Electrical Conductivity of Xenon at Megabar Pressures

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The electrical transport properties of solid xenon were directly measured at pressures up to 155 GPa and temperatures from 300 K to 27 mK. The temperature dependence of resistance changed from semiconducting to metallic at pressures between 121 and 138 GPa, revealing direct proof of metallization of a rare-gas solid by electrical transport measurements. Anomalies in the conductivity are observed at low temperatures in the vicinity of the transition such that purely metallic behavior is observed only at 155 GPa over the entire temperature range.

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With the ability to pressurize materials to megabar pressures (>100 GPa), it is possible to decrease the volume of compressed solids by over an order of magnitude [1]. This can drastically alter interatomic interactions, ultimately leading to the transformation of all substances to metals [2]. Indeed, these pressure-induced metals can have unique properties [1]. Rare-gas solids are the simplest substances for such studies: their atoms have completely filled electronic shells and therefore spherically symmetric charge distributions. As a result, the metallization pressures for these solids are expected to be high [3]. Xenon has the lowest predicted pressure of metallization and thus has been extensively studied [4–14]. Theory predicted that the transition to the metallic state occurs through indirect overlap of the valence and conduction bands [6,7]. Early estimates of the metallization pressure were obtained from extrapolation of the pressure dependence of the optical edge associated with the indirect gap [4,5]. X-ray diffraction measured at pressures up to 137 GPa showed that Xe at room temperature transforms at 14 GPa from the fcc structure to an intermediate close-packed phase and then completely to the hcp structure above 75 GPa [10,11]. Near infrared absorption and reflectivity appear at pressures above 140 GPa, which was interpreted as a Drude-type feature [12,13]. Extrapolation of the dependence of this feature gave 135–150 GPa as the pressure of metallization. Reichlin *et al.* [13] also showed that Xe remains in the hcp structure to at least 172 GPa.

If metallic at megabar pressures, xenon is an unusual material: it is reported to remain transparent in the visible region under these conditions [10,12,13]. This was explained by a small density of states at the top of the valence band, with overlap of the valence band (formed from antibonding 5*p* states) and the conduction band (5*d* states) generating a small concentration of free carriers [14]. However, the temperature dependence of metallic properties was not measured, and the contribution from the thermal excitation of carriers was not examined. Moreover, if the transition is isostructural, very general arguments indicate that there should be anomalies at low temperatures [15].

Ultimate and indispensable proof of metallization can be provided by electrical transport measurements, including the temperature dependence as $T \rightarrow 0$ K. Electrical measurements in a diamond anvil cell are among the most difficult techniques. Experiments for solidified gases at very high pressures are particularly challenging because one needs an insulating gasket capable of containing gas. Previous work barely reached the megabar range [16]. In this Letter, we report direct electrical conductivity measurements in solid xenon above 140 GPa and down to 27 mK. Distinct changes across its high-pressure transitions are observed.

In our experiments, pressure was generated by a pair of diamonds with 300 μm culets, a 10° bevel angle cone, and a 100 μm flat surface at the top (Fig. 1). The electrodes immersed in the sample are separated by ~5 μm. The part of the sample between the electrodes provides the largest contribution to the measured resistance [17]. The experimental arrangement for the electrical measurements was similar to that described in Ref. [18] but with a different insulating layer made from the mixture of 1 μm cubic boron nitride powder and epoxy. High purity xenon was loaded cryogenically in the 50 μm gasket hole. Four electrical leads made from platinum foil were arranged in two pairs in contact with each other, allowing a quasi-four-electrode measurement of the resistance. The direct electrical contacts between the pairs of electrodes allowed us to test whether electrodes were broken during loading, and were routinely checked to ensure that there was no

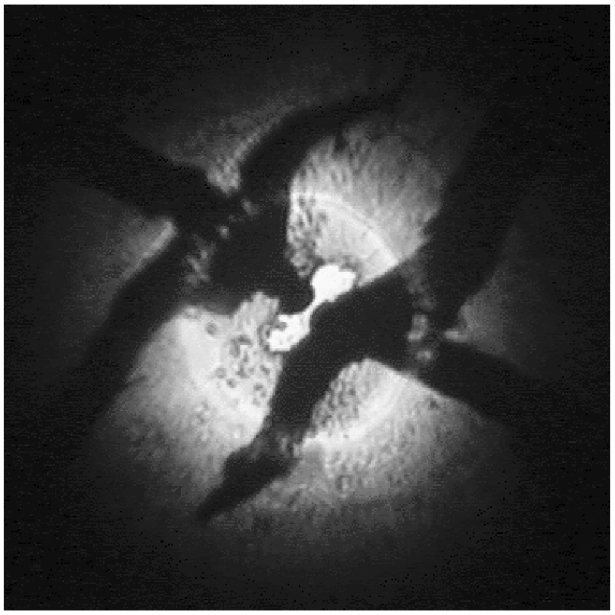

FIG. 1. Quasi-four probe electrode scheme at 120 GPa. A xenon sample is between the two electrodes in the center. The insulating gasket at the culet around the sample is semitransparent. The distance across the field of view is 250 μm.

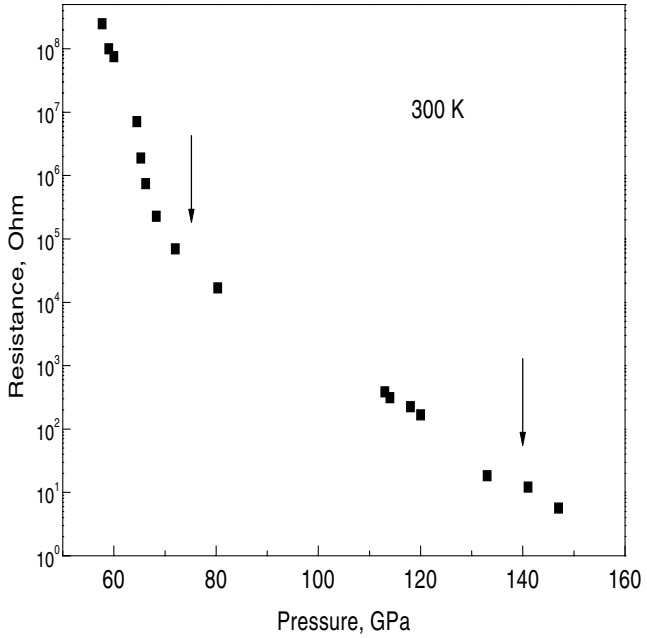

FIG. 2. Resistance of xenon measured by the quasi-four-electrode method as a function of pressure at room temperature. Arrows show the pressures corresponding to the completion of the transition to the hcp structure at 75 GPa measured by x-ray diffraction [10] and to the metallic state indicated by absorption and reflectivity [12,13].

contact between the electrodes and the gasket. The gasket was shown to be nonconducting up to at least 150 GPa as demonstrated by control experiments on other materials (e.g., H_2O ice) performed with identical gaskets up to 150 GPa. Samples were cooled in the ^{3}He refrigerator down to 0.4 K and ^{3}He/^{4}He refrigerator down to 0.027 K. Pressure was measured with ruby chips placed with the Xe sample at all temperatures down to 3 K in the optical cryostat [17]. Typically pressure increased by 8 GPa during cooling to low temperatures at pressures above 100 GPa [19]. This change was reproducible; therefore, pressure was measured only at room temperature in experiments with cooling of the cell in the ^{3}He [20] and ^{3}He/^{4}He [21] refrigerators. Luminescence from the ruby was measured with Ar^+ and Ti:sapphire lasers.

Above 60 GPa, a measurable resistance appeared which dropped with further increase in pressure. A noticeable change in slope was observed at pressure $\sim$75 GPa. This pressure coincides with the pressure of completion of the transformation to the hcp phase at room temperature [10]. Overall, the pressure dependence of the resistance shows a drop indicative of the approach to a metallic state (Fig. 2). The temperature dependence of resistance at different pressures (Fig. 3) clearly indicates a transition from semiconducting to apparent metallic behavior between 121 and 138 GPa. This is similar to the estimates based on room-temperature optical studies [12,13]. Low-temperature measurements are needed to prove that the material is metallic as $T \rightarrow 0$ K. Measurements performed down to 27 mK demonstrate that purely metallic behavior appears only at 155 GPa [22].

The low-temperature measurements reveal interesting features near the transition. At 138 GPa metallic behavior ($dR/dT > 0$) is observed from room temperature to low temperatures. However, at temperatures below 25 K the resistance noticeably increases. At 141 GPa an increase in resistance was detected at $T < 1$ K. At 155 GPa the resistance did not change in a wide temperature range and decreased slightly at $T < 2$ K (Fig. 4). The changes were

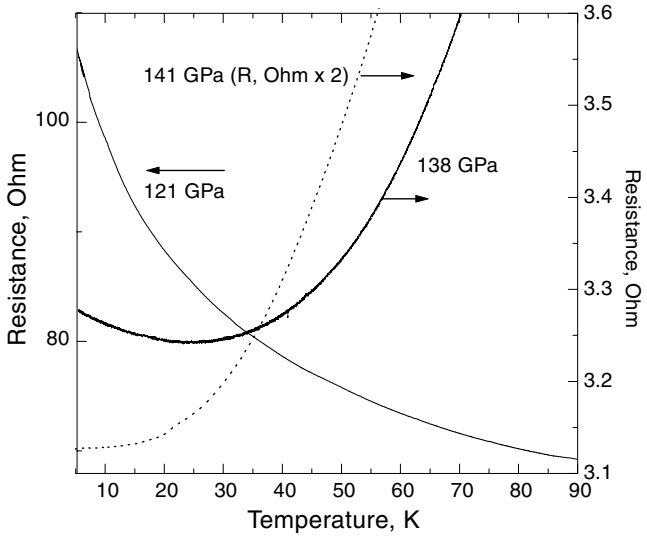

FIG. 3. Resistance of the xenon sample as a function of temperature measured at different pressures.

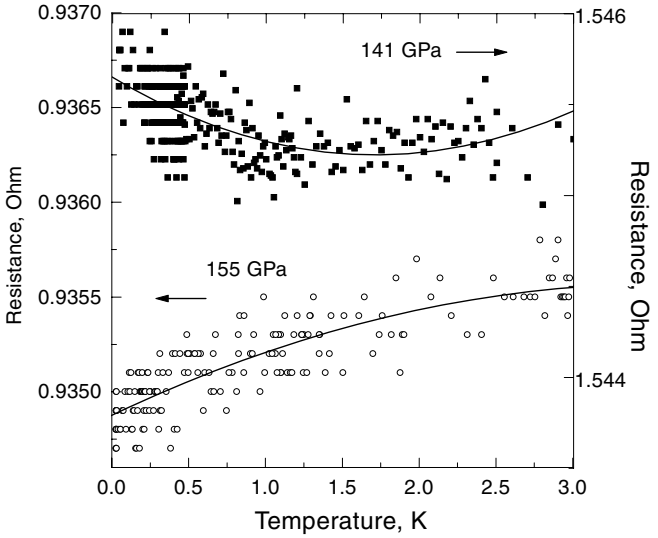

FIG. 4. Resistance of xenon at very low temperatures measured with the ^{3}He [20] and ^{3}He/^{4}He [21] refrigerators.

systematic and consistent for measurements in all three laboratories.

An increase of resistance at low temperatures is not typical for crystalline metals but can be observed in amorphous metals because of weak localization effects [23]. This requires a small value of $k_F l$, where l is the mean free path of electron and k_F is the radius of the Fermi surface. A very small l can be realized in highly disordered (e.g., amorphous) metals. This state seems unlikely in xenon at the transition to the metallic state because x-ray studies [10] show that the material is a close-packed crystalline solid (hcp) at these pressures and does not change at the transition. It is possible that defects accumulate at lower pressures, during the phase transition from the fcc to the hcp phase between 14 and 75 GPa [10], leading to a sufficiently small l. In addition, xenon has a small k_F because it is a very poor metal at these conditions. Alternatively, the observed increase in resistance may arise from contact resistance in the two-electrode technique where carriers may be localized at the electrodes. Despite the small measured pressure gradient [17] a mixture of semiconducting-metal phases could also develop near the transition and produce an increase in resistance with decreasing temperature.

Another attractive, but at this point speculative, explanation for the increase of resistance is the formation of an excitonic insulator state. This phenomenon is predicted to occur when the energy gap E_g becomes smaller than the binding energy E_b of an exciton and the ordinary ground state of the crystal becomes unstable with respect to the spontaneous formation of excitons [15]. In this phase, bound electrons and holes do not participate in the electrical current and the crystal behaves like an insulator. The theory of this phenomenon has been studied [15,24–26], but so far there has been no convincing experimental proof. One of the problems has been finding a proper material in which the conditions for observing this effect are satisfied. Xenon appears to be an excellent candidate as it fulfills all necessary criteria: it has a low density of carriers and therefore an unscreened Coulomb interaction can create a bound state between an electron and a hole (exciton). The gap closure occurs via indirect overlap of the bands, so the dielectric constant and E_b remain finite while E_g can be arbitrarily small. There are no structural transitions at the pressure of gap closure, which would obscure the effect [10]. The exciton binding energy in xenon is expected to be high: $\sim$0.2 eV. This value is much larger than estimated for many other materials [25]. Pressure could easily be controlled within the estimated pressure range ($\Delta P \simeq 8$ GPa) required to observe the effect.

In conclusion, we have carried out direct measurements of electrical transport properties in solid xenon up to 155 GPa over a wide temperature range (0.027–300 K), the highest pressure conductivity measurements on a solidified gas reported to date. The temperature dependence of the resistivity of the sample becomes predominantly metallic between 121 and 138 GPa and shows purely metallic behavior at 155 GPa. Even when exhibiting purely metallic behavior at 155 GPa the estimated value of conductivity is $\sim$500–2000 $\Omega^{-1}\,\mathrm{cm}^{-1}$, which is the minimum for metallic conductivity [24]. We confirm that the small conductivity correlates well with the fact that xenon remains transparent in the visible range at metallization (cf. Refs. [12,13]). Additional measurements, including Hall effect, four probe conductivity, and optical studies in the vicinity of the transition, as well as theoretical calculations that take into account localization effects, would provide further insight into the intriguing properties exhibited by this material at very low temperatures and megabar pressures.

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