Optical observations on xenon up to 63 GPa

I. Makarenko and G. Weill
Département Hautes Pressions, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France

J. P. Itie and J. M. Besson
Physique des Milieux très Condensés, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France
(Received 14 May 1982)

Xenon has been observed by optical methods up to 63 GPa in a diamond cell. At this pressure, its density is over 9.5 g/cm^3 and the optical dielectric constant has increased from 2 to 6. Nevertheless, it is still transparent and shows no metallic or semimetallic behavior, in contradiction with previous reports.

Metallization of simple systems has been the subject of a number of calculations and comparatively little experimental work. Rare-gas solids provide the simplest models to test theory and, among them, xenon stands out since its insulator-metal transition might occur in a range of pressures which is now accessible by static methods. In 1972 Ross[1] using a Slater exchange potential calculated a transition pressure for fcc xenon in the range of 200 GPa. In 1979 a drop in the resistivity of xenon at low temperature was observed in a diamond indentor system at a calculated pressure of 30–50 GPa and interpreted as metallization of xenon.[2] This discrepancy between experiment and theory has stimulated new calculations with different exchange potentials[3,4] or taking into account the possibility of a structural transition from fcc to bcc under pressure.[5,6] Recently Chan *et al.*[7] on the basis of plasticity considerations have reevaluated the maximum pressure actually attained in Ref. 2 above 100 GPa. In this Communication we report optical observation of xenon above 60 GPa. Although pressure causes an increase in density from 1 to over 9 g/cm^3, and an increase of the optical dielectric constant from 2 to 6, xenon remains a dielectric at least up to 63 GPa.[8]

The xenon sample we used was 4.5N grade gas from Prodair. Loading into a classical diamond anvil squeezer[9] was done directly from the 50-bars container, at room temperature, after the cell had been evacuated to eliminate residual air and moisture. Filling with xenon is done by simply capping the cell with a suitable casing, connecting it to the bottle, squeezing the anvils and gasket tight, and then releasing the external 50-bars pressure. Before loading with gas, a ruby chip is positioned in the center of the Inconel gasket and used as a pressure gauge under illumination from the green (514.5 nm) line of an Ar^+ laser. The pressure shift of the R_1 line has been taken to be 7.53 cm^{-1}GPa^{-1} throughout this work. The anvils culet plane, 500 μm in diameter, have a 3° bevel[9] leaving a flat octogon about 280 μm in diameter. The Inconel 750 gasket, 150 μm thick initially is reduced to 40 μm, after preindenting. The hole in the prestrained gasket is 200 μm in diameter at low (< 1 GPa) pressures and is reduced to 90 μm at 60 GPa (Fig. 1). In this photograph, the ruby chip which is less than 30 μm across and 10–15 μm thick, appears dark since its refractive index is much less than that of xenon. Pressure is 63 ± 2 GPa. This large uncertainty is due partly to a slight broadening of the ruby luminescence peak and mainly to a rapid decrease of the luminescent intensity above 55 GPa. This cannot be assigned to absorption either of the ruby emission in the near infrared or of the laser excitation in the visible since no absorption occurs in this range, as reported later on in this Communication. Since this behavior has not been reported by other authors, using higher-energy excitation from HeCd lasers, or Hg high-pressure lamps, it is likely that it is due to a pressure shift of some intermediate levels which are responsible for the luminescent

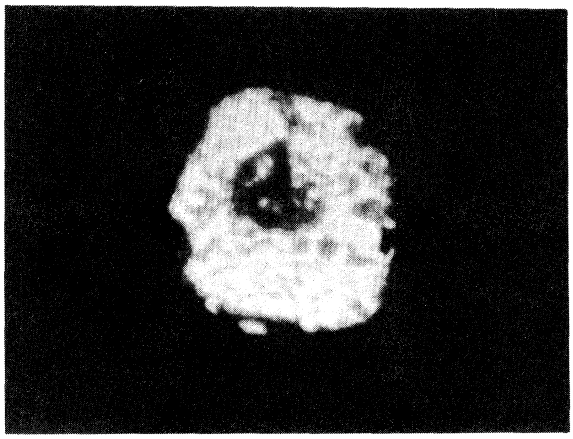

FIG. 1. Xenon microcrystals in the diamond anvil cell at 63 ± 2 GPa, $T = 300$ K. Dark spot is the ruby flake used as a pressure gauge. The cell is about 90 μm in diameter and 18 μm thick.

processes in ruby. The 488-nm line of the laser did give higher intensity than the 514-nm one but could not be used throughout the experiment. For the present, no further discussion on this point can be done here. Direct observation of the Xe sample (Fig. 1) shows that it is not metallic or semimetallic. Grain boundaries between xenon microcrystals appear as a faint network. This pattern does not show any abrupt change with increasing pressure, such as would be expected at a fcc → bcc transition. This, nevertheless, does not disprove the existence of the transitions since the difference in free energy between the two structures is expected to be small[5] and the transition might elude direct observation.

Figure 2 shows the refractive index n of the xenon sample versus density which was measured at two pressures by the index coincidence method. The transmittancy spectrum of the cell shows Fabry-Pérot fringe maxima and minima. Although strict parallelism of the diamond faces is not maintained under stress, because of the curvature of the anvil culets, it is still possible to observe the fringes at the highest pressures using an illumination diaphragm and an observation iris which narrow the observation field down to 20 μm. When this light spot is coincident with the ruby, a *maximum* in the fringe amplitude occurs at 6 GPa, that is when the index of the ruby is

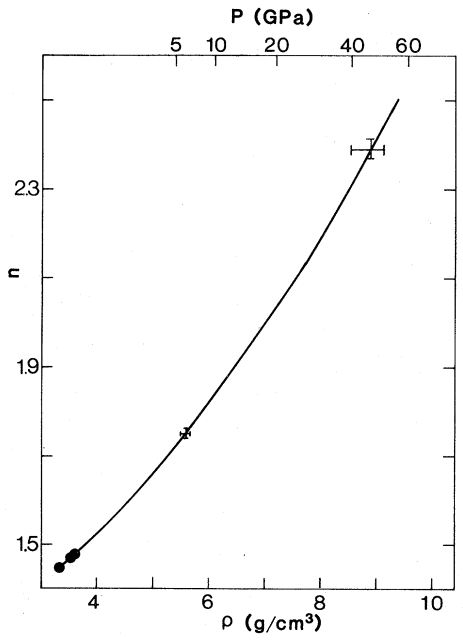

FIG. 2. Refractive index of xenon at 300 K under pressure around $\lambda = 650$-nm wavelength vs density. Pressure-density relations from Ref. 1. Full circles: low-pressure data from Ref. 10. The two values at 6 and 45 GPa are obtained by the index coincidence method. Full line is not fitted and simply goes through experimental data.

equal to that of Xe (the ruby sample "disappears" in the field). On the contrary, when the light goes through xenon alone, fringe amplitude recorded around a wavelength of 650 nm decreases and goes to zero around 45 GPa. This behavior corresponds to the expected minimum of fringe amplitude which occurs when the index of diamond equals that of xenon (zero reflectivity of the diamond-xenon interface). After applying high-pressure corrections for the indices[10] of the two crystals, we get an evaluation of $n = 1.75 \pm 0.02$ at 6 GPa and $n = 2.39 \pm 0.03$ around 45 GPa. The small index anisotropy of ruby is included in the error. Using known values of $n(\rho)$ for xenon at low densities,[11] we can plot n versus density, using the published equations of state (EOS).[3] Admittedly, this is a rough method, but, because of the very large variation of n in xenon, it still gives a useful evaluation of $n(\rho)$. The high-pressure value was checked by observing GaN in the cell. This crystal has an index of 2.4 and disappears in the field above 40 GPa.

The value of the Fabry-Pérot interfringe separation $\Delta\nu$ (wave-number distance between successive maxima and minima) decreases by less than 4% between 22 000 and 12 000 cm^{-1}, up to 30 GPa, showing a negligible dispersive term in the index. We can thus relate it to the index n and thickness of the cell by: $2ne\Delta\nu = 1$ and thus compute the actual thickness under pressure.[8] In our case, the cell was some 20 μm thick at 50 GPa. By measuring the relative variation in size of the cell, which deforms homothetically above 4 GPa, we get a rough estimate of the *relative* volume variation, and thus of the *relative* density variation, which is then fitted to the experimental[12] values below 10 GPa. We get a fit with the EOS of Ross and McMahan,[3] after correcting to room temperature, all over the range from 10 to 60 GPa, with only 1.5% mean deviation. Since we estimate our errors to be 4% at least, this good fit may be coincidental, and we will only state for the moment that our results do not contradict existing EOS's.

Transmission measurements of the cell were done under a microscope, with a Jarrell-Ash double monochromator. The reference level (zero absorbancy) was taken from the low-pressure spectrum which turned out to be identical at all pressures up to 30 GPa between 1.5- and 2.8-eV photon energy. High-energy absorption appeared between 35 and 53 GPa. This series of experiments is different from that displayed in Fig. 1 and was interrupted by anvil failure. Knowing $e(P)$ we could compute the absorption coefficient α (Fig. 3) taking the region between 1.5 and 2 eV to have $\alpha = 0$ since its spectral profile is identical from 0 to 53 GPa and shows no near infrared absorption. It should be clear here that Fig. 3 displays the total absorbancy of the setup that is anvil plus xenon α would be the actual absorption coefficient only if no absorption came from the diamonds.

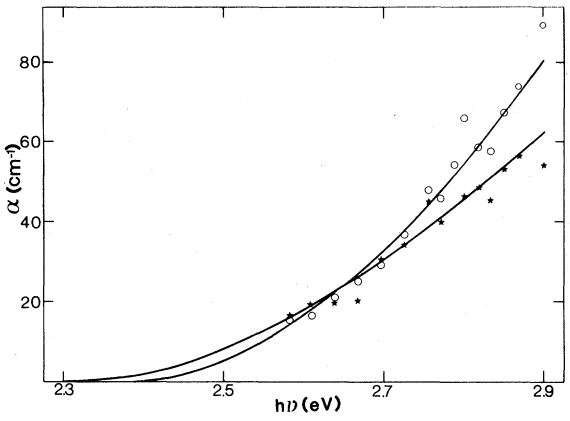

FIG. 3. $\alpha = (1/e)\log_{10}(I_0/I)$ vs photon energy $h\nu$ for the Xe sample and diamond anvils, e: cell thickness; $\log_{10}(I_0/I)$: absorbancy of the setup. Circles: 45 GPa; stars: 53 GPa; full line: fit of α with a quadratic law (see text).

Actually our anvils being type-I stones, the characteristic[13] absorption from nitrogen centers may well have been pressure-shifted down to this part of the spectrum. We nevertheless tentatively fitted the apparent absorption coefficient spectrum with a quadratic law, as would be expected from an indirect Γ_{15}^{V}-X_1^{C} process in xenon. This yields a value of 2.3 eV at 53 GPa for the indirect edge. This corresponds closely with predictions from Ref. 3 but this is probably coincidental since the pressure coefficient of the "edge" which one determines in this way from measurements at several pressures between 40 and 53 GPa is much smaller in absolute value than that calculated in Ref. 3. Moreover, recent results indicate that the gap is of the order of 3.9 eV at 44 GPa.[14] Therefore, we can only state that the gap in xenon is larger than 2.3 eV at 53 GPa.

This last result is nevertheless sufficient to allow some discussion of the high-pressure behavior of Xe.

The optical transparency of the sample up to 63 GPa rules out its being a metal, semimetal, or small-gap semiconductor, contrary to a previous report.[2]

The absorption of our setup shows that the absorption edge is still larger than 2.3 eV at 53 GPa, and may be considerably more.[14]

Grain boundaries in the sample show no discontinuous change up to 63 GPa. The experimentally determined EOS fits with previous calculations and dynamic data.[3] No sign of a transition to a different structure[5] (bcc?) is apparent.

A remarkable increase in the optical dielectric constant, from 2 to 6, is observed. This point and comparison with the Clausius-Mossotti relation and the variation of the polarizability of xenon (Lorentz-Lorentz coefficient) as well as the equation of state will be discussed at more length in a forthcoming paper.

In conclusion, if the decrease in conductivity observed in Ref. 2 is to be assigned to band overlap in the Xe sample this must occur at much higher pressures in accordance with more recent calculations.[7] Moreover, direct optical observations (this work and Ref. 14) tend to support existing predictions based on equations of state[3,4,12] which predict band crossing to occur in the vicinity of, or above 100 GPa, in the fcc structure.

ACKNOWLEDGMENT

This work has been supported in part by a DRET Contract No. 80/500.

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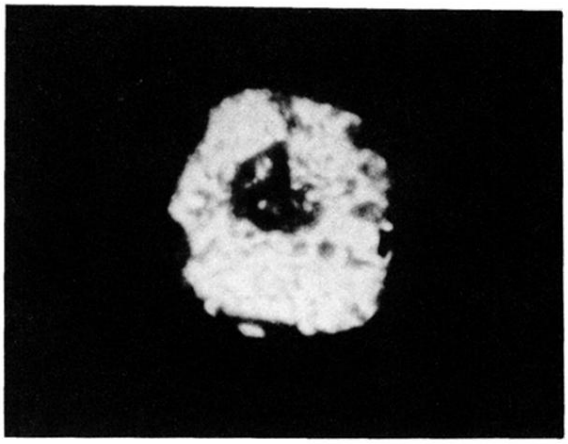

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