

## Specific Heat of LiF and KI at Low Temperatures\*

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The heat capacities of LiF and KI single crystals have been measured over the temperature range 2–7°K. An adiabatic calorimeter was employed making use of a mechanical contact "heat switch." A carbon resistor embedded directly in the specimen was used as thermometer. For LiF the heat capacity was found to be proportional to the cube of the temperature over the whole range of temperatures investigated, and the value of  $\theta_0$  was found to be 722°K. For KI variations from the  $T^3$  dependence were found above 3°K. An extrapolation of a smooth curve through the data to zero degrees temperature indicates a value of  $\theta_0=128^\circ\text{K}$ . These values of  $\theta_0$  are compared to values of  $\theta_0$  derived from elastic constants data.

## INTRODUCTION

RECENTLY a group at this laboratory has been making measurements at low temperatures needed for a fundamental understanding of alkali halides. Briscoe and Squire<sup>1</sup> reported elastic constants measurements on LiF. Their work has been extended to KI and KCl by Norwood and Briscoe.<sup>2</sup> The present experiment, whose results are to be tied in theoretically with these elastic constants data, is a measurement at low temperature of the specific heat of LiF and KI.

For dielectric crystals such as the alkali halides, there should be at low temperatures only one contribution to the specific heat, that due to thermal vibrations of the lattice. The form of the dependence of this contribution upon temperature has been well established by Debye<sup>3</sup> and by Born and von Kármán<sup>4</sup> who showed that at sufficiently low temperatures

$$C_v = 2(464.3)(T/\theta_0)^3 \text{ cal/deg mole,}$$

where  $C_v$  is the specific heat at constant volume and  $\theta_0$  is a constant characteristic of the substance. The  $\theta_0$  will be a function of the forces between particles of the lattice and thus will be basic to the understanding of phenomena in solids. The factor two in the above well-known equation is because there are  $2N$  atoms per mole in these substances.

The question of how low in temperature one must go before the true  $T^3$  region is reached was discussed by Born and von Kármán.<sup>4</sup> They showed that the  $T^3$  dependence of specific heat is a low-temperature limit independent of crystal structure and independent of any special assumptions concerning isotropy. They showed that the frequency distribution function for crystals such as the alkali halides involving two different masses will have two different "branches." One of these branches will relate to modes of vibration of high frequency, of the order of reststrahlen frequencies in

the infrared. These modes will not be excited above their ground states at low temperatures where only low energies are available. The other branch at low temperatures will have only the lowest frequencies excited above the ground state and will give rise to the  $T^3$  dependence of specific heat.

The problem has been further considered by Blackman.<sup>5</sup> He concludes that the true  $T^3$  region is attained only at a temperature of the order of  $\theta_0/50$  where  $\theta_0$  is the low-temperature limit of the Debye constant. For LiF with a  $\theta_0$  of about 722°K this is a temperature of 14°K. All the measurements reported in this work were made well below this limit. It is thus expected that the specific heat of LiF will obey a  $T^3$  law for all the data here reported. For KI, on the other hand, with a  $\theta_0$  of about 128°K the Blackman criterion leads to a temperature of about 2.5°K. By going to low enough temperatures, both for LiF and KI the present experiment should be able to indicate the true limiting value of the Debye temperature  $\theta_D$  for  $T$  approaching zero.

At the outset of the present work, the situation was as shown in Fig. 1. Here values of  $\theta_D$  for LiF and KI calculated on the basis of the Debye model are plotted as a function of temperature. The specific heat for these materials had been measured over a wide range of temperatures by Clusius and Eichenauer<sup>6</sup> and by Berg and Morrison.<sup>7</sup> As yet, however, there was no clear indication that the  $\theta_D$  as a function of  $T$  had approached a constant value. There was also no certain estimate of the value that  $\theta_D$  would assume near  $T=0^\circ\text{K}$ . The present experiment was set up to find these values. Moreover, the findings were to be used to verify determinations of  $\theta_0$  from elastic constants measurements and thereby help to establish agreement between theory and experiment. Further, just such measurements as these are needed to shed light on recent attempts to extend the simple Debye theory. A preliminary report of our work on LiF was given at the Low-Temperature Physics Conference, Madison, Wis-

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<sup>1</sup> C. V. Briscoe and C. F. Squire, *Phys. Rev.* **88**, 398 (1957).<sup>2</sup> M. H. Norwood and C. V. Briscoe, preceding paper [*Phys. Rev.* **112**, 45 (1958)].<sup>3</sup> P. Debye, *Ann. Physik* **39**, 789 (1912).<sup>4</sup> M. Born and T. von Kármán, *Physik. Z.* **13**, 297 (1912).<sup>5</sup> M. Blackman, *Reports on Progress in Physics* (The Physical Society, London, 1941), Vol. 8, p. 11.<sup>6</sup> K. Clusius and W. Eichenauer, *Z. Naturwiss.* **11A**, 715 (1956).<sup>7</sup> W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1957).

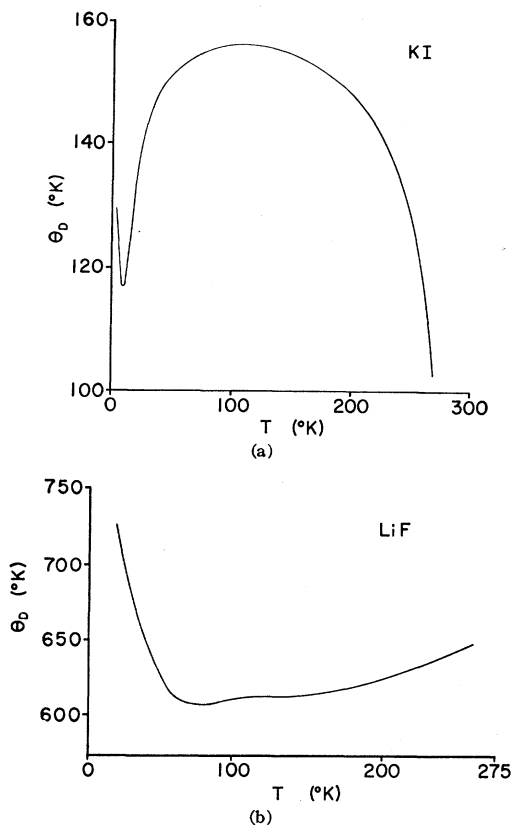


FIG. 1. Debye characteristic temperature,  $\theta_D$ , as a function of temperature (a) for KI and (b) for LiF. The values of  $\theta_D$  are those required to make the Debye theory of specific heat fit the experimental values of  $C_v$ . See references 6 and 7.

consin, August, 1957. Similar work was reported there by Berg and Morrison,<sup>7</sup> whose results on KI we shall compare with our own.

#### EXPERIMENTAL

The specimens of LiF and KI on which the measurements were performed were large pure single crystals obtained from the Harshaw Chemical Company. They were shaped in the form of cylinders about three inches long and one inch in diameter, giving a mass of 104 grams for the LiF and 125 grams for the KI.

The calorimeter was similar in design to one reported by Ramanathan and Srinivasan.<sup>8</sup> In this type of calorimeter cooling is brought about by bringing the specimen into mechanical contact with a constant temperature bath. This obviates the necessity of using helium exchange gas with the possibility that helium vapor be adsorbed upon the sample as it is cooled. Such adsorbed vapor would boil off during periods of heating with an accompanying heat of desorption, giving a spuriously high result for the specific heat.

We shall give a brief description of the equipment

<sup>8</sup> K. G. Ramanathan and T. M. Srinivasan, *Phil. Mag.* **46**, 338 (1955).

such that future work of this nature from this laboratory may refer to this paper. The apparatus is depicted in Fig. 2. The salt hangs freely in its normal position inside a brass can large enough to be one-half inch distant at closest approach. This can, the calorimeter, is attached at its top to a thin-walled Monel tube which secures it rigidly to the top-plate at the room temperature end of the apparatus. The calorimeter is surrounded by a double Dewar flask, the inner one of which can be filled with liquid helium to form a constant temperature bath. A high-speed vacuum pump is connected to this chamber making it possible to reduce the pressure above the liquid helium. This allows the bath temperature to be reduced from the normal boiling point of helium at 4.2°K to about 1.3°K. It was found in practice that quite adequate vacuum could be produced in the sample chamber by merely pumping out the chamber at room temperature with an ordinary forepump and allowing the liquid helium itself to freeze out what air remained. The vacuum obtained in this way was about  $10^{-6}$  mm of Hg. The calorimeter can had a low-melting-point indium solder seal which allowed it to be opened easily when adjustments were to be made. The salt specimen was suspended by nylon threads from a brass plate shown in the diagram. The plate was attached to a small stainless steel rod which extended up the inside of the Monel tubing. At the top the rod was attached to a Sylphon bellows, which gave a vacuum-tight connection with freedom of vertical motion of about an inch. The bellows was activated by a hand screw so that any vertical position within the limits of extension could be achieved and held. In this way the specimen could be lowered from a position in which it was hanging freely in vacuum to a position in which it was being pressed tightly by the rod to the bottom of the can. Pressures upon the salt which were obtainable by hand tightening the bellows screw were sufficient for adequate thermal conduction. The salt could be brought from several degrees above the liquid helium bath temperature to an equilibrium with the bath in about fifteen minutes. The initial cooling from liquid air temperatures down to liquid helium temperatures took about forty-five minutes. Upon breaking the contact some heating occurred so that there was initially a very rapid rise in the temperature of the salt. Consequently, the lowest temperatures at which accurate measurements could be made were higher than the lowest bath temperatures obtainable by about a degree.

Temperatures of the sample were measured with a carbon resistance thermometer, which was embedded in a groove at the upper edge of the salt itself. A constantan heater wrapped directly on the salt over about three-quarters of its length provided a means for admitting measurable amounts of heat. Good thermal contact between the salt and the heater and thermometer was assured by a very thin coating of red Glyptal. The carbon resistor was of the Allen-Bradley

type. It had a room temperature resistance of 57 ohms, a resistance at 4.2°K of about 1000 ohms, and a resistance at 2°K of about 10 000 ohms. This thermometer was calibrated after each run by admitting helium exchange gas to the calorimeter. Resistance readings of the thermometer were then compared to vapor pressure readings of the liquid helium bath as read on a manometer by a cathetometer. By-pass pumping lines with suitable valves allowed regulation of the pumping speed to such a degree that the bath could be held at essentially constant temperature (within a millidegree) for ten minutes or more for each calibration point so that equilibrium was assured. Extrapolation between the points directly determined was made using the formula suggested by Clement and Quinnell<sup>9</sup>; i.e.,

$$\log R + K/\log R = B + A/T,$$

where  $R$  is the resistance,  $T$  the temperature, and  $A$ ,  $B$ , and  $K$  are constants to be determined by calibration.

All measurements were made in point-by-point fashion using two Leeds and Northrup Type K potentiometers. One measured the voltage drop across the thermometer or heater directly, and the other measured the voltage drop across a standard resistance in the same circuit. In this way data were obtained for compiling plots of temperature *versus* time through a drift period on either side of a period of heating. Energy was supplied to the sample via the heating coil from a lead storage battery. Suitable variable resistance in the circuit allowed the temperature rise for a fixed period of heating to be kept reasonably constant at several hundredths of a degree. The heating period was fixed by a cam operated microswitch driven by a clock motor. This was calibrated using a scalar circuit set to read the peaks of the 60-cycle laboratory current. By this arrangement the time of the heating period was determined to be  $30.63 \pm 0.04$  sec.

In order to prevent heat leaking to or from the sample through the leads to the heater and thermometer, two things were done. First, the leads themselves were brought out of the calorimeter can through Kovar seals in its top, so that the leads outside the calorimeter passed through the liquid helium bath. The Kovar seals gave adequate performance even in the superfluid helium. Secondly, inside the calorimeter long leads of No. 38 manganin wire, about 50 cm in length, were used. The salt was protected from radiation by a concentric-cup baffle at the end of the Monel tube, and also by the plate from which it was suspended. The rod leading from the bellows was thermally linked to the bath by two flexible copper wires soldered to the lower end of the rod and to the top of the can. This was found necessary to prevent heat from leaking down the rod and reaching the specimen. The over-all heat leak to the sample could be determined by measuring the rate

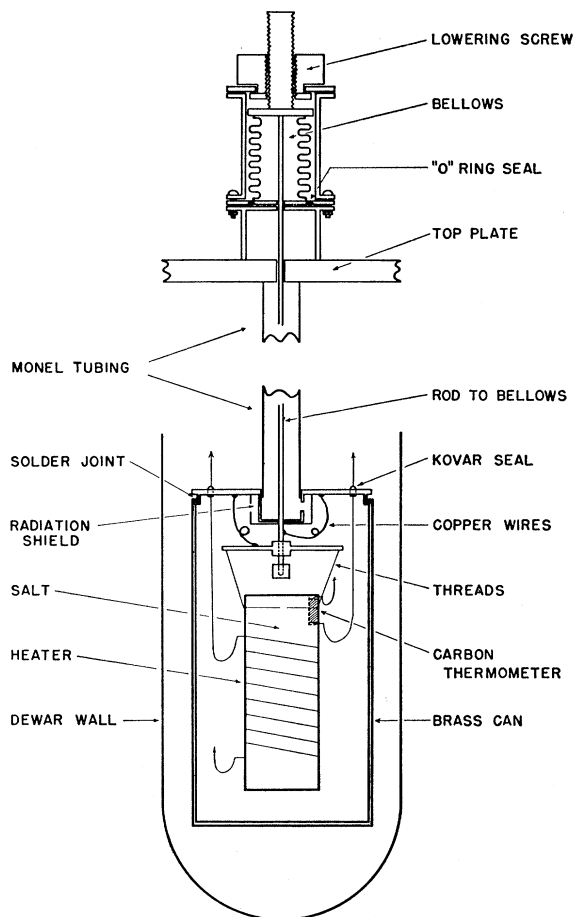


FIG. 2. Schematic diagram of the apparatus used in these experiments.

of temperature rise during drift periods. When this was done it was always found that there was heat leaking *to* the sample. The rate was found not to be strongly dependent on temperature. Generally the heat leak was on the order of several hundred ergs per minute.

#### METHOD OF ANALYSIS AND CORRECTIONS

From the data, plots could be compiled of temperature as a function of time. Each set of plots corresponded to a heating period, when a measurable amount of power was being delivered to the heater, and a preceding and following drift period, when no power was being delivered to the heater. The data for these curves were put into an IBM-650 computer made available through the generosity of the Shell Development Company, and a least squares fit to a parabola was made for each drift curve. These parabolas were then extrapolated to the midpoint time of the heating period. The difference between the two drift curves at this point was taken to be the rise in temperature for the measured input of heat. Provided the heat leak to or from the sample involves terms of no higher tem-

<sup>9</sup> J. R. Clement and E. H. Quinnell, *Rev. Sci. Instr.* **23**, 213 (1952).

perature dependence than the first, this is correct to a high order. In any case, it is a closely correct procedure if the drift curves are very nearly linear, as was the case in this work.

Several corrections were necessary, and we wish to emphasize these in reporting our results. Since the leads to the heater were of Manganin and of long length, they had a resistance of about twenty ohms each, compared to the heater resistance itself of about 295 ohms. Thus consideration had to be given to heat developed in the leads which subsequently leaked into the sample. In order to determine the magnitude of this effect a separate experiment was run. The heater coil was bypassed in such a way that the heating current passed through the *leads* to the heater only. Then, assuming the heat capacity of the sample to be known, the quantity of heat passing into the sample from the leads during a specified time could be determined from the rise in temperature of the specimen. This quantity of heat could then be compared to the total amount of heat developed in the leads as determined from the lead resistance and the heater current. It was found that 19% of the heat developed in the leads leaked into the specimen. This number was essentially independent of the specimen temperature over the range of low temperatures used in this work. It was also found that the heat leaking in from the leads did so with a long time constant. The upper drift curve, in this case, is representative of the *drift* in temperature only many seconds *after* the heating has stopped. With this effect taken into account, the slopes of the two drift curves were found to be very nearly the same.

For a measurement of heat capacity the heat input was calculated from the measured heater resistance and measured heater current, with a correction being made as mentioned for lead heating. The rise in temperature for this heat input was determined by extrapolating the drift curves as discussed above. The heat capacity was then obtained by using the relation

$$C = \Delta Q / \Delta T,$$

where  $\Delta Q$  is the heat input and  $\Delta T$  is the change in temperature. A correction to the heat capacity was made for the heat capacity of the Glyptal coating. Use was made of the formula for specific heat of Glyptal suggested by Pearlman and Keesom<sup>10</sup>; i.e.,  $0.22T^2 \times 10^4$  ergs/g deg. This quantity was calculated for every data point and subtracted from the heat capacity as determined above. For the LiF the correction to the heat capacity ranged from about 8% at the lowest temperatures to about 3% at the highest. For the KI the correction was a fraction of 1% at all temperatures. A separate experiment was made with the salt sample replaced by a thin aluminum shell to check this correction. The results indicated that the correction for the heat capacity of the addenda to the salt was quite

<sup>10</sup> N. Pearlman and P. H. Keesom, Phys. Rev. 88, 398 (1952).

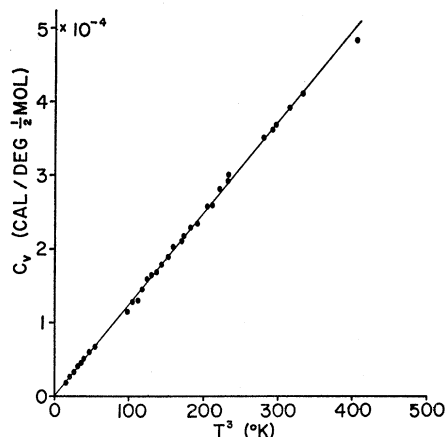


FIG. 3. Specific heat of LiF *versus*  $T^3$ . The experimental points fall on a straight line, indicating that the Debye theory is valid throughout the range investigated.

reasonably accounted for by the Glyptal correction alone.

In calibrating the thermometer against the vapor pressure of the liquid helium bath, no correction was made for the head of liquid helium above the thermometer. This is certainly correct at temperatures below the  $\lambda$ -point transition in liquid helium where the heat conductivity of the liquid helium is very high. A check may be made for the range of temperatures above the  $\lambda$  point by making a plot of the resistance of the carbon thermometer against the vapor pressure of the bath. One can demand a smooth transition of such a curve across the  $\lambda$  point. This was done as part of the calibration procedure, and the indication always was that negligible correction needed to be made to the vapor pressure readings.

It was found that the parameters involved as constants in the calibration equation of Clement and

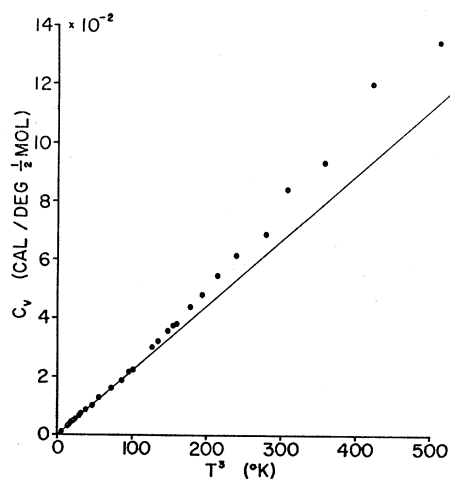


FIG. 4. Specific heat of KI *versus*  $T^3$ . The straight line is that determined by the lowest temperature experimental points.

Quinnell differed slightly but systematically depending on the range of temperature from which calibration points were chosen. The only time a difference of any consequence resulted so far as the derived temperatures were concerned was for the temperatures above those obtainable with the bath, where no calibration points could be determined. For these it was deemed adequate to extrapolate the Clement-Quinnell formula using constants determined from calibration points made between the lambda-point and the normal boiling point of helium. In this range the resistance was a comparatively slowly varying function of the temperature and seemed to be very well described by the formula over the whole range.

The results reported here are for  $C_v$ , the specific heat at constant volume. The actual measure quantities related to  $C_p$ , the specific heat at constant pressure. The two specific heats are related thermodynamically by

$$C_p - C_v = \beta^2 VT/k,$$

where  $\beta$  is the volume coefficient of thermal expansion and  $k$  is the isothermal compressibility. At sufficiently low temperatures the two are negligibly different. For KI the pertinent calculations were made by Berg and Morrison,<sup>7</sup> and they find that the difference is negligible below 20°K. A similar calculation for LiF was made in this laboratory and the same was found to be true.

Consideration was given to the question of thermal relaxation and thermal equilibrium. What sort of times are involved between the admission of heat at one point in the specimen and the diffusion of this heat throughout the specimen so that a thermometer at another point will read a reliable average temperature? For these salts, although the thermal conductivity is very small, the specific heat by comparison is even smaller. Consequently, the thermal relaxation time, which is determined by the ratio of the specific heat to the thermal conductivity, is very short. Calculations showed that in all cases in this experiment the thermal relaxation time was no more than a fraction of a second. Experimentally this was verified by the fact that the changes in slope between the drift curves and the heating curves always occurred at the time the heater was turned on, so far as could be determined.

#### RESULTS AND CONCLUSIONS

The results of the present investigation are presented in Figs. 3 and 4, where the specific heat as a function of  $T^3$  is shown. The LiF is seen to be linear in  $T^3$  throughout the range of measurements, while the KI veers from the line determined by the lowest temperature values and rises from this line as the temperature is increased. A more sensitive method of plotting is used in Figs. 5 and 6. In these figures the value of  $\theta_D$  from  $C_v = 2(464.3)(T/\theta_D)^3$  is shown as a function of  $T$ . For LiF the values are seen to cluster about a constant value, which may be taken to be the  $T=0^\circ\text{K}$  value

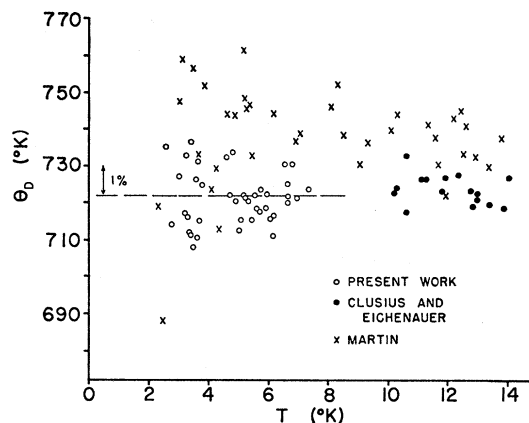


FIG. 5. Debye temperature for LiF versus temperature. The dashed line is the average of the experimental points of the present work.

of  $\theta_D$ . An average of the 42 points along with the average deviation is  $\theta_{\text{LiF}} = 722 \pm 6^\circ\text{K}$ . Also shown in Fig. 5 are the results reported by Clusius and Eichenauer<sup>6</sup> and Martin.<sup>11</sup> Martin's data are seen to be somewhat consistently higher, although there are a number of points in agreement. The work of Clusius and Eichenauer is in a slightly higher temperature range but is in excellent agreement. The present work forms a complementary extension of their work to liquid helium temperatures. Values of  $\theta_D$  reported by Martin and Clusius, respectively, are  $737 \pm 9^\circ\text{K}$  and  $723 \pm 7^\circ\text{K}$ . Briscoe and Squire<sup>1</sup> derive a  $\theta_D$  from low-temperature measurements on the elastic constants of LiF. They report a value of  $\theta_D$ , calculated using DeLaunay's tables,<sup>12</sup> of  $\theta_D = 734 \pm 5^\circ\text{K}$ . This is felt to be in agreement with  $\theta_D$  determined by specific heat measurements.

In Fig. 6 we show our values of  $\theta_D$  for KI along with values reported by Berg and Morrison.<sup>7</sup> The agreement

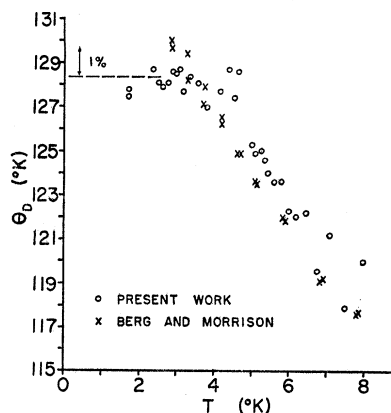


FIG. 6. Debye temperature for KI versus temperature. The dashed line is the average of the experimental points of the present work below 3.5°K.

<sup>11</sup> D. L. Martin, *Phil. Mag.* **46**, 751 (1955).

<sup>12</sup> J. DeLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

is seen to be favorable, but with an important difference in implication. From their data there is no indication that  $\theta_D$  has yet begun to level off toward a constant value. The present work, however, indicates a leveling off in the neighborhood of 3°K with an approach to a value between 128 and 129°K for  $T=0^\circ\text{K}$ . The average of the ten points below 3.5°K gives  $\theta_{\text{KI}}=128.3^\circ\text{K}$ . The value of 3°K is in rough agreement with Blackman's criterion of  $\theta_0/50=2.6^\circ\text{K}$ . Norwood and Briscoe,<sup>2</sup> in a companion paper to this one, describe measurements of the low-temperature elastic constants of KI. Again comparison of the elastic-constant  $\theta$  with specific-heat  $\theta$  may be made. They report two values, depending on the method of calculation. Using DeLaunay's tables,<sup>12</sup> they derive  $\theta_0=131\pm 2$ . Using Houston's method<sup>13</sup> as extended by Betts, Bhatia, and Wyman,<sup>14</sup> they get  $\theta_0=129\pm 2$ . The agreement with either is felt to be good.

In light of a recent paper by Ludwig,<sup>15</sup> the agreement may be even better between the data on elastic constants and the specific heat data. He indicates that because of anharmonic terms in the crystal potential which are normally neglected there will generally be a slight difference between the  $\theta_0$  derived from data on

elastic constants and that derived from specific heat data. For LiF he reports, as for certain other alkali halides, that this should have the effect of making  $\theta$ (elastic constants) a percent or two *higher* than  $\theta$ (specific heat). Barron and Morrison,<sup>16</sup> by another approach, consider the effect of anharmonic terms retained in the frequency distribution functions. They find a slight change in the specific-heat  $\theta$ .

The present work adds confirmation to the not very extensive body of low-temperature data that the Debye  $\theta$ 's derived by elastic means and by thermal means do substantially agree. It is hoped, further, that this work, coupled with the elastic constants experiments, will contribute to the increasing effort being made to evaluate anharmonic terms and their influence on the physical properties of crystals. More work of this nature is needed to test recent extensions of the simple Debye model.

#### ACKNOWLEDGMENTS

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<sup>16</sup> T. H. K. Barron and J. A. Morrison, *Can. J. Phys.* **35**, 799 (1957).

<sup>13</sup> W. V. Houston, *Revs. Modern Phys.* **20**, 161 (1948).

<sup>14</sup> Betts, Bhatia, and Wyman, *Phys. Rev.* **104**, 37 (1957).

<sup>15</sup> W. Ludwig, *J. Phys. Chem. Solids* **4**, 283 (1958).

## Vacancy Pairs in Ionic Crystals

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Equations for the thermal equilibrium concentrations of Schottky vacancies and vacancy pairs are presented; these equations allow for the effects produced by Debye-Hückel screening.

**I**N the study of lattice defects in ionic crystals and semiconductors the concept of "association" between defects bearing opposite effective charges—as borrowed from the theory of electrolyte solutions—has played a useful role.<sup>1-3</sup> In many applications it is good enough to treat the assembly of defects on the assumption that those pairs of oppositely charged defects which are close together are bound into neutral complexes, while defects at large separations move independently with their full effective charge available for interaction with external fields. It is sometimes desirable, however, to refine this picture and in a previous paper the question of the association between impurity ions

and vacancies in ionic conducting crystals has been discussed in higher approximation.<sup>4</sup> The notion of associated pairs is retained but the unassociated defects are described by the Debye-Hückel theory which takes account of the correlated motion caused by the long-range Coulomb interactions among the defects. The same approach can be used to refine the theory of the formation of Schottky and Frenkel defects.<sup>5,6</sup> This topic was reviewed again recently by Theimer<sup>7</sup> who suggests that these previous calculations are incomplete, in that they neglect the effect of the Debye-Hückel screening on the energies of formation of the defects,

<sup>1</sup> J. Teltow, *Halbleiterprobleme* (Friedrich Vieweg und Sohn, Braunschweig, 1956), Vol. 3, p. 26.

<sup>2</sup> Reiss, Fuller, and Morin, *Bell System Tech. J.* **35**, 535 (1956).

<sup>3</sup> A. B. Lidiard, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

<sup>4</sup> A. B. Lidiard, *Phys. Rev.* **94**, 29 (1954).

<sup>5</sup> E. G. Spicar, thesis, Technischen Hochschule Stuttgart, 1956 (unpublished); quoted by A. Seeger, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, p. 401.

<sup>6</sup> T. Kurosawa, *J. Phys. Soc. Japan* **12**, 338 (1957).

<sup>7</sup> O. Theimer, *Phys. Rev.* **109**, 1095 (1958).