Effect of Pressure on the Resistance of Three Thallous Halides*

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The effect of pressure to several hundred kilobars has been measured on TlI, TlBr, and TlCl at 25° and 120°C. Since the materials were not highly purified, the sources of conduction electrons at lower pressures, at least, are probably impurities. The resistance pressure curves show three regions. In the lowest pressure region, the resistance decreases rapidly with increasing pressure, corresponding to ionization of the impurities; in the second region the resistance depends only slightly on temperature. In this region the resistance is apparently controlled by mobility of impurities. In the third region the material appears to be a true metal. The electrical measurements are consistent with previous optical studies.

THE effect of pressure to several hundred kilobars was measured on the resistance of TlI, TlBr, and TlCl. The materials were all cp stock, but undoubtedly highly impure from the electronic viewpoint. The samples were pressure fused in layers 0.0005 in. thick. The experimental procedure has been previously described.[1-3] The samples were loaded in the same manner as the zinc blende samples.[2,3]

In order to test the temperature coefficient of resistance, a heating mantle was developed for the cell. Using a dummy piston with a hole, temperatures were measured as a function of time at the center of the cell, and a regime established to give a steady temperature of 120° at the cell center after 30 min which permitted the running of isotherms. The time–temperature curve was sufficiently reproducible to allow the establishment of resistance as a function of temperature along an isobar.

There seems, at present, to be no practical way to establish a pressure calibration at elevated temperature. The ion transition[1] was obtained at about 122–127 kbar at 120°C using the 25°C calibration. This compares reasonably with the 132 kbar obtained at 25°C. For the purposes of discussion of these results the room-temperature calibration was used. Since our discussion does not depend on precise numerical values, our conclusions should not be affected by any small error involved.

[1] A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. **32**, 308 (1961).
[2] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids **23**, 451 (1962).
[3] G. A. Samara and H. G. Drickamer, J. Phys. Chem. Solids **23**, 457 (1962).

Since the resistance of the bomb was usually about $10^7 \, \Omega$, it was not possible to make measurements in the low-pressure region. The figures show resistances from the point where they become measurably below the bomb resistance. It should be pointed out that there is no satisfactory method to correct for contact resistance so that the numbers are not resistivities. By measuring both current and potential, it was possible to establish that the contacts were Ohmic, at least within the accuracy of the data.

TlI

This material was obtained, in a "purified" form, from the Fisher Scientific Company. Six runs were made at 25°C, and the results were quite reproducible. The resistance drops to within range by 60 kbar. The resistance curve consists of three distinct regions. In region I, the resistance drops sharply, and linearly on a log resistance vs pressure plot, decreasing by 5–6 orders of magnitude between 60 and 100 kbar. Around 100 kbar, there is an abrupt change in slope. Between 100 and 160 kbar (region II) the resistance decreases with nearly half the slope of region I. Above 160 kbar (region III) a relatively small decrease in resistance is observed. The resistance decreases by only about 40% over the range of 170–250 kbar. A typical run is shown in Fig. 1. The resistivity in the high-pressure region is of the order $10^{-4} \, \Omega$–cm.

Three runs were made at 120°C. Typical results are also shown in Fig. 1. As can be seen the three regions of the resistance curve remain distinct; however, there are important differences. In the first region, the resistance decreases rapidly with increasing temperature, and the slope of the curve at 120°C is only about half

FIG. 1. Resistance vs pressure—TlI.
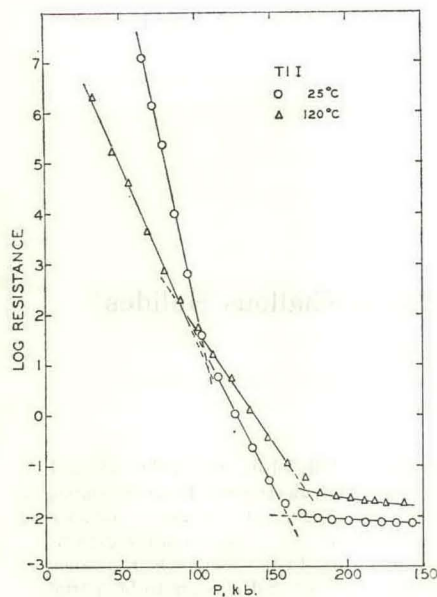
FIG. 3. Resistance vs pressure—TlCl.

that at 25°C (or nearly the same as that in region II at 25°C). The three isotherms cross each other in region II. In region III, the slopes are nearly equal, but the resistance is higher the higher the temperature.

Several runs were made starting at 25°C, increasing the pressure to 220 kbar and holding it there. At this point, the temperature was raised. The temperature coefficients of resistance obtained in region III checked those obtained in the isothermal runs.

TlBr

TlBr (cp) was obtained from the A. D. Mackay Company. Five runs were made at 25°C, and again, the resistance curve consists of three regions; however,
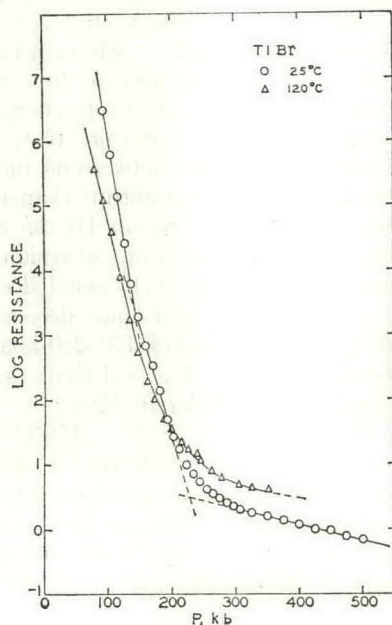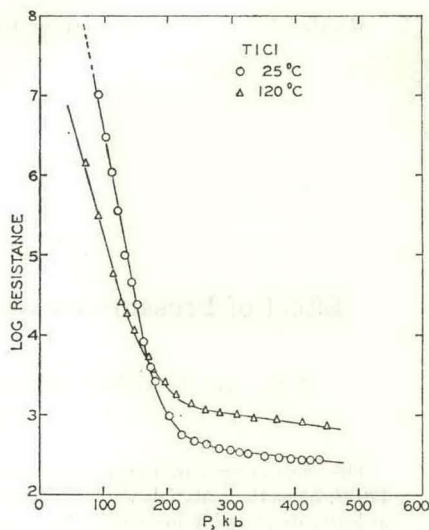
the transfer from region II to region III is less abrupt than that for TlI. The resistance comes to range by 80–90 kbar and drops by about four orders of magnitude between 80 and 150 kbar, at which point region II begins. The slope in this region is 40–50% smaller than that in region I. The third region starts around 230 kbar, and here the resistance decreases by a factor of 3–3.5 over the range 300–500 kb. The resistivity in this region is about 100 times higher than that for TlI.

Two isothermal runs were made at 120°C, and the main temperature effects are similar to those of the iodide; however, in this case, the "transition" between regions is much less distinct at 120°C. Typical runs are shown in Fig. 2. Again, we note that the isotherms cross in region II.

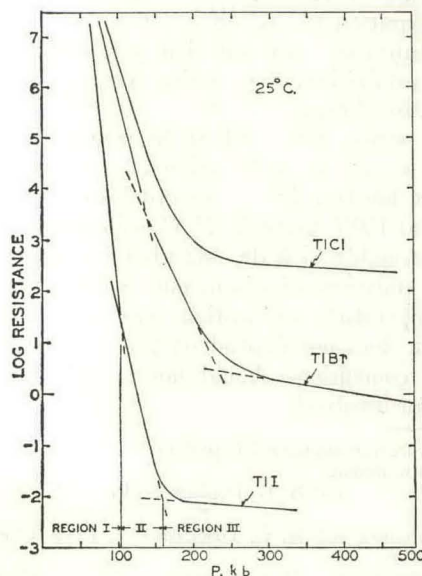FIG. 2. Resistance vs pressure—TlBr.

FIG. 4. Comparison of pressure—resistance curves for three thallous halides.
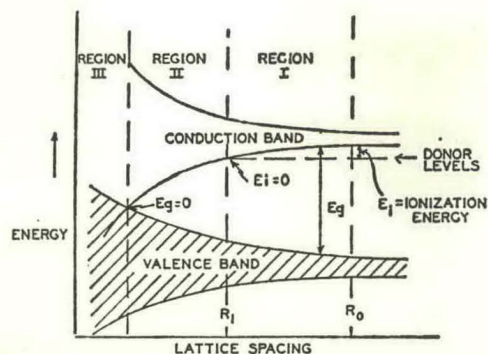
FIG. 5. Possible band picture of thallous halides as a function of interionic distance.

TlCl

This material (reagent grade) was obtained from the Fisher Scientific Company. Five runs were made at 25°C. Region II of the resistance curve is no longer distinguishable. The resistance comes within range by 90–100 kbar and drops sharply up to 200 kbar, after which it levels off (Fig. 3). The resistivity at the high-pressure region is about two orders of magnitude higher than that for TlBr (four orders of magnitude higher than TlI).

Two isothermal runs were made at 120°C. The behavior is very similar to that for the bromide.

DISCUSSION

TlCl and TlBr crystallize in the simple cubic (CsCl) structure, while TlI transforms from the green rhombic form to the red CsCl structure around 5 kbar. The CsCl structure, with a coordination number of eight, represents the most stable configuration for ionic crystals. Thus, no phase transitions were expected in the thallous halides at high pressure, and none were observed.

When pure, these compounds are good insulators having optical energy gaps of the order of 3 eV. With such large gaps, it is highly probable that any measurable conductivity, at least at low temperatures and pressures, is the result of carriers furnished by impurities or by the electrodes, rather than from the valence band of the crystal. Since the materials used in this work were not intensively purified, the major source of conduction electrons is almost certainly impurities.

A summary of the results at 25°C is given in Fig. 4. In region I, the large decrease in resistance is undoubtedly due to an increase in carrier concentration. This is probably caused by the deformation and movement of the bottom of the conduction band with respect to impurity levels. A possible representation is shown schematically in Fig. 5. At sufficiently high pressures, the impurities may all become ionized (i.e., $E_i \rightarrow 0$). This is the situation at R_1.

This picture is also consistent with the temperature dependence of the resistance in this region. At a given pressure, raising the temperature causes increased ionization of impurities, and hence higher conductivity. The activation energies at 75 kbar are about 0.6 eV for TlI and 0.4 eV for both TlBr and TlCl.

In region II, the decrease in resistance is primarily associated with an increase in carrier mobilities. This is probably caused by the broadening of the energy bands (Fig. 5). Here, the temperature coefficient of resistance depends on the scattering mechanism. The results indicate that this mechanism is the same for all three compounds. Since, in this region, all impurities are already ionized, no further increase in carrier concentration is expected. However, a secondary effect causing the decrease of resistance may be due to the excitation of some electrons across the energy gap. This is probably appreciable only at the high-pressure end of region II.

In region III, the resistance is "metallic" in the sense that it has a distinct positive temperature coefficient. If one considers a T^{-n} law for metallic conductivity, n is found to be equal to 1.2, 1.3, 1.8 for TlI, TlBr, and TlCl, respectively. Because of the problems of contact resistance, it is not reasonable to put too much significance in the exact numerical values.

The differences in resistivity among the three compounds, at high pressure, is considerably larger than one would intuitively anticipate from differences in band structure. These may well be impurity effects. The over-all picture will become much clearer when purer materials are investigated. A zone refining apparatus is being set up in this laboratory, and these halides will be examined further.

It is helpful to compare the present data with the results on the shifts of the absorption edges of the three compounds reported by Zahner and Drickamer.[4] The optical transitions are believed to be transitions to the exciton state or the conduction band.

All three compounds exhibit large red shifts with pressure, the ratio of the slopes (TlI/TlBr/TlCl) being about 2.3/1.4/1.0. These ratios are quite comparable to the ratio of the slopes of the log resistance vs pressure curves in region I, the latter being 2.7/1.3/1.0 for TlI/TlBr/TlCl. Thus, we see that the decrease in resistance caused by the decrease in the gaps between conduction band (and/or valence band) and impurity levels parallels the change in the optical energy gap.

It is interesting to note that the optical gaps of TlI and TlBr extrapolate to zero at (160–170) kbar and (230–240) kbar, respectively. It should be recalled here that region III of the resistance curves begins around 160 kbar for TlI and around 230 kbar for TlBr. Thus, it is quite reasonable that region III corresponds to the region of the overlap between valence and conduction band (see Fig. 5). The positive temperature coefficient of resistance in this region is certainly consistent with this behavior.

ACKNOWLEDGMENT

⁴ J. C. Zahner and H. G. Drickamer, J. Phys. Chem. Solids 11, 92 (1959).