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PRESSURE INDUCED METALLIC TRANSITIONS
IN INSULATORS

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UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Livermore, California

Contract No. W-7405-eng-48

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B. J. Alder and R. H. Christian

November 1957

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PRESSURE INDUCED METALLIC TRANSITIONS IN INSULATORS

B. J. Alder and R. H. Christian

Radiation Laboratory, University of California
Livermore, California

ABSTRACT

Experimental evidence is presented that several ionic and molecular crystals change their conductivity into the range of metallic conductivities when subjected to a pressure of about 250,000 atmospheres. For some of these substances the pressures at which this transition occurs are roughly defined.

INTRODUCTION

It is known from qualitative theoretical arguments that all materials will exhibit metallic behavior when subjected to a sufficiently high pressure. For systems under extreme pressures, for example, as found in astrophysical situations, the Thomas-Fermi model is applied. This model, in which all the electrons are assumed to be statistically placed about the nucleus, would exhibit metallic conductivity. For hydrogen a rough quantum mechanical calculation has been carried out¹ which predicts that a pressure in the neighborhood of one-half million atmospheres would be needed to produce the metallic state. Such pressures would be very difficult to reach by static means, however, the recent development of techniques utilizing high explosive systems permit measurements to be made at these pressures.^{2, 3} Although the shock wave generated by these explosive systems keeps the substance at these high pressures for only microseconds, this time is quite long compared to times required for the establishment of equilibrium for electrons.

Static experiments would be possible for those materials that conduct below approximately 100,000 atmospheres. Indeed such measurements would be preferable since they can be carried out under more controllable conditions. In fact, some such static experiments are in progress by Drs. D. T. Griggs, W. C. McMillan and C. P. Nash at the University of California at Los Angeles, having been started independent and previous to this work.

THEORETICAL CONSIDERATIONS

A treatment of an electron in a box, or a hydrogen atom in a box,⁴ has shown that compression has the effect of raising the energy levels of the electron. In fact, when the size of the cage is reduced to 1.835 Bohr radii, the kinetic energy of the electron of the hydrogen atom is greater than the attractive energy of the central positive charge. The pressure required for this is about 6.3 million atmospheres and the system would then certainly be metallic. However, in this model the walls of the box are infinite and prevent the escape of the electron. In solid materials the walls represent the repulsive interaction of neighboring atoms and the system has to be considered in its entirety, the energy levels being replaced by energy bands. Compression in the region where repulsive forces are dominant again has the effect of raising the bands and the further effect of broadening them. Metallic conduction will then be achieved when the highest filled band of an insulator overlaps with an unoccupied higher band (the conduction band). This must occur before pressure ionization takes place, that is, at a pressure lower than that necessary to overcome the central Coulomb attraction for an outer electron of an atom.

The choice of insulators that might conduct at the lowest possible pressures hence is governed by the criteria that they must have an empty band not far removed from the highest filled band. This certainly occurs when an atom has a loosely bound electron. Obviously, the hydrogen atom would be a poor choice since the 2p energy level is about 10 ev removed from the 1s level in the free atom. The materials that have been found in this work to give indication of metallic conduction are believed to have an empty band less than 5 ev above the occupied band. Other substances whose bands were separated by a larger energy were also tested and they

did not conduct at the highest pressures used so far. These substances were used to establish the validity of the experimental procedure.

EXPERIMENTAL METHOD

The pressure was created by a shock wave generated by a high explosive system similar to one previously used.² This assembly induced a strong plane shock into a series of plates in contact with the high explosive. This series of plates consists of three aluminum plates, individually grounded, and separated by two Teflon plates. This is believed to produce an uncharged shock at the samples although it might not be necessary to use such precautions.

Each sample was pressed against the last plate by spring-loaded pins. Several arrangements of these pins have been used, all yielding the same results. In one case two pins were merely pressed against the surface of the crystal.³ One of these pins was charged to 300 volts, while the other was grounded. These pins constituted part of an appropriate RC circuit. A "raster" type oscilloscope was attached across a resistor of this circuit, so that any discharge could be observed and photographed. The shape of the signal indicates roughly the resistance of the sample. In the second type of arrangement the pins were buried half way into the crystal. In the third case only the charged pin was inserted halfway into the crystal. The aluminum plate on which the crystal rested was substituted for the grounded pin, so that the resistance was measured in the perpendicular direction to the previous cases.

EXPERIMENTAL CONSIDERATIONS

The pressure was determined from the known equation of state of aluminum² by means of an accurate measurement of the velocity of the aluminum surface. This was accomplished by a group of seven pins, spaced at 1.5 mm intervals away from the aluminum plate. From a knowledge of the pressure in the aluminum, the pressure in the crystal itself can be estimated from its initial density and measured shock velocity.

A shock velocity was obtained by measuring the time difference between the signal from the pins in the crystal and the closure of an additional pin located beside the base of the sample and 0.2 mm away from the

surface of the aluminum plate. The shock velocity obtained from this transit time must be consistent with one predicted from compressibility data in order to interpret the data as implying metallic conduction. It sometimes happened that the pins in nonconducting material discharged also, which might be due to the arrival of the aluminum plate itself at the position of the pins. However, since this occurs considerably later the timing of this phenomena allows a clear distinction to be made between metallic behavior and spurious discharge.

At present no method is available for measuring the temperature of the sample during the time the shock passes through, however, an estimate² of it can be made. For most substances considered here the temperatures will range between 1000° and 2000°C. As the shock reflects off the free surface the sample will be adiabatically cooled by the rarefaction wave to somewhere near 600°C and the pressure resulting from the propagation of the shock in the gas phase surrounding the sample would maintain a pressure of about 500 atmospheres in the crystal. Although these ionic crystals have melting points in the region of 600 to 700°C and quite high conductivities⁵ in the molten state under atmospheric conditions, the experiments with buried pins rule out the possibility that ionic conductivity discharged the pins. This is because the conductivity with buried pins is certainly measured while the crystal is under high pressure, where melting occurs at much higher temperatures and ionic mobilities are quite low. An approximate calculation with the aid of the Clapeyron equation shows that at 2000°C the ionic crystals are solid above 50,000 atmospheres.

RESULTS

Initially all samples had a resistance greater than 10^8 ohms, except red phosphorous whose resistance was about 5×10^6 ohms. The materials that showed a resistance of less than a hundred ohms, the minimum observable, at a pressure in the aluminum plate of 280,000 atmospheres, were a single crystal of CsI, and the following powders which were compressed into pellets to densities near that of the crystal: commercial-grade I_2 , red phosphorous, $LiAlH_4$, and RbI . Furthermore, a powdered pellet of CsI seemed to behave similarly to a single crystal. The materials which

definitely did not conduct at this pressure were Teflon and pressed NaCl. Several substances had resistances of the order of hundreds of ohms to kilohms which might mean that they are in the transition region from an insulator to a conductor at this pressure, that is, the bands were approaching each other within thermal energies. RbI already gave some indication of having a resistance of the order of a hundred ohms while KI definitely did. CsBr and particularly CsCl had resistances of the order of kilohms.

When the pressure in the aluminum plate was about 100,000 atmospheres only phosphorous of the above materials conducted. It seems likely that the metallic transition observed is the same one, namely the one to black phosphorous, that was observed by Bridgman⁶ at about 40,000 atmospheres.

At 150,000 atmospheres in the aluminum plate, which corresponds to 50,000 atmospheres in the crystal, LiAlH_4 conducted but appeared to have a resistance of the order of kilohms. It should be mentioned that the LiAlH_4 might have contained a fair amount of metallic aluminum as an impurity, as evidenced by its grayish appearance. However, if these results are reliable, the transition for LiAlH_4 would be in this pressure region. It might be expected that LiAlH_4 would have the lowest transition pressure of all the ionic materials studied, since the AlH_4^- ion would hold the electron least tightly.

At the same pressure in the aluminum plate as the above experiment, the iodine sample conducted also. This corresponds to a pressure in the iodine of roughly 130,000 atmospheres. Hence, the transition occurs below this pressure and above 80,000 atmospheres where it did not conduct according to the previously mentioned experiment. Iodine absorbs in the visible and has an energy level roughly 1.3 eV above the filled band.

In another experiment in which a pressure of 220,000 atmospheres was obtained in the aluminum plate, CsI showed a resistance in the neighborhood of a kilohm. Thus a pressure in the CsI of 200,000 atmospheres must be near the transition point. RbI and KI seem to be in a similar position. CsBr, on the other hand, still had a resistance above 10^6 ohms under these experimental conditions and hence its transition lies at higher pressures.

Considerable more effort is planned in order to improve the precision of the resistance measurements, and to determine more accurately the transition pressure, the temperature dependence of this phenomenon and the nature of any volume change associated with the transition for these as well as other substances. A detailed comparison with theoretical predictions could then be made.

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