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High-pressure x-ray diffraction study of solid xenon and its equation of state in relation to metallization transition

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A high-pressure x-ray diffraction study of solid xenon was performed at pressures up to 32 GPa at room temperature using a diamond-anvil cell. The fcc structure was found to remain stable up to the maximum pressure used in the present study. An equation of state of Birch-Murnaghan type was fitted to the compression data reduced to 0 K to obtain the pressure-volume relation of solid xenon under an extremely high pressure. On the basis of this Birch-Murnaghan equation of state at 0 K and the optical absorption data reported previously, the pressure-induced metallization transition in solid xenon is expected to take place when the volume is compressed to about 10 $\mathrm{cm^3/mol}$ and the corresponding pressure is about 200 GPa. In the present work, the molar volume was reduced to 16.3 $\mathrm{cm^3/mol}$ at 32 GPa ($V_0 = 34.74$ $\mathrm{cm^3/mol}$ at 0 K).

There has been a considerable interest in the pressure-induced metallization transition in some simple crystallographic and electronic systems,[1] especially in isoelectronic series of solid Xe, CsI (Refs. 2–6) and BaTe (Ref. 7) and in other alkali halide crystals such as RbI and KI (Ref. 8). Among them, xenon is considered to represent the simplest case to exhibit pressure-induced metallization transition without, possibly, any change in crystal structure, since it has a closed-shell electronic configuration and a close-packed fcc lattice. Therefore, the metallization transition of solid xenon under very high pressure is still one of the most interesting problem in the high-pressure physics world.

Ross and co-workers[9–11] were the first to calculate the band-gap energy of solid xenon as a function of volume compression using both the augmented-plane-wave (APW) and pseudopotential methods. They obtained a volume ratio $V/V_0 = 0.28$ for solid xenon for the band-gap closure to occur, which shows remarkably good agreement with that obtained by the classical Herzfeld criterion.[12,13]

Nelson and Ruoff,[14] then, reported the metallization of solid xenon at 33 GPa and 32 K. They observed an abrupt resistance drop in a thin film of xenon deposited on an interdigited electrode arrangement in a diamond indentor. Subsequent theoretical works,[15,16] however, suggested the possibility of a metallic transition in solid xenon only above 130 GPa under the assumption that xenon will remain in a fcc lattice even in a very-high-pressure region. Hama and Matsui[17] have investigated the possibility of a fcc-bcc transition in solid xenon theoretically to explain the unusually low metallization pressure of 33 GPa by Nelson and Ruoff[14] and found that xenon will transform to a metallic bcc structure at 83 GPa. Furthermore, they also found that the spin-orbit coupling effect makes the transition pressure much lower to 66 GPa,[17] in closer agreement with the result of Nelson and Ruoff.[14] Subsequently, Ray, Trickey, and Kunz[18] have also investigated the possibility of a fcc-bcc phase transition theoretically and obtained the results that the fcc-bcc phase transition pressure is above 95 GPa and the bcc phase is metallic.

Recent diamond-anvil-cell optical measurements up to 44 GPa by Syassen[19] and those up to 55 GPa by Asaumi, Mori, and Kondo[20] showed that xenon remains an insulator up to those pressures with the band-gap energies (E_g) 3.9 eV at 44 GPa (Ref. 19) and 3.7 eV at 55 GPa.[20] Asaumi *et al.* estimated the metallization pressure to be around 200 GPa or greater by extrapolating the E_g versus pressure curve, under the assumption that xenon does not undergo any structural phase transition.[20] Later, Makarenko, Weill, Itie, and Besson[21] also confirmed that xenon is still transparent to the visible light even at 63 GPa. Thereafter, Ruoff and his co-workers[22] reanalyzed the elasticity theory of their experimental configuration of the diamond-indentor anvil and revised upward the metallization pressure of solid xenon to be above 100 GPa.

An x-ray diffraction study of solid xenon under high pressure was performed firstly by Syassen and Holzapfel up to 11 GPa at 85 K.[23] Fitting their data to Keane's equation of state,[24] they obtained the adjustable parameters: $B_0 = 2.65$ GPa, $B_0' = 7.69$, and $B_0'' = 4.80$. Here, the B_0 value was made fixed with that obtained by Anderson and Swenson[25] by piston-displacement data. Recently, Schiferl, Mills, and Trimmer[26] carried out an x-ray diffraction study of solid xenon up to 23 GPa at room temperature by using a diamond-anvil cell. They obtained relatively sharp lines from the first five reflections of fcc xenon below 12 GPa. Above 12 GPa, however, they obtained only x-ray diffraction patterns of poor quality compared with those at low pressure. They did not make a least-squares fitting to their data because some uncertainties in pressures existed and, moreover, the diffraction patterns above 12 GPa were very poor in quality. Nevertheless, their result is not inconsistent to that obtained by Syassen and Holzapfel.[23]

The present paper describes precise x-ray diffraction results of solid xenon up to 32 GPa obtained by the gasketed diamond-anvil cell at room temperature (295 K). The pressure-volume relation obtained at 295 K is reduced to that at 0 K using Mie-Grüneisen equation and Debye approximation. This P-V relation reduced to 0 K is fitted to an equation of state of the second-order Birch-Murnaghan type and compared to the theoretical P-V relations up to 200 GPa. On the basis of the present x-ray result and the optical absorption data reported previously, the possible metallization transition in solid xenon in an extremely high-pressure region is discussed.

High-pressure x-ray diffraction patterns were obtained by using a diamond-anvil cell devised by the author.[8] Diamond anvils were 0.23 carat with 0.7-mm cross-sectional diameter truncated faces. An x-ray beam generated by a 1.2-kW sealed-off Mo tube was focused onto the sample with a 0.1-mm cross-sectional diameter pinhole collimator. The diffraction pattern was recorded on a flat film located 45.0 mm from the sample. Typical exposure time was 20–50 h depending on the pressure. The sample loading procedure was as described in Ref. 20. The sample diameter was about 100 μm at low pressures (<10 GPa) and increased to about 150 μm at high pressure (~ 30 GPa). Pressures were calibrated by the ruby R_1 fluorescence scale.[27,28] All measurements were performed at room temperature.

Figure 1 shows the pressure dependence of the first five interplanar distances of solid xenon from 2.1 to 32 GPa at room temperature. These interplanar distances decreased monotonically with increasing pressure without any indication of phase transition. The lattice constants of solid xenon at high pressures were obtained by averaging the values for all observed lines. Eight diffraction lines were observed in the uttermost: $(111)\beta$, $(111)\alpha$, $(200)\alpha$, $(220)\beta$, $(220)\alpha$, $(311)\beta$, $(311)\alpha$, and $(222)\alpha$ in order of increasing diffraction angle.[29] Among them the lattice constant obtained from the (200) diffraction line showed a systematic discrepancy as compared with those obtained by other diffraction lines. The lattice constant obtained from the (200) line was always larger than those obtained from other diffraction lines. This discrepancy increased as the pressure was increased and amounted to 1.3% at 32 GPa. This discrepancy, however, is not so serious in obtaining the average lattice constant because it is reduced to within 0.2% by simply averaging those of the above mentioned eight diffraction lines. The effect of this systematic discrepancy on the crystal volume is, therefore, about 0.6% at the most and is considered well within the experimental error which is estimated to be about 1.0%.

The molar volumes of solid xenon plotted as a function of pressure is shown in Fig. 2. Solid circles are the present x-ray diffraction results obtained at room temperature. A dashed curve up to 11 GPa is a fitted one to the Keane-type equation of state by Syassen and Holzapfel[23] to their x-ray data at 85 K. Open circles represent the 0-K isotherm calculated by Ross and McMahan[15] with the APW Hedin-Lundqvist method. Crosses are some of the APW-$X\alpha$ results for $T=0$ K xenon obtained by Worth and Trickey[30] and by Ray, Trickey, Weidman, and Kunz.[16] Present result of molar volumes gives larger values than those obtained by Syassen and Holzapfel and than those of two theoretical calculations below 10 GPa. This is quite reasonable because the temperature of the present study is higher than that of Syassen and Holzapfel and of two sets of calculations. This was already confirmed by Schiferl *et al.*[26] whose data points, however, are not shown in this figure because precise values were not available. Above 10 GPa the present result shows excellent agreement with the values calculated by Worth and Trickey[30] and by Ray *et al.*[16] The result of Ross and McMahan[15] gives smaller volumes than the present study, but the difference is small.

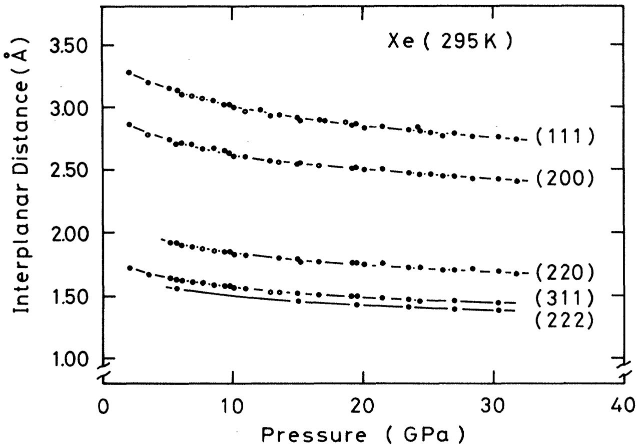

FIG. 1. Pressure dependence of the first five interplanar distances in solid xenon from 2.1 to 32 GPa obtained at room temperature. These interplanar distances decreased monotonically with increasing pressure without any indication of phase transition.

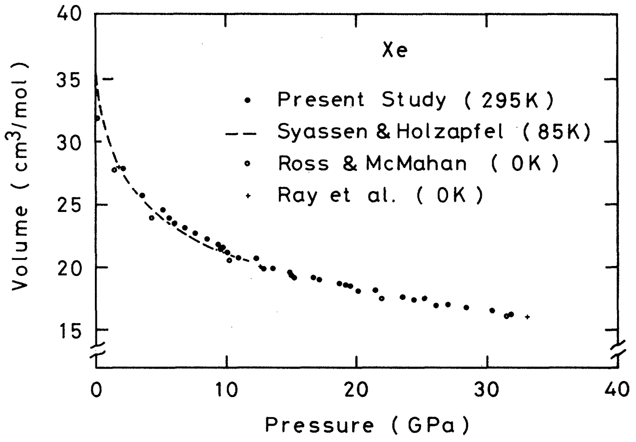

FIG. 2. Molar volumes of solid xenon at high pressure. The solid circles represent the present experimental result obtained at room temperature. Dashed curve up to 11 GPa is the experimental results of Syassen and Holzapfel at 85 K. Open circles show the theoretical calculation by Ross and McMahan at static lattice limit. Crosses are the theoretical result by Ray *et al.* (Ref. 16).

In order to obtain an equation of state in solid xenon up to above a 100-GPa region, the present experimental data are reduced to 0 K using the Mie-Grüneisen equation and the Debye model approximation.

In the Mie-Grüneisen approximation the equation of state can be written as

$$P(V,T)=P_{\mathrm{SL}}(V)+P_{\mathrm{ZP}}(V)+P_{\mathrm{TH}}(V,T) ,$$

where P_{SL}, P_{ZP}, and P_{TH} are potential pressure in the static lattice limit, zero-point pressure, and thermal pressure, respectively. In the Debye approximation

$$P_{\mathrm{ZP}}(V)=(9\gamma/8V)R\Theta ,$$

$$P_{\mathrm{TH}}(V,T)=(3RT\gamma/V)D\left[\frac{\Theta}{T}\right] ,$$

$$D\left[\frac{\Theta}{T}\right]=3\left[\frac{T}{\Theta}\right]^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx ,$$

where γ is the Grüneisen parameter, R the gas constant, Θ the Debye temperature, T the absolute temperature, and D the Debye function. The Debye temperature Θ is related to γ by

$$\Theta=\Theta_0\exp\int_V^{V_0}\left[\frac{\gamma}{V}\right]dV .$$

As the actual form of the volume dependence of γ is not known, the relation suggested by Holt and Ross[31] is adopted

$$\gamma=\gamma_1(V/V_0)+\tfrac{1}{2} \ ,$$

with γ_1 independent of volume.

The following parameters were adopted in the Mie-Grüneisen and Debye approximations: $V_0=34.74$ cm^3/mol ($T=0$ K),[25] $\Theta_0=64.0$ K,[32] $\gamma_0=2.90$,[25] and $\gamma_1=2.40$. Using these approximations we can calculate the P-V relation of solid xenon at $T=0$ K. The result is shown in Fig. 3. In the present study only the thermal pressure is subtracted from the observed pressure values to keep the consistency with the V_0 value determined experimentally by Anderson and Swenson[25] with piston-displacement technique. The zero-point pressure remained within 0.3 GPa below 32 GPa ($V>16$ cm^3/mol) and so is estimated to be well within the experimental error around the 30-GPa region.

The present P-V relation reduced to 0 K was fitted to the equation of state of Birch-Murnaghan (BM) type:

$$P=\tfrac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3}-\left(\frac{V_0}{V}\right)^{5/3}\right]\times\left\{1+\tfrac{3}{4}(B_0'-4)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\} .$$

The initial bulk modulus (B_0) and its pressure derivative (B_0') are determined as $B_0=5.18\pm0.32$ GPa and $B_0'=5.48\pm0.24$.

The bulk modulus (B_0) of solid xenon at $T=0$ K has already been obtained to be 3.65 GPa by Anderson and Swenson[25] from their piston-displacement data up to 2.0 GPa which differs significantly with the present B_0 value. It is inevitable that the two B_0 have much different values, because the fitted pressure range is expanded to over ten times in the present study. When this $B_0=3.65$ GPa was fixed in least-squares fitting to the above BM equation of state, we can obtain $B_0'=7.09$. The overall feature of the P-V relation is, however, far better reproduced with the former set of values than with the latter.

The solid line in Fig. 3 corresponds to the BM equation of state fitted to the present P-V data reduced to 0 K with $B_0=5.18\pm0.32$ GPa and $B_0'=5.48\pm0.24$. The extrapolated P-V relation to over 100 GPa agrees fairly well with those calculated by Ross and McMahan[15] and those by Ray and co-workers,[16,30] as shown in this figure.

In a previous optical absorption measurement,[20] we have reported the pressure dependence of the band-gap energy (E_g) of solid xenon from 44 to 55 GPa. By combining the E_g data and the present equation of state (extrapolated up to 55 GPa), the band-gap energies are replotted against the molar volume, as shown in Fig. 4. Solid circles represent the experimental result. Solid curves are the theoretical results by Ross and McMahan[15] where S and HL refer to the calculations using Slater and Hedin-Lundqvist exchange-correlation potential, respectively. The S result was extrapolated to zero gap (dashed portion).

The band structure of solid xenon has been investigated both theoretically[33,34] and experimentally.[35] The lowest band gap of solid xenon at 0 GPa is direct ($\Gamma_1-\Gamma_{15}$) and the gap increases with increasing pressure,[15] where the Γ_1 state is the bottom of the empty conduction band and is 6s character and the Γ_{15} state is the top of the filled 5p-type valence band. As the volume is decreased, the bottom of the 5d band (X_1 state) becomes the lowest level in the conduction band and then the band gap is expected to decrease monotonically with increasing pressure.[15]

As shown in Fig. 4 the band-gap energies obtained by the experiment lie between those by the two calculations S and HL.[15] From this figure we can estimate the metallization volume of solid xenon to be about 10 cm^3/mol which agrees with the value obtained by the classical Herzfeld theory.[12] The corresponding metallization pressure is estimated to be ~200 GPa with the help of the BM equation of state mentioned previously, under the assumption that xenon does not undergo any structural phase transition.

It would be of great interest to extend the x-ray diffraction and optical absorption studies for solid xenon up to

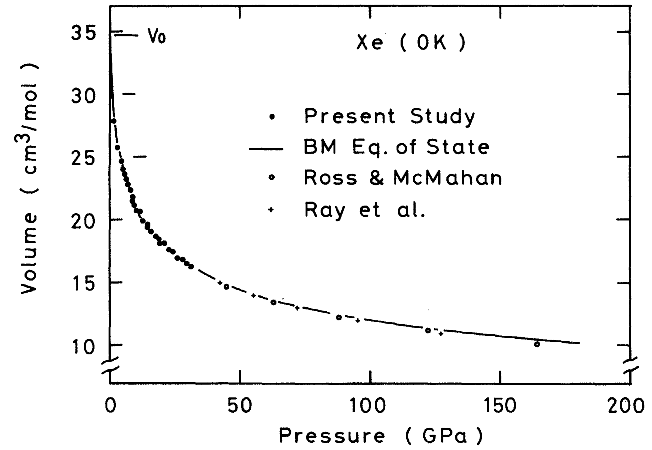

FIG. 3. Molar volumes of solid xenon at 0 K. Solid circles represent the present result reduced to 0 K using Mie-Grüneisen apposimation and Debye model. The solid line is an equation of state of Birch-Murnaghan type fitted to the present result. Here $V_0=34.74$ cm^3/mol is adopted obtained by piston-displacement technique by Anderson and Swenson. Open circles and crosses are same as in Fig. 2.

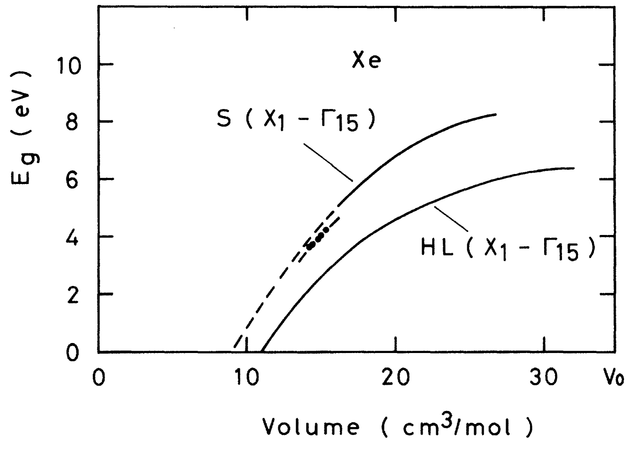

FIG. 4. Energy band gap in solid xenon as a function of volume compression. The solid circles represent the experimental result. S and HL curves are theoretical results by Ross and McMahan, where S and HL refer to the calculations using Slater and Hedin-Lundqvist exchange-correlation potentials, respectively. X_1-Γ_{15} is the smallest gap between 5d-like conduction band and 5p-like core state.

~100 GPa in the future, because the band-gap energy of solid xenon will cross the visible region at about 80 GPa so the xenon sample will show coloration when viewed through the diamond windows. X-ray diffraction study up to 100 GPa will, of course, test whether there is any crystallographic phase transition or not, to bcc or to any other crystal structures as some theories predict.[17,18]

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