Concerning one temperature anomaly in the spectra of layered impurity crystals $CdBr_2$–I_2

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The investigated crystals were grown by the Kiropoulos method in a helium atmosphere.[1] They have layered structures. The samples, split along the cleavage planes, were plane-parallel plates with specular surfaces of good quality. The z axis was perpendicular to the layers, i.e., the light propagated along the symmetry direction of the crystal. The spectra were measured in the temperature interval 77—300 °K on crystals $CdBr_2$–I_2 (1%) ($d = 8\ \mu$) and $CdBr_2$–I_2 (0.1%) ($d = 53\ \mu$). Since the ion radii of Br^{-1} and I^{-1} differ greatly (1.96 and 2.20 Å, respectively) and at a weight concentration of iodine of 1% the $CdBr_2$ lattice is distored, we analyze only the spectra of $CdBr_2$–I_2(0.1%) ($N = 8.54 \times 10^{18}$ cm^{-3}).

Figure 1 reveals the following singularity: at 77 °K one can see a distinct impurity band and a sharp absorption edge. The band is shifted below the edge by an amount $\delta E = 0.175$ eV. Raising the temperature leads to a smearing of both parts of the spectrum, and at room temperature a sharp edge is again seen.

FIG. 1. Absorption spectra of $CdBr_2$-I_2 crystals (0.1%) at 77, 122, 164, and 300 °K.

This anomaly is due to the different behavior of the fundamental and impurity spectra. We have found no published information on the absorption of pure $CdBr_2$ single crystals. To separate the indicated details we have therefore measured separately the spectra of $CdBr_2$ at various temperatures. By way of illustration, Fig. 2 compares the spectra of the impurity containing (points) and of the pure (dashed) crystals. The sections are easily separated.

The temperature dependences of the impurity-band parameters are shown in Fig. 3. The $H(T)$ dependence is described by the function[2]

$$H(T) = H(0)\left[\mathrm{cth}\frac{E_{ph}}{2kT}\right]^{1/2} \tag{1}$$

at $H(0) = 920$ cm^{-1} and $E_{ph} = 6.8$ meV (55 cm^{-1}). The temperature shift of the maximum of the band $E(T)$ is determined, as is well known, by two factors: electron-phonon interaction and thermal expansion of the lattice:

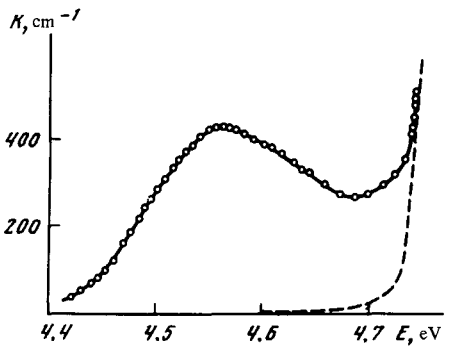

FIG. 2. Absorption curves of $CdBr_2$ (dashed) and of $CdBr_2$-I_2 (0.1%) (circles) at 77 °K.

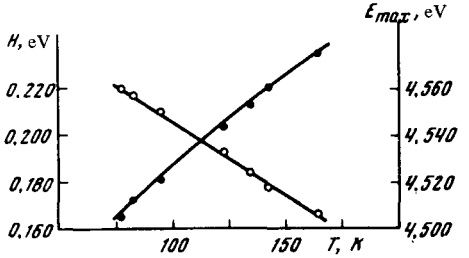

FIG. 3. Variation of the impurity-band parameters with temperature.

$$E_m(T) = E_m(0)\exp\left[A\left(1 - \operatorname{cth}\frac{E_{ph}}{2kT}\right)\right] - \int_0^T \frac{\beta}{K}\left(\frac{dE_m}{dP}\right)_T dT,$$

where $E_m(0)$ is the position of the maximum of the band, extrapolated to 0 °K, E_{ph} is the energy of the actual phonons, β is the volume coefficient of thermal expansion, K is the isothermal compressibility, and A is a constant ($A \ll 1$). Our analysis of the parameters of the band pertains to the region of low temperatures (77—170 °K), when single-phonon processes predominate. Taking (1) and the smallness of A into account, we write

$$\begin{aligned} E_m(T) &\approx E_m(0) + E_1\left(1 - \operatorname{cth}\frac{E_{ph}}{2kT}\right) - B\Delta E_T(T) \\ &= E_m(0) - E_1\left(\frac{H^2(T)}{H^2(0)} - 1\right) - B\Delta E_T(T). \end{aligned} \tag{2}$$

The function $\Delta E_T(T)$ was taken by us from[3], where it was obtained for the layered crystal PbI_2. The correction B takes into account the difference between β, K, and $(dE_m/dP)_T$. The experimental $E_m(T)$ curve is approximated by

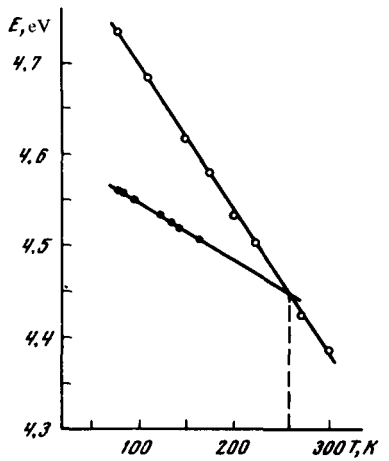

FIG. 4. Temperature shifts of the impurity band and of the intrinsic absorption edge of the system $CdBr_2$-I_2 (0.1%).

the function (2) with parameters $E_m(0) = 4.581$ eV, $E_1 = 5.44 \times 10^{-2}$ eV, and $B = -2.371$.

Thus, the temperature coefficients of the shifts of the impurity band and of the absorption edge do not coincide. For the interval 77—200 °K we have $\Delta E_g/\Delta T = -1.52 \times 10^{-3}$ eV/deg and $\Delta E_m/\Delta T = -6.21 \times 10^{-4}$ eV/deg. As a result, the spectra overlap at 256 °K and the impurity peak is then "lost" against the background of the fundamental band (Fig. 4). It is important to indicate that at 300 °K the long-wave wing of the impurity band should still be noticeable below the absorption edge (extrapolation of the function $H(T)$[1)]), and in fact the edge becomes sharp. A unique "transfer" of the oscillator strength from the impurity to the host takes place. This interesting fact (which is quite rare in experiments) is obviously due to the proximity of the impurity level to the band. We can therefore expect a shift in the configurations of the subsystems (the host lattice and the impurity). These questions have been investigated in detail in the literature for molecular crystals.[4] In the case of layered crystals, this effect was observed here for the first time.[2)]

The approach of the impurity level to the band can lead to temperature-dependent changes of the oscillator strength f of the impurity absorption, in contrast to the traditional theory. For the two temperatures (77 and 122 °K) for which the band was reliably investigated (see Fig. 1(a)), we obtained f by using the Smakula—Dexter formula[5] (Gaussian contour):

$$f = 0.87 \cdot 10^{17} \frac{1}{N} \frac{n}{(n^2+2)^2} \alpha_m H, \tag{3}$$

where α_m is the absorption coefficient at the maximum of the band (in cm^{-1}) and H is in eV. The refractive indices n at the given temperatures were measured by us by an interference method. We obtained $f^{(77K)} = 4.36 \times 10^{-3}$ and $f^{(122K)} = 4.13 \times 10^{-3}$. Indeed, as the fundamental edge is approached, the impurity band becomes depleted.

[1)]The real half width H at 300 °K exceeds the value extrapolated from (1) because of the possible turning on of the multiphonon mechanism.

[2)]Whereas in molecular crystals it is necessary to change the composition of the crystal in order to vary δE, in the present case the measurements are carried out on one and the same samples, since δE depends on T (Fig. 3).

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