Optical absorption of solid xenon at high pressure

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The optical absorption of solid xenon has been studied in a diamond anvil cell up to pressures of 44 GPa in the spectral range of 2.5 to 5 eV. The onset of weak uv absorption above 36 GPa is attributed to indirect $5p$ -$5d$ interband transitions of Xe. At 44 GPa the optical gap is 3.9 ± 0.3 eV, in reasonable agreement with band-structure calculations of Ross and McMahan, but in sharp contrast to the reported metallization of Xe at 33 GPa.

The metallization of xenon at 33 GPa as reported by Nelson and Ruoff[1] has stimulated the recent theoretical interest[2–6] in the high-pressure behavior of this heavy rare-gas solid. According to the calculations of Ross and McMahan[2] and some previous theoretical studies[7,8] the insulator-metal transition for fcc Xe should occur above 130 GPa. A similar result was obtained by Ray and co-workers.[3,6] The emphasis of the band-structure calculations by Hama and Matsui[4] and by Christensen and Wilkins[5] was to account for the unexpectedly low metallization pressure. Contrary to the widely spread theoretical predictions of the transitions pressure [37 GPa (Ref. 5) to 200 GPa (Ref. 2)] the calculated ground-state isotherms[2,4,9] are in reasonable agreement with the 0-K isotherm derived from measurements up to 11 GPa.[10] In view of the large discrepancies for the valence-conduction-band gap, it is highly desirable to perform an independent experimental study of the high-pressure behavior of Xe.

In the present work we report high-pressure optical-absorption studies extending to a pressure of 44 GPa. The onset of weak optical absorption above 36 GPa at photon energies below 5 eV is attributed to valence-conduction-band transitions in Xe.

The absorption measurements were performed using a gasketed diamond window high-pressure cell which is described in detail elsewhere.[11,12] The diamond windows were of near type-II quality with only weak absorption below the 5.4-eV optical gap of diamond. Samples were loaded into the cell by the following procedure: A xenon crystal was grown by condensing Xe gas of 99.99% purity onto a substrate held at a temperature slightly below the melting point of Xe. The crystal was then cooled to about 100 K and transferred under N_2 atmosphere into the cold diamond anvil cell. There the sample was squeezed into the gasket of 100 μm initial thickness with a gasket hole of 120 μm diameter. The cell was pressurized to 3 GPa and warmed up to room temperature. The sample was recrystallized at room temperature by first lowering the pressure below the melting line and then increasing the pressure again. The optical absorption has been measured between 2.5 and 5.5 eV using a 60-W deuterium lamp as a light source and mirror optics and uv achromats as image forming elements. Light was passed through a 0.75-m spectrometer and detected by a uv sensitive photon counting system. Transmission spectra through the Xe sample were divided by the transmission of the empty diamond anvil cell. Pressures were measured by the well-known ruby fluorescence method.[13]

Figure 1 shows absorption spectra for the most interesting range of pressures and photon energies. At 3.2 GPa the absorption shows a steep edge starting at about 5.0 eV. This absorption is due to excitations across the diamond window optical gap. The energy of the absorption edge in the highly strained diamonds is considerably less than the value of 5.4 eV

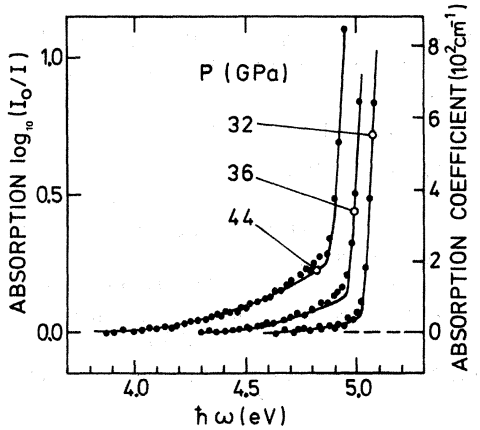

FIG. 1. Optical absorption of solid xenon measured in a high-pressure diamond anvil cell. The steep edge on the high-energy side of each spectrum is due to the absorption of the diamond windows, while the weak absorption feature below the diamond absorption edge at 36 and 44 GPa is attributed to $5p$ -$5d$ interband absorption of xenon. The solid line corresponds to a rough fit of an indirect absorption expression [Eq. (1)] to the experimental data points (see text).

for unstrained diamond. We emphasize that the position of the diamond absorption edge depends on the *strain* in the diamond window and can, in general, not be related to the pressure in the sample.

If the pressure is increased to 44 GPa the diamond absorption shifts further down in energy, but, in addition, a weak absorption feature occurs below the diamond gap. This weak absorption is already seen at 36 GPa. In order to clarify that this absorption indeed arises in the Xe sample and not in the diamond anvils, we measured the optical transmission through a LiF sample at 42.5 GPa using the same pair of diamonds. With LiF we did *not* find any indication for absorptions below the diamond edge. Therefore we attribute the absorption features below the diamond edge to the Xe sample.

According to the band-structure calculations the lowest valence-conduction-band excitation energy E_g in compressed fcc Xe is an indirect transition between a $5p(\Gamma_{15})$ state at the Brillouin-zone center and a $5d(X_1)$ state at the Brillouin-zone edge. From the theory of optical interband transitions we find that the absorption I/I_0 for allowed indirect transitions between parabolic bands is given by[14]

$$\ln(I/I_0) = -Cd\hbar\omega(\hbar\omega - E_g)^2 = -\alpha d \quad , \qquad (1)$$

where d is the sample thickness and C is a constant containing information about transition matrix elements and combined density of states. The solid lines in Fig. 1 correspond to a superposition of a weak indirect absorption for Xe ($Cd = 0.35$, when energies $\hbar\omega$ and E_g are measured in eV) and a strong indirect absorption edge for diamond ($Cd = 9.0$). The absorption coefficient $\alpha(\hbar\omega)$ can be estimated from the approximate sample thickness of about 30 μm. The rough fit of the indirect absorption expression Eq. (1) to the experimental data yields values for the Xe optical gap of 4.3 eV at 36 GPa and 3.9 eV at 44 GPa. If this procedure for determining the optical gap is correct, we estimate the uncertainty of the gap values to be ± 0.3 eV. The values for the optical gap are in agreement with the visual observation of Schiferl,[15] who could not detect any color change of Xe at 44 GPa.

In Fig. 2 we compare the experimental results with the optical gap calculated for fcc Xe by Ross and McMahan.[2] For the pressure volume conversion we used the 0-K shock-wave potential isotherm of the same authors. The optical gap lies in between the two theoretical lines corresponding to augmented plane-wave (APW) calculations with Slater (S) and Hedin-Lundqvist (HL) exchange correlation potentials. The Slater exchange is believed to be more reliable for the computation of highly excited electronic states, while the Hedin-Lundqvist approximation is believed to be correct close to the gap closure.[16] Therefore it is not unexpected that the experimental

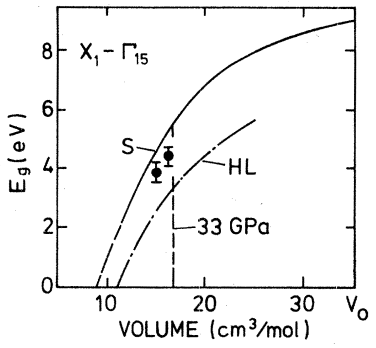

FIG. 2. Comparison between the experimental optical gaps of xenon (●) and the theoretical predictions by Ross and McMahan (Ref. 2). S and HL refer to Slater exchange and Hedin-Lundqvist approximation, respectively.

gap at around 40 GPa is somewhere in between these two approximations.

For comparison, we list in Table I the calculated optical gaps at 44 GPa and the predicted metallization pressures. The computations of Hama and Matsui,[4] Christensen and Wilkins,[5] and Ray *et al.*[6] yield an optical gap considerably lower than the experimental result. All three groups have considered the influence of a structural fcc-bcc transition and found even lower values for the optical gap. Furthermore, the question of the extent to which an fcc to hcp transition would influence the optical gap has been raised.[3,16] From visual observation we do not have any indication for a structural phase transition within our experimental pressure range of 44 GPa.

It is outside the scope of the present paper to discuss the theoretical aspects of compressed xenon in any detail or to add any speculations. However, it is obvious to make a comparison with CsI. CsI is isoelectronic with Xe and the compressed state is expected to undergo similar changes in band structure.[16] The band gap of CsI is 6.4 eV at normal conditions compared to 9.3 eV for Xe. The metallization pressure of CsI is expected to be lower than in Xe. According to the optical absorption measurements of Asaumi and Kondo,[18] the optical gap of CsI is between 1.0 and 1.5 eV at 44 GPa. At this pressure there is still a difference of more than 2.0 eV between the gaps of Xe and CsI. The close relationship between CsI and Xe suggests, that further experimental studies of the metal-insulator transition in Xe can be guided by first studying the metallization of CsI.

We summarize our conclusions as follows.

(1) The metallization of Xe does not occur at a pressure as low as 33 GPa. However, we cannot rule out the Nelson and Ruoff[1] indeed measured the insulator-metal transition, but considerably underestimated the transition pressure because of their in-

TABLE I. Experimental and predicted optical gap E_g of xenon at a pressure of 44 GPa. The calculated metallization pressures are also listed.

	E_g (eV) at 44 GPa	Metallization pressure (GPa)
Experiment[a]	$.9 \pm 0.3$	. . .
Ross and McMahan[b]		
Slater	4.7	200
Hedin-Lundqvist	2.6	130
Hama and Matsui[c]		
fcc	~ 2.6	130
bcc	~ 1.9	82
Christensen and Wilkins[d]		
fcc	0.4	48
bcc	0	37
Ray *et al.*[e]		
fcc	2.7	126
bcc	2.0	≥ 95

[a] Present result.
[b] Reference 2.
[c] References 4 and 17.
[d] Reference 5.
[e] Reference 6.

direct method of determining the actual pressure on the sample. Also the effect of nonuniform strain has to be considered in the Nelson-Ruoff experiment.

(2) The experimental value of 3.9 eV for the optical gap of Xe at 44 GPa is not unexpected on the basis of the APW calculations reported by Ross and McMahan[2] and on the basis of the experimental absorption edge of CsI at the same pressure.[18]

(3) In view of the present experimental results for Xe and the optical absorption measurements for CsI,[18] it appears likely that the metallization of xenon does occur well above 50 GPa. This is in agreement with the theoretical arguments of Ross and McMahan[2,16] and also with the observation by Besson[19] that Xe is not metallic at pressures slightly above 60 GPa.

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