Changes caused in the energy structure of self-trapped excitons by hydrostatic pressure in CsI and RbI crystals

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Experiments reveal a change in the sign of the baric shift and a sharp decrease in the intensity of the photoluminescence band of self-trapped excitons in CsI near 8 kbar. It is suggested that the effects are due to an inversion of radiating states of self-trapped excitons. The photoluminescence of singlet self-trapped excitons disappears from RbI at an $O_h^5 \rightarrow O_h^1$ phase transition.

A self-trapping of excitons occurs in many crystals and is the reason for such effects as a change in the mobility of excitons, a change in energy transport by excitons, the induction of radiation effects, and heat evolution.[1,2] An external pressure may, by changing the band structure of the crystal, affect the processes by which excitons undergo self-trapping and also the self-trapped states themselves. The effect of pressure on self-trapped excitons has recently attracted increased interest because of the suggested instability of self-trapped excitons during compression of a crystal.[3,4] The possibility of manipulating the properties of self-trapped excitons by means of an external pressure might present a way to control certain properties of crystals.

As samples for the present experiments we selected crystals of cesium iodide, CsI, with the CsCl structure (O_h^1), and of rubidium iodide, RbI, with the NaCl structure (O_h^5). In the cesium iodide crystals, a relatively modest hydrostatic pressure ($P < 10$ kbar) can cause radical changes in the (reflection) spectrum of free excitons,[5] while in the rubidium iodide an $O_h^5 \rightarrow O_h^1$ phase transition occurs at $P \approx 4$ kbar. Both of these circumstances increase the heuristic value of pressure experiments.

We have studied the effect of hydrostatic pressure, in a gaseous medium (helium), up to 11 kbar at $T = 80$ K, on the photoluminescence bands of self-trapped excitons in CsI with $E_{max} = 3.65$ eV (Refs. 6 and 7) and in RbI with $E_{max} = 3.9$, 3.0, and 2.3 eV (Ref. 8). For comparison, we have also studied the photoluminescence band of bound excitons in a CsI-Na crystal.[9] The samples are compressed in an optical chamber with leucosapphire windows, surrounded by liquid nitrogen. The pressure in the chamber is produced by a 15-kbar helium compressor.[10] The photoluminescence spectra are measured with an MDR-23 monochromator, an FÉU-106 photomultiplier, and a photon counting system. The photoluminescence is excited by a deuterium lamp through appropriate filters.

To excite the photoluminescence of the self-trapped excitons in CsI and RbI, we use the spectral interval 5.5–6.1 eV, in which there are three (reflection) bands of free excitons ($n = 1$), at 5.76, 5.90, and 5.97 eV in CsI (Ref. 5); in the RbI, there is a free-exciton band ($n = 1$) in this interval, at 5.7 eV. Separate measurements of the excitation spectra of the photoluminescence of self-trapped excitons in CsI show that at
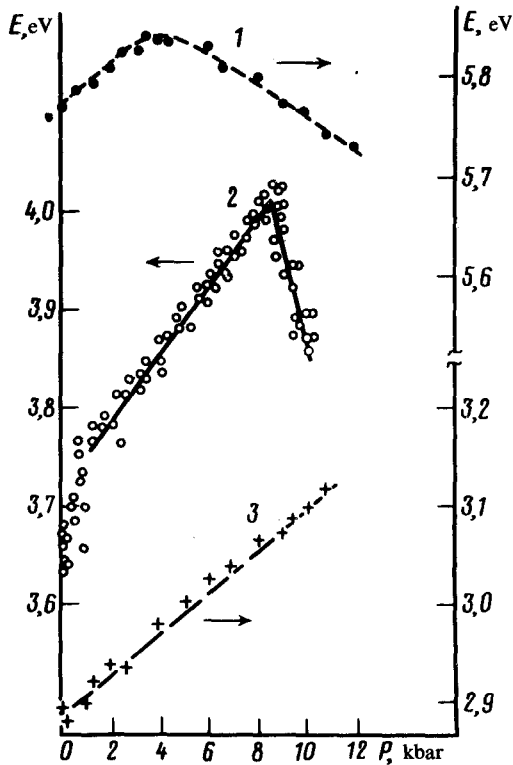
FIG. 1. Pressure dependence of the position of the peaks of the exciton bands in CsI crystals at $T = 80$ K and in CsI-Na crystals at $T = 295$ K. 1—Long-wave reflection band of free excitons in CsI (Ref. 5); 2—luminescence band of self-trapped excitons in CsI; 3—luminescence band of bound excitons in CsI-Na.

pressures up to ≈ 9 kbar the excitation bands are essentially identical to the reflection bands in terms of both positions and baric shifts. To determine the RbI excitation region, we measured reflection spectra at pressures P up to 10 kbar.

Figures 1 and 2 summarize the results on the behavior of the photoluminescence spectra of the self-trapped excitons in CsI. We see (curve 2 in Fig. 1) that the peak of the photoluminescence band at 3.65 eV shifts with increasing pressure (up to ~ 8.5 kbar) in the short-wave direction, at a rate of 36 ± 1 meV/kbar over the interval 1–8.5 kbar; beyond this interval, there is a sharp long-wave shift with a coefficient[1] of
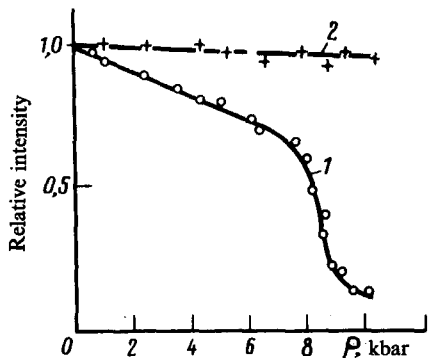

FIG. 2. Intensity of the exciton luminescence bands versus the pressure. 1—Self-trapped excitons in CsI ($T = 80$ K); 2—bound excitons in CsI-Na ($T = 295$ K).

$- 70 \pm 10$ meV/kbar. Near 8 kbar, there is again a sharp decrease in the photoluminescence intensity (curve 1 in Fig. 2), with the result that the spectral measurements at $P > 8$ kbar are less accurate and less reliable (because of a possible effect of stray light). In the pressure range 0–7.5 kbar, on the other hand, the photoluminescence intensity varies considerably less, decreasing by $\sim 30\%$. Both effects—the change in the direction of the shift and the sharp decrease in the intensity of the photoluminescence band of self-trapped excitons in the interval 7.5–9 kbar—are completely reversible with the pressure.

Curve 1 in Fig. 1, based on data from Ref. 5, shows the pressure dependence of the energy of the lowest free-exciton level, E^1_{free}, in CsI; this level is the "starting point" for the process of self-trapping of the excitons. The change in the slope on this curve at $P = 3.5$–6 kbar corresponds to a region in which the electron component of the exciton wave function changes from an s-type function ($P \lesssim 5$ kbar) to a d-type function. The overall symmetry of the free-exciton states (Γ_{15}) is conserved.[5]

It can be seen from Fig. 1 that the changes in the states of free excitons and self-trapping excitons are not rigidly coupled with each other: In the region of the non-monotonic change in E^1_{free} (curve 1), the photoluminescence band of the self-trapped excitons shifts monotonically (curve 2), and vice versa. The apparent reason is that at the rather high temperatures in our experiments ($T = 80$ K) the change at $P \approx 5$ kbar in the internal structure of a free exciton, which has a small radius in the $n = 1$ state, does not affect the thermally activated surmounting of the self-trapped barrier.[2] On the other hand, the smooth decrease in the photoluminescence intensity of the self-trapped excitons in the pressure range 0–7.5 kbar (curve 1 in Fig. 2) may be due to a decrease in the probability for a surmounting of the self-trapped barrier because of a possible increase in the width of the exciton band, B, as a result of compression of the crystal, since the barrier height w increases with increasing B. Evidence in favor of this explanation is the fact that during direct excitation of the photoluminescence of bound excitons in CsI-Na ($E_{\text{exc}} \approx 5.0$ eV, $E_{\text{rad}} \approx 2.9$ eV), in which case there is no need to surmount a self-trapped barrier, the decrease in the intensity does not occur (curve 2 in Fig. 2).

When we also take into account the nature of the sharpness of the changes in the photoluminescence of the self-trapped excitons, we get the impression that a change occurs in the energy spectrum of self-trapped excitons in CsI at $P \approx 8.5$ kbar. According to the model of Ref. 6, the complete wave function at self-trapped excitons in CsI is constructed from the $5p$ states of two I^- anions, forming a V_k center, and $6s$ and $5d$ states of the four surrounding Cs^+ cations. These cations contribute the lowest-energy states, Γ_1^+ (s-type) and Γ_3^+ (d-type), for the electrons in the self-trapped excitons and give rise to two types of self-trapped excitons, with lowest-lying triplet radiating levels $^3\Gamma_2^-$ and $^3\Gamma_4^-$, respectively. It may be that these levels lie extremely close together along the energy scale. The photoluminescence band of self-trapped excitons at $E_{\text{max}} = 3.65$ eV in CsI corresponds to transitions from the $^3\Gamma_2^-$ lower level.

By analogy with the free excitons in CsI (Ref. 5), it might be suggested that pressure causes the s-states and d-states of electrons and the corresponding $^3\Gamma_2^-$ and $^3\Gamma_4^-$ states of self-trapped excitons to move closer together along the energy scale, and at $P \approx 8.5$ kbar an inversion of these states occurs. The result would be sharp

changes in the characteristics of the self-trapped excitons, since the luminescence from the $^3\Gamma_4^-$ level is quenched[7] at $T = 80$ K. For bound excitons in CsI-Na, whose spatial and energy structure differs from that of self-trapped excitons, no change in structure occurs (curve 3 in Fig. 1). In this case the shift of the photoluminescence band is 21 ± 1 meV/kbar.

In the photoluminescence spectra of self-trapped excitons in RbI we have observed (1) an intensification of the photoluminescence band at 2.6 eV, associated with α centers,[8] as the pressure is increased; 2) the disappearance of the photoluminescence of singlet self-trapped excitations with $E_{max} = 3.9$ eV at $P > 4$ kbar (after the $O_h^5 \to O_h^1$ phase transition) and the restoration of this photoluminescence after the removal of the pressure $(O_h^1 \to O_h^5)$. The latter effect supports the theoretical conclusion[6] that a radiative transition from a particular singlet level of self-trapped excitons may be forbidden in structures of the CsCl type (O_h^1).

We wish to thank Ch. B. Lushchik and G. S. Zavt for discussions of this study.

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[1]To the best of our knowledge, these are the highest rates of baric shifts that have ever been observed in luminescence spectra.

[2]Although the height of the self-trapped barrier in CsI is not known, it is apparently small, since at $T = 80$ K the luminescence of free excitons is completely quenched.[11]

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Translated by Dave Parsons