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I. E. Paukov, Corresponding Member of the Academy of Sciences of the USSR P. G. Strelkov,

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Abstract

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PHYSICS

**I. E. Paukov, Corresponding Member of the Academy of Sciences of the USSR P. G. Strelkov,
V. V. Nogteva, V. I. Belyi**

HEAT CAPACITY OF BLACK PHOSPHORUS AT LOW TEMPERATURES

Black phosphorus was first obtained by Bridgman (^{1}) from the white modification of this element at a pressure of ~ 12 000 atm and a temperature of ~ 200°C. Subsequently, other investigators (^{2,3}) established that there are two modifications of black phosphorus–crystalline and amorphous–and also determined the conditions for obtaining them. However, the physical properties of both modifications of black phosphorus have so far been studied incompletely.

The purpose of the present work was to investigate the true heat capacity of the crystalline modification of black phosphorus, and also to calculate the values of the absolute entropy and enthalpy under standard conditions. This modification was chosen as the object of study because it is apparently the most stable modification of phosphorus (^{4}). In addition, it is the only form of phosphorus for which the lattice parameters have been determined precisely (^{5}). The crystal consists of corrugated layers of phosphorus atoms, each layer consisting of two sublayers located at a distance of 2.28 Å from one another. Neighboring layers, situated at considerably greater distances, are bound to one another less strongly, which explains the layered character of crystalline black phosphorus, similar to the layered character of graphite.

The sample whose heat capacity was studied was obtained with the aid of a high-pressure bomb capable of operating up to pressures of 13,000–14,000 kg/cm^2 and temperatures of ~ 300°C. To obtain the necessary pressure, the MOP-10000 apparatus was used.

Twice-distilled white phosphorus was used as the starting material for preparing the sample; chemical analysis of it showed the presence of impurities in an amount of less than 0.03%. The white phosphorus, in a sealed lead ampoule, was placed in the bomb and held at a pressure of 13,500 kg/cm^2 and a temperature of 220° for 15–20 min. Under these conditions it was practically entirely converted into black phosphorus. The samples thus obtained were subjected to chemical and spectral analyses, according to which the total phosphorus content in the sample was 99.12%. The principal impurities, carbon $\sim 0.3\%$ and lead $\sim 0.3\%$, were introduced during preparation of the sample in the high-pressure bomb. In addition, small amounts, about 0.01%, of Ni, Sn, Mg, Fe, and Co were present.

A phase x-ray analysis of the sample was also carried out, using an RKD chamber. The exposure was made with Cu K_α radiation, with the Cu K_β radiation filtered out. It was found that the sample consists of a single phase of rhombic syngony, which is confirmed by the good agreement of the d/n values obtained in the analysis with the literature data (^{5}). The presence of other phases was not detected by x-ray analysis. The diffuse ring characteristic of amorphous black phosphorus was likewise not found on the x-ray pattern.

The apparatus and the method for measuring the true heat capacity at low temperatures were basically similar to those described earlier (^{6}). We note only that the temperature measurements were carried out with the aid of a platinum-

of the resistance thermometer, made of "Pobeda" platinum and calibrated at the All-Union Scientific Research Institute of Physicotechnical and Radiotechnical Measurements. The resistance of the thermometer at 273.15°K was $R_0 = 91.712$ ohm, $\alpha = 0.003925$.

Table 1

T,° K	Heat capacity, cal/deg • g-atom	$S^0_T - S^0_{13}$, entropy units	$H^0_T - H^0_{13}$, cal/g-atom
13.0	0.0398	0	0
15.0	0.0524	0.00644	0.0904
17.0	0.0760	0.0143	0.2175
20.0	0.1135	0.0296	0.5006
25.0	0.1867	0.0636	1.275
30.0	0.3009	0.1081	2.499
40.0	0.5652	0.2296	6.784
50.0	0.8362	0.3852	13.81
60.0	1.108	0.5614	23.51
80.0	1.658	0.9568	51.26
100.0	2.166	1.382	89.57
150.0	3.297	2.483	227.3
200.0	4.137	3.555	414.6
250.0	4.686	4.539	635.6
298.15	5.158	5.429	882.4

Adiabatic conditions during the calorimetric experiment were maintained automatically with the aid of an apparatus described in detail in (7).

The heat capacity of the empty calorimeter (more precisely, of the calorimeter filled with dry pure helium to a pressure of ∼ 25 mm Hg) was measured in the temperature interval 12.9–297.5°K. Ninety-four calorimetric experiments were carried out, and from them a graphically smoothed curve $c - T$(°K) was constructed. The deviations of individual experimental points from the smoothed curve did not, as a rule, exceed 0.2% in the temperature interval 45–297.5°K, but gradually increased below 45°K and became equal to ∼ 1.5% in the region 13–20°K.

A total of 32.713 g of substance was placed in the calorimetric vessel, which amounted to 1.056 g-at. The linear dimensions of the individual crystals of the sample were several millimeters; in this form was almost the entire sample. A small part (∼ 5% of the total amount) consisted of pieces of the sample less than 1 mm in size and of dust.

The heat capacity was measured in the temperature interval from 13.0 to 293.8°K, and 118 calorimetric experiments were carried out. The measurement results, obtained from the graphically smoothed curve $c_p - T$, are given in Table 1.* In Fig. 1, experimental values of c_p are given in part. The deviations of the experimental values of the measured heat capacities from the smoothed curve $c_p - T$(°K) averaged less than 0.1% in the interval 40–293.8°K and, gradually increasing, reached ∼ 1.7% at the lowest temperatures.

The calculation of the values of the absolute entropy at 298.15°K by numerical integration of the curve $c_p - \ln T$ led to the value

$$S^0_{298.15} = 5.457 \pm 0.010 \text{ entropy units.}$$

The value of the enthalpy difference at 298.15 and 0°K was likewise calculated by numerical integration of the curve $c_p - T$:

$$H^0_{298.15} - H^0_0 = 882.6 \pm 1.5 \text{ cal/g-at.}$$

Fig. 1. Temperature dependence of the heat capacity of black phosphorus in logarithmic coordinates

* In the calculations of c_p, S^0_T, and $H^0_T - H^0_0$, it was assumed that 1 cal = 4.1840 J.

For the calculation of the quantities $S^0_{298.15}$ and $H^0_{298.15} - H^0_0$, the smoothed curve of the dependence of heat capacity on temperature was graphically extrapolated to 0° K. In our estimate, the error in the quantities $S^0_{298.15}$ and $H^0_{298.15} - H^0_0$ due to extrapolation should not exceed ∼ 0.003 entropy units and ∼ 0.02 cal/g-atom, respectively.

No anomalies were found in the behavior of the $c_p - T$ curve. In Fig. 1 the temperature dependence of the heat capacity is presented in the coordinates $\ln c_p - \ln T$. The straight line drawn through the experimental points in the temperature interval 20–37° K corresponds to the heat capacity in this region being proportional to temperature to the power 2.3. However, upon more careful examination of the curve, it is seen that the exponent changes gradually and, below 20° K, in the interval 13–20° K, becomes equal to 2.7. At lower temperatures the heat capacity will apparently be proportional to the third power of temperature, i.e., for black phosphorus Debye' s "cube" law will become valid. In any case, measurement of the heat capacity of black phosphorus at lower temperatures is highly desirable.

It should be noted that there have as yet been no literature data on measurements of the heat capacity of black phosphorus.

Institute of Thermophysics
Siberian Branch of the Academy of Sciences of the USSR

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