

Heat Capacity of Laminar Lattices at Low Temperatures

E. S. ITSKEVICH AND P. G. STRELKOV

Institute of Physico-technical and Radiotechnical Measurements

(Submitted to JETP editor November 3, 1956)

J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 467-477 (March, 1957)

The heat capacity of three anhydrous cadmium salts — CdI_2 , CdBr_2 , and CdCl_2 — which are classical laminar crystals has been measured in the temperature interval from 1.6 to 100° K. Possible thermal effects of sorption were excluded by carrying out the measurements on pressed preparations without heat exchanging gas. At helium temperatures, the heat capacities of all three salts obey a cubic law. In the 4-10° K range, the exponent in this relationship exceeded three for all three salts. Above 10° K, the exponent starts to decrease continuously and in a certain region the relation becomes quadratic; the region in which this relation holds decreases from the iodide to the chloride. Still higher, the relation is linear, the region of which increases from the iodide to the chloride. Attempts are made to compare the experimental results with theory.

THE study of the heat capacity of anisotropic crystals, in particular, laminar crystals, is of great value in the development of our representations of solid bodies. During the last ten years, a large quantity of theoretical work has been published on this question¹⁻⁷. The conclusions arrived at by the various authors do not coincide. Very few experimental investigations of the heat capacity of laminar lattices below 50° K have been made; they have been carried out only up to hydrogen temperatures, and on a limited group of substances^{8, 9}. Quite recently, three articles appeared on the heat capacity of graphite in which measurements were also made at helium temperatures¹⁰⁻¹², and a communication appeared concerning measurements of the heat capacity of MoS_2 and BN at 5° K and higher¹³.

We have studied the temperature dependence of the heat capacity of anhydrous iodide, bromide, and chloride of cadmium over the temperature range from 1.6 to 100° K. Measurements were also made above 100° K, but they cannot be used in the present article since we are interested in C_v , which practically coincides with C_p at low temperatures, but begins to differ strongly above 100° K.

A short report concerning our results at temperatures above 11° K has been published¹⁴. CdCl_2 , CdBr_2 , and CdI_2 represent classical laminar crystals. Their layers are formed of two networks of closely packed halide atoms, and a network of cadmium atoms located in the octohedral vacancies between them. These triple layers are bound by Van der Waal forces, the bond in the layers is basically ionic. CdCl_2 , CdBr_2 , and CdI_2 form a series with regular varying properties, in particular, the binding forces between layers increases as we

go from the iodide to the chloride^{15, 16}.

The absence of free electrons allows us to attribute the entire measured heat capacity to the lattice (in distinction from graphite).

1. METHOD OF MEASUREMENT

We used preparations obtained from IONKH, Academy of Sciences, U.S.S.R.* The CdCl_2 and CdI_2 were marked "ChDA." According to analysis, the total impurity content was 0.18% for CdI_2 , and 0.12% for CdCl_2 . The CdBr_2 was marked "Ch" and contained 0.47% impurities. This preparation was purified by three recrystallizations in an aqueous solution.**

Measurements above 11° K and in the helium region were made on identical samples. The preparations were dehydrated and were guarded against moisture during the filling of the calorimeters. For measurements in the region above 11° K, we used 0.287 moles of CdI_2 , 0.887 moles of CdCl_2 , and 0.696 moles of CdBr_2 . In the region of helium temperatures, we used 0.517, 0.830, and 0.843 moles, respectively.

To prevent possible sorption of heat-exchanging helium by the preparation during measurements at hydrogen temperatures, we selected large particles of the substance with linear dimensions of the order of 1 mm, comprising about 90% by weight. Furthermore, helium is adsorbed weakly at these temperatures. Deterioration of heat exchange in the

*The authors are grateful to E. I. Banashek and V. A. Sokolov for kindly giving them preparations.

**The authors thank T. N. Rezukhin (Professor of Physical Chemistry, Moscow State University) for his help in the purification of the CdBr_2 .

calorimeter, which would lead us to think of sorption, was not noted over the entire range of measurements. The effects of sorption at helium temperatures were avoided by the use of special measures, described below.

Part of the preparation was in the form of a powder, and it was necessary to consider its possible influence. However, from the work of Dugdale, Morrison, and Patterson^{17,18}, it appears that the presence in the calorimeter of ~ 10% of crystals with mean dimensions of the order of 100μ will not alter the results.

For experiments above 11° K, we used an adiabatic vacuum calorimeter described in Refs. 19 and

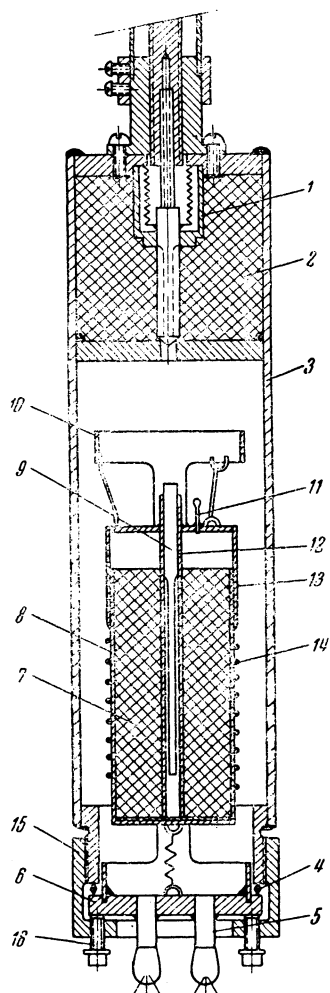


FIG. 1. Calorimeter for helium temperatures. 1—carbon pump valve; 2—activated carbon; 3—body of the calorimeter vacuum jacket; 4—sealing ring; 5—copper-glass unions for leads; 6—vacuum jacket cover; 7—pressed preparation; 8—glass calorimeter; 9—thermometer; 10—calorimeter holder; 11—capillary for evacuating the calorimeter; 12—tube with disc for the thermometer; 13—calorimeter cover; 14—heater; 15—support ring for the jacket; 16—sealing screws.

20. The platinum resistance thermometer used in the measurements was calibrated at 10.7, 14.0, 20.4, and 90.19° K by direct comparison with a secondary reference thermometer made of the same kind of platinum. The temperature dependence of the latter was found by comparison with a gas thermometer²¹.

At 1.6° K and above, we used a vacuum system of the type accepted here, with a carbon pump²² and a removable seal¹⁹ (Fig. 1).

To avoid the effects of sorption, having in mind that the selected crystals of CdI_2 , $CdBr_2$, and $CdCl_2$ have sufficiently developed surfaces, heat-exchanging gas was not introduced, and the preparation was located in a high vacuum. In order to provide proper thermal contact between the sample and the walls of the calorimeter, the heater, and the thermometer, without heat-exchanging gas, we used a modified type of calorimeter (Fig. 1). The salt being studied was pressed into the glass container 8, which is 60 mm high, 30 mm in diameter, has a wall thickness of 0.2 mm, and in which a tube 12 is set for the thermometer. In order not to disturb the tube during pressing, a centering disc was soldered to it, restraining it at the bottom of the calorimeter, after which the tube was filled with Wood's metal. The pressed salt was in good thermal contact with the wall, the bottom, and the tube, and the particles of the salt were in good thermal contact with one another.

A special die and plunger were made for pressing the salt in the thin walled glass vessel. The pressing pressure was 300-400 kg/cm². Cover 13 with capillary 11 was put on the glass vessel with the salt pressed in it and the tube, and the place where they joined was soldered. All parts of the calorimeter were made of pure copper. Identical calorimeters were used for $CdCl_2$, $CdBr_2$, and CdI_2 . The calorimeters were pumped out through the capillaries for about 10 hours at 120° C. Then the capillaries were pinched under vacuum and unsoldered.

The heater 14 was made of enameled constantan wire, 0.1 mm diameter, wound on the surface of the glass vessel which was first covered with polymerized adhesive BF. To ensure good thermal contact, the constantan windings were again covered with BF. To ensure good thermal contact, the constantan windings were again covered with BF and polymerized. The heater resistance was ~ 150 at liquid helium temperatures.

The calorimeters were suspended by nylon threads from girder 10, soldered to the removable cover of the jacket 6, which simplified the assembly. The leads to the heater and to the thermometer were

made of tinned constantan. The wires entered the vacuum system through platinum lead-ins, fused into the glass of copper-glass unions 5. The carbon pump was located in the upper part of the jacket and was controlled from the cover of the Dewar.

Two thermometers were used. For the range from 1.6-4.2° K, a bronze resistance thermometer was used, calibrated by the vapor pressure of liquid helium using a specially built condensation thermometer. The calibration was based on the 1948 scale. However, the final results were recalculated on the basis of the 1955 scale²³. The thermometer was a copper tube with a bifilar-wound two-section wire of phosphor bronze with diameters of 40 and 70 μ .

The carbon thermometer, made of a radio resistance from the firm of Allen Bradley, was mounted in a copper case, filled with heat exchanging helium and sealed. The electrical leads to the sensitive element of the thermometer were led in with the aid of a well sealing layer of polymerized BF²⁴.

The thermometers, lubricated with a thin layer of Ramsay coating, were inserted tightly into tube 12. The carbon thermometer served mainly for measurements in the intermediate temperature range (4.2-11° K); therefore it was calibrated at one temperature in liquid helium, and at the temperatures of normal boiling and the triple point of hydrogen. For these temperatures, the coefficients in the formula $\lg R + k/\lg R = A + B/T$ proposed by Clement and Quinell²⁵ were calculated.

2. MEASUREMENTS

The sequence of measurements in the range from 11° K and above was similar to that described in previous works¹⁹. The heat capacity of the empty calorimeter was determined over the temperature range from 10.67 to 302.92° K. The values were smoothed graphically. Individual experimental points deviated from the smoothed curve by no more than 1%. The magnitude of the heat capacity of the empty calorimeter compared with the measured value for CdI₂ went from ~ 20% at 10.7° K to 60% at 100° K, and for CdBr₂ and CdCl₂ went from ~ 15% at 10.9° K to ~ 37% at 83° K.

The measurements in the range 1.6-4.2° K were carried out in a bath of liquid helium boiling under reduced pressure. The calorimeter was cooled to the temperature of the bath by means of heat-exchanging helium let into the jacket by a special measuring valve. This gas was then pumped off by the carbon pump, providing a high vacuum. Opening the carbon

pump was always accompanied by some pulsations which warmed the calorimeter. To cool the calorimeter to the bath temperature with an open pump, a portion of heat-exchanging helium was let into the jacket. Since the heat capacity of the calorimeter is very small ($2-3 \times 10^{-3}$ cal/deg), it is possible to cool it during the time the heat-exchanging helium is being absorbed by the carbon. We started the measurements at 1.48° K.

Measurements in the range 4.2-16° K were carried out in a bath of liquid helium boiling at normal pressure. Before the start of each experiment, the resistance of the carbon thermometer was determined. This was done by letting heat-exchanging gas into the jacket, and measuring the vapor pressure over the helium in the Dewar precisely. To compare data obtained with the bronze and with the carbon thermometers, we started some series of measurements with the carbon thermometer (at least one for each salt) at temperatures ~ 3° K, so that the intervals of measurements with the different thermometers overlapped.

At the conclusion of the measurements of heat capacity in the helium bath, the remaining helium evaporated. Liquid hydrogen was quickly poured into the cold apparatus and the resistance of the carbon thermometer was determined at the point of normal boiling and at the triple point. This was done in each experiment because the carbon thermometers showed inadequate reproducibility from test to test.

Near 6° K, the tinned constantan leads to the heater lost their super-conductivity and began to dissipate energy. However, because of the cold-flow from the liquid helium bath, the portion of the wire adjacent to the bath remained superconducting. To measure the resistance of the nonsuperconducting part, an auxiliary potentiometer arrangement was used. The data were corrected for the power dissipated in these parts.

Equilibrium was established quickly in the pressed sample. We noticed no difference in the variation of calorimeter temperature with time between the pressed sample and the sample with heat-exchanging gas.

Since we measured the sum of the heat capacities of the preparation and the calorimetric vessel, it was necessary to know the heat capacity of the empty calorimeter, all parts of which were made of pure copper. The heat capacity of the calorimeter was calculated. The weight of copper in the calorimeter was 63.97 g for CdI₂, 36.66 g for CdCl₂, and

T°K	Heat capacity in % of the measured value					
	for the copper			overall for the empty calorimeter		
	CdI ₂	CdBr ₂	CdCl ₂	CdI ₂	CdBr ₂	CdCl ₂
1.6	15.1	9.8	13.9	16.5	11.5	17.0
2.0	11.7	7.7	11.8	12.8	9.3	14.6
2.5	9.2	5.0	8.6	10.3	6.8	11.9
4.0	5.2	3.0	5.0	6.2	4.7	7.9
7.0	2.9	1.7	3.0	4.2	3.7	7.0
10.0	2.9	1.6	2.4	4.4	4.0	6.2
14.0	—	1.6	—	—	4.1	—
16.0	3.7	—	2.7	5.2	—	6.2

36.63 g for CdBr₂ (the copper in the latter two calorimeters weighed less because thinner parts were used). The contribution of the copper²⁶ to the calculated heat capacity is given in the table for each calorimeter. We feel that the error involved in this determination of the heat capacity of the copper parts is hardly greater than 1/10 of the tabulated values. Corrections for the heat capacity of the solder used were introduced by calculations based on published data. We also introduced a correction for the polymerized BF.* In the region of helium temperatures, these corrections were considerably smaller than the corrections for the heat capacity of the copper. The total contribution of the heat capacity of the empty calorimeter is also given in the table.

We estimate the possible error associated with this method of determination of the heat capacity of the empty calorimeter to be approximately 1% above 3° K and up to 2% below 3° K.

The satisfactory agreement between our hydrogen and helium data in the region where they join between 11 and 17° K confirms the reliability of the method used. The high vacuum maintained by the carbon pump allowed us to raise the temperature of the calorimeter up to 17° K at a bath temperature of 4.2° K with a small change of temperature paths.

3. RESULTS OF THE MEASUREMENTS

The measured heat capacities of CdI₂, CdBr₂, and CdCl₂ from 1.6 to 30° K are shown on a logarithmic scale in Fig. 2. It is clear that the results obtained in the helium region conform with the results ob-

tained in the hydrogen region. Except for the article by Dworkin *et al*²⁷ concerning measurements of CdI₂ above 16° K, already considered in Ref. 14, no published data exist concerning the heat capacities of CdI₂, CdBr₂, and CdCl₂ in the low temperature region.

The results are presented in Fig. 2 in the form of points (1 cal = 4.185 abs. joules). The authors plan to publish the numerical data separately. The intervals from 1.6 to 100° K for CdI₂, from 1.6 to 60° K for CdBr₂, and from 1.6 to 80° K for CdCl₂ were covered by the measurements without gaps; phase transitions were not observed.

The heat capacities of all three salts exhibit a cubic temperature dependence at helium temperatures. The straight lines in Fig. 2, corresponding to the points in the helium region, show this cubic relation. Fig. 3 also confirms this.

The cubic dependence is maintained up to 4.0° K for CdI₂ and CdBr₂, and up to ~ 5.0° K for CdCl₂, and is described by the following formulas: for CdI₂, $C_p = 0.76 T^3$ mcal/deg mole, for CdBr₂, $C_p = 0.470 T^3$ mcal/deg mole, and for CdCl₂, $C_p = 0.275 T^3$ mcal/deg mole.

At higher temperatures the dependence becomes stronger and the exponent increases. CdCl₂ deviates from the cubic dependence somewhat more than the other salts. The maximum deviation of the CdCl₂ curve (Fig. 2) corresponds to a temperature exponent equal to 3.4. The deviation from cubic dependence is outside the limits of experimental error, and amounts to more than 20% for CdI₂ and CdBr₂, and more than 30% for CdCl₂.

Around 10° K the temperature exponent begins to decrease, and in the region of hydrogen temperatures the relation becomes quadratic over a certain interval. The region of "quadraticity", as was noted in Ref. 14, decreases as we go from CdI₂ to CdCl₂. At higher temperatures there is a region of linear dependence (Fig. 4), which broadens strongly as we go

*The authors take this opportunity to thank I. N. Kalinkin for making available to them his measurements of the heat capacity of polymerized coatings of BF at helium temperatures.

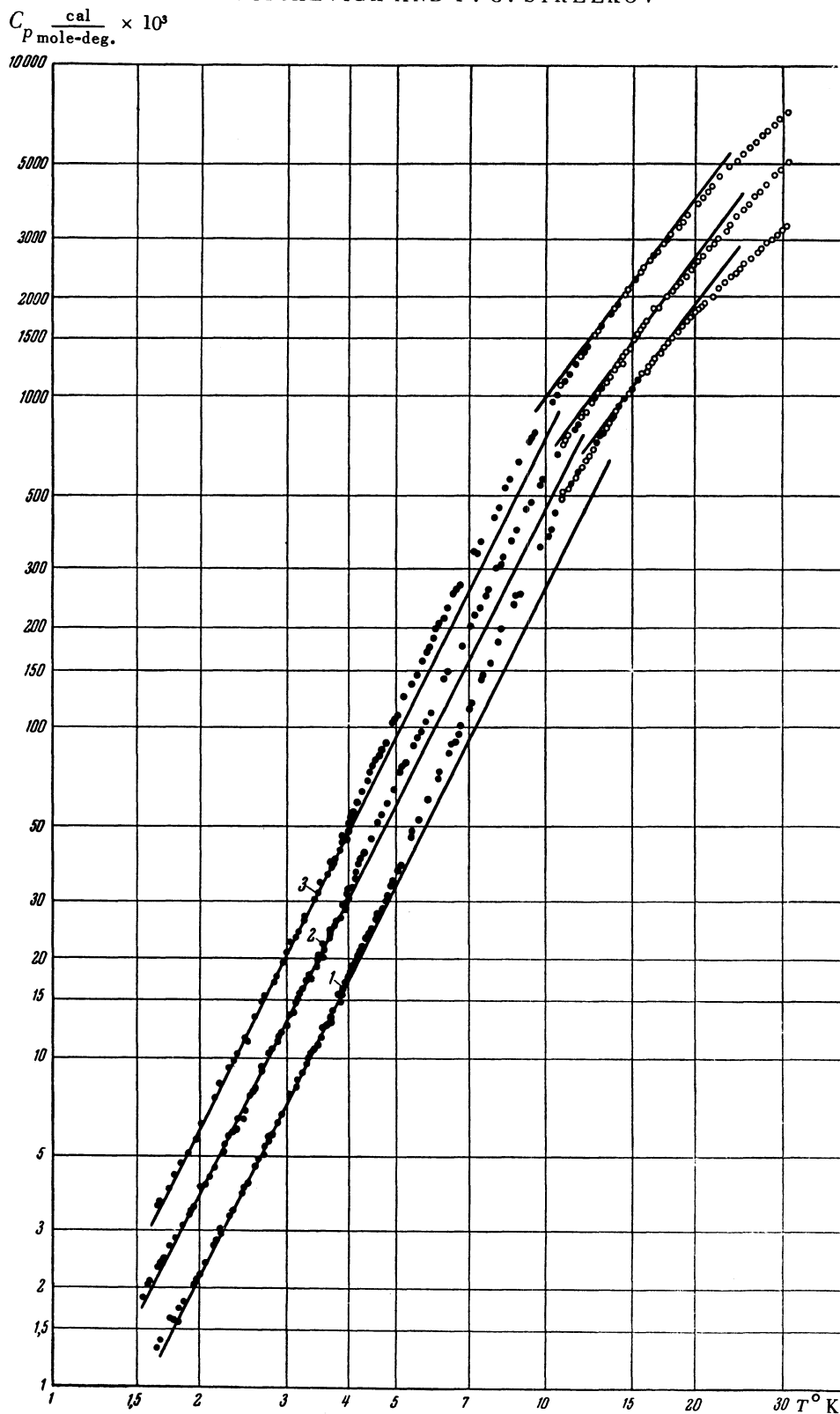


FIG. 2. Heat capacity of halide salts of cadmium from 1.6 to 30° K (● refers to the helium bath, ○ refers to the hydrogen bath¹⁴). 1—CdCl₂, 2—CdBr₂, 3—CdI₂. The straight lines in the region 1.6-10° K correspond to a cubic relation. A series of points ●, coinciding with points ○, have been omitted in the region 10-20° K.

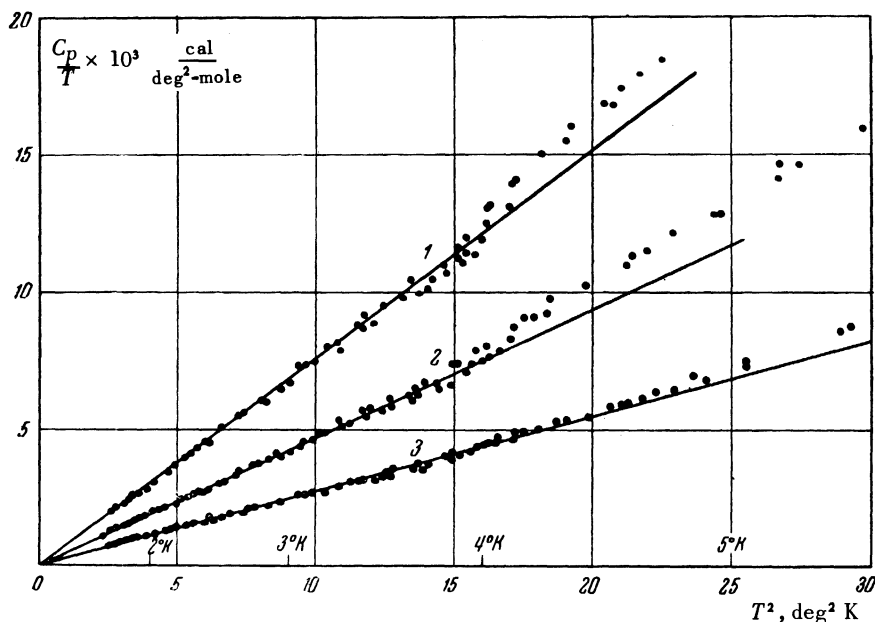


FIG. 3. The relation $C_p/T = f(T^2)$ for halide salts of cadmium at helium temperatures. 1— CdI_2 , 2— CdBr_2 , 3— CdCl_2 .

from the iodide to the chloride¹⁴.

We estimate the mean experimental error to be generally 1% in the hydrogen region and 3% in the helium region. In the region 3.5–4.5° K, the error increases somewhat (up to 5%) due to the rough calibration of the carbon thermometer at one helium point between 3 and 4.2° K. However, this does not affect the conclusions, especially since the curve is rectified by the measurements with the bronze thermometer.

4. DISCUSSION OF THE RESULTS

During 1945–1950, Tarasov¹, in a series of articles, pointed out for the first time that the heat capacity of laminar lattices must have specific singularities, and cannot be described by the interpolated Debye formula. Using a method similar to that of Debye, he proposed interpolation formulas describing the heat capacity of laminar crystals at low temperatures. According to Tarasov, the heat capacity of a laminar crystal obeys a cubic law at very low temperatures, and at higher temperatures where the interaction energy between layers is less than kT , it becomes quadratic. Later Krumhansl and Brooks⁴, Rosenstock⁵, and others obtained relations similar to those of Tarasov based on models.

In 1952, Stepanov³ criticized the basic assumptions used by Tarasov to obtain his formulas. At the same time, I. M. Lifshitz² examined the question again in detail, and constructed a completely phenomenological theory of the heat capacity of

laminar crystals. He pointed out the specific contribution to the heat capacity of laminar structure of waves similar to bending waves in layers. He obtained a dispersion law (relation between the frequency and the wave vector) pertaining to laminar crystals with axial symmetry with respect to the elastic properties, in particular hexagonal properties for long waves, yielding a major contribution to the heat capacity at low temperatures. Lifshitz showed that in the temperature region in which the energy of interaction between layers may be neglected, the heat capacity depends linearly on temperature, which is determined by the bending waves. This differs significantly from the trend of Tarasov's ideas.

Lifshitz obtained an analytic expression for the heat capacity in the temperature region in which the interaction is significant. This expression was integrated which made it possible to tabulate heat capacity as a function of temperature²⁸. It appeared possible to compare the heat capacity according to Lifshitz with experimental data without appealing to the unknown values of the elastic constants of a laminar lattice in this temperature region, because the elastic constants enter the formulas only in the form of determined combinations. The numerical values of these combinations may be determined if the heat capacity is known in the regions of pure cubic law, and pure quadratic law, and the expected values of the heat capacity may be calculated in the intermediate region between the cubic and the quadratic regions. We attempted to carry out such a comparison

between theory and experiment for CdI_2 , CdBr_2 , and CdCl_2 , whose heat capacities were measured in the regions of cubic, quadratic, and intermediate temperature dependence. However, the theoretically calculated values did not agree with the experimental values. This may be explained by the fact that the theoretical values were calculated on the assumption of a very large difference between the magnitudes of the elastic moduli in a layer and between layers², which apparently does not hold for CdI_2 , CdBr_2 , and CdCl_2 . The anisotropy required² is such that the numerical values of the temperatures at which the purely cubic law and purely quadratic law hold, must differ by more than an order of magnitude. Judging from the published data, this relation is satisfied to a large extent by graphite; a comparison was carried out in Ref. 28.

It would be extremely laborious to obtain an expression for the heat capacity of a crystal using the complete dispersion law². A possible way out of the situation was discussed in Ref. 28.

A quantitative comparison between theory and experiment is not possible in the region of linear temperature dependence. In addition to the fact that the Lifshitz theory deals with anisotropies which are not possessed by the real crystals investigated by us, a comparison would require further knowledge of the magnitude of the transverse rigidity of the layer.

Qualitatively, however, the lengthening of the linear part of the curve as we go from the iodide to the chloride is contained in Lifshitz's theory², taking into account Ref. 15, from which it follows that the bond between the layers increases from the iodide to the chloride.

Newell⁷ made an attempt to consider the question of the heat capacity of laminar lattices, based on models. Using the concept of two types of vibration in a laminar crystal, he obtained results agreeing qualitatively with Ref. 2. Newell shows that valence forces having a specific dispersion law (similar to the dispersion law for bending waves in Ref. 2) are responsible for the linear behavior of heat capacity. Nevertheless, Newell's conclusions remain qualitative. We agree with Newell that for almost isotropic substances, it is not possible, within the limits of existing theories, to obtain satisfactory information concerning molecular forces from heat capacity data, because almost all the data may be described by a Debye curve with one parameter θ_D . But data on the heat capacity of strongly anisotropic substances in the low temperature region may give some useful information concerning the forces of interaction in crystals—information which would be difficult to obtain directly.

The works of Lifshitz, Newell, and others show that to determine the vibratory spectrum of the lattice of a laminar crystal, at least four parameters

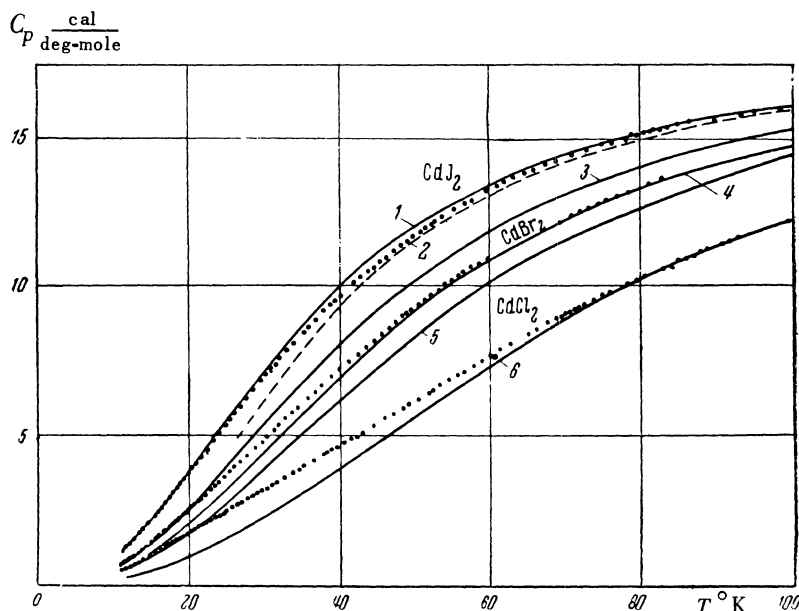


FIG. 4. Heat capacity of CdI_2 , CdBr_2 , and CdCl_2 in the region 11-100° K. The points represent the experimental results. The solid lines represent the value of heat capacity calculated according to Tarasov: 1— CdI_2 with $\theta_2 = 163^\circ\text{K}$, $\theta_3 = 32.6^\circ\text{K}$; 3— CdBr_2 with $\theta_2 = 200^\circ\text{K}$; 4— CdBr_2 with $\theta_2 = 223^\circ\text{K}$; 5— CdCl_2 with $\theta_2 = 240^\circ\text{K}$; 6— CdCl_2 with $\theta_2 = 320^\circ\text{K}$. The dashed line 2 represents the heat capacity of CdI_2 , calculated according to Debye ($\theta_D = 155^\circ\text{K}$).

must be known. Therefore it is doubtful *a priori* that Tarasov's functions with two parameters can be universal for the description of the heat capacity of laminar crystals. However, there are indications in the literature that the formulas proposed by Tarasov give a good representation of the temperature dependence of the heat capacities of a series of laminar crystals^{1,9,29}. In view of this, we tried to use Tarasov's formulas with two parameters¹ to describe our data on CdI₂, CdBr₂, and CdCl₂.

In Fig. 4, the experimental results in the region 11-100° K are shown by points, and the solid lines show the values calculated according to Tarasov's formulas over the same interval. One-parameter curves are shown for CdBr₂ and CdCl₂ because the introduction of a second parameter does not change the calculated results above 16° K. We see that the experimental points for CdI₂ from 11 to 100° K are described well by the curve, with only a certain systematic deviation in the region 30-60° K (up to 4%). The deviation is stronger for CdBr₂ and is very sharply evident for CdCl₂. Their heat capacities are not at all well described by Tarasov's formulas in this temperature interval.

If the heat capacity curve calculated for CdI₂ according to Tarasov (Fig. 4) is extrapolated to lower temperatures, it diverges sharply from the experimental data. In the helium region it differs by a factor of two. If, in reverse, we determine the parameters in the Tarasov functions using experimental data in the helium region and in the neighborhood of 20° K, then there is a systematic divergence ~ 20% in the region 6-20° K. It should be noted that above 40° K, the heat capacity of CdI₂ is also satisfactorily described by the Debye function.

A comparison of the experimental data for CdCl₂ and CdBr₂ with Tarasov's curves below 11° K would have no meaning since the divergencies are already large in the hydrogen region. Thus, the Tarasov formula is not universal.

The experiment shows that for all three salts there is an interval in which the dependence of the heat capacity on temperature is greater than the third degree. It is possible that this is a consequence of the contribution of optical branches to the heat capacity. Optical branches corresponding to interlayer interactions may be sufficiently soft. The existence of such branches may be due to the fact that in our lattices the layers are not monatomic, and the surfaces of each layer, facing neighboring layers, are different⁴. In CdI₂ the iodide ions on one side of the layer are turned through an angle of 60° about the axis passing through the cadmium ions, with respect to the iodide ions on the other side of the layer. In CdCl₂ the picture is even more complicated: the triple layers of which it is formed repeat their configura-

tion after two layers.

CONCLUSIONS

1. The heat capacities of anhydrous cadmium chloride, cadmium bromide, and cadmium iodide were measured over the range 1.6-100° K.

2. The heat capacity of all three salts obeys a cubic law in the interval 1.6-4° K.

3. The temperature exponent in the relation between heat capacity and temperature became greater than three between 4 and 10° K for all three salts. This is assumed to be due to the influence of the soft optical branches of interlayer interaction.

4. In the region of hydrogen temperatures a quadratic dependence occurs over an interval which decreases as we go from the iodide to the chloride.

5. At still higher temperatures a linear dependence occurs over an interval which increases as we go from the iodide to the chloride.

6. Our results do not qualitatively contradict the Lifshitz theory. A quantitative comparison was not possible because the particular case considered theoretically which led to tabulated results refers to lattices with sharply differing elastic constants in the layer and between layers, in any case, with far greater differences than occur in CdI₂, CdBr₂, and CdCl₂.

7. The two-parameter Tarasov functions cannot describe the experimental data referring to all three salts.

In conclusion, the authors consider it their pleasant duty to express their genuine gratitude to Academician P. L. Kapitza for making it possible for them to carry out measurements at helium temperatures at the Institute for Physical Problems, Academy of Sciences, U.S.S.R., and to Prof. I. M. Lifshitz for numerous and fruitful discussions on the questions considered in this article.

¹ V. V. Tarasov, Dokl. Akad. Nauk, U.S.S.R., **46**, 22 (1945); **54**, 803 (1946); **58**, 577 (1947); J. Phys. Chem. (U.S.S.R.) **24**, 111 (1950).

² I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) **22**, 471, 475 (1952).

³ P. E. Stepanov, J. Phys. Chem. (U.S.S.R.) **26**, 1642 (1952).

⁴ J. Krumhansl and H. Brooks, Chem. Phys. **21**, 1663 (1953).

⁵ H. R. Rosenstock, Chem. Phys. **21**, 2064 (1953).

⁶ K. Komatsu and T. Nagamiya, J. Phys. Soc. Japan **6**, 438 (1951); K. Komatsu, J. Phys. Soc. Japan **10**, 346 (1955).

⁷ G. F. Newell, Chem. Phys. **23**, 2341 (1955).

- ⁸W. de Sorbo, Chem. Phys. **21**, 168 (1953); Am. Chem. Soc. **77**, 4713 (1955).
- ⁹Dworkin, Sasmor and van Artsdalen, Chem. Phys. **21**, 954 (1953); Smith, Brown, Dworkin, Sasmor and van Artsdalen, Chem. Phys. **78**, 1553 (1956).
- ¹⁰Bergenslid, Hill, Webb and Wilks, Phil. Mag. **45**, 367, 851 (1954).
- ¹¹P. H. Keesom and N. Pearlman, Phys. Rev. **99**, 1119 (1955).
- ¹²W. de Sorbo, Chem. Phys. **23**, 1970 (1955).
- ¹³E. F. Westrum and J. J. McBride, Phys. Rev. **98**, 270 (1955).
- ¹⁴E. S. Itskevich, P. G. Strelkov, Dokl. Akad. Nauk, U.S.S.R. **106**, 805 (1956).
- ¹⁵Z. G. Pinskar, J. Phys. Chem. (U.S.S.R.) **15**, 599 (1951); **16**, 1 (1942); Izv. Akad. Nauk, U.S.S.R., ser. khim. **6**, 415 (1943); Z. G. Pinsker and L. I. Tatarinova, J. Phys. Chem. (U.S.S.R.) **15**, 1005 (1941).
- ¹⁶L. A. Smirnova, A. Kh. Breger, G. S. Zhdanov, J. Phys. Chem. (U.S.S.R.) **18**, 309, 425 (1944).
- ¹⁷J. S. Dugdale, J. A. Morrison, D. Patterson, Proc. Roy. Soc. (London) **224A**, 228 (1954).
- ¹⁸J. A. Morrison, D. Patterson, Trans. Farad. Soc. **52**, 764 (1956).
- ¹⁹Strelkov, Itskevich, Kostriukov, Mirskaia and Samoilo-
lov, J. Phys. Chem. **28**, 459 (1954).
- ²⁰Astrov, Itskevich and Sharifov, J. Phys. Chem **29**, 424 (1955).
- ²¹Borovik-Romanov, Orlova and Strelkov, *Establishment of a low temperature scale between 90, 19 and 10° K by means of a graduated table of a group of standardized platinum resistance thermometers*, Moscow, 1954.
- ²²M. O. Kostriukova and P. G. Strelkov, Dokl. Akad. Nauk, U.S.S.R. **90**, 525 (1953).
- ²³H. van Dijk and M. Durieux, *Helium vapour pressure scale T_L⁵⁵*. Kamerlingh Onnes Laboratory, Leiden, 1955.
- ²⁴B. N. Samoilov, J. Tech. Phys. (U.S.S.R.) **22**, 888 (1952).
- ²⁵J. R. Clement and E. H. Quinell, Rev. Sci. Instr. **23**, 213 (1952).
- ²⁶Corak, Garfunkel, Satterthwaite and Wexler, Phys. Rev. **98**, 1699 (1955).
- ²⁷Dworkin, Sasmor and van Artsdalen, Am. Chem. Soc. **77**, 1304 (1955).
- ²⁸E. S. Itskevich and V. M. Kontorovich, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 175 (1957).
- ²⁹W. de Sorbo, Acta Metallurgica, **2**, 274 (1954).

Translated by D. Lieberman

