Investigation of the optical absorption spectra of cesium iodide (CsI) under pressures up to 60 GPa

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The optical absorption spectra of single crystals of CsI were measured in a cell with diamond anvils at pressures up to 60 GPa. The fine structure of the spectra near the characteristic absorption edge of CsI is investigated at high pressures for the first time. It is shown that exciton effects play a significant role in this region of the spectrum. Based on the experimental results obtained, an estimate of the pressure of metallization of CsI (~ 110 GPa) is given.

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In recent years, due to the development of the technology of diamond anvils, it has become possible to investigate condensed noble gases and alkali-halide compounds from the point of view of the metal-insulator transition. Among these substances, Xe and its isoelectronic analog CsI, whose metallization pressure according to different estimates falls within experimentally attainable limits, are of greatest interest.[1] Recent

investigations of optical absorption under ultrahigh pressures have shown that Xe apparently transforms into the metallic state at pressures considerably exceeding 100 GPa.[2-4] The corresponding estimates for CsI ($P = 70$–80 GPa), made in Ref. 5, appear to be more optimistic. It must be admitted, however, that the interpretation of the experimental results given in Refs. 2–4 is not without faults, since the authors of these papers, for different reasons, could not observe the fine structure of the absorption edge of Xe and CsI attributed to exciton effects (measurements at atmospheric pressure[6-8] definitely show that exciton absorption makes an important contribution to the absorption spectra of Xe and CsI).

In this paper we report on the investigation of optical absorption of CsI at pressures up to 60 GPa at room temperature. It is shown for the first time that near the characteristic absorption edge of CsI, exciton absorption peaks are observed at high pressures. The metallization pressure of CsI is estimated from the experimental data obtained (~ 110 GPa).

To measure the absorption spectra at high pressures, we used a cell with diamond anvils. The medium for transmitting the pressure was solid xenon.[3] As a result, nearly hydrostatic conditions were maintained in the cell up to the maximum attainable pressure of 60.3 GPa (the pressure drops in the working volume of the cell did not exceed 0.5 GPa). The optical density was determined from measurements of the transition spectra of Xe and of two specimens of CsI with different thickness. The CsI specimens consisted of cleaved plane-parallel single-crystalline plates with dimensions 30×20 μm and thickness 5–15 μm. The measured absorption measured was 10^3–10^4 cm^{-1}. The transmission spectra were recorded on a double DFS-24 monochromator (1.5–3 eV) and a modified DFS-12 monochromator[1)] (1.4–2.5 eV at pressures above 57 GPa) with the help of a specially developed optical microattachment. The pressure in the diamond cell was determined with the help of a ruby manometer in accordance with the calibration proposed in Ref. 9. The experimental error in determining the pressure was ± 0.2 GPa. All measurements were performed at room temperature.

The typical absorption spectra of CsI with different pressures in the range 40.4–60.3 GPa are shown in Fig. 1. As is evident from this figure, as the pressure is increased, the curves of the optical density are displaced monotonically into the long-wavelength region of the spectrum. For all measured spectra, the presence of a distinct peak near the absorption edge is characteristic (1). In addition, a second diffuse absorption peak is observed in the short-wavelength region of the spectra (2).

Figure 2 shows the pressure dependences of the spectral positions of peaks 1 and 2. This figure also shows the coordinates of the first two exciton absorption peaks at atmospheric pressure (~ 5.6 and 6.0 eV, Refs. 7 and 8), corresponding to direct interband transitions $\Gamma_8^- \rightarrow \Gamma_6^+$ and $\Gamma_8^- \rightarrow \Gamma_8^+$ from I^-5p to Cs^+6s and $5d$ bands.[10] As follows from the data in Ref. 11, the indicated exciton levels undergo inversion at a pressure above 0.7 GPa,[2)] so that the peaks 1 and 2 observed by us can be identified with the excitons (Γ_8^-, Γ_8^+) and (Γ_8^-, Γ_6^+), respectively (see Fig. 2).

To clarify the nature of the behavior of the minimum forbidden band E_g and the binding energy of the exciton R at high pressures, we shall use the theory in Ref. 12, which describes the optical absorption in the region of the unbound state of the exciton. Simple considerations,[3)] showing that at high pressures the minimum energy gap

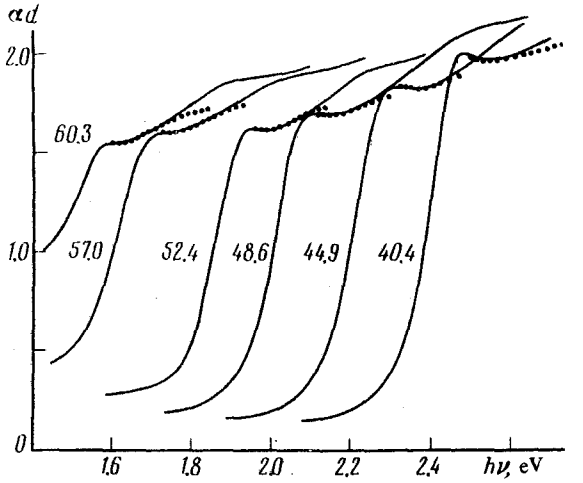

FIG. 1. Curves of the optical density in CsI at different pressures (GPa). The points show the results of calculations using the theory in Ref. 12. We call attention to the fact that the theoretical description does not include the second absorption peak.

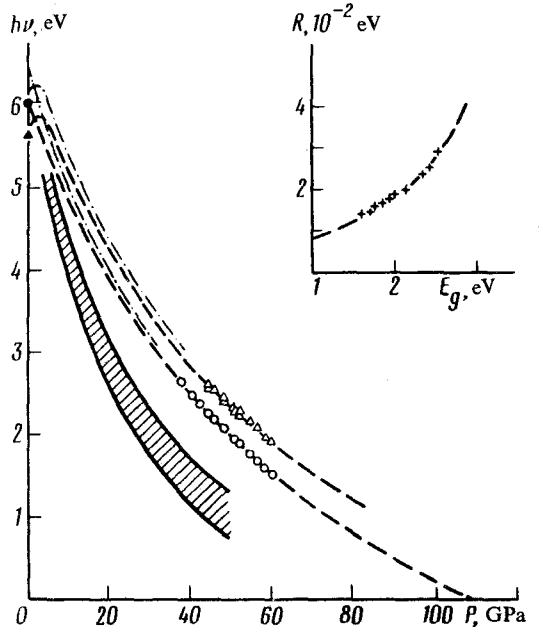

FIG. 2. Energy characteristics of absorption spectra of CsI at high pressures. ○, △ — The spectral positions of the first and second absorption peaks (see Fig. 1) at different pressures; ▲, ● — the same for the first two absorption peaks at atmospheric pressure and at room temperature.[7,8] The dashed lines and the dot-dashed lines indicate the pressure dependences of the positions of the exciton levels and the corresponding energy gaps. The shaded region corresponds to the estimates of E_g in Ref. 5. The insert shows the dependence of the binding energy R of the lower exciton state on the quantity $E_g(+)$, calculated using the theory in Ref. 12.

corresponding to the interband transition $\Gamma_8^- \rightarrow \Gamma_8^+$ is situated in direct proximity to the first exciton peak or, in other words, the binding energy R of the exciton (Γ_8^-, Γ_8^+) is small compared to the distance between the two exciton peaks ($\sim$0.4 eV), can serve as a justification for using this theory in the case of the complex exciton spectrum of CsI. The results of the corresponding calculations are shown in Figs. 1 and 2.

As is evident from Fig. 2, the behavior of the quantity $R(E_g)$ indicates the rapid convergence of the lower exciton level E_{ex} to the corresponding energy gap E_g. For this reason, to estimate the metallization pressure of CsI, it is natural to make use of the dependence $E_{ex}(P)$, determined reliably in the experiment. Extrapolation of this dependence to zero (see Fig. 2) gives the estimate $\sim$110 GPa for the metallization pressure of CsI. We might note that this result differs appreciably from the estimate 70–80 GPa in Ref. 5.

[1)]We are grateful to G. N. Zhizhin and N. N. Mel'nik for kindly making it possible for us to perform the measurements using this apparatus.

[2)]We note that the rearrangement of the conduction band of CsI under the action of pressure is analogous to the inversion of the electronic s and d states in metallic Cs.[13,14]

[3)]The red shift of the absorption edge of CsI under pressure indicates that E_g decreases with incresing pressure, which in turn leads to a strong decrease in the binding energy of the exciton $R \sim E_g^4$ ($R \sim \epsilon^{-2}$, $\epsilon \sim E_g^{-2}$, ϵ is the dielectric constant).

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