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► **To cite this version:**

J. Itie, A. Polian, J. Besson. VARIATION OF THE OPTICAL ABSORPTION EDGE OF CsI AT HIGH PRESSURE. Journal de Physique Colloques, 1984, 45 (C8), pp.C8-47-C8-51. 10.1051/jphyscol:1984809 . jpa-00224307

HAL Id: jpa-00224307

<https://hal.science/jpa-00224307>

Submitted on 4 Feb 2008

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VARIATION OF THE OPTICAL ABSORPTION EDGE OF CsI AT HIGH PRESSURE

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Résumé - L'absorption optique d'un monocristal de CsI a été mesurée à température ambiante jusqu'à des pressions de 58 GPa, en utilisant le xénon comme milieu transmetteur de pression. La forme et la position du front d'absorption mesuré diffèrent de façon significative des résultats obtenus sur des poudres, alors que seule la forme diffère des résultats précédents obtenus sur des monocristaux.

Abstract - Optical absorption was measured in single crystals of CsI at room temperature at pressures up to 58 GPa, using xenon as a pressure transmitting medium. The shape and position of the absorption edge are shown to differ significantly from results obtained on powders, whereas only the shape differs from results obtained on single crystals.

Investigations of the transition from isolating to conducting behavior of solids under pressure have been actively pursued lately. In cesium iodide, which is ionically isoelectronic with xenon, band closure should be attainable with a diamond anvil cell.

It has been studied among other techniques by optical absorption measurements either on powder⁽¹⁻³⁾ or on single crystals⁽⁴⁻⁵⁾. X-ray measurements show one⁽²⁻⁴⁾ crystallographic phase transitions around 40 GPa.

In this paper, we report optical absorption results on monocrystalline CsI up to 57,5 GPa using Xe as a pressure transmitting medium and compare it with previous results.

Experiment

Xenon was used as a pressure transmitting medium. A $50 \times 40 \times 10 \mu\text{m}^3$ single crystal of CsI and a ruby chip were placed at the center of the hole of the stainless steel gasket. Sample and gasket hole stay centered with respect to the diamond culets during the experiment, within $10 \mu\text{m}$. This minimizes the pressure gradient within the active volume of the sample. Pressure was measured by pressure shift of the luminescence line of ruby⁽⁷⁾. Unpolarized transmission spectra was measured under a microscope, through a $15 \mu\text{m}$ region selected by a focal iris. Transmitted and reference beams went through the CsI sample and xenon at all pressures.

No correction was made for reflexion losses at the Xe-CsI interface⁽⁵⁾. Two sets of correction were made on the raw spectra.

- In the highly absorbing, high energy range, diffused stray light induces a constant apparent transmittancy which has been subtracted.
- In the low-energy range, geometrical factors in the setup and structural inhomogeneity in the sample induce a constant apparent absorbancy which must be fitted to $\alpha \approx 0$.

Pressure inhomogeneity within the sample was less than 2GPa, by comparison with the line broadening of the ruby emission.

Results and analysis

Several features are apparent in fig. 1.

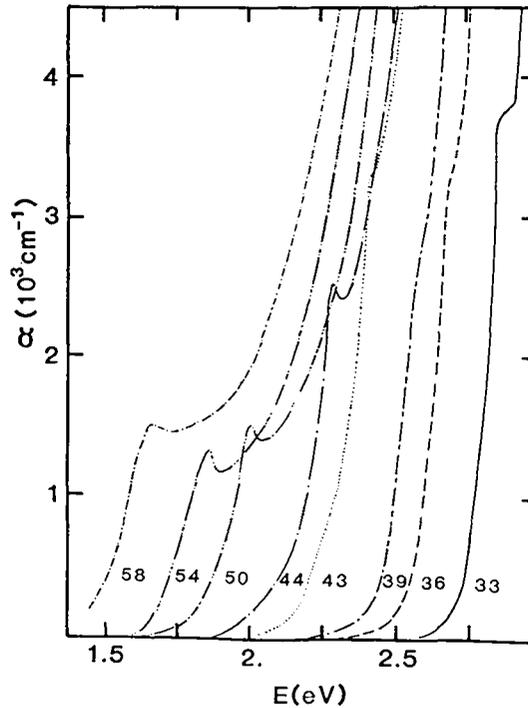


Fig. 1 : Absorption coefficient of a CsI sample ($d \approx 10 \mu\text{m}$ at $P = 0$ in xenon at $T = 300 \text{ K}$. Pressures are in GPa.

- 1) The absorption edge shifts continuously to lower energies with increasing pressure.
- 2) The shoulder on the absorption edge disappears when the pressure is increased up to 40 GPa.
- 3) When the pressure is further increased, it reappears a well-defined peak.
- 4) The apparent absorption spectrum is steeper at lower pressure.

The electronic band gap energy cannot be derived from the absorption edge without some physical model for the transition. Here we will examine the most likely process : allowed direct transition. In this case, it is natural to examine the assignment of the shoulder which appear below 40 GPa to an exciton. If we compare with the room pressure spectrum⁽⁸⁾ we note that the integrated intensity decreases between 0 and 40 GPa by a factor of 60.

For a Wannier exciton, the integrated intensity can be written⁽⁹⁾

$$\alpha \Gamma \propto \frac{\mu^3 |M|^2}{\epsilon^{7/2} E_G^d}$$

α : absorption maximum, Γ : full width at half maximum
 μ : reduced mass of the exciton, ϵ : the dielectric constant,
 M : the matrix element of the transition and E_G^d : the direct gap.

We take M to be independent of pressure, and ϵ to have the same pressure dependence as in Xe, while E_G^d decrease from 6 to ~ 2 eV⁽¹⁰⁾. Then a decrease of μ factor of 3 to 4 will account for the observed intensity and is consistent with the latest band structure calculations. This evaluation depends on several assumptions, and is only meant to show that the kink we observe, despite its small intensity, may be assigned with a direct exciton. Nevertheless, the shape of the high energy absorption is not that of direct continuum, with Coulomb interaction and must be related to the low-energy tail of a deeper level⁽⁹⁾. In any case, the exciton energy (circles in fig. 2) certainly represent a lower value for E_G^d .

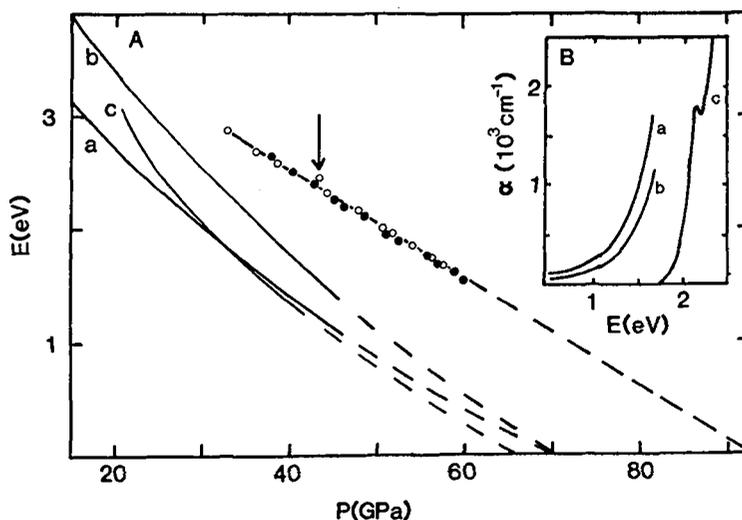


Fig. 2 A : Energy gap (eV) vs pressure (GPa) in CsI. a and b are threshold energy gap E_{th} and direct energy gap of ref. 1. c : absorption edge (ref. 2). Circles : exciton energy E_x (this work). Points : "Exciton energy" (ref. 4). Dashed lines : extrapolations to zero energy. The arrow indicate the location anomaly of the exciton peak near the phase transition.

B. : Comparison of our results with those of K. Asaumi (réf. 6) a and b : absorption coefficient of ref. 1, with samples thicknesses of 20 and 30 μm at 46 GPa. e : absorption coefficient at 48 GPa (this work).

Above 44 GPa, polarized light measurements should be done, in order to determine the optical gap. However, we have an indication of the position of the band edge. It should be noted on figure 2 that apart from the transition pressure (arrow) E_x versus P has a continuous variation, which fits with a very small volume variation at the transition, and presumably a small optical anisotropy.

Discussion and Conclusion

Comparison of our results (figure 2A and B) with the preceding shows clearly two sets of results : on the one hand, results obtained on powders⁽¹⁻²⁾, and on the other hand, those obtained on single crystals with a pressure transmitting medium⁽⁴⁻⁵⁾.

The shape and position of the edge are very different between the two set of results, whereas only the shape of the edge (see fig. 2A) differentiates the "single crystal" results.

We interpret the differences between single crystal and powder by the higher pressure homogeneity over the active volume of single crystals, the use of a reference beam, and the nature itself of the crystal and the powder. This discrepancy in the raw data leads to significant differences in the variation of the gap and of the extrapolated band closing pressure. Whereas powder results predict a band closing between 65 and 70 GPa⁽¹⁻²⁾, our linear extrapolation, which is a lower limit gives 93 GPa and Makarenko et al.⁽⁴⁾ predict 110 GPa, using a non linear extrapolation.

These two last results fit reasonably well with band structure calculations which predict 100 ± 10 GPa. If the variation of the position of the energy gap fits very well (fig. 2A) the shape of the absorption curve is quite different. (fig. 3).

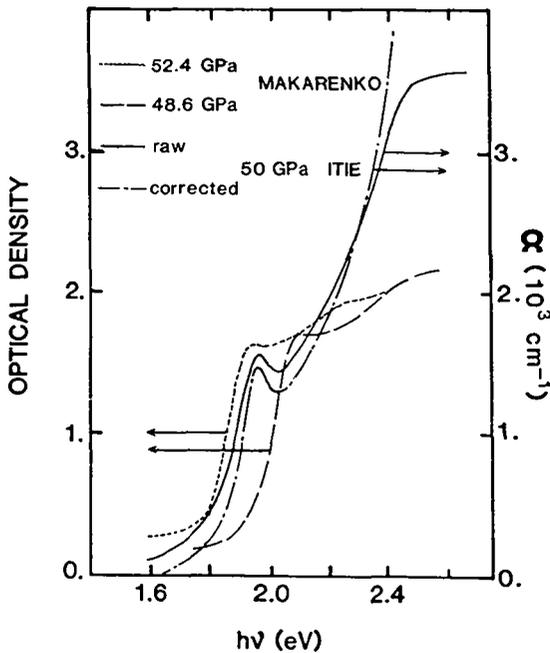


Fig. 3 Comparison of our results with those of Makarenko (ref. 4)----- and -----: optical density (left hand scale) at 52.4 and 48.6 GPa, respectively from ref. 4, -----: raw and corrected absorption coefficient (right hand scale) at 50 GPa (this work).

In conclusion, it should be emphasized that the difference between the two set of results is very big. Then it seems to be necessary to use monocrystalline samples in transparent quasihydrostatic pressure transmitting medium, in order to extract meaningful data.

Note added in proof :

Absorption and X-ray measurements were performed recently on polycrystals⁽¹³⁾. The band gap variation does not fit with neither set of results discussed above. Indeed, in this work, samples are polycrystals and the stray low energy absorbancy is not corrected for. Moreover, the gap is arbitrarily located at a constant absorption coefficient ($9 \times 10^3 \text{ cm}^{-1}$) for all pressures.

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