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To cite this version:

J P Itic, A Polian, J M Besson. Optical-absorption edge of CsI up to 58 @Pa. Physical Review B: Condensed Matter (1978-1997), 1984. hal-03085341

HAL Id: hal-03085341

https://hal.science/hal-03085341v1

Submitted on 21 Dec 2020

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RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 4 15 AUGUST 1984

Optical-absorption edge of CsI up to 58 GPa

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(Received 13 February 1984; revised manuscript received 30 April 1984)

The optical transmittancy of cesium iodide single crystals has been studied up to 58 GPa, using xenon as a pressure-transmitting medium. The shape and position of the absorption edge under pressure has been measured under controlled stress-homogeneity conditions. It is found to differ significantly from previous results obtained on highly strained powder samples. The data are analyzed in terms of band-to-band transitions and show that band closing in cesium iodide is not to be expected below 90 GPa.

INTRODUCTION

Transitions of insulators to a conducting phase under high pressure are actively investigated at the present time, using dynamic and static methods. A rough evaluation of the "metallization" pressures can be obtained using Herzfeld's criterion;[1] although, for a variety of elements and compounds, a detailed study of the band-closing process is necessary using standard solid-state methods. Cesium iodide is expected to evolve to a conducting state in the range of attainable static pressures, possibly below 100 GPa. Recent results on the absorption edge[2,3] point to closing of the band gap to occur in the vicinity of 70 GPa. X-ray measurements[3–5] indicate the presence of two crystalline phase transitions between 40 and 70 GPa, which may significantly modify these predictions. Moreover, the equation of state (EOS) of CsI is somewhat uncertain at the present time,[3–8] above 30 GPa.

In this Rapid Communication, we report optical-absorption experiments on CsI monocrystals where the pressure gradient on the sample has been kept below 2 GPa, up to 57.5-GPa nominal pressure. The results for the absorption edge are shown to differ significantly from published data,[2] obtained under inhomogeneous conditions. We then analyze the observed absorption edge in terms of band-to-band transitions and show that the expected band closing pressures are considerably higher than those which have been previously proposed.[2,3]

EXPERIMENT

Xenon has been used as a pressure transmitter in a diamond anvil cell.[9] A cleaved $50\times40\times12$-μm^3 sample of monocrystalline CsI was placed in the center of the gasket hole. The hole in the AISI 301 stainless-steel gasket was 200 μm across and 40 μm thick at the filling pressure (5 MPa) and shrank down to 95 μm in diameter and 20 μm in thickness at 50 GPa. The sample and gasket hole were kept centered with respect to the anvil culets within 10 μm. This is an important condition for minimizing pressure gradients since at the center of the cell, both the gradient of the hydrostatic component of stress, and radial strain are minimum. Pressure was measured by the R_1 line shift of a 10-μm ruby chip close to the sample.[10] Transmission under a microscope through a 15-μm region of the experimental space was measured by a suitable focal iris. Transmitted and reference beams were measured through the CsI sample and the xenon, at all pressures. Unpolarized transmitted light was analyzed on a T 800 Coderg monochromator. No allowance was made for reflection losses at the CsI-Xe interfaces since both media have similar EOS, and were taken to have analogous indices. In the high-absorption region, the apparent transmission was corrected for diffused stray light by subtracting the constant ($\sim 2\%$) transmission background. We thus do not expect the accuracy on the absorption coefficient α to be better than 20% in absolute value. In contrast, the relative dispersion of the points on a given

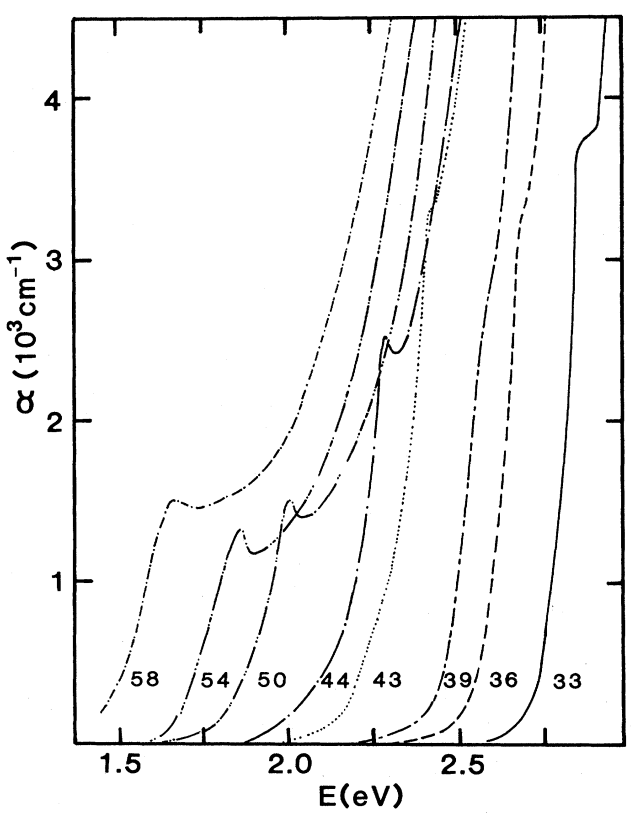

FIG. 1. Absorption coefficient of a 10-μm-thick sample of CsI in xenon $T=300$ K. Pressures are given in GPa according to the scale of Ref. 10. Absorption coefficient was scaled down to zero below 1.3 eV. Diffuse stray light level corresponds to $\alpha > 4000$ cm^{-1}.

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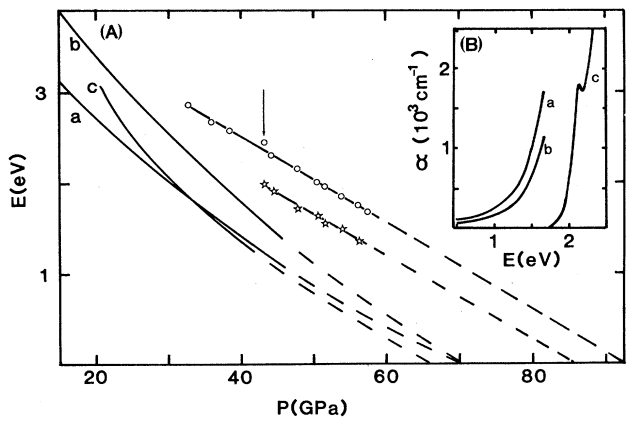

FIG. 2. (A) Energy gap (electron volts) vs pressure in CsI. a and b are threshold energy gap E_{th} and direct energy gap E_g from Ref. 2; c is the absorption edge from Ref. 3. Circles: "exciton" energy (this work), E_x. Stars: indirect gap energy E_g^i (this work, see text). Dashed lines are extrapolations to zero energy. All pressures scales are along Ref. 10. The arrow indicates a singular location of the exciton peak, in the vicinity of the first phase transition. (B) Comparison of our absorption data with other work at similar pressures. a and b are the absorption coefficient at 46 GPa from Ref. 2, sample thicknesses of 20 and 30 μm, respectively. The evaluation of upper and lower values for sample thickness is from K. Asaumi (private communication). c is the absorption coefficient at 48 GPa (this work).

spectrum is less than 1%. The pressure inhomogeneity within the active region of the sample was evaluated to be less than 2 GPa, by reference with the apparent broadening (7 $cm^{-1} \simeq 1$ GPa) of the R_1 line of the ruby reference chip.

Under these conditions, the absorption edge of CsI shifts to lower energies under pressure, as shown in Fig. 1. Several features may be pointed out.

(i) An absorption shoulder (kink) disappears with increasing pressure up to some 40 GPa. A well-defined peak reappears above 44 GPa. This feature had not been reported before.

(ii) At 43 GPa, this absorption peak is off, in energy with respect to the points for the other pressures (Fig. 2).

(iii) The shape of the absorption edge is different above and below this pressure.

ANALYSIS OF RESULTS

The relevant quantity to be extracted from our results is the optical band gap and this just cannot be guessed from the location of the optical edge without some physical justification. Here, we shall discuss two possibilities: direct and indirect (phonon-assisted) processes.

In the first case it is worthwhile to examine whether the shoulder which appears on the spectrum below 40 GPa can be related to one of the excitons in the room-pressure spectrum of CsI.[11] At room pressure, the lowest-energy exciton in CsI has an integrated intensity $\alpha\Gamma \simeq 60\times10^6$ cm^{-2}, Γ is the width at half maximum. Under pressure, that is between 30 and 55 GPa, we estimate $\alpha\Gamma$ of the peak to be between 1.6 and 0.6×10^6 cm^{-2}, that is a factor of 40–100 smaller. Now, using a Wannier exciton model,[12] we find for the integrated intensity

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

where μ is the reduced mass of the exciton, ϵ the dielectric constant, M the matrix element of the transition, and E_g^d the direct energy gap.

Taking M to be constant when E_g^d decreases from 6 to ~ 2 eV at 40 GPa and ϵ to increase from ~ 3 to 5 as it does in Xe (Ref. 13), we find that a decrease of μ by a factor of 3–4 only, would account for the decrease of $\alpha\Gamma$ that we observed. Recent band-structure calculations[14] show that this order of magnitude is entirely expected in view of the strong decrease of the electron and hole effective masses, at the direct gap. This evaluation admittedly rests upon a number of hypotheses. Among others, a hydrogenic exciton behavior is assumed at all pressures, which may not be the case. Also, the dielectric constant used here (Xe) does not take into account the reststrahl contribution in CsI: this implies either that the static ϵ varies the same way or that the $n=1$ exciton frequency is higher than the LO mode (10 meV).

Nevertheless, the calculation shows that, for lack of other evidence, the kink we observe, despite its small intensity, may be tentatively assigned to a direct exciton. The direct gap itself cannot be directly linked to the observed absorption edge above the exciton since a band-to-band continuum has a completely different shape.[12] To be consistent, we have to relate it to the low-frequency tail of deeper level.[11] In this scheme, experiments show that, with increasing pressure, the edge of this level catches up with the exciton below 40 GPa, then separates from it above 44 GPa, which is consistent with the existence of the phase transition in this region. Thus, the exciton energy E_x [starred circles in Fig. 2(A)] certainly represents a lower value for E_g^d.

Above 44 GPa, our unpolarized light measurements should not yield exact values for α. Nevertheless, we still have an indication of the location of the optical edge with lowest energy. Note that apart from transition region (arrow), E_x vs P has a continuous behavior, which fits with the fact that the volume change at the transition is very small.[3–5]

For the sake of completeness, we examined the possibility that the phase transition around 40 GPa would turn CsI into an indirect-gap structure and found it possible to fit the absorption edge above 44 GPa with a quadratic law (indirect transitions) after subtraction of an *ad hoc* Lorentzian representing the absorption maximum, using lattice modes in the range of 400 cm^{-1} which is reasonable in view of the low-pressure Grüneisen constant.[15] The location of E_g^i (indirect) is indicated in Fig. 2(A). This assignment nevertheless is rather unlikely: apart from leaving the absorption peak unexplained (impurities? F center? exciton linked to a higher-lying edge?), it contradicts the band-structure calculations[14] which show CsI to be strongly direct under pressure. A weak tetragonal distortion around 40 GPa is not exactly expected to strongly modify the band structure. One should note also that the weak pressure inhomogeneity discussed in the experimental part (up to 2 GPa at 55 GPa) will also account for the apparent "flattening" of the edge above 40 GPa. This may be mistaken for a quadratic dependence of α on energy.

DISCUSSION AND CONCLUSION

Comparison of our $\alpha(E)$ curves [insert Fig. 2(B)] with previously published data shows large differences on the shape and position of the edge. The reason for this might be sought in the use of the xenon as a pressure transmitting medium: it might be argued that Xe diffuses into CsI at high pressure and modifies the absorption spectrum. In this case we would expect the apparent absorption edge to start at a lower energy than in pure CsI, because of band tailing, and to flatten out at higher energies, because of the superposition of the absorbancy of Xe-diffused CsI at the surface, and of pure CsI in the bulk. The observed behavior is exactly the opposite [Fig. 2(B)]: the edge starts at higher energies and its shape is steeper. On decreasing the pressure, moreover, the process is reversible and no alteration of the crystal could be detected. Therefore, although we cannot absolutely rule out the possibility of Xe diffusion, we have no positive evidence for it.

More likely reasons for the difference in results would be the higher-pressure homogeneity over the active region of our samples, the use of a reference beam, and the monocrystalline nature of our samples versus powders in Ref. 2. This discrepancy in the raw data, together with the difference in analysis of the absorption edge, leads to striking differences in the variation of the gap with pressure and in the extrapolation to higher pressures [Fig. 2(A)] between this work and previously published data. Whereas band closing is expected to occur between 65 and 70 GPa in Refs. 2, 3, and 5, our data, using the most likely band structure (direct gap) linearly extrapolate to 93 GPa at least. This fits rather well with band-structure calculations[6,14] which predict 100 ∓ 10 GPa. This evaluation, of course, implies that no reconstructive phase transition occurs above 60 GPa. If one uses the equation of state of Refs. 3, 6, 8, and 13 one finds that band closing should occur for a reduced volume V/V_0 of 0.43, whereas the equations of states[4,5,7] yields a prediction for V/V_0 of 0.46.

Although, in conclusion, both values seem to fit well with that obtained from Herzfeld's criterion,[1] that is $V/V_0 = 0.42$, it should be pointed out here that there is a sizeable difference for the experimentalist between pressures in the range of 60 to 80 GPa which have been attained by a number of laboratories and the range over 100 GPa, where optical measurements have not yet been published. Thus, straight application of this rule to interpret band closing in compounds and elements should be replaced by analysis of the band parameters with variable band gap. Moreover, to extract meaningful data for comparison with variable band-to-band transition schemes, there seems to be no alternative but to use in the future crystalline samples in transparent quasihydrostatic pressure media, helium being probably the only choice in the region above 60 GPa.[16]

Note added in proof. Similar results for the pressure variation of the optical edge energy in CsI have been independently reported.[17] Nevertheless, the shape of the optical edge given by the authors of Ref. 17 markedly differs from our results in the high-energy region, because they did not correct for stray light which completely alters the spectrum at low transmittancies.

ACKNOWLEDGMENTS

This work has been supported in part through a Direction des Recherches, Etudes, et Techniques Grant No. 80/500.

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