Effect of Very High Pressure on the Optical Absorption Edge in Solid Xe and Its Implication for Metallization

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The pressure dependence of the fundamental optical absorption edges in solid Xe has been investigated up to the maximum pressure of 55 GPa by using a diamond-anvil–type high-pressure cell at room temperature, and the band-gap energies as a function of pressure have been obtained from 44 to 55 GPa. The metallic transition pressure for solid Xe is estimated to be about 200 GPa or greater from the present pressure versus band-gap energy measurements, under the assumption that the solid Xe does not undergo any structural phase transition above 55 GPa.

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The properties of solids in the ultrahigh-pressure region are of considerable interest from the point of view that an insulator may become metallic at very high pressure. Rare-gas solids (Ne, Ar, Kr, and Xe) represent simple insulators with the crystal structure of a close-packed fcc lattice and with the closed-shell electronic configurations. They are expected to become metallic at very high pressures without any change in crystal structure. Among these rare-gas solids, Xe is of particular interest because it is expected to transform into a metallic state at the lowest pressure.

Since the work of Ross,[1] theoretical studies on the pressure-induced insulator-metal transition of solid Xe have been made by several authors.[2,3] Two static compression experiments on solid Xe have been reported.[4,5] Syassen and Holzapfel performed an x-ray diffraction study of solid Xe and obtained the pressure-volume isotherm up to 11 GPa at 85 K.[4] Nelson and Ruoff, on the other hand, claimed to have found a metallic transition in solid Xe at 33 GPa and 32 K, using a "diamond indentor" technique.[5] Subsequent theoretical studies, however, suggest the possibility of a metallic transition in solid Xe only above 130 GPa.[6,7] Since there are significant discrepancies between the theoretical predictions and the experimental result of Nelson and Ruoff on the metallic transition pressure in solid Xe, it is important to obtain experimentally quantitative information on the band-gap decrease with pressure in the ultrahigh pressure region.

We have shown in our previous papers that the optical absorption and reflection measurements at high pressure using a diamond-anvil high-pressure cell can be a useful tool for the quantitative study of the pressure dependence of the band-gap energies in such ionic solids as CsI[8] and LiH.[9] In the present paper we report the optical-absorption spectra and band-gap energies in solid Xe as a function of pressure up to the maximum pressure of 55 GPa at room temperature. This is the first report that deals with the pressure effect on the band-gap energy in solid Xe. A possible metallic transition in the megabar range is also discussed.

The optical-absorption spectra of solid Xe at high pressures were obtained by using a diamond-anvil–type high-pressure apparatus. Type-II*a* diamonds were used throughout this study since the absorption edge of solid Xe remained above that of the type-I diamonds up to the maximum pressure of 55 GPa. The transmission spectra of the present type-II*a* diamonds are already shown in our previous paper.[8] The pressure dependence on the absorption edge energy of the present type-II*a* diamonds was investigated by using LiF as a transparent material up to 55 GPa.

The sample loading procedure was as follows. The metal gasket was precompressed to ~ 80 μm thick and a hole of 60 μm diameter was drilled at the center of the precompressed gasket. The diamond-anvil cell was cooled slowly in a cryostat by cold N_2 gas down to about 150 K, and then Xe gas, guided by a glass capillary tube, was condensed over the metal gasket. Then the sample was confined within the diamond-anvil cell by pressing down the moving piston firmly. The initial pressure in excess of 0.4 GPa was applied at low temperature in order to keep the Xe in a solid phase at room temperature in the diamond-anvil cell.[10] The pressurized cell was transferred from the cryostat into a desiccator to avoid the precipitation of dew drops on the diamond windows during the warmup process. The experimental setup adopted in the present optical investigation has been described in our previous paper.[8] A combination of a D_2 lamp, a Suprasil prism monochromator, and a photomultiplier (Hamamatsu R955) was used in the absorption measurements. Pressures were calibrated by the ruby fluorescence scale.[11] All measurements were performed at room temperature.

Since the initial band gap of solid Xe (~ 9 eV) is larger than the absorption edge energy of the type-IIa diamonds (~ 5.5 eV) the absorption spectra below 30 GPa show only the pressure effect on the absorption edge of the diamond anvils. From 30 GPa the absorption tail of solid Xe begins to appear just below the absorption edge of the diamond anvils. The optical absorption of Xe becomes apparent as pressure is increased.

According to the energy-band calculation of Ross and McMahan,[6] the lowest band gap of solid Xe below 1.3 GPa is direct (Γ_1-Γ_{15}) and the gap increases with increasing pressure. Above 1.3 GPa the indirect gap (X_1-Γ_{15}) becomes lower than the direct one and the gap decreases with increasing pressure. According to Elliot,[12] the absorption coefficient of the indirect transition rises as $(\hbar\omega - E_g \pm \hbar\omega_{\rm ph})^2$ above the indirect gap E_g, where $\hbar\omega_{\rm ph}$ is the energy of the phonon relevant to the indirect transition. Thus E_g can be obtained from the square-root plot of the optical densities. In Fig. 1, the square roots of the optical densities in solid Xe from 43.8 to 55.0 GPa are shown. The straight lines in the lower-energy region represent the optical absorption in solid Xe, whereas the steep rises at higher energy are considered to show the effect of abrupt rising of optical absorption in type-IIa diamond anvils. Since the sample thickness was estimated to be 20–30 μm, the absorption coefficient corresponding to the optical densities in Fig. 1 should be $\sim 10^2$ cm^{-1}. Judging from the absolute values of their absorption coefficients, we infer that band gaps are indirect. The energy of the relevant phonon, $\hbar\omega_{\rm ph}$, around 50 GPa can be estimated from the pair potential and the equation of state of Ross and McMahan,[6] with reference to the phonon data[13] at 1 bar, to be within 40 meV, which is negligible compared with the experimental error (~ 0.1 eV) in determining E_g. With these facts taken into account, energy band gaps of solid Xe at very high pressures are obtained at energies where the square roots of the optical densities go to zero. The energy band gaps thus obtained are plotted in Fig. 2 as a function of pressure.

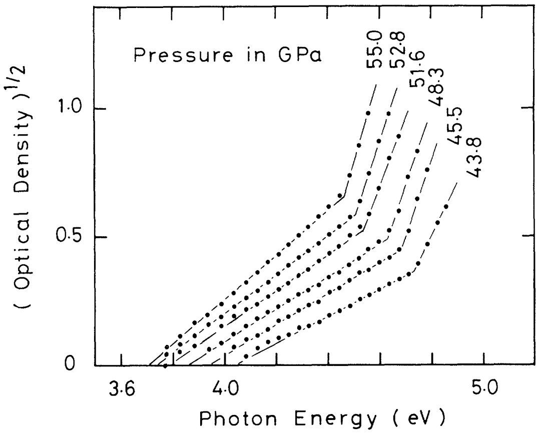

FIG. 1. The square-root plot of the optical densities in solid Xe at high pressures. Below 30 GPa the band gap of solid Xe is larger than the absorption edge of type-IIa diamonds and so absorption spectra are not observed. From about 30 GPa, the absorption tail of solid Xe becomes gradually apparent as pressure is increased. From the band theoretical calculations the band gap in solid Xe at high pressure is predicted to be indirect. The straight lines in the lower-energy region represent the optical absorption in solid Xe. The steep rises in the higher-energy region are considered to show the effect of abrupt rising of optical absorption in type-IIa diamond anvils. The energy band gaps of solid Xe at high pressures are obtained at energies where the square roots of the optical densities go to zero.

From the linear extrapolation of the tangent line of this pressure versus band-gap energy curve above 45 GPa, we can estimate the metallic transition pressure for solid Xe to be approximately 200 GPa (2 Mbar) or greater. This does not conflict with the value of 2.0 Mbar calculated by Ross and McMahan[6] but is much larger than 1.28 Mbar calculated by Ray *et al.*[7] We have found no anomaly in the absorption spectra of solid Xe around 33 GPa where Nelson and Ruoff claimed to have found the metallic transition at 32 K.

Figure 2 also shows the pressure dependence of the absorption edge of the present type-IIa diamonds which was obtained by compressing the LiF as a transparent material with the same configuration as in solid Xe. It decreases almost linearly with increasing pressure at the rate -1.57×10^{-2} eV/GPa.

Since CsI and solid Xe have the same electron-

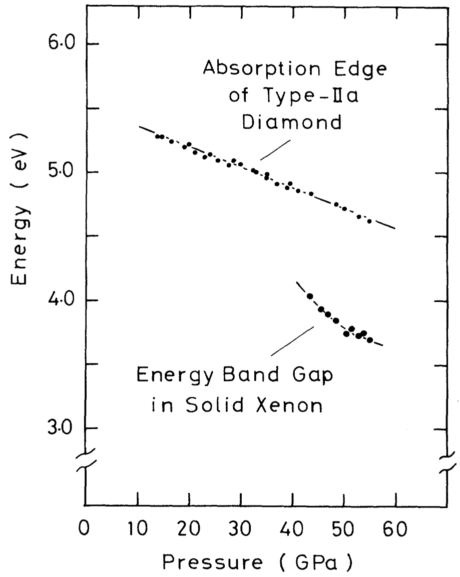

FIG. 2. Band-gap energies in solid Xe at high pressures. From the linear extrapolation of the band-gap energies between 45 and 55 GPa, the metallic transition pressure in solid Xe is estimated to be approximately 200 GPa (2 Mbar) or greater. The pressure dependence of the absorption edge of the present type-II*a* diamonds is also shown. The absorption edge decreases almost linearly at the rate -1.57×10^{-2} eV/GPa. No anomaly in absorption spectra was found around 33 GPa where Nelson and Ruoff claimed to have found the metallic transition.

ic configuration of a $(5p)^6$ closed shell, it is interesting to compare the behavior of these materials at very high pressure. Solid Xe has the cubic close-packed structure (fcc) whereas CsI has the CsCl-type (simple cubic) structure. The bulk modulus of solid Xe is 3.65 GPa[14] while that of CsI is 11.9 GPa.[15] Thus, solid Xe is initially far more compressible than CsI. The band gap of solid Xe at 0 GPa is 9.28 eV (21 K)[16] and that of CsI is 6.3 eV (80 K).[17] As already mentioned we have reported in our previous paper[8] the pressure dependence of the optical absorption spectra in CsI up to 46.2 GPa, where we have found that the threshold energy for the rising of optical absorption in CsI has decreased below 1 eV at 46.2 GPa. From the present study we see that the pressure dependence of the band-gap decrease in solid Xe around 50 GPa is not so remarkable compared with that in CsI in spite of the small initial bulk modulus. Probably the difference between the two materials when subjected to very high pressure comes from the fact that in CsI the Coulombic attractive force exists between nearest-neighbor atoms while in solid Xe the attractive force is of van der Waals nature and is very weak.

In the course of this experiment the vanishing of the phase boundary between solid Xe and a ruby particle was observed at 6.3 GPa, indicating that the refractive index of solid Xe crossed over that of ruby with increasing pressure. Using the Clausius-Mossotti relation and the other relevant data,[4, 10, 18] we can estimate the electronic polarizability of solid Xe at 0 and 6.3 GPa to be 4.11 and 3.73 in units of 10^{-24} cm^3, respectively.

The hydrostatic nature of solid Xe up to 30 GPa has been reported by Liebenberg[19] who observed the change of ruby fluorescence line shapes up to 30 GPa with solid Xe as a pressure transmitting medium. In the present experiment no significant change was observed in the line shapes of the ruby fluorescence up to 55 GPa: The doublet lines *R*1 and *R*2 were clearly resolved. Present results on solid Xe mean that the inhomogeneity of the pressure distribution was quite small and solid Xe showed almost hydrostatic behavior at least up to 55 GPa.

Is there any phase transition in solid Xe above 55 GPa? Can solid Xe be obtained in a metallic phase below 200 GPa? These are very interesting questions and to answer these, optical absorption measurements in the megabar range are necessary. Further optical-absorption measurements and x-ray diffraction study of solid Xe at high pressures are in progress.

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Noted added.—A recent communication from Professor Ruoff states "Chan *et al.* have shown on the basis of plasticity considerations that the pressure attained in the experiment of Nelson and Ruoff when electrical conduction occurred was above one megabar." [K. S. Chan, T. L. Huang, T. A. Grezybowski, T. J. Whetten, and A. L. Ruoff, J. Appl. Phys. (to be published)]. This supports the present experimental result.

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