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ELECTRICAL RESISTIVITY OF LIQUID CESIUM AT HIGH PRESSURES

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The melting curve of cesium and the electrical resistivity of its melt were investigated in the range of pressures up to 30×10^3 kg/cm^2. It was found that at low pressures the pressure dependences of the electric resistivity of liquid and solid cesium were qualitatively similar. At high pressures, these dependences become essentially different. The cesium melting curve was in agreement with Simon's equation only up to 10×10^3 kg/cm^2. It is concluded that, beginning from 10×10^3 kg/cm^2, a transition accompanied by a volume anomaly occurred in liquid cesium and that this anomaly was responsible for the maxima in the melting curve.

CESIUM is the only substance whose melting curve has two maxima (Fig. 4). The existence of maxima in a melting curve is basically due to the anomalous behavior of the volume of the liquid along its line of equilibrium with the liquid phase.[1] However, many questions associated with the nature of such anomalies still remain unanswered. A study of the electrical resistivity of liquid tellurium[2] has also indicated a maximum in the melting curve. The results have shown that the anomalies exhibited by tellurium are localized in very narrow pressure and temperature intervals and are in the nature of phase transitions. Such a situation is not quite self-evident in the case of cesium because, in contrast to tellurium, cesium is a typical metal. The present investigation was undertaken to determine the nature of these anomalies of liquid cesium.

Bridgman was the first to investigate the phase diagram of cesium: he studied its melting curve up to 4×10^3 kg/cm^2.[3] He also found that, in the pressure range up to 100×10^3 kg/cm^2, cesium underwent two phase transitions: one at a pressure of 22×10^3 kg/cm^2, at which the volume decreased by 2%, and another at 42×10^3 kg/cm^2, at which the volume changed by 10%.[4] Since the structure of cesium at atmospheric pressure is of the bcc type, the phase transition at 22×10^3 kg/cm^2 was interpreted[6] as a transition to the fcc structure[5] and the transition at 42×10^3 kg/cm^2 as a 6s–5d electronic transition in Cs. This suggestion was confirmed later by Hall et al.[7] Hall and his colleagues also found one more phase of cesium which exists in a very narrow range of conditions. The melting curve of cesium up to 50×10^3 kg/cm^2 has been investigated also by Kennedy et al.[8] (cf. Fig. 4).

We present here the results of an investigation of the electrical resistivity of liquid cesium at high pressures. We also investigated the melting curve of cesium in order to find more accurately the coordinates of the melting curve maxima.

EXPERIMENTAL TECHNIQUE AND RESULTS

The technique used to establish and measure both pressure and temperature has been described earlier.[2,9] The melting curve was investigated by thermal analysis.[9] The electrical resistivity was measured using a circuit incorporating a R-308 potentiometer. The following system was used to maintain isothermal conditions in a high-pressure chamber during measurements of the resistivity.[10]

The exceptionally strong reactivity of cesium forced us to develop special measuring cells (Figs. 1 and 2) in which the basic principle of construction was to protect the substance from contamination by a layer of the substance itself. Experiments showed that such cells ensured that the cesium remained pure after many experimental cycles.

The cell used in the thermal analysis (Fig. 1) was an iron container, 8 mm in diameter, with a thermocouple sheath along its axis. A cover, 6 mm in diameter, protected the investigated part of the cesium from direct contact with the pressure-transmitting medium. The

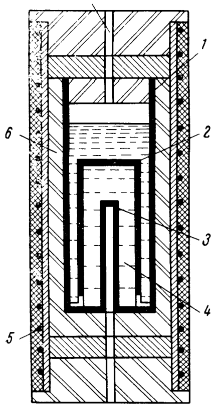

FIG. 1. Apparatus used for the thermal analysis of cesium at high pressures. 1) Armco iron container; 2) Armco iron cover; 3) thermocouple sheath; 4) cesium; 5) resistance furnace; 6) thermal insulator; 7) aperture for the admission of pressure-transmitting liquid.

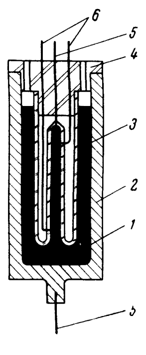

FIG. 2. Cell used to measure the electrical resistance of liquid cesium at high pressures. 1) Cesium; 2) Armco iron container; 3) glass ampoule; 4) Teflon stopper; 5) current leads; 6) potential leads.

cell was heated by an electrical resistance furnace, wound on a copper casing which ensured a more uniform temperature distribution. Copper inserts at the ends of the cell served the same purpose. To improve the recording of the areas under the thermographic curves, a teflon insulating layer was inserted between the measuring cell and the heater.

The cell used to measure the electrical resistivity (Fig. 2) was constructed similarly. Cesium filled the cavity between an iron container and a double-walled glass ampoule. The iron container acted also as one of the electrodes. The potential probes and the second electrode were made of platinum wire, 0.1 mm in diameter, sealed into the core of the ampoule. The diameter of this core was about 2 mm at the positions of the potential probes, and the distance between the probes was approximately 5 mm. A thermocouple was placed in the cavity between the two walls of the glass ampoule.

To fill a cell with cesium, we used the device shown in Fig. 3. It consisted of two funnels and a heater wound on a glass tube. The lower funnel ended in a steel capillary which entered the cell. All apertures and gaps were carefully smeared with a vacuum grease so that the steel capillary was the only channel which connected the internal cavity of the cell to the atmosphere. A cell, together with the filling device, was placed in a box and pure dry argon was passed through both of them. Next, the upper funnel was filled with solid cesium in an argon atmosphere and the whole device was placed under a vacuum hood. The heater was switched on in vacuum and the molten cesium flowed into the lower funnel. At the end of the procedure, argon was admitted into the vacuum chamber and cesium was pushed into the cavity in the cell. In all these experiments, cesium of 99.995% purity was employed.

The pressure and temperature were measured to within 0.1×10^3 kg/cm^2 and 0.5 deg C, respectively. The error in the measurement of the electrical resistance did not exceed 0.5%. The measured electrical resistance was used to calculate the resistivity of liquid cesium. The factor necessary in such a calculation, which was governed by the cell geometry, was determined to within 0.1% by measuring the resistance of pure mercury at atmospheric pressure. The resistivity of cesium was not corrected for the thermal expansion or for the deformation of the ampoule under pressure. The maximum value of the sum of these corrections at a pressure of the order of 30×10^3 kg/cm^2 did not exceed 2%.

Figure 4 shows the melting curve of cesium. This curve is in qualitatively good agreement with the results of Kennedy et al.[8] but there are some quantitative differences. The table below gives our values of the coordinates of the maxima and of the first triple point.

For the sake of comparison, we have included the results of Kennedy et al.[8]

The discrepancies are evidently due to the fact that Kennedy et al.[8] carried out their study under quasi-hydrostatic conditions, as a result of which there were considerable uncertainties in the pressure measurements and some uncertainties in the temperature measurements. The results of our measurements can be regarded as more accurate.

The availability of accurate results allowed us to check whether the melting curve of cesium obeys Simon's equation at low pressures. Using Simon's equation $(p + a)/a = (T/T_0)^c$ (T and p are the melting temperature and pressure; a, c, and T_0 are constants), we can easily obtain a linear relationship between the

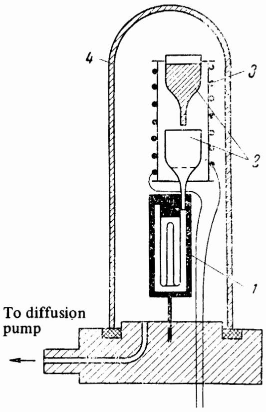

FIG. 3. Device used to fill measuring cells with cesium. 1) Cell; 2) funnels; 3) heater; 4) vacuum hood.

	Our data		Results of Kennedy et al.[8]	
	10^3 kg/cm^2	T, °C	p, 10^3 kg/cm^2	T, °C
Triple point	24.2	194.5	25.9	191
First maximum	20.5	199	22.9	197
Second maximum	28	201.5	31.1	198

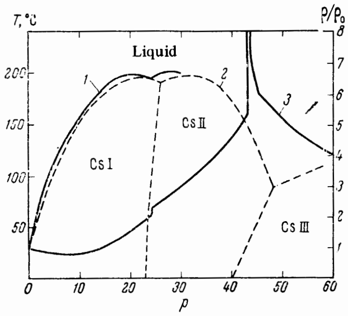

FIG. 4. Phase diagram of cesium; 1) according to our data; 2) according to Kennedy et al.[8]; 3) pressure dependence of the electrical resistivity of solid cesium at 25°C[7] (here and in Figs. 5 and 6 the pressure is expressed in units of 10^3 kg/cm^2).

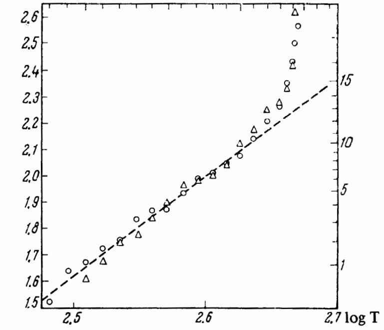

FIG. 5. Dependence of the logarithm of the slope of the melting curve of cesium on the logarithm of the melting point. Triangles and circles refer to the results obtained in different experiments.

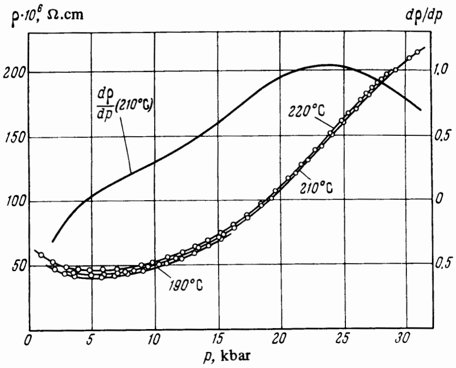

FIG. 6. Pressure dependence of the electrical resistivity of cesium at 190, 210 and 220°C.

logarithm of the derivative dT/dp and the logarithm of temperature. This relationship is plotted in Fig. 5, which shows that the melting curve of cesium agrees with Simon's equation only up to pressures of the order of 10×10^3 kg/cm^2.

Figure 6 shows the results of measurements of the electrical resistivity of liquid cesium at pressures up to 31×10^3 kg/cm^2. Comparing Figs. 6 and 4, the latter which includes the pressure dependence of the electrical resistivity of solid cesium,[7] we can easily see a qualitative similarity between the electrical resistivity curves of solid and liquid and cesium at low pressures. It is interesting to note that liquid cesium exhibits a definite electrical resistivity minimum, which is so characteristic of solid alkali metals.[3,11] However, at high pressures, the curves in question differ considerably.

DISCUSSION OF RESULTS

These results include two observations which can be used to obtain information on the nature of the volume anomaly of liquid cesium.

1. The pressure dependence of the electrical resistivity of liquid cesium has an inflection point in the region of 24×10^3 kg/cm^2. Comparison of the dependences $\rho(p)$ for liquid and solid cesium suggests that this inflection point marks a transition from one functional dependence $\rho(p)$ to another. Then, using the coordinates of the maxima in the melting curve, we may conclude that the range of pressures corresponding to the inflection point in the $\rho(p)$ curve represents the central part of the volume anomaly in liquid cesium.

2. The melting curve of cesium deviates from Simon's equation beginning from 10×10^3 kg/cm^2. To interpret this observation, we must recall the following data.

a) According to Bridgman,[3] the melting curves of various substances can be divided, in accordance with their sign of dT/dp, into "normal" (dT/dp > 0) and "anomalous" (dT/dp < 0). Only the "normal" substances obey Simon's equation.

b) The thermodynamic properties of the melts of substances with a "normal" melting curve are very similar to the corresponding characteristics of a solid. Structural analysis of such substances establishes a close correlation between the number and the mutual positions of particles in the first coordination spheres of the liquid and the crystal. In the case of substances with an "anomalous" melting curve, the short-range order and physicochemical properties of the melts are considerably different from the short-range order and corresponding properties of the crystalline phase.

Since a melting curve with a maximum has "normal" and "anomalous" branches, we may conclude that the transformation, accompanied by a change of the structure and of the thermodynamic properties, takes place in the liquid phase in the region of a maximum. It follows from the reported results that a deviation from Simon's law should indicate the onset of the transformation in the liquid. Consequently, we may conclude with a fair degree of certainty that the investigated anomaly in liquid cesium appears at 10×10^3 kg/cm^2 and extends to pressures higher than 15×10^3 kg/cm^2. In this respect, the behavior of liquid cesium differs basically from that of liquid tellurium.[2]

In our opinion, the temperature maxima in melting curves reflect partly some special processes in the liquid associated with regrouping of the component particles. The close similarity between the structures of liquids and the corresponding solids suggests that these transformations in a liquid reflect, to some extent, the high-pressure phase transitions in solids.

In general, we cannot expect total agreement between the coordinates[1)] of the corresponding transformations in a liquid and a solid and, consequently, the transformation in a liquid may occur at pressures lower or higher than the transition in a solid. It is quite clear that if the transformation in a liquid involving a decrease in the volume occurs earlier than a phase transition in a solid, maxima may be observed in the melting curve. On the other hand, if the transformation in a liquid takes place at a pressure higher than the transition in a solid, the only result is some decrease of the slope of the melting curve.

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[1)] By the coordinate of a transformation in a liquid, we understand the middle point of the transformation interval.