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Metallic Xenon at Static Pressures

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Using a diamond indentor, diamond anvil technique along with nonshorting interdigitated electrodes produced on the anvil by lithographic processes, we have shown that the electrical resistance of a xenon sample at 32°K drops from $10^{13}\ \Omega$ (or greater) to about $10^{4}\ \Omega$ at 0.33 Mbar. Further studies using a second method reveal that the resistivity has dropped to below $10^{-1}\ \Omega$ cm and possibly much lower.

The present paper demonstrates the production of a conducting state in xenon which is produced by the application of high pressure on a solid sample of xenon at 32°K. The experimental techniques are described first. Then there is a brief discussion of why xenon is expected to become metallic at high pressures.

When a spherical diamond tip of radius R is pressed against a flat diamond, a contact pressure is established. The pressure distribution can be accurately calculated by the Hertz contact theory,[1] from a knowledge of the tip radius R, the applied force F, Young's modulus E, and Poisson's ratio ν.[2,3] The fact that diamond is nearly isotropic elastically, and hence can be represented by an isotropic elastic solid, has been described elsewhere.[3] If a is the radius of the contact circle and r is a variable radius, then the pressure distribution is given by

$$P = P_0(1 - a^2/r^2)^{1/2}, \quad (1)$$

where

$$P_0 = (\tfrac{3}{2})^{1/3}\pi^{-1}[E/(1-\nu^2)]^{2/3}R^{-2/3}F^{1/3}. \quad (2)$$

We use $E = 1141$ GPa and $\nu = 0.07$.[3] For diamond at 50 GPa, the pressure computed from Hertz contact theory agrees with the directly measured value obtained by the use of Newton's-ring techniques.[3,4] Ruoff and Wanagel have used this indentor-anvil technique to obtain pressures of 1.4 Mbar.[2]

Measurements of insulator-to-metal transitions can be made using the interdigitated-electrode technique developed by Ruoff and Chan.[5] A schematic drawing of this electrode system is shown in Fig. 1. The actual electrodes involve 75 or more fingers. They are produced by photolithography although electrodes with smaller finger widths and smaller spacing can be produced by electron-beam lithography. The value of d in the present experiments is 3 μm. The electrodes used in these experiments are nickel, deposited by sputtering; they are 350 Å thick. Electrical leads are attached to the anvil base. Then the sample is deposited on the anvil. Finally, the indentor is pressed against the sample-electrode-anvil assembly resulting in contact over the region shown by the dashed circle in Fig. 1. When the pressure near the center reaches a sufficiently high value, the sample undergoes an insulator-to-metal transition and the electrode circuit is closed. The metallic region is represented by a solid circle in Fig. 1 for two different cases of indentor location. The center pressure will be different for these two cases when the transition is observed; by making the finger widths and spacings sufficiently small, the pressure at which the transition is observed will approach the center pressure. The technique used with ZnS led to a transition pressure[5] of 14.0 ± 0.5 GPa; this transition is observed at 15.0 ± 0.5 GPa on the ruby scale.[6]

In the present experiment the anvil (with its interdigitated electrodes) is placed in a vacuum chamber. Following evacuation, the anvil, which rests on a plate through which helium can flow, is cooled to 32°K. The temperature is measured with a platinum resistance thermometer. Xenon is then introduced into the chamber and condenses on the anvil. The thickness of the xenon is measured by a quartz thickness monitor, the quartz crystal being located adjacent to the dia-

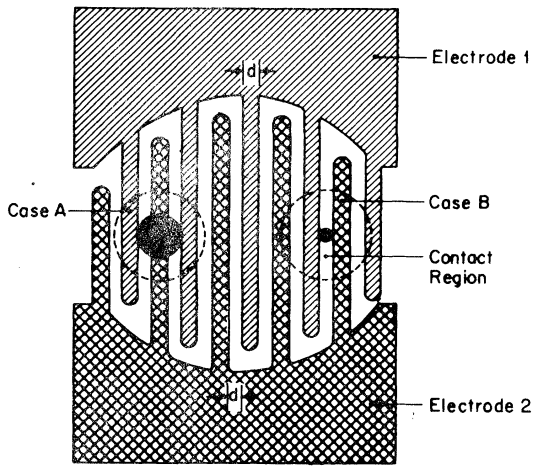

FIG. 1. Schematic of interdigitated electrodes on diamond. Actual electrodes have 75 or more fingers. A thin sample is present on top of these electrodes. Dashed circle shows the perimeter of the contact circle when the indentor is applied with a specific force. The black center circle shows the sample material which has become conducting.

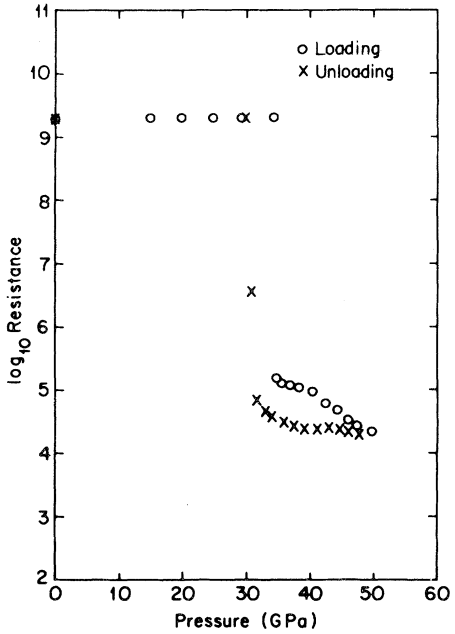

FIG. 2. Insulator-to-conductor transition in xenon at 32°K using the interdigitated electrodes. Transition may be first order or may involve continuous decrease in the band gap. The final resistance is the lead resistance; the sample resistance is substantially less.

mond anvil on the cold plate. Another quartz crystal located on the plate but within a permanently evacuated chamber is used as part of the quartz thickness monitor. The xenon sample thickness used herein ranged from 800 to 1200 Å in different samples.

The diamond indentor is attached to a rod. A flexible aluminum foil is connected between a cold plate and the rod. A thermocouple is attached to the rod just above the indentor. The cold indentor is then pressed against the sample and the force is then measured by a calibrated load cell. The force measurement is expected to be accurate to 1%.

When the sample thickness, t, is sufficiently small the pressure distribution will be essentially that for diamond-diamond contact as computed from Hertz contact theory. This will be the case where $t \ll \delta$. Here δ is the relative displacement of two points along the axis of revolution, one point located in the indentor far from the contact surface, and the other in the anvil far from the contact surface. From Hertz contact theory

$$\delta = (a/R)^2 R \tag{3}$$

and

$$\frac{a}{R} = \pi \frac{1-\nu^2}{E} P_0. \tag{4}$$

Experiments by Gupta and Ruoff[7] using Newton's-ring techniques to measure area show that Eq. (1) gives nearly the correct pressure even when $t = \delta$. For our experiments on xenon, at 33 GPa, $t \leq \delta/5.6$. Tip radii of 39 and 100 μm were used, with most of the experiments involving the latter.

Resistance measurements made with a Keithley 160B multimeter are shown in Fig. 2 (the upper resistance is the limit of the device); the resistance drops by a factor of 10^4 to 10^5. [In a few experiments a Keithley 610BR electrometer capable of measuring a resistance of 10^{13} Ω (10^{14} ideally) was used; then the total resistance drop observed was by a factor of 10^9.] These experiments were repeated seven times always with a new xenon sample and led to essentially the same results. The resistance drop occurs at about 33 GPa.

The following two types of control experiments were performed. In one, H_2O was used (at 78°K) in place of xenon; ice remains an insulator to 72 GPa, the highest pressure used. The second type of experiment involves bringing the indentor down directly on the electrodes with no sample present[5]; no resistance drop was observed by the multimeter at the highest pressure. Also at the highest pressure used (45 GPa) subsequent

examination of the electrodes in the scanning electron microscope revealed the area of contact. Similar scanning electron microscope studies following experiments on xenon did not reveal the region of contact, thus clearly establishing that the indentor did not punch through the xenon. This is not surprising since the ratio of the contact radius to the sample thickness at 33 GPa is about 50; in experiments on ungasketed sodium chloride, a ratio of 5–10 provides sufficient friction to contain the sample at pressures of 30 GPa at room temperature.[8] The shear strength of xenon at 32°K ($T/T_m = 0.2$) is about 25 MPa as obtained from Fig. 3 of Towle.[9] The shear strength of heavily deformed sodium chloride is 100 MPa at room temperature.[10]

In order to follow the resistance drop to lower resistances a second procedure was used. In this case a solid metal coating was placed on both the indentor and the anvil and leads were attached to both. The experiment was then carried out as before. This method had been used earlier to study sulfur.[11] The resistance behavior was similar to that obtained with the interdigitated electrodes, but because of the lower lead resistance, smaller final resistances could be obtained. Since the relation between resistance and resistivity had been analyzed for this geometry,[12] the final resistivity could be calculated. Curves similar to those shown in Fig. 2 were obtained although they extended to lower resistance. Altogether the transition was observed in eighteen different experiments with seven using the interdigitated-electrode method and eleven using the coated-piston method. We found that $\rho < 10^{-1}\ \Omega$ cm at the highest pressure. The technique would have to be modified—for example, by using a four-lead measurement—to obtain accurately the final value of resistivity.

It is not surprising that xenon should become metallic. Both iodine (Group VII*B*) and sulfur (Group VI*B*) become metallic by a band-overlap process. Iodine has been studied experimentally[13] and theoretically[14] and the band gap reduces to zero at about 15–17 GPa. Sulfur exhibits a similar behavior. In this case the band gap reduces to zero at about 30 GPa.[11,12,15] One study suggests 470 kbar.[16] From a study of the pressures at which iodine and sulfur and other insulating elements become metallic, it was expected that xenon would become metallic at 30–50 GPa. Ross[17] has studied the variation of the band gap of xenon with pressure using the Wigner-Seitz model. He predicted band-gap closure at 11.7 cm^3/mole. From pressure-volume relations by Ross and Alder,[18] a transition pressure (band gap overlap) of 70 GPa was predicted. The present result showing that band-gap overlap occurs in xenon at 33 GPa is more or less consistent with these predictions considering the potential for error in the P-V relations. It should be pointed out that the results of the present experiment do not distinguish between a continuous closing of the band gap which is complete at 33 GPa or a first-order transition at 33 GPa. If the band gap decreases linearly with pressure, the negative of the slope of $\log_{10}R$ vs P is given by[12]

$$\beta = \Delta E_0 / 4.6kTP^*, \tag{5}$$

where ΔE_0 is the zero-pressure band gap, P^* is the pressure at which band-gap closing is complete, and T is the absolute temperature. For a large-gap material such as xenon ($\Delta E_0 = 9.3$ eV)[19] and for studies at low temperature ($T = 32$°K), the magnitude of the slope is very large; a drop in resistance by a factor of 10^5 occurs over a pressure range of only 0.2 GPa. Hence it is experimentally impossible to distinguish between a continuous band-closing mechanism and a first-order transition in the present experiments. [For comparison, Eq. (5) predicts that in iodine a factor of 10^5 change in resistance at room temperature occurs over a pressure range of 8 GPa.]

Although the present experimental arrangement did not allow for studies of possible superconductive or magnetic behavior of metallic xenon, such studies would be of interest. Additional studies also requiring further development should obtain the actual value of the final resistivity. Finally, it would be of interest to know the crystal structure of the conducting phase. The most exciting experiments on this conducting form of xenon lie ahead. The present results lead us to infer that radon will become metallic at 15 GPA, bromine at 30 GPA, and krypton at 60 GPa.

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Microscopic Calculations of the Stability of Metallic Glasses

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We show that metallic glasses are stabilized by the close matching between the minima in the interionic potentials and the maxima of the partial pair-distribution functions. We use an *ab initio* pseudopotential method to calculate the interionic potentials for transition-metal–free glasses (Mg-Zn, Ca-Mg, and Ca-Al). The amorphous structure is determined using cluster relaxation and thermodynamic variational techniques. Our theory demonstrates that there is a close relation between glass formation and the formation of topologically close-packed intermetallic compounds.

Metallic glasses obtained by rapid quenching from the liquid state are of particular scientific and technological interest because of their many unusual physical properties.[1] Models based (i) on the destabilization of the crystalline mixture[2] and (ii) on the stabilization of the liquid phase[3] by packing effects[4] or electronic effects[5] have been proposed for the stability of amorphous metallic alloys. Very recently the study of metallic glasses formed by simple metals only has attracted much attention. The discovery[6] of the first transition-metal–free amorphous alloy $Mg_{0.7}Zn_{0.3}$ has been followed by the production of metallic glasses in the systems Mg-Ga and Ca and Sr with Mg, Al, Ga, and Zn.[7]

We present here the first microscopic calculations of the stability of metallic glasses, based on the pseudopotential approach to the interionic forces and model calculations of the amorphous and liquid structures. We show that the glassy and the liquid states are stabilized by the close matching of the minima in the interionic potentials and the maxima in the pair distribution functions (PDF's). At a majority concentration of the smaller atoms, the interionic distances of a topologically close-packed intermetallic com-

