

Intrinsic-defect mechanism of crystal acoustoluminescence

I. V. Ostrovskii

T. G. Shevchenko Kiev State University

(Submitted 25 April 1981; resubmitted 15 September 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 8, 467–471 (20 October 1981)

It is shown that an acoustic wave (AW) of above-threshold power generates optically active crystal-structure defects that lead to the appearance of the acoustoluminescence (AL) effect.

PACS numbers: 78.60.Mq, 61.70. — r, 62.65. +k, 43.35.Ty

A new type of crystal luminescence—acoustoluminescence (AL)—was reported in Ref. 1. The present paper is devoted to an investigation of the AL mechanism, since it is unknown. AL was excited experimentally in high-resistance CdS wafers, which were grown from the vapor phase, and in three-dimensional uncolored NaCl single crystals (Fig. 1). Ultrasonic AW were excited in the CdS wafers using the intrinsic piezoelectric effect of the CdS by connecting a high-frequency voltage $V(\omega)$ to the metal electrodes 2. The AW were excited in NaCl by the piezoelectric transducers 6 or 7. To eliminate charge carrier injection into the CdS, we used the 5- μm -thick Teflon films 3 or spring-loaded unpolished brass contacts, which provide an air gap between the electrode 2 and sample 1. As the amplitude of the excitation voltage was increased to a certain threshold V_{thr} , luminescence appeared along the propagation path of the ultrasound. The threshold ultrasonic energy flux density in the CdS was measured from the amplitude of the acoustoelectric current (I_a) at 300 K. The thresh-

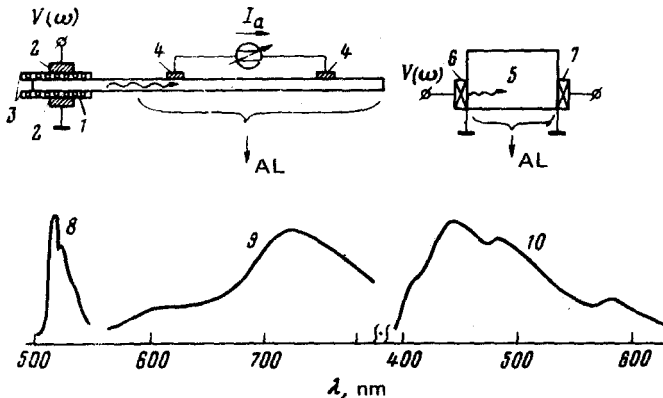


FIG. 1. Excitation schemes and AL schemes. 1—CdS sample; 2—AW excitation electrodes; 3—Teflon film; 4—indium contacts for removal of acoustocurrent; 5—NaCl sample; 6 and 7—*x*-cut LiNbO_3 piezoelectric transducers; 8—AL spectrum for sample *L45* ($\omega/2\pi = 5.9$ MHz, 77.4 K); 9—AL spectrum for sample *L81*, $\omega/2\pi = 15$ MHz, 77.4 K; 10—AL spectrum for sample *N16*, $\omega/2\pi = 9.6$ MHz, 300 K.

hold energy flux density, which ranged from one to several W/cm^2 for different samples, was calculated from the amplitude of I_a at $V(\omega) = V_{\text{thr}}(\omega)$. In NaCl the AW energy was determined from the acoustic radiation resistance of the piezoelectric transducers. At $V = V_{\text{thr}}$ the ultrasound intensity is of the order of $10 \text{ W}/\text{cm}^2$.

Figure 1 shows typical AL spectra for CdS (8 and 9) and NaCl (10). The AL spectra shown for CdS are attributed to luminescence centers that include intrinsic lattice defects: the red band with a maximum at 720 nm is attributed to radiative electron transitions between sulfur vacancies (V_S) and cadmium vacancies (V_{Cd}),² the orange band with a maximum at $605 \pm 5 \text{ nm}$ is attributed to interstitial cadmium (Cd_i),³ and the emission in the green region is attributed to interstitial sulfur (S_i).⁴ The AL spectrum of NaCl has a maximum in the 440 to 460-nm region, i.e., in the F -center absorption-band region; this corresponds to the α luminescence of NaCl caused by the intrinsic defects.⁵

The NaCl and CdS crystals were etched in order to reveal the dislocation structure. It was found that for above-threshold ultrasound power ($V > V_{\text{thr}}$) the dislocations can move and multiply in the crystal. This is understandable, since the dislocations have a long-range elastic-stress field and can concentrate the AW energy in the region of the dislocation center. Structural defects of the interstitial atom-vacancy type may be produced as a result of rotational and translational slippage of dislocations with thresholds in the ultrasonic elastic-stress field.

To determine the optical activity of the defects that appear in the field of an above-threshold-power AW, we have investigated the influence of the AW on the optical spectra of CdS. Figure 2 shows the variation of the energy position of the transmission and reflection (A exciton) spectra. The long-wave displacement of the A exciton is caused by a variation of the forbidden-band gap and is equal to its decrease, which amounts to 11 meV. The shift of the absorption spectra is equal to 50 meV. The excess shift of T_v compared to R_v indicates the appearance of optically active Cd_i ,⁶ which is a shallow donor. The spectra of excitons, which are localized in the acceptors (J_1) and donors (J_2) increase after the crystals have been ultrasonically loaded (Fig. 3). The intensity of spectrum 2, which was measured after a five-minute AW excitation, increased by 20%; this indicates an increase in the number of

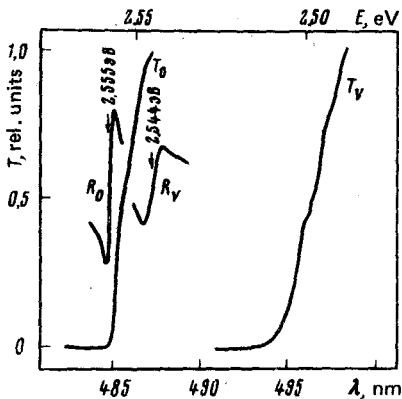


FIG. 2. Transmission (T) and reflection (R) spectra measured in sample L45 at 4.2 K. T_0 and R_0 are without AW ($V = 0$); T_v and R_v are for above-threshold AW ($V = 1.2 V_{\text{thr}}$).

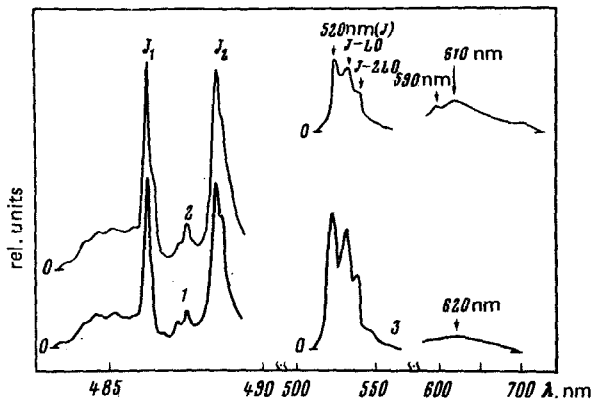


FIG. 3. Effect of AW on photoluminescence of CdS. Sample RL82B (4.2 K). 1- $V=0$; 2- $V > V_{\text{thr}}$, $\omega/2\pi = 7.4$ MHz. Sample L46 (77.4 K). 3- $V=0$; 4- $V > V_{\text{thr}}$, $\omega/2\pi = 7.4$ MHz.

acceptors and donors. The emission in the green region decreases and the orange luminescence of CdS increases; this can be seen from a comparison of spectra 3 and 4 in Fig. 3. The changes in the luminescence spectra caused by the AW indicate a generation of optically active pairs of defects of the type $V_{\text{Cd}} - \text{Cd}_i$ and $V_{\text{S}} - \text{S}_i$. This follows from the fact that the J_1 and J_2 excitons can be found by the S_i and V_{S} acceptors and Cd_i donors, respectively^{7,8}; an increase in the Cd_i concentration leads to an increase of the orange luminescence,³ and the V_{Cd} suppresses the luminescence of the green region.⁹

The intrinsic-defect mechanism for the AL can be described as follows: 1) an AW of above-threshold power generates the defect pairs; 2) radiative electron transitions to these donor-acceptor pairs form the AL spectra. For example, for CdS an electron transition from the Cd_i donor to the S_i acceptor gives green luminescence with a maximum at 520 nm, the transition from the V_{S} donor to the V_{Cd} acceptor gives the red band with a maximum at 720 nm, and transitions from the Cd_i -trap complexes to the S_i acceptor (or to the valence band) give orange luminescence. This AL mechanism in CdS agrees with the known energy levels of singly charged intrinsic defects in the forbidden band.

Singly charged donors and acceptors in the pair correspond to the electron-excited state of a Frenkel pair in CdS. The generation of singly charged intrinsic defects in A_2B_6 compounds requires smaller energy expenditures than neutral defects¹⁰; and doubly charged vacancies, such as V_{Cd}^- , are encountered seldom in special, undoped crystals.¹⁰ After a radiative electron transition, the vacancies and interstitial atoms become doubly charged and effectively annihilate each other, returning the crystal to the original state. Annihilation is caused by the migration of Cd_i^{++} (Ref. 11) and S_i^- ions (Ref. 11) with stable electron shells along the crystal. The decay time of the AL brightness in CdS is $< 10^{-5}$ sec at 77.4 K; this corresponds to annihilation of close Frenkel pairs, which are annealed starting at 60 K.¹¹ An analogous scheme is also applicable for the defect pairs in NaCl.

The intrinsic-defect mechanism of AL differs from the luminescence mechanism if there is a plastic deformation, since the deformation luminescence in A_2B_6 is caused by the transfer of electric-charge dislocations to the surface and subsequent electroluminescence, or by the ionization of the impurity levels¹²; the latter also applies to colored alkali-halide crystals.

In conclusion, we wish to thank A. Kh. Rozhko for his assistance with the recording of the spectra at 4.2 K, and also M. D. Galanin, Yu. V. Gulyaev, S. G. Kalashnikov, V. A. Krasil'nikov, and M. V. Fok for their interest in this work and its discussion at the seminars.

1. I. V. Ostrovskii, A. Kh. Rozhko, and V. N. Lysenko, XXVII Soveshchanie po lyuminesentsii (25th Conference on Luminescence), Ezerniki, 1980, p. 185.
2. I. G. Ermolovich, V. V. Gorbunov, and P. D. Konozenko, *Fiz. Tekh. Poluprovodn.* **11**, 1812 (1977) [*Sov. Phys. Semicond.* **11**, 1061 (1977)].
3. B. A. Kulp, *Phys. Rev.* **125**, 1865 (1962).
4. B. A. Kulp and R. H. Kelly, *J. Appl. Phys.* **31**, 1057 (1960).
5. I. K. Vitol, *Izv. Akad. Nauk SSSR Ser. Fiz.* **30**, 564 (1966).
6. P. D. Ekbote, S. V. Moharil, and I. K. Zope, *Indian J. Pure Appl. Phys.* **16**, 488 (1978).
7. K. F. Lider, B. V. Novikov, and S. A. Permogorov, *Phys. Status Solidi* **18**, K1 (1976).
8. V. F. Grin', V. E. Lashkarev, and E. A. Sal'kov, *Ukr. Fiz. Zh.* **18**, 118 (1973).
9. M. Gamaguchi, *Jpn. J. Appl. Phys.* **15**, 1675 (1976).
10. *Fizika i khimiya soedinenii A_2B_6* (Physics and Chemistry of A_2B_6 Compounds), Mir, Moscow, 1970, Chap. 4, p. 135.
11. *Tochechnye defekty v tverdykh telakh* (Point Defects in Solids), Mir, Moscow, 1979, Chaps. 1 and 5.
12. Yu. A. Ossipyan and V. F. Petrenko, *J. Phys.* **40**, C6-161 (1979).

Translated by Eugene R. Heath

Edited by S. J. Amoretty