

The Heat Capacity of KCl below 4°K*

P. H. KEESOM AND N. PEARLMAN

Department of Physics, Purdue University, West Lafayette, Indiana

(Received June 10, 1953)

The heat capacity of KCl has been found to be proportional to T^3 below 4°K, with a Debye θ of 233°K. This agrees with values calculated from elastic constants and also from the vibration spectrum.

I. INTRODUCTION

THE heat capacity of KCl at liquid helium temperatures was first measured by Keesom and Clark¹ shortly after linear terms were found in the low-temperature atomic heats of silver and zinc.² Since these linear terms were attributed to the heat capacity of the degenerate electron gas in metals,³ it was expected that such a term would be absent in the insulator KCl, and this expectation was borne out. Keesom and Clark¹ made their measurements with powdered KCl in a calorimeter which also contained a small amount of He gas for heat exchange. As a result they found it difficult, at their lowest temperatures (about 2°K), to separate the heat capacity of the KCl from the desorption heat of that part of the exchange gas which had been adsorbed on the powder. In par-

ticular, it was impossible to ascertain if the heat capacity of the KCl was proportional to T^3 .

Blackman and others have shown⁴ that independently of crystal structure, the lattice contribution to heat capacity should be proportional to T^3 for T less than $\theta/50$ or $\theta/100$, where θ is the Debye temperature at very low temperatures. Since θ is about 230°K for KCl,¹ this "true T^3 region" should be found at liquid helium temperatures. Despite the fact that Keesom and Clark themselves pointed out the limited accuracy of their results, various authors⁵ have since concluded from these data that the low-temperature heat capacity of KCl shows no T^3 dependence, even at the lowest temperatures.

We have also experienced difficulty due to adsorption in measurements on crushed germanium.⁶ Since our results on ingots of germanium were much more reliable, we considered it worth while to remeasure the heat capacity of KCl at liquid helium temperatures using a large single crystal, as had already been suggested by Keesom and Clark.¹ As they pointed out, this would be feasible if the thermal conductivity, k , is high enough at low temperatures. Measurements by De Haas and Biermasz⁷ show that the thermal conductivity of KCl decreases from about 2 watt (cm degree)⁻¹ at 4°K to 0.6 at 2°K. This is considerably larger than the thermal conductivity of germanium in the same temperature range.⁸ When the larger specific heat c , and smaller density, ρ , of KCl compared to Ge are also taken into account, the thermal diffusivity $k/\rho c$, on which the rate of approach to thermal equilibrium depends, is seen to be somewhat larger for KCl than for Ge at liquid helium temperatures. Since we experienced no difficulty from this source in our measurements on Ge, we anticipated that KCl would also be suitable for this type of measurement.

II. EXPERIMENT

A single crystal of KCl, diameter 37 mm, length 88 mm, weight 189 g, was procured from the Harshaw

TABLE I. Data for heat capacity of KCl.

Point	T (°K)	ΔT (°K)	C_v
			millijoules half-mole °K
February 4, 1953			
1	4.231	3.106×10^{-2}	11.52
2	4.230	3.106	11.52
3	3.912	3.912	9.142
4	3.929	3.858	9.270
5	3.567	2.404	7.093
6	3.567	2.394	7.123
7	3.312	3.096	5.507
8	3.316	2.987	5.709
9	2.924	4.419	3.856
10	2.925	4.419	3.856
March 9, 1953			
1	1.466	3.107×10^{-2}	0.4678
2	1.434	3.480	0.4277
3	1.441	3.553	0.4253
4	1.656	4.379	0.6903
5	1.667	4.422	0.6855
6	1.670	4.415	0.6861
7	1.985	3.823	1.221
9	2.012	3.721	1.259
10	2.324	3.957	2.006
11	2.322	4.105	1.935
12	2.335	4.015	1.962
13	4.247	1.333	12.07
14	4.293	2.883	12.02

* This work was supported by the Signal Corps Contract.

¹ W. H. Keesom and C. W. Clark, *Commun. Kamerlingh Onnes Lab., Leiden, No. 238c; Physica 2, 698 (1935)*.

² W. H. Keesom and J. A. Kok, *Commun. Kamerlingh Onnes Lab., Leiden, No. 232d; Physica 1, 770 (1933-34)*.

³ A. Sommerfeld, *Z. Physik 47, 1 (1928)*.

⁴ M. Blackman, *Repts. Progr. Phys. 8, 11 (1941)*.

⁵ See, e.g., F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 114; R. B. Leighton, *Revs. Modern Phys. 20, 165 (1948)*.

⁶ P. H. Keesom and N. Pearlman, *Phys. Rev. 91, 1347 (1953)*.

⁷ W. J. De Haas and Th. Biermasz, *Commun. Kamerlingh Onnes Lab., Leiden, No. 249a; Physica 4, 752 (1937)*.

⁸ I. Estermann and J. E. Zimmerman, *Technical Report No. 6, Department of Physics, Carnegie Institute of Technology, June 1951 (unpublished)*.

Chemical Company. Constantan heater wire and phosphor-bronze thermometer wire were secured to the crystal with Glyptal lacquer. No correction was necessary for the heat capacity of the wires and the lacquer. The crystal was hung with Nylon thread in a vacuum can, and the measurements were carried out in the manner described earlier.⁹

III. RESULTS

The results of our measurements are collected in Table I. These data are plotted in the form C_v/T versus T^2 in Fig. 1, where C_v is the heat capacity of one-half mole of KCl. The method of least squares applied to the data gives for the equation of the line in Fig. 1

$$C_v/T = (15.37 \pm 0.09) \times 10^{-5} T^2 - (0.37 \pm 0.39) 10^{-5} \\ \times \text{joules/mole degree}^2. \quad (1)$$

The coefficient of the quadratic term corresponds to a value for θ of $(233 \pm 3)^\circ\text{K}$, and it is evident that there is no other significant contribution to the heat capacity. The results of Keesom and Clark¹ are also plotted in Fig. 1 for comparison.

IV. DISCUSSION

It appears from Fig. 1 that the data of Keesom and Clark¹ agree well with ours above about 3.6°K. They found larger values of the molar heat at lower temperatures, which would be expected if, as they suspected, some of their helium exchange gas was being desorbed from their KCl powder during the heating periods. This effect would not be noticeable in the case of our single crystal of KCl.

The excellent agreement of our data with the calcu-

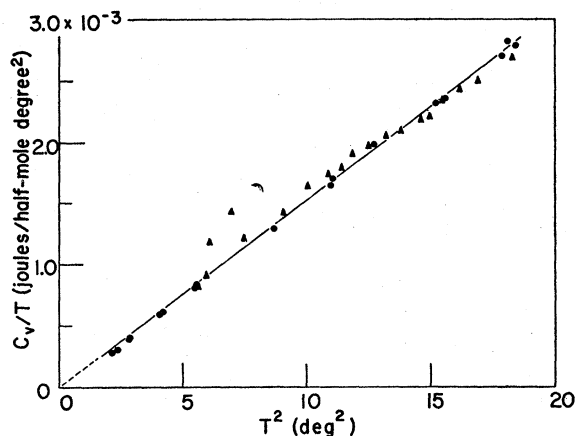


FIG. 1. C_v/T vs T^2 for KCl. ●—Our results. ▲—Keesom and Clark.

lated straight line drawn in Fig. 1 leads us to the conclusion that below about 4°K (about $\theta/50$), the molar heat is proportional to T^3 , as predicted by Blackman.⁴ The reported deviations from this relation⁵ would appear to be nonexistent. They apparently were based on attributing higher accuracy to the original measurements of Keesom and Clark¹ than the authors themselves claimed. Our value of θ , 233°K, agrees fairly well with that of Durand,¹⁰ 246°K, calculated from his estimates of the elastic constants at 0°K, based on measurements down to liquid nitrogen temperatures, and also with Iona's value, 230°K, found from his calculation of the elastic frequency spectrum.¹¹

We would like to express our appreciation of the support of Dr. K. Lark-Horovitz, who suggested the problem and provided valuable guidance in its execution.

⁹ N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).

¹⁰ M. Durand, Phys. Rev. **50**, 449 (1936).

¹¹ M. Iona, Phys. Rev. **60**, 822 (1941).