2×10^{-16} cm^2.

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JUMP IN VOLUME AND MELTING CURVE OF CESIUM AT PRESSURES UP TO 17,000 kg/cm^2

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The lack of a finished theory of melting does not allow us to predict the course of the melting curve and to state whether it has a maximum, whether it approaches some temperature asymptotically, or whether it increases continuously with increasing pressure. This question can be answered only by experiment. Until recently the melting temperature increased continuously with increasing pressure in all experiments. Recently, however, a maximum on the melting curve was observed for several substances [1-6]. Unfortunately, the experiments in which a maximum was observed on the melting curve were carried out in apparatus with a quasihydrostatic medium. The presence of the maximum is therefore subject to doubt and can be attributed to the appearance of a new phase in the solid, a phase that might have been overlooked as a result of the crude nature of the experiment.

Confirmation of the maximum on the melting curve would be provided by measurement of the jump of volume along the melting point. On approaching the maximum, the magnitude of the volume jump should tend to zero, in accord with the Clayperon-Clausius equation. We report below the results of an experiment on the determination of the volume jump in cesium, for which Kennedy [1] observed a maximum on the melting curve.

The apparatus in which the present experiments were carried out, together with the procedure for determining the volume jump, is described in detail in [7]. The experiments were made in a hydrostatic medium (benzene). The volume jump was determined from the break in the continuity of the volume-pressure curve. At the instant of melting the volume was measured at constant pressure, and the magnitude of its change was determined from the deflection of the pointer of a special device. The temperature and pressure along the melting curve were measured simultaneously with the volume jump.

The experimental results are shown in Figs. 1 and 2. The first figure shows the experimental data on the dependence of the volume jump $\Delta\bar{V}$ on the melting temperature T. The error

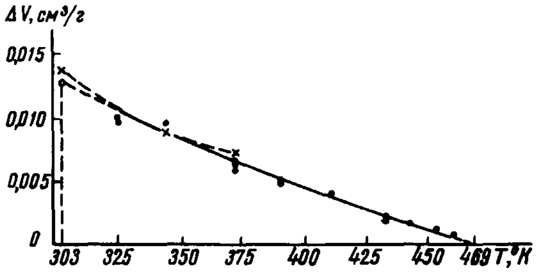

Fig. 1. Jump in volume of cesium vs. melting temperature.

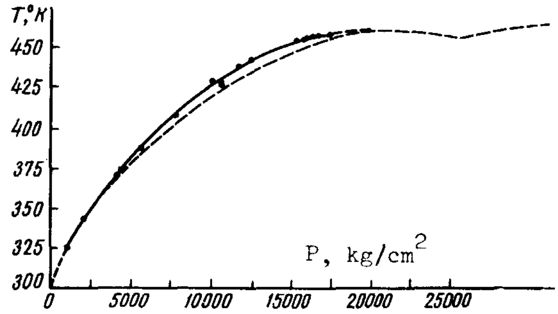

Fig. 2. Melting curve of cesium.

in the determination of the volume jump was estimated to be not more than 0.0005 cm^3/g, while the temperature error was ±0.3°C. The temperature was measured with a chromel-copel thermocouple placed directly in the cesium and protected with a steel case. The pressure was measured with a manganin manometer of relative accuracy ±0.5%.

The experimental data obtained agree well with the empirical formula

$$\Delta\overline{V} = \Delta\overline{V}_0 - a \log (T/T_0),$$

where $\Delta\overline{V}$ and T_0 are the jump in volume and the melting temperature at atmospheric pressure, and a is an experimentally determined constant. For cesium the formula becomes

$$\Delta V = 0.0125 - 0.066 \log (T/302.9). \qquad (1)$$

The jump in volume at atmospheric pressure was not measured, but was determined by extrapolating the experimental data obtained at high pressures. The plot of Eq. (1) is the solid curve of Fig. 1. The dashed curve shows, for comparison, Bridgman's experimental data [8].

The variation of $\Delta\overline{V}$ with T could be followed experimentally only to values of $\Delta\overline{V}$ not lower than 0.0005 cm^3/g. Extrapolation of the experimental data to $\Delta\overline{V} = 0$ by means of Eq. (1) yields a value T = 469.2°K for the maximum. This agrees well with the temperature of the maximum on the melting curve (470°K) obtained by Kennedy [1].

The circles in Fig. 2 show the values of the pressure P and of the melting temperature T obtained in our experiments. The smoothing curve is shown solid, and the dashed curve represents Kennedy's data.

The systematic discrepancy in our experimental data can be explained as follows. Kennedy's experiments were made in equipment with a quasihydrostatic medium. This made the estimated pressure uncertain. On the other hand, the temperature in his experiment was measured with accuracy not worse than ±0.5°C. It is therefore natural to expect differences in the data on the pressure, and not on the temperature, as seen in Fig. 2.

We can therefore conclude that the experimental measurement of the jump in the volume of cesium, as a function of the melting temperature, also points to the existence of a maximum on the melting curve.

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Article by V. S. Bogdanov, "Jump in Volume and Melting Curve of Cesium at Pressures up to 17,000 kg/cm^2," in line 2 of the second paragraph "jump of volume along the melting point" should read "jump in volume along the melting curve."