ON THE TEMPERATURE DEPENDENCE OF PHOTOCONDUCTIVITY IN CADMIUM IODIDE LAYERED CRYSTALS

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The temperature dependence of photoconductivity in pure and PbI_2-doped cadmium iodide crystals in the temperature range 4.2–80 K is investigated. As the temperature decreased from 70 to 40 K, a growth of the photocurrent by more than four orders of magnitude was discovered; in the region $T<40$ K, the magnitude of the photocurrent didn't depend practically on the temperature down to 4.2 K. The results are explained by the rise of the mobility of charge carriers in the case of their scattering by membrane vibrations of the CdI_2 layered lattice, variations of elastic constants, and the phenomenon of spontaneous deformation of the crystal in this temperature region. In the CdI_2–PbI_2 crystal system, the photocurrent at $T<70$ K increases by at most two orders of magnitude; moreover, the behavior of its temperature dependence also changes. The influence of the impurity on bending vibrations of the host lattice is discussed.

1. Introduction

Cadmium iodide crystals belong to the family of MX_2 halogenides with a layered structure formed by a close hexagonal arrangement of iodine atoms, a half of whose octahedral cavities is filled with cadmium atoms. Strong ion-covalent bonds that arise between cadmium and iodine atoms result in the formation of two-dimensional triple I–Cd–I layers (or sandwiches), whose superposition forms a three-dimensional crystal. In this case, neighbor "sandwiches" are coupled by weak van der Waals forces, which allows one to consider them as free ones in the first approximation.

It was established in work [1] that there appeared a peculiarity in the spectrum of acoustic phonons of such crystals linked with bending vibrations of layered packets (the membrane effect). These vibrations make a main contribution to thermal capacity, thermal conductivity, and linear expansion of layered crystals at low temperatures, where their influence is a determining one [2], the consideration of the dispersion of phonons is important for investigation of transport phenomena in superlattices [3]. For cadmium iodide, the temperature range of the existence of bending vibrations is 10–65 K [4, 5].

The given work is devoted to the investigation of the temperature dependence of photoconductivity in pure and PbI_2-doped crystals of cadmium iodide in the temperature region $T<70$ K.

2. Experimental Technique

Crystals used for investigations were grown with the help of the Stockbarger method in evacuated quartz ampoules from the raw material purified by means of multiple floating-zone refining. The content of the PbI_2 impurity in the charge amounted to 0.1 mol.%. The samples for investigations were cleaved out according to cleavage planes 0.15 mm in thickness, while their area was equal to 5×10 mm^2. Gallium-indium contacts were applied to the basic (0001) surface of the samples. The electric field with an intensity of 5 kV/cm was formed between them. The photocurrent was registered with the help of a V7-30 electrometer in the direction normal to the crystallographic axis.

The wavelength of the exciting light was separated by means of an SF-4 monochromator from the continuous spectrum of a DKsSh-1000 xenon lamp or a DrSh mercury lamp that has intense lines in the region of fundamental absorption of cadmium iodide. In the case of luminescent investigations, the spectral composition of luminescence was analyzed using an MDR-12 monochromator.

In Fig. 1, curve *1* shows the temperature dependence of the photocurrent of pure CdI_2 crystals in the temperature range 4.2–80 K in the case of excitation

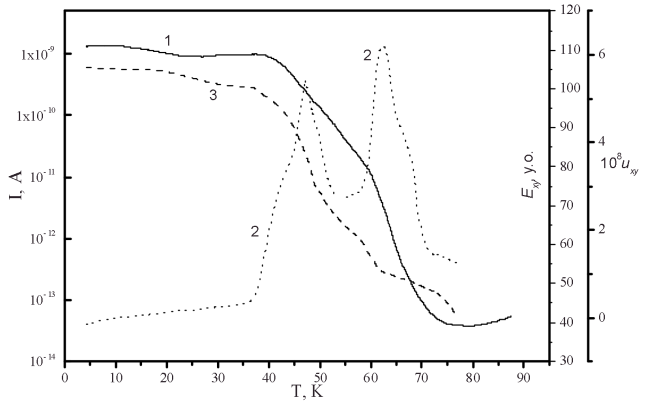

Fig. 1. Temperature dependences of the photocurrent of CdI_2 crystals in the case of excitation in the region of proper absorption (curve *1*), spontaneous deformation U_{xy} (curve *2*) [7], and elastic constants E_{xy} (curve *3*) [7]

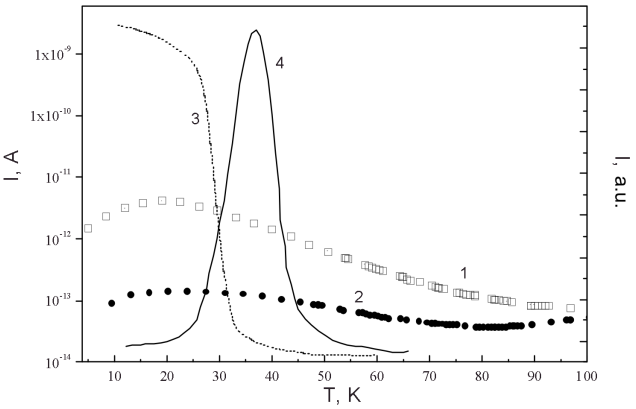

Fig. 2. Temperature dependences of the photocurrent of CdI_2–PbI_2 crystals in the case of excitation in the region of proper absorption (curve *1*) and 384-nm impurity band (curve *2*), 515-nm (curve *3*), and 397-nm (curve *4*) luminescence bands

with the help of the 334-nm mercury line (region of indirect transitions). As the temperature decreases from 70 to 40 K, one observes an abrupt increase of the photocurrent I (by more than a factor of 10^4). In this case, there appear two regions with different rates of change of the photocurrent: one of them for which $\frac{\Delta \lg I}{\Delta T} \approx 0.2$ lies in the range 70 – 60 K, while the other, where the rate of change is twice as less, lies in the range 60 – 40 K. At $T<40$ K, the photocurrent reaches the saturation, and its magnitude is not practically changed up to a temperature of 4.2 K. In the region of high temperatures ($T>80$ K), one observes a thermoactivated growth of the photoconductivity of CdI_2 (this temperature region isn't presented in Fig. 1).

For the sake of comparison, Fig. 1 presents the temperature dependences of the elastic constants E_{xy}(curve *2*) and the spontaneous deformation U_{xy} (curve 3) of the cadmium iodide crystals with stoichiometric cation excess [7]. The position of the maxima on curve *2* rather well coincides with two regions of the increase of the photocurrent on curve *1*, whereas the behavior of the change of the spontaneous deformation (curve *3*) is similar to the form of the temperature dependence of the photocurrent of CdI_2 crystals.

In Fig. 2, we display the temperature dependence of the photocurrent of CdI_2–PbI_2 crystals in the case of excitation in the regions of fundamental absorption (curve *1*) and the impurity 348-nm band (curve *2*). A rise of the photocurrent is observed both in the case of excitation of the host CdI_2 lattice, as well as under the excitation of layers of the PbI_2 microphase.

In both cases, as the temperature decreases from 70 K, one doesn't observe a region of abrupt increase of the photocurrent; instead, there occurs a smooth rise of its magnitude to 20 K and a further decrease down to 4.2 K. However, in the case of excitation close to 384 nm, the photocurrent rises by a factor of four (with respect to the dark one), whereas this ratio approximately amounts to 75 in the case of normalized excitation in the region of fundamental absorption of the crystal.

Thus, in the CdI_2–PbI_2 crystal system, one also observes an increase of the photocurrent at $T<70$ K, but the relative change of the photocurrent is less than that in nonactivated CdI_2 crystals. In addition, the photocurrent reaches its maximal value (at 20 K) not so abruptly as for CdI_2 and has a falling region at $T<20$ K.

Curves *3* and *4* in Fig. 2 demonstrate the temperature dependences of the intensities of two photoluminescence bands of the CdI_2–PbI_2 crystal: the 397-nm one (in the case of excitation with the 313-nm mercury line) and the 515-nm one (in the case of 380.2-nm excitation), respectively. One can see that the intensity of the long-wave band starts to increase from 45 K, abruptly rises with the approach to 36 K and steeply decreases after that down to 25 K. The characteristic "burst" of the intensity of the given photoluminescence band in a narrow temperature range was also observed in [8]. The intensity of the short-wave 397-nm luminescence band abruptly increases in the range 35–20 K and after that remains constant down to 4.2 K.

3. Discussion of the Results

When explaining the effect of essential increase of the photocurrent of CdI_2 crystals in the region $T<70$ K, we paid attention to the qualitative similarity of its temperature behavior and the corresponding change of the spontaneous deformation of the crystal (Fig. 1, curves *1* and *3*).

The authors of [7] explain the peculiarities of the mechanical properties of CdI_2 crystals with stoichiometric cation excess in the temperature region $T<70$ K by the influence of the nonlinear electron-phonon interaction. Indeed, an elastic wave creates a deformation of the crystal characterized with a negative coefficient in the plane of the layer and a positive one in the normal direction. This phenomenon can manifest itself as a spontaneous deformation in CdI_2 crystals at $T<70$ K (Fig. 1, curve *3*).

The temperature dependence of the photocurrent of CdI_2 crystals in this temperature range can be caused by a similar reason, namely by the interaction of charge carriers with bending vibrations of the lattice. The authors of [6] also noted a considerable increase of the photocurrent of CdI_2 crystals at the liquid-helium temperature close to the region of the appearance of high-energy excitons (5.7 and 6.2 eV). Moreover, they have demonstrated that the photocurrent is caused to a great extent by the motion of electrons.

In the general form, the photoconductivity is determined by the formula

$$\sigma = e_n\mu_n\Delta n + e_p\mu_p\Delta p, \tag{1}$$

where e_n and e_p are the electron and hole charges, respectively; $\mu_n and \mu_p$ are their mobilities; and Δn and Δp denote the excess concentrations of carriers created by light.

It's known that, in the case of scattering of charge carriers by acoustic vibrations of a specific lattice, the temperature dependence of the mobility is determined by the expression

$$\mu = \mu_{0T}T^{-3/2}, \tag{2}$$

i.e. a decrease of the temperature results in an increase of the mobility of charge carriers [9]. However, in order to explain the observed anomalously large increase of the photoconductivity, it's obviously worth also analyzing the temperature dependence of the proportionality coefficient μ_{0T} related to the characteristics of the given substance:

$$\mu_{0T} \sim c_{ll}N^{-1}\Delta_c^{-2}m^{*^{5/2}}, \tag{3}$$

where c_{ll} stands for the coefficient of elasticity, N denotes the concentration of atoms of the host substance, Δ_c is the constant of the deformation potential, and m^* is the effective mass.

As one can see from Fig. 1 (curve *2*), the elastic constants of CdI_2 crystals can determine different behaviors of the increase of the photocurrent in the range $40 < T < 70$ K.

The influence of such characteristics of the crystal as the deformation potential constant and the effective mass of charge carriers on the temperature dependence of the quantity μ_{0T} can be explained in the following way: under the membrane vibrations of layered crystals, a decrease of the distance between atoms within the layer increases the overlap of atomic wave functions and results in an increase of the exchange energy. In this case, the widths of the bands of allowed energy values increase, whereas the energy gap width decreases. As the effective electron mass is inversely proportional to the exchange integral, the compression of the lattice in the plane of the layer in the case of membrane vibrations causes a decrease of the effective mass, which results in a rise of the mobility.

Thus, analyzing dependence (3), one can see that, in the course of the interaction of charge carriers with acoustic vibrations of the lattice of cadmium iodide, the partial contribution of each of the basic characteristic parameters of the crystal results in an essential rise of the mobility of carriers and, consequently, in the growth of the photocurrent as the temperature falls from 70 to 40 K. The saturation of the photocurrent at 40 K can be conditioned by properties of the deformation potential, which is confirmed by the similarity of the behavior of the temperature dependence of the photocurrent and that of the spontaneous deformation (Fig. 1, curves *1* and *3*).

The influence of the PbI_2 impurity on the photoelectric properties of CdI_2 crystals manifests itself not only in the quantitative decrease of the photocurrent value but also in the change of the pattern of its increase in the region $T<70$ K (Fig. 2, curves *1* and *2*). The absence of the region of abrupt growth of the photocurrent for the crystal system CdI_2–PbI_2 in the case of decrease of the temperature from 70 to 40 K can be related to the fact that PbI_2 phase inclusions evidently hamper the free propagation of membrane vibrations of the CdI_2 lattice. The difference of the parameters of the lattices (for CdI_2 $a = 4.24$ Å, $c = 6.84$ Å; for PbI_2 $a = 4.56$ Å, $c = 6.96$ Å) contributes to the disordering of the crystal lattice [10].

The comparison of the temperature dependences of the photocurrent and the luminescence (Fig. 2) allows us to trace the process of migration of the excitation energy in the CdI_2–PbI_2 lattice. From curve *4* (Fig. 2), one can see that, in the case of excitation of PbI_2 phase inclusions, the intensity of the 515-nm luminescence band steeply rises in the temperature range 30–45 K. The temperature (36 K) that corresponds to the "burst" of the intensity of this band is close to the temperature of 40 K, at which the photocurrent in CdI_2 crystals reaches its maximal value (Fig. 1, curve *1*), and practically coincides with the temperature (35 K), at which the dynamics of extinction of the 2.44-eV radiation band of PbI_2 nanoparticles located in SiO_2 films abruptly changes [11]. One can assume that acoustic vibrations of the layers of the PbI_2 microphase also influence the pattern of luminescent processes in the CdI_2–PbI_2 crystal system. Below the temperature of 30 K, there occurs a steep rise of the 397-nm photoluminescence band in these crystals (Fig. 2, curve *3*) that can be interpreted as the luminescence of free high-energy excitons of PbI_2 [12], which correlates, in turn, with the decrease of the probability of exciton scattering by bending vibrations of the lattice in activated CdI_2 crystals.

Thus, the phenomenon of abrupt increase of the photoconductivity in CdI_2 layered crystals in the case of decrease of the temperature from 70 to 40 K, that was observed in this work, is related to both a high efficiency of scattering of charge carriers by bending vibrations of the lattice and a considerable increase of the mobility of charge carriers accompanying it. The decrease of the photoconductivity in the CdI_2–PbI_2 crystal system is caused by a decrease of the mobility of charge carriers due to the disordering of the CdI_2 lattice by PbI_2 microphase inclusions.

4. Conclusions

We have discovered the increase of the photocurrent in CdI_2 by more than 4 orders of magnitude with decrease in the temperature of the crystal from 70 to 40 K. At $T < 40$ K, the photocurrent reaches the saturation and its value is not practically changed down to the liquid helium temperature.

The experimental results are explained by both the scattering of charge carriers by membrane vibrations of the CdI_2 layered lattice and a rise of their mobility. A steep growth of the photocurrent in the range 70–40 K correlates with essential changes of the elastic constants of CdI_2 in this temperature region, while the saturation of the photocurrent at $T<40$ K is probably related to the properties of the deformation potential of the cadmium iodide lattice.

The PbI_2 impurity results in a smoother transition of the system to the state with a high photoconductivity, whose magnitude is two orders of magnitude lower than that in pure crystals. Obviously, the PbI_2 impurity "suppresses" bending vibrations of the CdI_2 lattice, which is adequately reflected in the value and the temperature dependence of the photoconductivity of CdI_2–PbI_2 crystals. The decrease of the photocurrent in the CdI_2–PbI_2 crystal system is related to a reduction of the mobility of charge carriers due to the disordering of the CdI_2 lattice by PbI_2 microphase inclusions.

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1. I.M. Lifshitz, Zh. Eksp. Teor. Fiz. **22**, 478 (1952).
2. N.A. Abdulaev, R.A. Suleimanov, M.A. Aldzhanov, and L.N. Alieva, Fiz. Tverd. Tela **44**, 1775 (2002).
3. Y. Chen, D. Li, J.R. Lukes, Z. Ni, and M. Chen, Phys. Rev. **B72**, 174302 (2005).
4. M.S. Brodin and S.V. Blonskii, *Exciton Processes in Layered Crystals* (Naukova Dumka, Kyiv, 1986) (in Russian).
5. O.N. Yurchenko, S.A. Pyroga, and S.D. Olekseyuk, Zh. Prikl. Spektr. **68**, 771 (2001).
6. D.K. Wright and M.R. Tubbs, Phys. Stat. Sol. **37**, 551 (1970).
7. I.M. Bolesta, I.V. Kityk, J. Filipecki, and H. Zount, Phys. Stat. Sol. **B189**, 357 (1995).
8. T. Hayashi, T. Ohata, M. Watanabe, and S. Koshino, J. Phys. Soc. Jap. **63**, 4629 (1991).
9. P.S. Kireev, *Physics of Semiconductors* (Vysshaya Shkola, Moscow, 1975) (in Russian).
10. V.V. Artamonov, M.Y. Valakh, V.A. Korneichuk, *et al.*, Ukr. Fiz. Zh. **27**, 1046 (1982).
11. E. Lifshitz, M. Yassen, L. Bykov, and I. Dag, J. Lum. **70**, 421 (1996).
12. A.V. Gloskovskii, M.P. Panasyuk, L.I. Yaritskaya, and N.K. Gloskovskaya, Fiz. Tverd. Tela **45**, 390 (2003).

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ПРО ТЕМПЕРАТУРНУ ЗАЛЕЖНІСТЬ ФОТОПРОВІДНОСТІ ШАРУВАТИХ КРИСТАЛІВ ЙОДИСТОГО КАДМІЮ

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Р е з ю м е

Досліджено температурну залежність фотопровідності чистих та легованих йодистим свинцем кристалів йодистого кадмію

в температурному діапазоні 4,2–80 K. Зі зниженням температури від 70 до 40 K виявлено ріст фотоструму, більший ніж на 4 порядки; для температур $T<40$ K величина фотоструму практично не залежить від температури до 4,2 K. Результати пояснюються ростом рухливості носіїв заряду при розсіянні на мембранних коливаннях шаруватої кристалічної ґратки CdI_2, змінами пружних констант та явищем спонтанної деформації кристала в цій температурній області. У кристалічній системі CdI_2–PbI_2 при $T<70$ K фотострум зростає менше ніж на 2 порядки, при цьому змінюється і характер його температурної залежності. Обговорюється вплив домішки на згинні коливання основної кристалічної ґратки.