Evidence for the Insulator-Metal Transition in Xenon from Optical, X-Ray, and Band-Structure Studies to 170 GPa

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The equation of state and optical absorption of condensed Xe have been measured in a diamond-anvil cell up to 172 GPa. Pressures were determined by use of the ruby-fluorescence technique or from the equation of state of the Re gasket used to confine the sample. Xe transformed to an hcp structure between 70 and 90 GPa that remained stable to 172 GPa. At 150 GPa we observed sudden changes in absorption and reflection spectra of Xe that we attribute, on the basis of electron band calculations, to the onset of metallization.

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In this paper we present evidence for the appearance of metallic Xe at 150 GPa. The pressure-induced transformation of condensed Xe from insulator to metal has long been the subject of intense interest.[1-4] Herzfeld[1] first predicted such a transition at a volume of 10.2 cm^3/mol, where the molar volume of Xe would become equal to its gas-phase molar refractivity. Electron band-structure calculations[3] have shown that transition of Xe to the metallic state at high pressure is due to crossing of the empty $5d$ conduction and full $5p$ valence bands, and that the insulating gap for volumes less than 30 cm^3/mol is indirect. Subsequent calculations[4] produced an equation of state (EOS) and predicted the insulator-metal transition to occur, via band overlap, in the range from 11 to 9 cm^3/mol, corresponding to pressures from 130 to more than 200 GPa. Recently, Goettel *et al.*[5] have measured an ir reflection spectrum of Xe at an estimated pressure of 230 GPa and used it to estimate metallization of Xe at 190 GPa.[5]

Structural studies of Xe using x-ray techniques have shown that Xe freezes in an fcc structure that has been reported to remain stable at room temperature up to a maximum pressure of between 23 and 55 GPa.[6-8] Recently, Jephcoat *et al.*[9] reported phase transitions in Xe at 14 GPa from fcc to an intermediate, close-packed phase, and at 75 GPa, to an hcp structure that remained stable to 137 GPa. Their measured EOS was found to be in close agreement with theory.[4] Transition of the heavy rare-gas solids to the hcp phase prior to metallization was also predicted theoretically.[9]

Optical absorption studies of Xe have been reported by Syassen[10] and Asaumi, Mori, and Kondo[11] at pressures up to 44 and 55 GPa, respectively. Both attributed weak uv absorption below the diamond absorption edge to interband transitions across the indirect insulating gap. Their findings, which show a decrease in the band gap with increasing pressure, are consistent with theoretical predictions,[4] and extrapolate to gap closure in the vicinity of 10 cm^3/mol.

In this Letter we describe the results of high-pressure optical absorption, ir reflection, and x-ray diffraction experiments on solid Xe using the diamond-anvil cell (DAC). Pressures were generated in Xe using "megabar" DAC's with either single- or double-beveled diamond anvils.[12] Both type-I and type-IIa diamonds were used in a series of experiments employing various anvil designs. Bevel angles as well as the flat and culet dimensions were varied to optimize the pressure performance.

Gaskets were made of 250-μm-thick Re, which we selected on the basis of our earlier calculations and experiments that indicated superior performance with high-yield-strength gasket materials in the DAC.[12] Gaskets were preindented to a thickness of 15 to 20 μm and a 50-μm-diam hole was drilled to form the sample chamber. A small amount of ruby powder (<3-μm-diam grain size) was placed on the culet of the cylinder diamond for pressure calibration.[13] Samples generally contained less than 10% ruby. The gasket-diamond interface was lightly dusted with fine ruby powder, which yields steeper pressure profiles across the gasket in tests made on gaskets alone,[12] and with CsI as a sample material,[14] which ultimately resulted in higher pressures in the sample chamber for a given load.

Xe samples were loaded in the DAC by condensing gas on the tip of the diamond anvils and remotely closing the cell to trap the liquid (observed visually) in the sample chamber. Once a sample was sealed in a DAC, the cell was warmed to room temperature.

Absorption spectra were measured between 1.3 and 5.0 eV at Lawrence Livermore National Laboratory using an optical system similar to that described elsewhere.[15] Single-beam transmission spectra were measured using a 75-W-Xe-arc source and reflecting uv or visible achromatic optics for imaging. A Spex model 1702 $\frac{3}{4}$-m spectrometer with 1800-grooves/mm grating and GaAs photomultiplier tube detector was used to collect the optical data. Transmission spectra were collected and normalized to a spectrum measured in the sample at low pressure. Reference spectra were collected through a pinhole placed at the sample position before and after each sample spectrum to compensate for small changes in lamp intensity and spectral character over time. The area of the sample illuminated was 15 μm in diameter.

ir reflection spectra were collected in the range 0.5 to 1.5 eV at the Xe-diamond interface from 50 to 160 GPa. The details of our experimental technique are described in Ref. 16.

X-ray data were collected at the Cornell High Energy Synchrotron Source bending-magnet white-beam station using energy-dispersive x-ray diffraction techniques. Details of the technique and apparatus are published elsewhere.[17] Diffraction data were used to obtain the EOS of Xe to 172 GPa and to measure pressures within the sample when ruby fluorescence was masked by fluorescence in the diamond anvils, typically between 120 and 150 GPa in these experiments. X-ray pressures were determined from the EOS of the Re gasket.

This experiment is the first in which the EOS of a material in a DAC has been measured using the gasket as the calibrant. This is difficult because the two materials are in contact only along the xenon-rhenium interface and because of the presence of pressure gradients in both materials. We constructed the EOS by using Xe diffraction lines taken with the collimator at the sample-gasket interface and Re diffraction lines from spectra taken with the collimator centered 5–10 μm from the center of the sample. This method, although not as satisfying or as straightforward as an internal standard, minimizes the effect of large pressure gradients, and the resulting data, shown in Fig. 1, are in good agreement with the work of Jephcoat *et al.*[9] These measured pressures are also in reasonable agreement (about 3%–5%) with theory.[4] By fitting our data with the Birch first-order EOS,[18] we obtained the parameters $B_0=10.17$ GPa and $B_0'=4.03$, which can be used without extrapolation between 111 and 172 GPa. The zero-pressure volume (V_0) used was 34.7 cm^3/mol, which is the 4-K value used by Refs. 4 and 9.

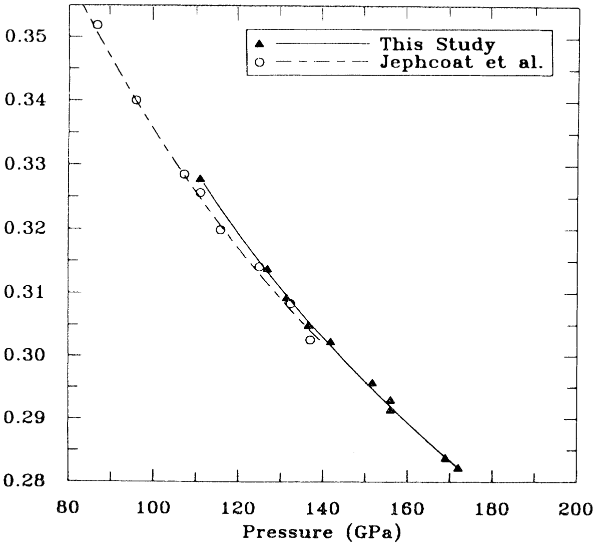

FIG. 1. The measured high-pressure equation-of-state of Xe.

Pressure measurements with the ruby-fluorescence technique were made using the 457.9-nm line of an argon-ion laser focused to a 5-μm diameter. Pressures based on x-ray measurements were collected with a 5×20-μm^2 sampling area. This enabled us to carefully characterize the pressure distribution within the sample chamber. Pressures determined from x-ray data obtained at 5-μm intervals varied by less than 12 GPa in Xe at a peak pressure of 160 GPa. The sample was approximately 70 μm long and 40 μm wide. Xe appears to be a weaker solid than isoelectronic CsI at comparable pressures based on the larger pressure gradient supported by CsI under similar conditions.[16] In fact, the pressure in the center of the sample is 30 GPa lower than the maximum pressure in the gasket.

Diffraction and optical absorption data were collected from a sample during unloading from a peak pressure of 172 GPa. At 172 GPa Xe is hcp and shows no evidence for the onset of any crystallographic phase transitions. The intermediate phase appeared between 90 and 70 GPa, which was one increment of unloading. The details of x-ray studies of the hcp and intermediate phases will be described in detail elsewhere.[19]

Optical absorption measurements, made at pressures up to 172 GPa, are shown in Fig. 2. ir reflectivity spectra to 160 GPa are shown in Fig. 3. Two important features should be noted: (1) Above 150 GPa a significant increase in absorption (Fig. 2) and reflectivity (Fig. 3) takes place at the lowest photon energies studied (1.3 and 0.5 eV, respectively); and (2) near 150 GPa a new absorption peak appears at 2.0 eV that is pressure insensitive and increases in prominence with increasing pressure. On the basis of linear muffin-tin orbital[20] band-structure calculations,[21] we interpret both features as arising from the metallization of hcp Xe. The first is the expected low-energy Drude absorption due to intraband transitions. The latter is a new feature that we believe to arise from interband transitions in hcp metallic Xe.

Metallization in hcp Xe occurs via closure of the indirect gap $\Gamma_2^- - K_2$ shown in Fig. 4. As the Fermi level drops below the top of the 5_p valence band, empty states are provided near Γ that we believe are responsible for the 2-eV absorption peak seen in Fig. 2(a). In hcp Xe, unlike fcc, the top of the $5p$ valence band is split into two subbands, near Γ_2^- and Γ_6^- on the one hand, and Γ_5^+ on the other hand, separated by about 2 eV. We identify the absorption peak with this $\approx$2-eV splitting. Specifically, the transition from Γ_5^+ to hole states at Γ_6^- is direct and allowed both by parity selection and a 4%

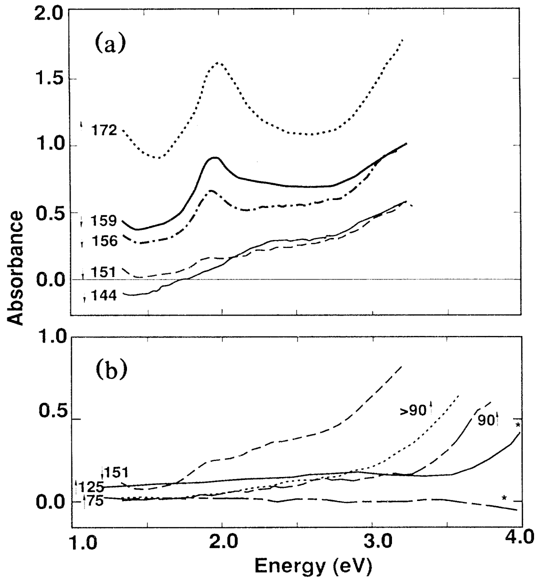

FIG. 2. (a),(b) Xe absorbance $\{\log[(I_0/I_p)(R_p/R_0)]\}$ vs energy (eV), where I_0 is the transmission spectrum of Xe at P_0 (30 GPa), I_p is the transmission spectrum of Xe at pressure, R_p is the reference spectrum collected at pressure, and R_0 is the reference spectrum collected at P_0. Pressures are indicated for each spectrum in GPa. ↑ indicates spectrum collected on loading, ↓ indicates spectrum collected on unloading. Absorbance falls below zero at high energies during unloading because the sample of I_0 is thicker than at I_p. (b) Low-pressure spectra plotted on an expanded vertical scale. * indicates spectra collected through type-IIa diamond anvils.

admixture of *d* character at and near Γ_6^-. Although we have not calculated the transition probabilities, the valence bands are quite parallel, which leads to a large density of states that would account for the intense 2-eV peak. Calculations were made at several densities to verify the near pressure independence of this transition. An inspection of the band structure fails to show any other transition that can lead to a relatively pressure-insensitive 2-eV absorption and also account for the abrupt appearance of this feature as would suggest involvement of hole or electron pockets created by metallization. Both criteria rule out transitions from the valence to the conduction band. Phonon-assisted excitations to M_1^+ from the electron pocket at K_2 will also be pressure dependent as a result of the low density of states between K_2 and M_1^+ and the consequent rapid rise of the Fermi level in the conduction band after metallization. By contrast, the Fermi level moves slowly into the valence band after metallization due to the large density of states at the top of that band.

A careful inspection of the absorption spectra (Fig. 2) actually shows a very small shift in the $\approx$2-eV peak to higher energies with increasing pressure of the order 0.002 to 0.003 eV/GPa. At 172 GPa the peak position is 2.05 eV. This observation is in agreement with the band-theory prediction that with increasing pressure, the position of the lower states of the split valence band decrease in energy relative to the Fermi level. This leads to a predicted increase in the absorption peak energy with pressure at the rate of 0.003 eV/GPa, in excellent agreement with experiment. Estimates of the plasma frequency obtained from our band calculations show that the electron density is small, so that the sample is expected to be transparent over the pressure range investigated, which is consistent with our observations. It is important to note that we have made identical optical absorption measurements on a sample of H_2 in type-I diamond anvils up to 200 GPa and have observed no absorption below the diamond edge, indicating that our measurements indeed represent absorption in xenon.

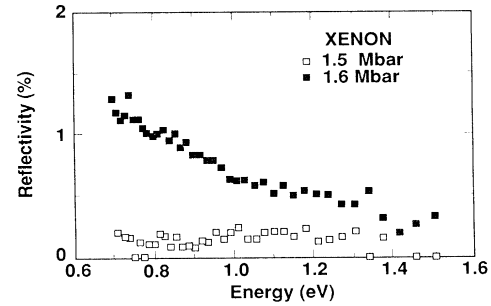

FIG. 3. ir reflectivity (%) vs pressure for xenon at 150 and 160 GPa. At pressures below 150 GPa, reflectivities were less than 0.25%.

The metallic character of Xe above 150 GPa is further supported by the ir reflectivity spectra shown in Fig. 3. The first appearance of detectable reflectivity at 150 GPa, and the overall low reflectivity and the factor-of-2 increase in reflectivity from 1.5 to 0.7 eV at 160 GPa are consistent with a low-carrier-density metal.

At pressures below 150 GPa, in contrast to our results at higher pressure, we observe weak absorption that may be evidence of the indirect interband transition between Γ and *K*. This transition should be decreasing in energy with increasing pressure. The low-pressure spectra be-

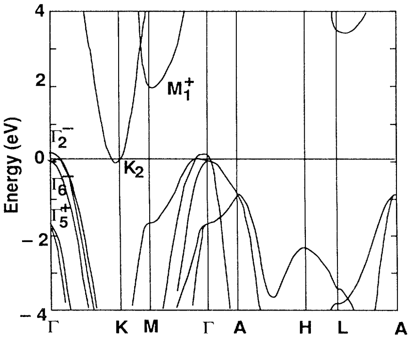

FIG. 4. Electron band structure of hcp Xe at 11.1 cm^3/mol (1.2 Mbar), near calculated metallization.

tween 73 and 125 GPa show some weak absorption below the diamond edge in both type-I and type-IIa diamonds [Fig. 2(b)]. Whether this is caused by absorption across the indirect gap in Xe or is stress-induced absorption in the diamonds cannot be determined with our experimental technique.[22] Previous studies concluded that weak absorption such as we find in our measurements is the result of excitations across the indirect gap. If that is so, then the indirect gap may be below 1.3 eV at 130 GPa, as evidenced by the criteria of these earlier works.[10,11] Wolford and Bradley's[23] work on III-V compounds in the DAC has demonstrated that the intensity of absorption across the indirect gap can be several orders of magnitude weaker than that across a direct gap.

The transformation of Xe to a metallic state near 150 GPa has been inferred using band theory to interpret optical absorption and reflection data. At metallization, the volume is 10.2 cm^3/mol, which is the volume predicted by Herzfeld in 1927.

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[22] Ring fracturing of beveled anvils during unloading precludes making calibration experiments on that exact pair of diamonds with a nonabsorbing sample such as LiF before or after the Xe experiment, as others have done at low pressure (Refs. 10 and 11).

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