals with a high flow limit for small values of the PPE. In addition, in crystals with τ_f, the absolute value of the photostrengthening is well described by the mechanism whereby the dislocations overcome the photoobstacles, if it is assumed that $\cos \varphi_{br} \approx 1$.

Figure 6 shows the dependence of the photostrengthening on the degree of deformation. For all samples we observed a decrease of the photostrengthening with increasing degree of deformation, and at $\epsilon_n > 15\%$ the PPE vanished almost completely, although the photocurrent changed by not more than 20%. As already mentioned above, the decrease of the PPE with increasing deformation can be attributed to an increase in the concentration of such opticals as point defects, "scaffold" dislocations, etc., against the background of which the photo-obstacles become less and less noticeable.

The temperature dependences of the photoplastic effect and of the photoconductivity are shown in Fig. 7 for two cadmium-sulfide samples. The thermal quenching of the photoconductivity is observed at T = 330°C, whereas the PPE vanishes already at 250°C. Such a temperature "gap" can be attributed, in particular, to the increase of the break-away angle φ_{br} with increasing temperature, i.e., to the decrease of the "height" of the photo-obstacles. In principle, the height of the energy barrier for the dislocations at the photo-obstacles can be calculated from the temperature dependences of $\Delta\tau_f$ and I_{ph}.

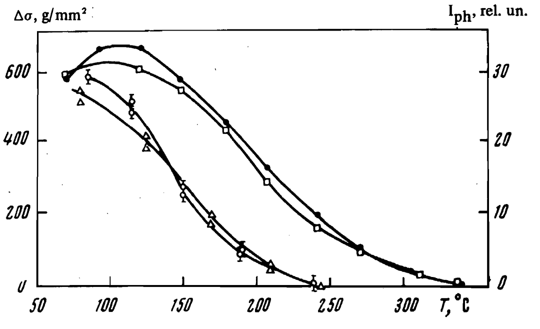

FIG. 7. Temperature dependence of the photostrengthening (○, △) and of the photoconductivity (●, □).

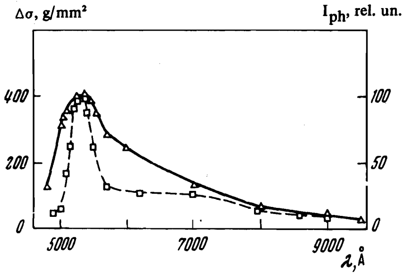

FIG. 8. Spectra of the photoplastic effect (Δ) and photoconductivity (□) at T = 100°C.

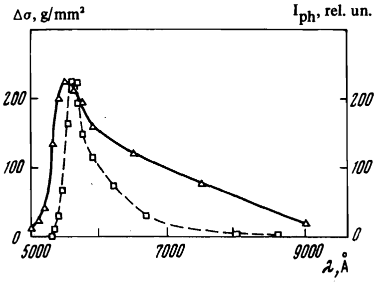

FIG. 9. Spectra of the photoplastic effect (Δ) and photoconductivity (□) at T = 100°C.

The results of spectral investigations of the PPE and of the photoconductivity are shown in Figs. 8 and 9. We choose for the comparison samples that differ greatly from one another in the parameters of the electron subsystem. The sample with the spectral characteristics shown in Fig. 8 was grown from the gas phase and had at 100°C a conduction-electron concentration on the order of 10^{12} cm^{-3}, thus indicating a low concentration of the shallow donor levels. The most noticeable difference between the PPE spectrum and the photoconductivity spectrum is its broadening in the short-wave and long-wave directions. Within the framework of our model, the broadening in the short-wave direction can be explained in the following manner: the strongly absorbed short-wave radiation penetrates only into the very thin surface layer and makes a small contribution to the photocurrent[11]. The same radiation produces at the crystal surface a greatly strengthened layer, which prevents the dislocations from emerging to the surface, and thus affects directly the bulk plastic deformation. In other words, whereas volume absorption of light is necessary to obtain large values of the photocurrent, to hinder the motion of dislocation it suffices to produce the photoobstacles in the surface layer.

The broadening in the long-wave direction can be attributed to the fact that the processes in which electrons are transferred from the valence band (with formation of photoholes) to a deep level in the forbidden band contribute to the PPE without increasing the electron concentration in the conduction band, since the probability of thermal transfer of the electron from the deep level into the conduction band is small. The small "tail" of impurity photoconductivity (6000–7000 Å) that can be seen on the photoconductivity spectrum has no analog in the PPE spectrum, since the transfer of the electron from the local level to the conduction band does not produce a photohole in the valence band.

Figure 9 shows the spectra of a single crystal grown from the melt, with a conduction electron concentration 7×10^{17} cm^{-3} at 100°C, indicating a high density of shallow donors. As seen from the figure, this sample is also characterized by a broadening of the PPE spectrum on both sides, in comparison with the photoconductivity spectrum. An essential difference between the spectra shown in Fig. 9 and the spectrum shown in Fig. 8 is the 300 Å shift of the maxima of the photoplasticity and photoconductivity toward the long-wave side, which can be attributed to an analogous shift of the absorption edge as a result of the high density of the shallow donor states. For all samples, the positions of the maxima of the PPE and of the photoconductivity coincided within the measurement error (70 Å). The maxima were shifted toward the long-wave side with increasing temperature (~ 1 Å per °C), and also with increasing degree of deformation (~ 15 Å per 1% deformation).

The authors thank I. S. Smirnova for the results of the calculation of the energies of the different dislocations in hexagonal cadmium sulfide, and V. Ya. Kravchenko for a useful discussion of the work.

---

[1] Yu. A. Osip'yan and I. B. Savchenko, ZhETF Pis. Red. **7**, 130 (1968) [JETP Lett. **7**, 100 (1968)].

[2] L. Carlsson and Ch. Svensson, Solid State Commun. **7**, 177, 1968.

[3] L. Carlsson and Ch. Svensson, J. Appl. Phys. **41**, 1653, 1970.

[4] C. N. Ahlquist, M. J. Carroll and P. Stroempl, J. Phys. Chem. Solids **33**, 337, 1972.

[5] Yu. A. Osip'yan, V. F. Petrenko, and I. B. Savchenko, ZhETF Pis. Red. **13**, 622 (1971) [JETP Lett. **13**, 442 (1971)].

[6] Yu. A. Osip'yan, Fiz. Tverd. Tela [Sov. Phys.-Solid State], in press.

[7] A. Rose, Concepts in Photoconductivity and Allied Problems, Wiley, 1963.

[8] Y. A. Osipyan and I. S. Smirnova, Phys. Stat. Sol. **30**, 19, 1968.

[9] G. L. Pearson, W. T. Read and F. J. Morin, Phys. Rev. **93**, 666, 1954.

[10] Yu. A. Osip'yan, Yu. I. Fedyaev, and S. A. Shevchenko, Zh. Eksp. Teor. Fiz. **54**, 1706 (1968) [Sov. Phys.-JETP **27**, 916 (1968)].

[11] R. R. Holms and C. Elbaum, Phys. Rev. **173**, 803, 1968.

[12] L. Carlsson, J. Appl. Phys. **42**, 677, 1971.

[13] R. H. Bube, Photoconductivity of Solids, Wiley, 1960.

[14] A. V. Lyubchenko, Fiz. Tverd. Tela **12**, 1593 (1970) [Sov. Phys.-Solid State **12**, 1263 (1970)].

[15] A. J. E. Foreman and M. J. Makin, Phil. Mag. **14**, 911, 1966.

Translated by J. G. Adashko
192