

Specific Heat and Elastic Constants of Sodium Iodide at Low Temperatures*

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(Received June 13, 1960)

Measurement of specific heat from 2.4°K to 8°K and of elastic constants from 4.2°K to 300°K have been made on single crystals of sodium iodide. The Debye theta at 0°K, θ_0 , as calculated from the specific heat data is $163 \pm 1^\circ\text{K}$. Values of the elastic constants at 4.2°K are $C_{11}=3.761$, $C_{12}=0.798$, and $C_{44}=0.781$ in units of 10^{11} dynes/cm². θ_0 calculated from the velocity of sound waves is $167 \pm 1.5^\circ\text{K}$. The manner in which the experimental specific heat compares with the work of Berg and Morrison and with the theoretical concepts of Barron and Morrison is discussed.

INTRODUCTION

EXPERIMENTAL results¹⁻⁴ at this laboratory on the elastic constants and specific heats of some alkali halides at low temperatures have stimulated some criticism⁵ concerning interpretation. At the same time the experiments have been of some value to theoretical studies⁶⁻⁸ on lattice vibrations. The simple Debye theory of specific heat would not be expected to be valid for a substance like NaI where a more general lattice theory^{7,8} would predict a frequency distribution of the vibrational modes of greater complexity. Even so, at sufficiently low temperatures the high-frequency oscillators are in their zero-point energy state, and long-wavelength modes of motion contribute to a specific heat of the crystal in a manner which approaches the familiar T^3 law of Debye. The experimental work reported in this paper demonstrates that in NaI a T^3 law does in fact set in with lowering of temperatures, and that the characteristic Debye temperature at 0°K as calculated from the specific heat data is slightly lower than that which one may calculate from the velocity of sound data taken also at very low temperatures. We believe that the arguments of Barron and Morrison⁵ are refuted by these experimental observations.

EXPERIMENTAL

The single crystals of NaI used in these measurements were grown by Harshaw Chemical Company and are of the high purity, optically clear, type supplied by that company. We have sometimes found several parts per million of paramagnetic impurity (such as Fe) in such alkali halides. The specific heat measurements were made in a high-vacuum calorimeter into which no heat exchange gas of He had been admitted. In this way the

common source of error caused by adsorption of helium gas on the sample is eliminated. Details of the calorimeter and techniques have been described in earlier papers.^{3,4} Similarly, we may refer to earlier papers^{1,2} from this laboratory concerning the equipment and techniques for determining the values of the velocity of sound in such single-crystal specimens over the temperature range from 4°K to 300°K. Briefly the technique of pulsed sound waves at 10 megacycles/sec was used and the well-known echo ranging method gave the round trip time through the specimen. Longitudinal and transverse waves were sent along two directions in the crystal so that elastic constants could be calculated.

RESULTS

I. Specific Heat

The measured values of the specific heat, C_p , are listed with their corresponding temperatures in Table I. Figure 1 is a plot of C_p/T^3 versus T . Scatter in the data is due to the low specific heat at low temperatures, and

TABLE I. The specific heat of sodium iodide at low temperatures.

$T^\circ\text{K}$	C_p cal/mole deg	$T^\circ\text{K}$	C_p cal/mole deg
2.321	0.002661	4.483	0.02040
2.387	0.002933	4.728	0.02495
2.462	0.003263	4.752	0.02488
2.538	0.003472	4.958	0.02931
2.643	0.003977	4.980	0.02899
2.721	0.004304	5.149	0.03341
2.806	0.004707	5.181	0.03344
2.890	0.005186	5.318	0.03736
2.979	0.005619	5.466	0.04149
3.054	0.005998	5.581	0.04361
3.059	0.006165	5.585	0.04501
3.103	0.006390	5.707	0.04871
3.137	0.006574	5.738	0.04810
3.152	0.006654	5.819	0.05097
3.202	0.006925	5.910	0.05447
3.211	0.007056	6.390	0.07117
3.274	0.007513	6.678	0.08613
3.304	0.007658	6.834	0.09079
3.343	0.007976	6.980	0.09944
3.358	0.008103	7.114	0.1087
3.439	0.008738	7.246	0.1129
3.477	0.008935	7.396	0.1227
3.650	0.01047	7.584	0.1365
4.061	0.01499	7.752	0.1493
4.142	0.01544	7.909	0.1583
4.441	0.02016		

* Supported in part by a grant from the National Aeronautics and Space Administration, and assisted by the Office of Naval Research.

¹ C. V. Briscoe and C. F. Squire, *Phys. Rev.* **88**, 398 (1957).

² M. H. Norwood and C. V. Briscoe, *Phys. Rev.* **112**, 45 (1958).

³ W. Scales, *Phys. Rev.* **112**, 49 (1958).

⁴ D. R. Huffman and M. H. Norwood, *Phys. Rev.* **117**, 709 (1960).

⁵ T. H. K. Barron and J. A. Morrison, *Phys. Rev.* **115**, 1439 (1959).

⁶ W. Ludwig, *J. Phys. Chem. Solids* **4**, 283 (1958).

⁷ A. M. Karo, *J. Chem. Phys.* **31**, 1489 (1959).

⁸ C. Oliphint, *Phys. Rev.* **115**, 296 (1959).

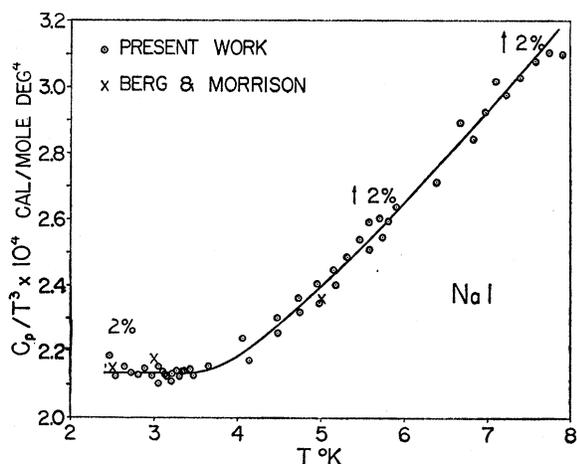


FIG. 1. The specific heat at constant pressure divided by T^3 plotted against the temperature, $T^\circ\text{K}$, for sodium iodide.

to the reduced sensitivity of the carbon resistance thermometer at the higher temperatures. It can easily be seen that below 3.5°K the specific heat follows a Debye T^3 relation to within 2%. The specific heat in the T^3 region has been used to determine the 0°K limit of the Debye theta, θ_0 . The arithmetical average of the 22 data points below 3.5°K gives a value of

$$\theta_0 = 163.2 \pm 1.0^\circ\text{K}.$$

The low-temperature T^3 behavior is in agreement with Blackman's⁹ criterion that the specific heat follows the simple Debye law below $\theta_0/50 = 3.3^\circ\text{K}$.

It will be noted that smoothed values of the specific heat at rounded values of the temperature taken from Table II of Berg and Morrison¹⁰ are included in the plot of Fig. 1. Agreement with the present work is well within the experimental error, but there are important differences in interpretation and method of measurement. In the present work, the salt was suspended in a high vacuum; in that of Berg and Morrison an exchange gas was employed. Further, reference to Fig. 4 of Berg and Morrison, a plot of θ_D versus temperature, does not show a region of true T^3 dependence. This may be attributed to the large scatter in their experimental points ($\pm 3\%$ in θ_D , or $\pm 9\%$ in C_D), and to the fact that the measurements do not extend below 2.8°K . An average of their lowest points, which must be in the T^3

TABLE II. Debye characteristic temperature, θ_0 , at $T \rightarrow 0^\circ\text{K}$ for NaI.

Source	Elastic constants	Specific heat
Berg and Morrison		$164.2 \pm 1.0^\circ\text{K}$
Present work	$167.6 \pm 1.5^\circ\text{K}$	$163.2 \pm 1.0^\circ\text{K}$

⁹ M. Blackman, in *Reports on Progress in Physics* (The Physical Society, London, 1941), Vol. 8, p. 11.

¹⁰ W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1959).

region, would indicate a value of $\theta_0 = 162 \pm 2^\circ\text{K}$, but rather they extrapolate the curve from higher temperatures to give a value of $164.2 \pm 1.0^\circ\text{K}$.

Comparison of θ_0 from the two methods is given in Table II, along with that derived from velocity of sound measurements. Substantially, the θ_0 from the Berg and Morrison data on specific heat is in agreement with the θ_0 from the present specific heat data and both values are smaller than the value of θ_0 from elastic wave velocity data.

II. Elastic Constants

Table III gives the values of the elastic constants which were calculated from the longitudinal and transverse sound wave velocities in the $[1,0,0]$ direction and the longitudinal wave velocity in the $[1,1,0]$ direction. In order that the velocities may be re-obtained the densities are also included in the table. There are data¹¹ available on the density from 300°K to 89°K . These data were extrapolated to 0°K using available specific

TABLE III. Density in g/cm^3 and elastic constants in units of 10^{11} dynes/cm² as a function of temperature ($^\circ\text{K}$) for sodium iodide.

T	ρ	C_{11}	C_{44}	C_{12}
300	3.6689	3.007	0.733	0.912
280	3.6789	3.034	0.739	0.905
260	3.6884	3.078	0.742	0.900
240	3.6969		0.746	
220	3.7050		0.750	
200	3.7124		0.754	
50	3.7595	3.703	0.780	0.809
40	3.7606	3.721	0.781	0.805
30	3.7613	3.738	0.781	0.799
20	3.7619	3.749	0.781	0.799
10	3.7620	3.758	0.781	0.798
4.2	3.7620	3.761	0.781	0.798

heat data¹⁰ and applying the Grüneisen relationship.¹² The linear expansion coefficient was determined as a function of temperature from the densities. The total change in length of the specimen between 300°K and 4.2°K was approximately 0.8%. The change of density was approximately 2.5%. Binder corrections of $0.04 \mu\text{sec}$ for transverse and $0.03 \mu\text{sec}$ for longitudinal waves¹³ were subtracted from the observed delay times. The estimated errors at 4.2°K for C_{11} , C_{12} , and C_{44} were $\pm 0.6\%$, $\pm 7.1\%$, and $\pm 0.3\%$, respectively. The large error in C_{12} is obtained by a propagation of error analysis involving errors in the other elastic constants as well as the travel time.

Dalven and Garland¹⁴ have measured the elastic constants from 300°K to 180°K . Our values agree within experimental error with the values which they obtained

¹¹ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929).

¹² Charles Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1954), p. 154.

¹³ L. J. Slutsky and C. W. Garland, *Phys. Rev.* **107**, 972 (1957).

¹⁴ R. Dalven and C. W. Garland, *J. Chem. Phys.* **30**, 346 (1959).

at 300°K. Therefore, we have concentrated on the temperature range from 50°K to 4.2°K.

The Debye theta (θ_0) at 0°K has been calculated from the elastic wave velocities. Using de Launay's tables,¹⁵ a value of $167.6 \pm 1.5^\circ\text{K}$ was obtained. The Betts, Bhatia, and Wyman method¹⁶ yielded a value of $167.3 \pm 1.5^\circ\text{K}$. The error in the Debye theta was estimated by taking all possible combinations of plus and minus errors of the elastic constants.

DISCUSSION AND CONCLUSIONS

The experimental results and calculated quantities from the elastic wave measurements add useful data on another alkali halide. Löwdin¹⁷ has given a theoretical analysis of the binding energy and elastic constants at very low temperatures of a few alkali halides, but at that time experimental data were meager and inadequate. It is our hope that with such new experimental results these theoretical problems will be re-examined. Once again, we have evidence that the Debye theta evaluated at 0°K from elastic wave velocities is perhaps as much as 1% higher than that computed from the heat capacity studies. These derived results again support an interesting theoretical conclusion by Ludwig⁶ that the inclusion of anharmonic terms would predict such a difference in the two derived Debye thetas, θ_0 .

We turn our attention now to the experimental results on the specific heat of NaI. Figure 1 supports the contention that at temperatures below 3.5°K the so-called T^3 region has been achieved and that a theoretical term involving T^5 would require a very small coefficient. On the high-temperature side of 3.5°K, it is evident that a large number of normal modes of oscillation are being excited out of their zero-point energy state and hence give rise to a rapid increase of the specific heat with temperature. The oversimplified approach of Briscoe

and Squire¹ to an understanding of the frequency versus density of oscillators spectrum does not give theoretical agreement with experiment. This lack of agreement was most unexpected because the ratio of masses and of ionic radii of the Na to the I were anticipated to give an ideal situation wherein the large iodine ions formed the lattice continuum (Debye type term) and the small sodium ions behaved like independent Einstein oscillators with a frequency taken from the infrared absorption maximum. We are thus led to the conclusion that the density of oscillators versus frequency spectrum is probably more complex. Karo⁷ has described the spectrum of NaI wherein the acoustic and optical modes are indeed separated in frequency and the acoustic branch has a considerable density of oscillators in its upper frequency range. In any case, the remarks by Barron and Morrison⁵ on the earlier work from this laboratory are refuted by the present investigation. It would be ill-advised to fit the single power series, $C_v = aT^3 + bT^5 + cT^7$, to the data above 4°K and from such a theory deduce the behavior of C_v below 3°K or to derive a Debye theta, θ_0 , valid for temperatures approaching 0°K. Yet this is the basis for the Barron and Morrison approach to these questions and they consistently ignore experimental low-temperature data³ to the contrary. We do not deny that a power series in temperature does in fact exist for the specific heat and may be valid in substances like KCl or CaF₂ over a range of temperature from 0°K to 10°K. But the possibility does exist that for substances like LiF, KI, and NaI the spectrum of density of oscillators versus frequency permits a T^3 law of specific heat at very low temperatures—e.g., below 3°K for NaI. However, above 3°K the specific heat rapidly departs from a T^3 law.

ACKNOWLEDGMENTS

The authors are indebted to Professor C. F. Squire for many suggestions and discussions during the course of this research. It is a pleasure to acknowledge the considerable assistance of Dr. Marcus H. Norwood on the elastic waves portion of this work.

¹⁵ J. de Launay, *J. Chem. Phys.* **30**, 91 (1959).

¹⁶ D. D. Betts, A. B. Bhatia, and M. Wyman, *Phys. Rev.* **104**, 37 (1956).

¹⁷ Per-Olov Löwdin, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 15, No. 17.