Optical absorption spectra of cesium iodide (CsI) at pressures up to 60 GPa

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The optical absorption spectra of CsI single crystals have been measured in a diamond anvil cell at pressures up to 60 GPa. For the first time, the fine structure of the absorption edge of CsI has been observed at high pressures. The exciton effects are shown to be responsible for the fine structure of the absorption edge. The pressure of metallization of CsI is estimated to be approximately 110 GPa.

The recent progress in the diamond anvil technique has made possible the experimental study of the insulator-to-metal transitions in relatively simple systems, such as rare-gas solids and alkali halide crystals. Xe and its isoelectronic analog CsI are of particular interest for their metallization pressures are believed to be in the experimentally accessible region.[1] The recent optical absorption studies at ultrahigh pressures show that the metallization pressure of Xe is probably much higher than 100 GPa.[2-4] The corresponding estimates for CsI look more encouraging and fall in the range 70–80 GPa.[5] However, there is a reason to believe that the interpretation of the experimental data given in Refs. 2–5 is oversimplified and exciton effects, which are typical of those substances at normal pressure,[6-8] were not properly taken into account.

In the present Rapid Communication we report the optical absorption spectra study of CsI at pressures up to 60 GPa at room temperature. To the best of our knowledge this is the first report where the exciton absorption effects at ultrahigh pressures are described. On the basis of our experimental data the metallic transition in CsI is expected to occur at about 110 GPa.

The experiments were carried out by means of the gasketed anvil cell. Solid Xe was used as a pressure transmitting medium.[3] The pressure gradient in the cell did not exceed 0.5 GPa up to the maximum pressure of 60 GPa. The optical density of CsI was obtained on the basis of the transmission spectra measurements of Xe and two CsI samples of different thickness. The CsI samples were flat monocrystalline chips with in-plane dimensions 30×20 μm^2 and 5–15 μm thick. The absorption coefficient which could be measured was confined to 10^3–10^4-cm^{-1} range. The transmission spectra were recorded with the aid of double grating monochromators[9] and a specially designed optical microsample system. The pressure was measured by the well-known
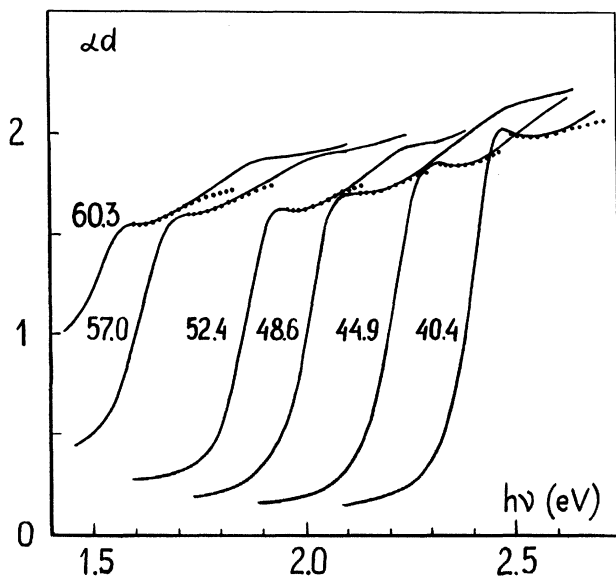

FIG. 1. Optical density curves of CsI at various pressures (GPa). The dotted lines represent the results of the calculations carried out using the theory (Ref. 15). Note that the theoretical description does not include the second absorption maximum.
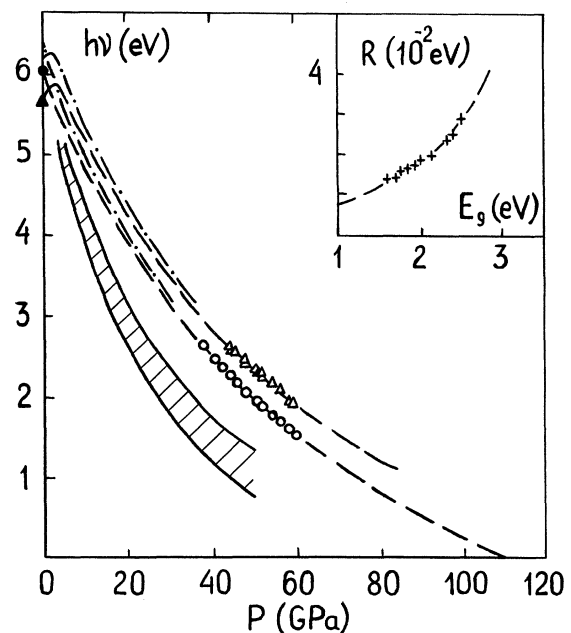

FIG. 2. Energy characteristics of the CsI absorption spectra at high pressures. O, Δ: spectral positions of the first and the second absorption maxima (Fig. 1) at various pressures; ▲, ●: the same at room temperature and atmospheric pressure (Refs. 7 and 8). The dashed and dot-dashed lines represent the pressure dependence of the exciton maxima and the corresponding band-gap energies. The shaded area corresponds to the band-gap energy E_g estimations obtained in Ref. 5. The inset shows the exciton binding energy R corresponding to the lowest interband transition vs the band-gap energy E_g (+) according to the theoretical calculations (Ref. 15).

ruby fluorescence method[10] with a precision of ± 0.05 GPa. All the measurements were performed at room temperature.

The typical optical absorption spectra at various pressures from 40.4–60.3 GPa are shown in Fig. 1. One can see that the optical density curves shift monotonically to the low-energy side as pressure increases. All the spectra reveal the existence of the well-formed maximum (1) near the absorption edge. Apart from that there is a second broad absorption maximum (2) on the high-energy side of the spectra.

In Fig. 2 the pressure dependences of the spectral positions of the 1 and 2 maxima are shown. In the same diagram we also plot the coordinates of the first two exciton absorption peaks at 0 GPa [5.6 and 6 eV (Refs. 7 and 8)], corresponding to the $\Gamma_8^- \to \Gamma_6^+$ and $\Gamma_8^- \to \Gamma_8^+$ direct interband transitions from the I^- $5p$ state into the Cs^+ $6s$ and $5d$ ones.[11] Since these bands cross at pressures more than 0.7 GPa,[12] we assign the 1 and 2 maxima to the (Γ_8^-, Γ_8^+) and (Γ_8^-, Γ_6^+) excitons (Fig. 2), respectively.[13,14]

In order to elucidate the behavior of the band-gap energy E_g and the exciton binding energy R at high pressures we tentatively use the theory,[15] describing the optical absorption in the vicinity of the absorption edge.

The use of theory[15] in the case of complex exciton absorption spectrum of CsI may be justified on the basis of simple consideration,[16] which shows that at high pressures the lowest band gap, corresponding to the $\Gamma_8^- \to \Gamma_8^+$ direct transition, is very close to the first exciton maximum, or, in other words, the exciton binding energy R is small as compared with the energy difference between the two stated exciton maxima. The results of the corresponding calculations are presented in Figs. 1 and 2.

As seen from Fig. 2, the exciton binding energy R rapidly decreases with the pressure which results in the fact that the first exciton maximum energy and the band-gap energy become very close at high pressures. Thus, the metallization pressure of CsI may be estimated by the extrapolation of the $E_{ex}(P)$ dependence which can be reliably obtained from the experiment. This extrapolation yields the pressure of the metallic transition in CsI of approximately 110 GPa, which is surprisingly close to the theoretical estimate,[17] but differs considerably from the results reported by Asaumi and Kondo.[5]

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