ELECTRIC RESISTANCE OF LIQUID TELLURIUM AT HIGH PRESSURES

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The results of a study of the electric resistance of liquid tellurium at high pressures are presented. It is shown that the curves for the dependence of the electric resistance on the temperature and pressure (in log $\rho - 1/T$ and $\rho -$ log p coordinates, respectively) can be represented by curves consisting of a series of linear segments with different slopes. The $T - p$ coordinates of the intersection points of the segments group together in a regular manner and divide the region of existence of the liquid phase in tellurium into four fields. It is proposed that phase transformations occur in liquid tellurium.

TELLURIUM belongs to the special group of the now rather numerous substances whose melting curves have a temperature maximum. The reasons for the existence of the maxima on the melting curves are not clear in many respects. However, it is quite evident that at the maximum point the change in the volume upon melting is equal to zero; consequently, the volume of the liquid phase decreases anomalously along the melting curve.[1] Undoubtedly, the explanation of the nature of this anomaly will also mean the solution of many problems connected with the existence of maxima on the melting curves. It seems to us that it is first necessary to establish whether or not the compressibility curve of the liquid is completely smooth in the region of the maxima, or whether it has singularities which indicate some sort of transformation in the liquid.

In reference[1] an anomaly was discovered in the melting curve of tellurium (see Fig. 1) which, in all probability, is an indirect proof of the existence of a definite transformation in the liquid. Nevertheless, it is scarcely worth pointing out that only a direct study of the properties of the liquid above the melting curve can give information necessary for the solution of the problem under consideration. There are appreciable difficulties along this path, brought about by the specific technology of high pressures, aggravated further by the requirement of high temperatures. Results are given below of a study of the electric resistance of liquid tellurium at high pressures. Undoubtedly the measurement of the specific heat and the compressibility is preferable in the solution of this problem; however, the measurement of the electric resistance can be carried out with much higher accuracy and,

consequently, has advantages over the former in the search for small effects.

EXPERIMENTAL TECHNIQUES

The pressure was produced by means of the compression of gasoline in a multiplier with a dual variable mechanical holder. The sealing of the high pressure piston and plug with electrical leads was performed with the aid of metallic and rubber washers.[2] Conical electrical leads, set in the plug, were sealed and insulated by means of paper liners.[3] The electrical leads for the chromel-alumel thermocouple were made from chromel-alumel alloys.[4] The pressure was measured by a specially constructed manganin resistance manometer (Fig. 2) which was made up of a coil of manganin wire of 0.05 mm diameter, packed in a steatite casing. Copper wires, serving as contacts, were welded to the manganin coil, thus also producing a steady mounting for the coil in the casing. The setting of the manometers after aging was
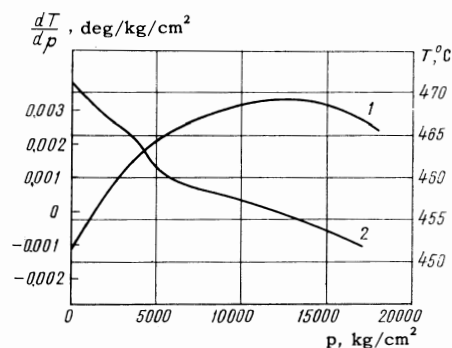
FIG. 1. Melting curve of tellurium (1) and the dependence of the slope of the melting curve on the pressure (2).
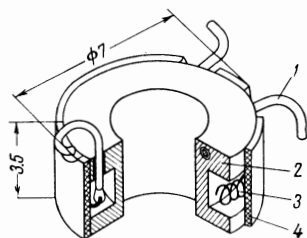
FIG. 2. Manganin resistance manometer: 1 – copper leads, 2 – talc casting, 3 – manganin wire, 4 – teflon cover.

FIG. 3. Measuring cell: 1 – soapstone container, 2 – volume filled with liquid tellurium, 3 – container for thermocouple, 4 – nichrome spiral of electric furnace, 5 – iridium probes.

stable within ±0.001 ohm for a total resistance of 100 ohms. Calibration of the manganin manometers was made by means of a deadweight manometer up to 15×10^3 kg/cm². During the course of the research, the resistance of the manganin manometers was measured and recorded by means of a circuit consisting of a R-329 dc bridge, photoamplifier, and an ÉPP-09 recorder, which made it possible to measure the pressure with a reproducibility error of ±25 kg/cm². The absolute error of the pressure measurements did not exceed 50 kg/cm².

Heating was carried out by means of an electric resistance furnace, whose temperature could be set and maintained by a servomechanism with an accuracy of ±0.02°.[5]

The electrical resistance of liquid tellurium was measured by means of a conventional dc potentiometer circuit using a UPL-60 potentiometer and an F-116/1 photocompensator as a galvanometer. The error in measurement of the resistance was no greater than 0.02%. Moreover, the resistance of several samples was measured with at 1000 Hz ac by the ammeter-voltmeter method. Both methods gave completely consistent results.

The greatest difficulties were encountered in the preparation of a container for the liquid tellurium and the choice of the material for the electric probes. Of the materials studied by us, only iridium did not react appreciably with liquid tellurium at temperatures up to 600°C, and at the same time was satisfactorily wetted by it, thus assuring reliable contacts. The container for the sample was made of untreated soapstone. After mounting the iridium probes, all apertures and grooves were sealed with a cement consisting of liquid glass and powdered talc. In addition, the assembled container was dried in a drying oven, and then annealed in vacuum at 900°C. After annealing, the container was filled with tellurium of 99.999 purity. The cell is shown in Fig. 3.

EXPERIMENTAL RESULTS

By means of the technology described above, we succeeded in carrying out several isobaric and isothermal experiments on the measurement of the electrical resistance of liquid tellurium in the reg-
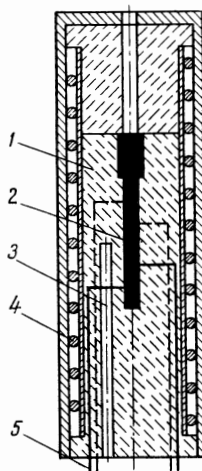
ion from the melting temperature up to 520°C, and at pressures up to 16,000 kg/cm².

Figure 4 shows two typical plots of the dependence of the electrical resistance of liquid tellurium on the temperature in the coordinates ρ and $1/T$ (ρ is the resistivity). As is seen from the drawing, one can discern two linear portions with different slopes (marked I and II in the drawing) and a junction region characterized by a positive anomaly in the resistance curve. It must be noted that in two cases, i.e., on the isobars p = 4000 kg/cm² and p = 6000 kg/cm², a third linear portion was noted in the region of high temperatures. However, no appreciable resistance anomalies were observed at the junction of the second and third regions. It is interesting that the electrical resistance ($\rho \sim 10^{-4}$ ohm-cm) of liquid tellurium is close in order of magnitude values of that of the liquid metals, but the negative temperature coefficient of the resistance compels us to regard it as a semiconducting liquid. Assuming that the theory developed for the temperature dependence of the resistance of crystalline semiconductors is applicable also to a
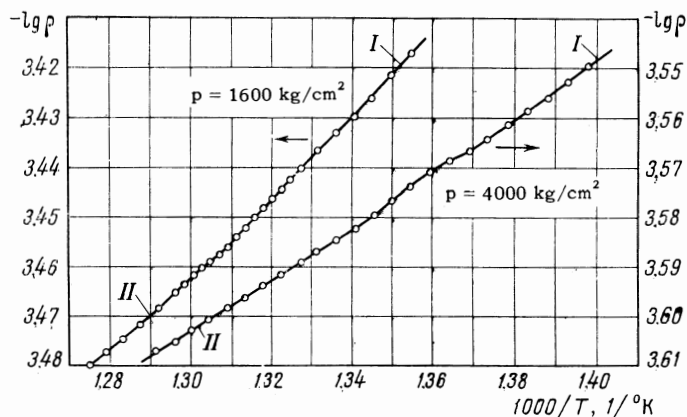

FIG. 4. Dependence of the electric resistance of liquid tellurium on the temperature.
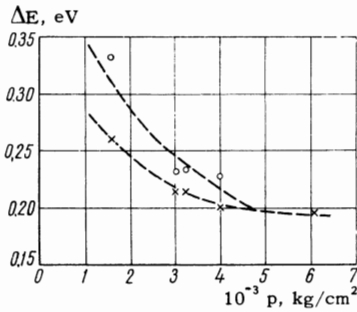
FIG. 5. Pressure dependence of the activation energy for conduction of liquid tellurium: O — region I, × — region II.

liquid semiconductor, we can compute the conductivity activation energy for the different regions observed in liquid tellurium. Figure 5 shows the results of these calculations.

In the work of Epstein et al.,[6] the conclusion is reached that in the melting of tellurium the conductivity activation energy does not change in radical fashion. Comparing our data with the known values of the width of the forbidden band of solid tellurium,[7] we can extend this conclusion also to the region of high pressures.

Very interesting results were obtained in the study of the pressure dependence of the electrical resistance of liquid tellurium at constant temperature. Figure 6 shows one such dependence for $T = 485°C$ in the coordinates ρ and log p. As is clearly seen, the ρ (log p) dependence breaks up into several portions (in the given case, four), on each of which there is a linear relation between the electrical resistance and the logarithm of the pressure. According to Bridgman,[8] there is a linear relation between the volume change ΔV and log p for many liquids. Consequently, the linear ρ (log p)
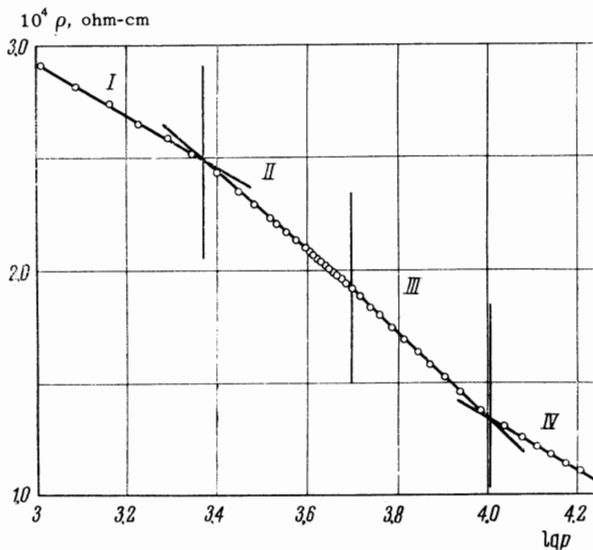
dependence can be transformed to the linear ρ (ΔV) dependence. However, this does little to clarify things, inasmuch as the data given in Fig. 5, are insufficient to draw any conclusion as to the analytic form of the dependence of the activation energy on the pressure.

The principal conclusions which can be drawn on the basis of both the isothermal and the isobaric measurements are the following:

1) Liquid tellurium reveals semiconducting properties in the investigated region of temperatures and pressures.

2) The liquid phase of tellurium is not homogeneous with respect to its electrical properties.

In order to establish the correlation between the individual parts which are set up in different cross sections in the region of existence of liquid tellurium, we have marked on the p − T diagram (Fig. 7) the coordinates of the points of intersection of the linear portions of the corresponding curves (see Figs. 4 and 6). As is seen, the coordinates of these points are grouped quite regularly and divide the region of existence of the liquid phase of tellurium into four parts.

It is notable that the boundary 1[1]) (see Fig. 7) intersects the melting curve precisely in the region of the previously noted anomaly.[1] On this same boundary there is an additional anomaly in the resistance on the temperature curves. The totality of these data allows us to consider this boundary and the regions immediately adjacent to it as a region of an unusual phase transition in the liquid tellurium, accompanied by compressibility anomalies (see the conclusions of[1]). In connection with this conclusion, the positive resistance anomaly can be attributed to the additional scattering of the car-
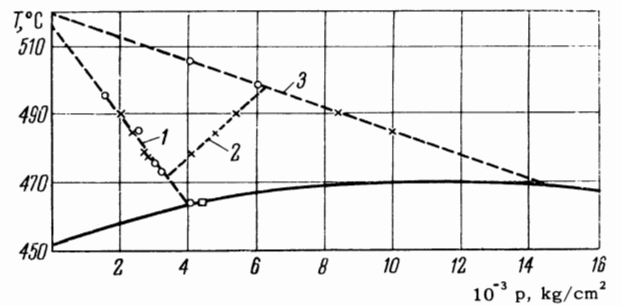

FIG. 6. Pressure dependence of the electrical resistance of liquid tellurium.

FIG. 7. Coordinates of the "boundaries" of different parts in liquid tellurium: O — points obtained along isobaric paths, × — points obtained along isothermal paths; solid curve — melting curve of tellurium; □ — according to [1].

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[1])The term "boundary" is used here in a conditional sense.

riers by inhomogeneities of the potential, which arise in the phase transition process. Assuming this explanation, we can conclude that the discussed interval of the phase transition extends over no more than 15°C. As to the boundaries 2 and 3 (Fig. 7), the information here is less detailed, but, in all probability, we must ascribe to them the same nature as boundary 1.

The reported results were quite unexpected, inasmuch as it would be difficult to assume such a number of transformations in an elementary liquid. Therefore it is quite evident that further investigations are necessary here.

We turn again to the maximum on the melting curve of tellurium. Two of the three boundaries discovered in the liquid tellurium cross the melting curve and consequently one must expect an anomalous behavior in the melting curve in just this region. But boundary 3 crosses the melting curve at much higher pressures than the pressure corresponding to the maximum; therefore it cannot have any relation to it. Thus, only boundary 1 remains to be discussed; this curve crosses the melting curve in the region of 4500 kg/cm^2. Here, just as was established earlier,[1] a rapid decrease takes place in the slope of the melting curve. For an explanation of all these facts, it can be assumed that the volume of liquid undergoes an anomalous decrease on boundary 1; however, this decrease is insufficiently large and the condition of a maximum, i.e., the equality of the volumes of the solid and liquid phases, is not achieved here. However, inasmuch as the compressibility of the liquid phase is always greater than the compressibility of the

solid,[2] the difference in the volumes of the liquid and solid becomes smaller and smaller and finally reaches zero at a pressure of 12,400 kg/cm^2.[9]

[1] S. M. Stishov, N. A. Tikhomirova and E. Yu. Tonkov, JETP Pis'ma 4, 161 (1966), JETP Lett. 4, 111 (1966).

[2] S. M. Stishov and V. A. Zil'bershteĭn, PTÉ No. 6, 209 (1966).

[3] S. M. Stishov, PTÉ No. 4, 219 (1966).

[4] S. M. Stishov and N. A. Tikhomirova, PTÉ No. 5, 251 (1965).

[5] V. A. Ivanov and S. M. Stishov, PTÉ (in press).

[6] A. S. Epstein, H. Fritzsche, and K. Lark-Horovitz, Phys. Rev. 107, 412 (1957).

[7] D. Long, Phys. Rev. 101, 1256 (1956).

[8] P. W. Bridgman, Physics of High Pressures (Russian Translation) ONTI, 1935.

[9] S. M. Stishov and N. A. Tikhomirova, JETP 49, 618 (1965), Soviet Phys. JETP 22, 429 (1965).

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[2] It must be emphasized that, as experiments have shown, [8] it is impossible to achieve a sign change of ΔV as a result of the large compressibility of the liquid only, without assuming structural transformations in it.