Supplemental Material to the article

“Non-standard features of the interaction of single luminescent centers formed by the partial dislocation cores in CdTe and ZnSe with longitudinal optical phonons”

1. Description of spectra presented in Fig. 1. Figura 1a of the manuscript shows typical emission spectra of thin ZnSe/GaAs films recorded near the fundamental absorption edge of ZnSe at a 5 K temperature. Similar spectra can be found, for example, in [1, 2].

To clearly illustrate the phonon replicas of emission lines of bound excitons and donoracceptor pairs with the participation of shallow impurities, a 200-nm thick ZnSe epitaxial film was selected. The film was grown by vapor phase epitaxy from organometallic compounds at 450 °C on a GaAs substrate. The growth was carried out in an H_2 atmosphere at atmospheric pressure; $ZnEt_2$ and Et_2Se were used as precursors. A feature of this film, which is important for this work, is the good separability of emission lines and the presence of several well-pronounced phonon replicas for emission lines of bound excitons and donor-acceptor pairs. To excite the photoluminescence, 405-nm laser was used. The luminescence spectrum was analyzed by the system described in the main text of the article.

Figure 1b of the manuscript shows typical emission spectra of an oxygen impurity (O_{Te}) in bulk ZnTe crystals at a temperature of 5 K. Similar spectra can be found, for example, in [3, 4]. To obtain illustrative O_{Te} spectra, in this work,we used bulk ZnTe crystals grown by chemical vapor deposition at a temperature of 670 °C. The features of crystal growth and their properties are described in detail in [4]. To excite the photoluminescence, 488-nm laser was used. The luminescence spectrum was analyzed by the system described in the work.

1. *Topics in Current.* 14 Excitons, ed. by K. Cho, Springer-Verlag, Berlin–Heidelberg–N.Y. (1979).

2. V. I. Kozlovskiy, V. S. Krivobok, P. I. Kuznetsov, S. N. Nikolaev, E. E. Onistchenko, A. A. Pruchkina, and A. G. Temiryazev, Semiconductors **50**, 688 (2016).

3. M. J. Seong, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **58**(12), 7734 (1998).

4. V. S. Bagaev, Yu. V. Klevkov, V. S. Krivobok, V. P. Martovitskii, V. V. Zaitsev, S. G. Chernook, and E. E. Onishchenko, Phys. Solid. State **50**, 808 (2008).

2. Description of samples under study.

CdTe/Si

CdTe/Si(103) heteroepitaxial structures were grown in the Ob' multi-chamber ultra-high vacuum installation for molecular beam epitaxy [5] using the developed production process described in detail in [6]. Reflection high-energy electron diffraction (RHEED) and single-wave ellipsometry (wavelength of $\lambda = 632.8$ nm) were used for in situ monitoring of preepitaxial preparation and growth. Commercially available boron-doped p-type silicon wafers (resistivity $\rho \sim 10\,\Omega\,\mathrm{cm}$) with a diameter of 76.2 mm oriented along the (103) plane were used as the substrates.

ZnSe QW

The 20-nm wide ZnSe quantum well was placed between two $Zn_{0.84}Mg_{0.16}S_{0.12}Se_{0.88}$ barrier layers. The structure was grown by molecular beam epitaxy on a GaAs substrate. The bandgap energy in the ZnSe layer, estimated using a spectral position of excitonic resonances, was $E_G \sim 2.825$ eV. The typical background impurity concentration was about $10^{15}\,\mathrm{cm}^{-3}$. See [7] for details.

5. Yu. G. Sidorov, S. A. Dvoretskii, N. N. Mikhailov, M. V. Yakushev, V. S. Varavin, and A. P. Antsiferov, J. Opt. Technol. **67**, 31 (2000).

6. M. V. Yakushev, D. V. Brunev, V. S. Varavin, V. V. Vasiliev, S. A. Dvoretskii, I. V. Marchishin, A. V. Predein, I. V. Sabinina, Yu. G. Sidorov, and A. V. Sorochkin, Semiconductors **45**, 385 (2011).

7. V. S. Krivobok, S. N. Nikolaev, S. I. Chentsov, E. E. Onishchenko, V. S. Bagaev, V. I. Kozlovskii, S. V. Sorokin, I. V. Sedova, S. V. Gronin, and S. V. Ivanov, JETP Lett. **104**, 110 (2016).

3. Typical example of deviation from the Huang–Rhys formula for single centers associated with dislocations in CdTe/Si.

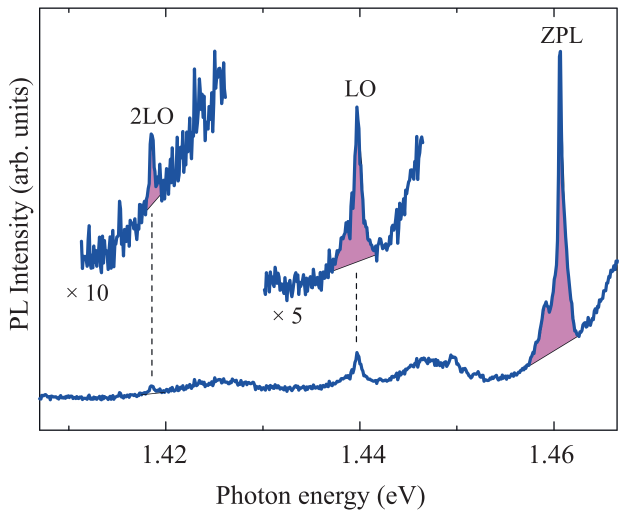

Fig. S1. A typical example of an individual luminescent center formed by a dislocation in a CdTe/Si thin film. ZPL stands for a zero phonon line. Temperature is 5 K.

Figure S1 shows a typical micro-photoluminescence (MPL) spectrum of an individual luminescent center, formed by (partial) dislocation in CdTe/Si. A narrow zero-phonon line (ZPL, 1.460 eV), which corresponds to the Y line region in Fig. 1a of the manuscript, is dominant in the MPL spectrum. Phonon replicas corresponding to the excitation of one (LO, 1.439 eV) and two (2LO, 1.418 eV) optical phonons are also recorded. The energy shifts between the lines reproduce the energy of the LO phonon of CdTe corresponding to the center of the Brillouin zone (21 meV). When comparing the integrated intensities of phonon replicas, it turns out that the S value calculated as the ratio of the ZPL line area to the LO line area is 0.125 ± 0.002. In turn, according to the Huang–Rhys model, this means that the intensity ratio between the second and first phonon replicas should be $S/2 = 0.063 \pm 0.001$. At the same time, the intensity ratio measured experimentally is 0.16 ± 0.02, which is 2.5 times higher than the expected value.

4. Results of calculating scalar products of oscillator wave functions. Following the standard theory based on the Franck–Condon principle, we consider the transition matrix element for a luminescent center with a ground state i and an excited state f:

$$\langle i|\mathbf{M}|f\rangle \to \langle \mu'|e\mathbf{x}|\mu''\rangle \int X^*_{\mu'\nu'}(X)X_{\mu''n''}(X)dX. \tag{1}$$

In (1), μ symbolizes the wave functions corresponding to the electronic subsystem, X – the wave functions of the phonon subsystem. The intensity of the transition from the initial state i to the final state f is determined by the Fermi golden rule:

$$I \sim \frac{2\pi}{\hbar}|\langle i|\mathbf{M}|f\rangle|^2\delta(E_f - E_i). \tag{2}$$

For a qualitative description of the phonon subsystem, consider a model of two quantum harmonic oscillators corresponding to the potentials $U(x) = \beta_1 x^2$ and $U(x) = \beta_2(x-a)^2 + u$. The parameters $\beta_i = \frac{\omega_i^2 m}{2}$ obviously depend on the eigenfrequencies (ω_i) and the particle mass (m). The wave function for the oscillator n-th state is described by the well-known formula:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-\frac{m\omega}{2\hbar}x^2} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right), \tag{3}$$

where $H_n(\xi)$ Hermite polynomials of order n. In the general case, $\beta_1 = \frac{\omega_1^2 m}{2} \neq \beta_2 = \frac{\omega_2^2 m}{2}$ due to a change in the bonds rigidity.

At low temperatures, the decisive role is played by the fundamental vibrational sublevel ($n = 0$) of the electronic state from which the transition occurs. Using the substitutions $\gamma = \frac{\omega_2}{\omega_1}$, $x_1 = \sqrt{\frac{\hbar}{m\omega_1}}$ and $x_2 = \sqrt{\frac{\hbar}{m\omega_2}}$, $x_2 = \frac{x_1}{\sqrt{\gamma}}$ one can obtain the following expression for the matrix element:

$$\int X^*_{\mu' n'}(X) X_{\mu'' n''}(X) dX = \int\limits_{-\infty}^{\infty} \psi'_n(x)\psi''_0(x)dx = \frac{\sqrt[4]{\gamma}}{x_1\sqrt{\pi}} \frac{1}{\sqrt{2^n n!}} \int\limits_{-\infty}^{\infty} H_n\left(\frac{x}{x_1}\right) e^{-\frac{\gamma(x-a)^2+x^2}{2x_1^2}} dx. \tag{4}$$

To calculate the integral, one can use the substitutions $k = \sqrt{\frac{\gamma+1}{2x_1^2}}$ and $b = \frac{a\gamma}{x_1\sqrt{2(\gamma+1)}}$, then:

$$\int X^*_{\mu' n'}(X) X_{\mu'' n''}(X) dX = \frac{\sqrt[4]{\gamma}}{kx_1\sqrt{\pi}} \frac{1}{\sqrt{2^n n!}} e^{-\frac{b^2}{\gamma}} \int\limits_{-\infty}^{\infty} H_n\left(\frac{y+b}{kx_1}\right) e^{-y^2} dy. \tag{5}$$

While maintaining the bond rigidity $\beta_1 = \beta_2$. In this case, the dependence of the square of the overlap integral on the displacement a and the phonon repetition number n is described by the well-known Huang–Rhys dependence:

$$\frac{e^{-s}S^n}{n!}, \tag{6}$$

where S is the ratio of the intensities of the first phonon replica and the zero phonon line. In the Huang–Rhys model, the parameter S is determined by the shift of potentials in the ground and excited states relative to each other

$$S = \frac{a^2}{2x_0^2} = \frac{a^2 m\omega}{2\hbar}. \tag{7}$$

In the case when $\beta_1 \neq \beta_2$, the intensity of phonon replicas is no longer described by the Huang–Rhys dependence. The results of calculating integrals (5) for the first seven values of n are shown in Table 1.

Table 1. Results of calculating the overlap integral for $n = 0{-}6$

n	Value
0	$\frac{\sqrt[4]{\gamma}}{kx_1} e^{-\frac{b^2}{\gamma}} = I_0$
1	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{\sqrt{2}} e^{-\frac{b^2}{\gamma}} \frac{2b}{kx_1} = I_1 = \sqrt{S} \times I_0$
2	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{\sqrt{2}} e^{-\frac{b^2}{\gamma}} \frac{(1+2b^2-k^2x_1^2)}{k^2x_1^2} = I_2 = I_0 \frac{S+(1-\gamma)/(1+\gamma)}{\sqrt{2}}$
3	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{\sqrt{3}} e^{-\frac{b^2}{\gamma}} \frac{b(3+2b^2-3k^2x_1^2)}{k^3x_1^3} = I_3 = I_0 \frac{\sqrt{S}}{\sqrt{6}} \left(2S + \frac{3(1-\gamma)}{1+\gamma}\right)$
4	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{2\sqrt{6}} e^{-\frac{b^2}{\gamma}} \frac{(4b^4-12b^2(-1+k^2x_1^2)+3(-1+k^2x_1^2)^2)}{k^4x_1^4}$
5	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{2\sqrt{15}} e^{-\frac{b^2}{\gamma}} \frac{b(4b^4-20b^2(-1+k^2x_1^2)+15(-1+k^2x_1^2)^2)}{k^5x_1^5}$
6	$\frac{\sqrt[4]{\gamma}}{kx_1} \frac{1}{12\sqrt{5}} e^{-\frac{b^2}{\gamma}} \frac{(8b^6-60b^4(-1+k^2x_1^2)+90(-1+k^2x_1^2)^2-15(-1+k^2x_1^2)^3)}{k^6x_1^6}$

5. Quenching of emission lines with temperature increasing. The luminescent centers discussed in this work demonstrate rapid quenching with increasing temperature. In particular, in the case of a ZnSe quantum well, the intensity of the zero phonon line decreases by a factor of 30 with an increase in temperature to 10 K (Fig. S2). Under such conditions, the lines corresponding to optical phonon replicas also become indistinguishable and it is not possible to estimate the ratio of the integral intensities of the lines.

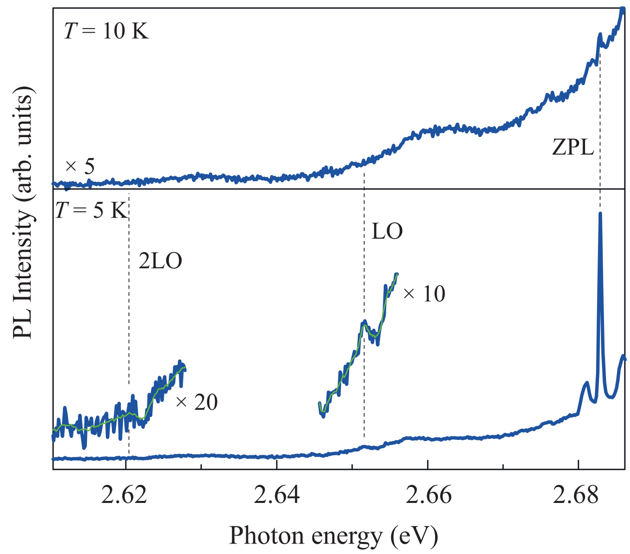

Fig. S2. Microphotoluminescence spectra of an individual luminescent center formed by a dislocation in a ZnSe-based quantum well at temperatures of 5 K (lower curve) and 10 K (upper curve). The effect of lines quenching with increasing temperature is seen