Metallic CsI at Pressures of up to 220 Gigapascals

M. I. Eremets,* K. Shimizu, T. C. Kobayashi, K. Amaya†

Direct electrical transport measurements in a diamond anvil cell provide evidence for the metallization of cesium iodide (CsI) at a pressure of 115 gigapascals. A drop in the temperature dependence of the resistance was found at pressures above 180 gigapascals, indicating that the CsI was superconductive. The superconductivity changed under the influence of a magnetic field to a lower critical temperature and disappeared above 0.3 tesla. The highest critical temperature at which superconductivity was observed was 2 kelvin, and the critical temperature decreased with increasing pressure.

Exposing a material to high pressures can alter its physical properties. Static high pressures, achieved with diamond anvil cells (DACs) (*1*), can decrease the volume of compressible solids. Volume reduction increases the interaction between the atomic valence orbitals, broadens the electronic bands, and ultimately closes the energy gap between the valence and conduction band states. Thus, a broad range of physical structures, from wide-gap dielectrics to metals, are open to investigation. One well-known solid for pressure-induced metallization is hydrogen, which is predicted to be a metal with high-temperature superconductivity at pressures of 300 to 400 GPa (*2*).

Transport electrical measurements in a DAC at high pressures can provide proof of metallization and be used to study superconductivity. In geophysics, the knowledge of conductance of minerals is necessary to understand phenomena such as the origin of Earth's dynamo. Development of electrical experiments in a DAC is also interesting for comparison of static pressure data with data obtained in shock-wave experiments (*3*). In spite of these objectives, electrical experiments in a DAC were limited to pressures <70 GPa (*4*), and conductive measurements seemed too difficult to perform at high pressures because of the small sample size. We have performed electrical experiments and conductivity measurements above 100 GPa in a DAC (*5–7*).

CsI is a prototype for the study of the dielectric-to-metal transition. Because it has the lowest energy gap (about 6 eV) among the alkali halides and because of its high compressibility, it is a favorable material for the study of metallization. CsI is also interesting because it is isoelectronic to solid xenon. The state equations of both materials are indistinguishable at high pressures (*8*). At ambient pressure, CsI has a simple B2 structure. Earlier experiments indicated that CsI undergoes transition to the tetragonal phase at 25 GPa, followed by a transition to the orthorhombic phase at 65 GPa (*9*). However, it was later shown that CsI undergoes a continuous distortion starting from the B2 phase at 15 GPa to the hcp phase, with hexagonal symmetry and close packing of the ions up to at least 200 GPa (*8*). The intermediate phase between 15 and 200 GPa has orthorhombic symmetry. Theoretical work showed that the CsI metallization is caused by overlapping at the Γ point of the filled 5p-like I band with the empty 5d-like Cs band at pressures of about 100 GPa (*10*, *11*). This mechanism is rather insensitive to the crystal structure of CsI. Optical experiments confirmed the metallization of CsI at about 100 GPa (*12*, *13*).

In our experiment, pressure was generated by a pair of diamonds with 300-μm-diameter tips, a 10° beveled angle cone, and a 50-μm-diameter flat surface at the top (Fig. 1). The rhenium gasket that lies between the diamonds was preindented with its thinnest part removed. In its place, an Al_2O_3 powder of 1-μm grain size was added and pressed to form a transparent Al_2O_3 gasket. It reliably insulated the sample and electrodes against the Re gasket. A 20-μm-diameter hole was drilled in the center of the Al_2O_3 gasket with a thickness of 7 to 10 μm, and a piece of 15- to 20-μm CsI was placed inside. Four electrodes made of platinum foil were placed on the Al_2O_3 layer. In other runs with CsI (*5*, *7*), electrodes were sputtered on the surface of the diamond and successfully operated. No contact between the electrodes and the gaskets was found at any stage in the experiment. At the beginning of pressurizing to about 10 GPa, the sample shifted from the center, but the sample configuration remained stable at higher pressures. No electrical contact between electrodes was detected at pressures below 45 GPa when the sample had a high resistance. The position and shape of the electrodes observed under a microscope in reflection light did not change at higher pressures.

To determine metallization and superconductivity, we measured the resistance of CsI in the region from 50 mK to 300 K at pressures of up to 206 GPa. In the temperature range of 2 to 300 K, an optical cryostat with a loading system and a DAC were used as described in (*14*). The pressure was measured with ruby grains of ~1-μm diameter placed on top of the CsI sample. To demonstrate the validity of the pressure measurements, we documented the ruby spectra (Fig. 2). The spectra were resolved up to the highest pressures with shape and width close to that taken for high-pressure experiments on hydrogen (*15*). This shows that shear stresses in CsI are small, which is also true in hydrogen. Therefore, we used quasi-hydrostatic pressure cal-

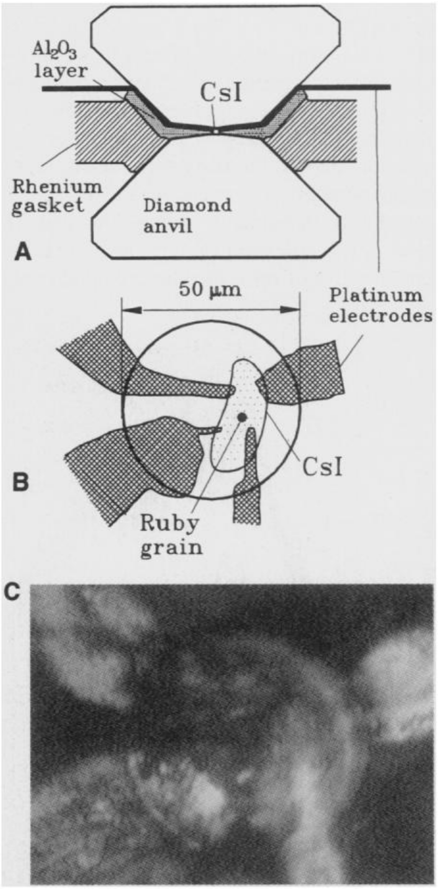

Fig. 1. (**A**) The experimental arrangement for electrical measurements in a DAC shown schematically. (**B**) The sketch shows the position of the electrodes in the photograph (**C**) taken in reflected light at 220 GPa and 300 K.

M. I. Eremets and T. C. Kobayashi, Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan. K. Shimizu, Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan. K. Amaya, Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, and Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Nakagun, Ibaragi 319-1195, Japan.

*On leave from Institute of Spectroscopy, Academy of Sciences of Russia, and Center for Superhard Materials, Ministry of Science, 142092, Troitsk, Moscow Region, Russia.

†To whom correspondence should be addressed.

ibration (*16*), correcting for the temperature dependence of the ruby luminescence peak (*17*). The temperature dependence (Fig. 2) showed that pressure inside the clamped cell (*14*) is nearly constant during cooling, increasing by only 8 GPa at 180 GPa. The temperature of the clamped cell was lowered to 50 mK in ^{3}He/^{4}He dilution refrigerators. One of the refrigerators was supplied with a magnet of up to 14 T, and the magnetic field was applied to the DAC, which was made from nonmagnetic NiCrAl alloy (*14*). Temperature was measured with a germanium thermometer attached to the DAC near the sample. Pressure in the clamped cell was measured at room temperature. We assumed that the pressure increases to 8 GPa upon cooling to millikelvins. The shift of the high-frequency edge in the Raman spectra of diamond taken from the tip of the low-luminescence diamond anvil provides a useful cross-check of the pressure. The edge shifted to 1710 cm^{-1} at 206 GPa from the Raman peak at 1332 cm^{-1} at ambient pressure.

Under compression, the resistance of CsI became measurable near 45 GPa (Fig. 3). The resistance decreased with increasing pressure and leveled off at about 115 GPa (Fig. 3A). This pressure behavior is consistent with our previous runs (*5*, *7*) at 300 K and 135 and 120 GPa. To confirm the metallization, we measured the temperature dependence of resistance (Fig. 3A, inset). At pressures below 117 GPa, the sample displayed semiconducting behavior; that is, the resistance increased as the temperature decreased. At 117 GPa, the temperature dependence changed to that of metal. From the temperature and pressure dependencies of resistance, we conclude that CsI metallizes at 115 ± 3 GPa. This result is consistent with optical experiments (*12*, *13*).

In the metallic state, conductivity and reflectivity simultaneously increase with increasing pressure. At about 120 to 140 GPa, CsI is gray and has low reflectivity, in accordance with (*13*). Above 200 GPa, its reflectivity is comparable to that of the platinum electrodes (Fig. 1). The increase in conductivity with increasing pressure is qualitatively explained by an increased concentration of electrons in the d-like conduction band and holes in the p states near the top of the valence band (*10*, *11*).

At 150 to 160 GPa, the second stepwise drop in resistance was observed (Fig. 3A). This drop might be associated with a transition to the hcp phase. The transition is not sharp, and the hcp phase is reported to appear at about 210 GPa in the x-ray spectra (*8*). At about 180 GPa, we observed a small but abrupt drop in the temperature dependence of resistance (Fig. 4). We explain this drop as the development of superconductivity in CsI. The step was reproduced for all combinations of the four-probe electrodes (Fig. 1B). A similar value of the change of resistance was determined in the experiment with two probes at 216 GPa. The onset of this step in resistance occurred at about 2 K and 180 GPa and shifted to 1.3 K at 216 GPa (Fig. 4). The most valuable argument for superconductivity of CsI is the characteristic dependence of the resistance drop on the magnetic field (Fig. 5). The step observed at 1.3 K at 206 GPa shifted to lower temperatures with increasing magnetic field strength. Extrapolation of the magnetic dependence to zero temperature gave the value of the critical magnetic field for initiation of superconductivity in CsI as 0.3 T. Application of the magnetic field above this value caused the step in the resistance to disappear. At higher magnetic fields, resistance increased by 5% to 8 T measured at 206 GPa and 0.2 K. A similar magnetic field dependence was also observed at 216 GPa.

The observed drop of the resistance was ≈2% of the resistance of the sample. A substantial residual resistance is common for these kinds of measurements at pressures above 100 GPa because of pressure gradients (within 10 GPa at the maximum pressure of 206 GPa measured over the 50-μm anvil tip), inhomogeneity of the sample, or poor alignment of electrodes and sample. The drop in resistance is small and may be due to the development of superconductivity in other substances in the experimental arrangement. The influence of the Re gasket on the observed step is definitely excluded because it is situated far from the pressurized region (Fig. 1), and no contact of the electrodes with the gasket was observed at any stage of the experiment. The platinum electrode material may become superconductive, and because the dimensions of the electrode tips are similar to those of the sample, the measured signal of resistance can include some signal from the electrodes. We checked the effect of the platinum electrodes by performing an experiment at 216 GPa with a two-probe configuration. We measured the same drop in resistance (Fig. 5), despite the addition of pieces of Pt from the two electrodes in series with the sample. We also have to estimate the effect of a possible dissociation of CsI $\rightarrow$ Cs + I at pressures above 5.5 GPa (*18*) and the input of superconductivity from Cs or I. CsI can become unstable under high pressures because its volume is higher than the volumes of the combined elements of Cs (*19*) and I

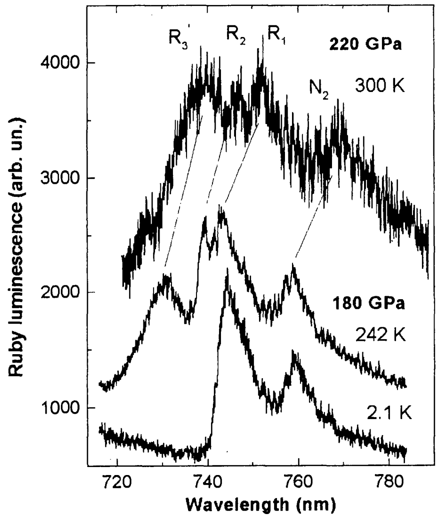

Fig. 2. Ruby luminescence spectra at high pressures taken from ruby grains situated in the center of the CsI sample. The spectra at 180 GPa are shown for two different temperatures. The peaks were assigned in accordance with (*15*); arb. un., arbitrary units.

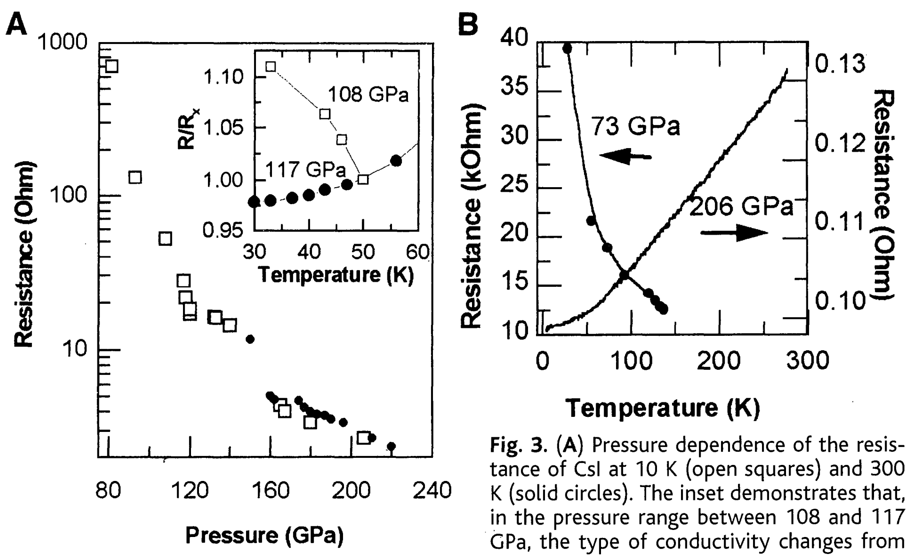

Fig. 3. (**A**) Pressure dependence of the resistance of CsI at 10 K (open squares) and 300 K (solid circles). The inset demonstrates that, in the pressure range between 108 and 117 GPa, the type of conductivity changes from semiconducting to metallic. The temperature dependence of the resistance *R* shown is ratioed to their values of R_x taken at 50 K. (**B**) Typical semiconducting and metallic resistance behavior over a wider temperature range.

(*20*). This difference is about 10% at 120 GPa and about 5% at 200 GPa. However, CsI shows no sharp volume changes, and it is difficult to expect substantial diffusion of the atoms to reconstruct the lattice to the clusters of Cs or I. If this disproportionation really exists, it has to be small, because it was observed only after laser heating at high pressures (*18*) and was not observed in experiments at room temperature. However, properties of the above discussed substances are not well known in this unexplored pressure region. Therefore, additional experiments are needed to exclude these other effects.

Calculations of the critical temperature of superconductivity in the hcp phase of CsI give $T_c = 0.04$ K (*11*). However, many uncertain parameters are involved in these calculations, and further theoretical studies are needed. In particular, it would be interesting to calculate the pressure dependence of T_c. We found that the maximum value of T_c is in the vicinity of the phase transition to the hcp phase and that T_c decreases with increasing pressure. This finding is consistent with the pressure dependence of T_c near the phase transitions observed for other superconductors.

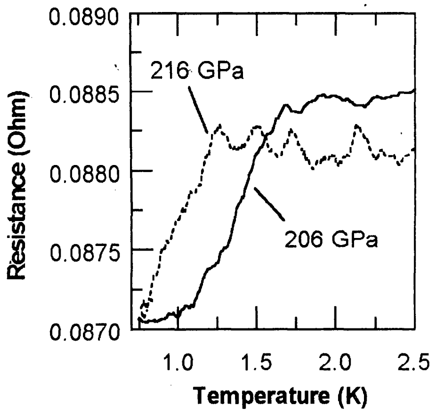

Fig. 4. Pressure dependence of the superconductive transition in CsI shown for 206 and 216 GPa. The plot at 216 GPa was obtained with a two-probe method with $R = 3.1315$ ohms at 2 K. It was shifted in the resistance scale to facilitate comparison with the plot for 206 GPa, which was obtained with the four-probe method.

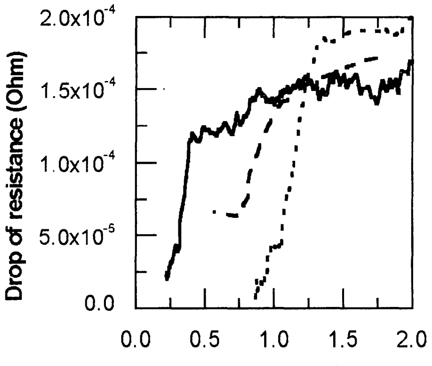

Fig. 5. Temperature dependence of resistance of CsI at 206 GPa taken at different magnetic fields: solid line, 0.5 T; dashed line, 0.07 T; and dotted line, 0 T.

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21. We thank K. Syassen for his critical reading of the manuscript, discussions, and valuable comments and K. Takemura for providing the state equation data for Cs before publication. This work was supported by Core Research for Evolutional Science and Technology and a grant-in-aid from Center of Excellence research (10CE20004), Japan.

20 May 1998; accepted 10 July 1998

Response of Flexible Polymers to a Sudden Elongational Flow

Douglas E. Smith and Steven Chu*

Individual polymers at thermal equilibrium were exposed to an elongational flow producing a high strain rate, and their dynamics were recorded with video fluorescence microscopy. The flow was turned on suddenly so that the entire evolution of molecular conformation could be observed without initial perturbations. The rate of stretching of individual molecules is highly variable and depends on the molecular conformation that develops during stretching. This variability is due to a dependence of the dynamics on the initial, random equilibrium conformation of the polymer coil. The increasing appearance at high strain rates of slowly unraveling hairpin folds is an example of nonergodic dynamics, which can occur when a statistical mechanical system is subjected to nonadiabatic, or "sudden," external forces.

The theoretical study of the dynamics of flexible polymer molecules in fluid flows has been an active area of research for more than 60 years, starting with the work of W. Kuhn in 1934 (*1*). It is also an area of practical interest because dilute polymer solutions exhibit many interesting non-Newtonian rheological properties such as viscosity enhancement and turbulent drag reduction (*2*). Classic experiments on the dynamics of polymers in elongational flow have measured averaged quantities such as light scattering (*3*), birefringence (*4*), and rheological stress (*5*). These results have been compared with many

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Departments of Physics and Applied Physics, Varian Building, Stanford University, Stanford, CA 94305, USA.

*To whom correspondence should be addressed. E-mail: schu@leland.stanford.edu