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Specific Heat and Elastic Constants of Calcium Fluoride at Low Temperatures*

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Measurements of specific heat from 3.5°K and of elastic constants from 4°K to 300°K have been made on single crystals of calcium fluoride. The Debye theta at 0°K, θ_0, as calculated from the specific heat data is 508±5°K. Values of the elastic constants at 4.2°K are $c_{11}=17.4$, $c_{12}=5.6$, and $c_{44}=3.593$ in units of 10^{11} dynes/cm². θ_0 calculated from elastic constants is 513.6±2.5°K. The two θ_0's are now in good agreement and are significantly greater than the value calculated from previous specific heat work.

INTRODUCTION

At this laboratory in recent years measurements have been made on elastic constants and specific heats of some alkali halides at low temperatures.[1–3] The simple cubic structure of these alkali halides appeared to make them the most suitable for comparison of measured properties with predictions of lattice theory. In the present work we have begun a study of single crystals with a structure slightly different from the alkali halides by measuring specific heats and elastic constants of CaF_2 at low temperatures. At sufficiently low temperatures the temperature dependence of the specific heat is given by the familiar T^3 law,[4]

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

where C_v is the specific heat at constant volume and θ_0, the Debye characteristic temperature, is a constant characteristic of the substance. The factor three in the above expression is because there are $3N$ atoms per mole in CaF_2.

The specific heat measurements and the elastic constant measurements complement one another as a comparison can be made between the values of θ_0 obtained from the low-temperature specific heat measurements and the θ_0 calculated from elastic constant measurements near the absolute zero. The only previous determination of θ_0 from elastic constants appears to have been derived from an extrapolation of room temperature measurements to give $\theta_0=510$.[5] Specific heat measurements made in 1913[6] in the temperature range from 17.5°K to 80°K seemed to show a T^3 law for the specific heat at temperatures below 40°K. This apparently gave confirmation to the newly published Debye theory[4] and indicated that the Debye theta, θ_D, had a constant value of approximately 474°K as indicated in Fig. 1. Thus as the present work began a difference of 36°K existed in the θ_0 values determined by the two methods. In an effort to see if the observed T^3 law extended to 0°K and to investigate the difference in θ_0's, the present measurements were made and the θ values computed from the data.

EXPERIMENTAL

All specimens used for these measurements were single crystals of CaF_2 grown from the melt by Harshaw Chemical Company. Specific heat measurements were made on a cylindrical specimen about three inches long and one inch in diameter, weighing about 123 grams. The experimental techniques used by us have been described in an earlier paper.[3] The specific heat values were corrected for the Glyptal lacquer used on the sample and for heat produced in the electrical leads as described by Scales.[3] The combined effect of these two corrections produced a 0.1% change in the measured specific heats at the lowest temperatures and a 0.6% change at the highest temperatures. Although the Glyptal correction is about 0.5% at the lower temperatures this is almost canceled by the opposite effect produced by heating in the leads.

The experimental values of the velocity of sound in CaF_2 were obtained in the same way as reported in this journal by Norwood and Briscoe.[2] The use of solid natural gas (mostly CH_4) as a binder between the quartz transducer and the specimen made possible accurate time measurements at 4°K on the pulsed

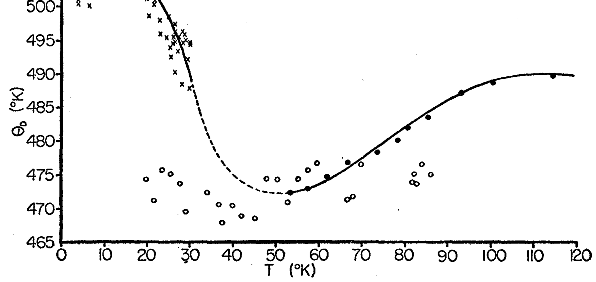

Fig. 1. Debye temperature for CaF_2 *versus* temperature. The solid line from 0°K to 30°K is a least squares fit to the expression $\theta=A+BT^2+CT^3$.

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[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] P. Debye, Ann. Physik **39**, 789 (1912).

[5] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 48.

[6] A. Eucken and F. Schwers, Verhandl. deut. physik Ges. **15**, 578 (1913).

ultrasonic waves. The echoes at these very low temperatures are sharp and no specimen has ever been damaged using this binder. The elastic constants are computed from the velocity of sound values and from the density of the crystal at each temperature by well-known relationships.

RESULTS

Specific Heat

The measured values of the specific heat, C_p, and the derived quantities θ_D with their corresponding temperatures taken from four separate runs are tabulated in Table I. Figure 1 displays the θ_D values as a function of temperature from the present work, along with the θ_D values derived from the work of Eucken and Schwers[6] and the higher temperature work of Todd.[7] There is a disagreement of from 4% to 5% in the θ_D values between the present work and the 1913 values. The work of Todd, however, can be smoothly joined to the present work by the dashed curve of Fig. 1. The solid line between 0°K and 30°K is a least squares fit of the θ_D values to the expression

$$\theta = A + BT^2 + CT^4.$$

The root mean square deviation from the smoothed curves is 3°K which is taken to be a measure of the random error in the θ_D values. Possible systematic errors are more difficult to assess. As no helium exchange gas is admitted into the calorimeter until all data have been taken, the common source of error in the helium temperature range caused by adsorption of helium gas on the sample is eliminated. We estimate the over-all possible error as 5°K and report the θ_0 determined from specific heat measurements to be

$$\theta_0 = 508 \pm 5\text{°K}.$$

TABLE I. Measured specific heat values for CaF_2 with calculated values of θ_D. Between 3–8°K the specific heat is in units of 10^{-3} cal/mole °K. Between 14–30°K the units are just cal/mole °K.

T	C_p	θ_0	T	C_p	θ_0	T	C_p	θ_0
3.617	0.513	505	14.59	0.0333	507	21.81	0.1144	502
3.666	0.545	501	14.81	0.0343	509	22.90	0.1357	498
3.707	0.560	502	15.01	0.0371	503	23.10	0.1408	496
3.735	0.561	505	15.28	0.0390	503	24.49	0.1683	495
3.762	0.566	508	15.61	0.0411	505	24.95	0.1746	499
3.764	0.585	509	15.91	0.0438	504	25.33	0.1879	494
3.785	0.603	500	16.07	0.0439	509	25.47	0.1925	493
3.789	0.576	512	16.93	0.0513	509	25.99	0.2020	495
3.814	0.581	511	17.20	0.0542	508	26.13	0.2039	496
3.920	0.651	505	17.40	0.0555	510	26.25	0.2079	495
4.050	0.717	505	17.56	0.0576	508	26.38	0.2168	490
4.167	0.765	509	17.81	0.0603	507	26.52	0.2108	497
4.278	0.835	507	17.86	0.0603	509	26.66	0.2156	496
4.376	0.907	505	18.17	0.0643	507	27.02	0.2287	493
4.581	1.026	507	18.19	0.0635	509	27.26	0.2319	496
4.771	1.144	510	18.53	0.0681	507	28.01	0.2502	496
4.874	1.239	507	18.63	0.0694	506	28.11	0.2652	489
5.005	1.325	509	18.92	0.0732	505	28.22	0.2585	495
5.035	1.359	508	19.39	0.0776	508	28.78	0.2724	496
5.127	1.486	502	19.69	0.0825	505	28.95	0.2783	495
5.180	1.501	505	19.96	0.0878	501	29.37	0.2957	492
5.386	1.668	508	20.19	0.0911	501	29.59	0.2978	495
5.485	1.696	514	20.40	0.0952	499	29.83	0.3179	488
5.575	1.807	511	20.58	0.0961	502	30.08	0.3135	495
5.855	2.104	510	21.09	0.1026	503			
6.351	2.730	508	21.30	0.1051	504			
6.465	2.804	512	21.35	0.1075	501			
7.590	4.693	507	21.56	0.1114	500			
8.171	5.766	509	21.61	0.1119	501			

Another method of deriving θ_0 from the data is shown in Fig. 2 as C_v/T^3 is plotted against T^2. From the general temperature expansion of the specific heat

$$C_v = aT^3 + bT^5 + cT^7 + \cdots,$$

it is seen that the intercept at $T^2 = 0$ will be a number which is proportional to θ_0^{-3}. This method of displaying the data shows clearly the scatter of the experimental points. At the lowest temperatures the scatter arises largely because of the small value of the specific heat, whereas the high-temperature scatter results primarily from decreased sensitivity of the carbon resistance thermometer. The solid curve in Fig. 2 is a least squares analysis which gives a value of "a" $= 1.068 \times 10^{-5}$ cal/mole deg^4, "b" $= 7 \times 10^{-11}$ cal/mole deg^6, and "c" $= 1 \times 10^{-12}$ cal/mole deg^8, with a standard deviation for all points calculated as 2.0×10^{-7} cal/mole deg^4. This value of "a" gives $\theta_0 = 507.2$, which is in good agreement with the value from Fig. 1.

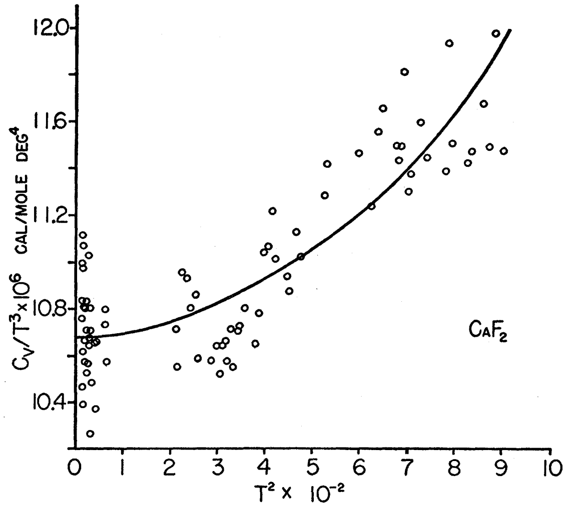

FIG. 2. A graph of C_v/T^3 *versus* T^2 for CaF_2. The solid line is a least squares fit to the expression $C_v/T^3 = a + bT^2 + cT^4$.

Elastic Constants

Table II shows 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 velocity in [1,1,0] direction. The densities used are listed also in order that the velocities

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[7] S. Todd, J. Am. Chem. Soc. **71**, 4115 (1949).

may be reobtained if desired. These densities were calculated from available data on the thermal expansion of calcium fluoride.[8,9] These data were extrapolated to 0°K by using previous low-temperature specific heat data[6] and applying the Gruneisen relationship.[10] The total change in length of the specimen between room temperature and 4°K is about $\frac{1}{3}\%$ and the change in density is about 1%. With these corrections it is felt that the error in the elastic constants is due almost entirely to the error in the time of travel. The estimated errors at 4°K for c_{11}, c_{12}, and c_{44} were $\pm 0.8\%$, $\pm 4\%$, and $\pm 0.2\%$. The large error in c_{12} is obtained by a propagation of error analysis involving errors in the other constants since the value of c_{12} involves a difference between quantities of about the same size. For this reason it is difficult to say whether the slight variation of c_{12} can be taken seriously in regard to maxima and minima. There were no maxima or minima in the velocity function.

TABLE II. Density in g/cm^3 and elastic constants in units of 10^{11} dyne/cm^2 as a function of temperature (°K).

T	ρ	c_{11}	c_{44}	c_{12}
300	3.1795	16.4	3.370	5.3
280	3.1830	16.4	3.390	5.4
260	3.1864	16.4	3.409	5.7
240	3.1898	16.5	3.429	5.6
220	3.1931	16.5	3.449	5.6
200	3.1962	16.6	3.465	5.7
180	3.1991	16.7	3.487	5.5
160	3.2017	16.8	3.506	5.4
140	3.2042	16.9	3.518	5.5
120	3.2063	17.0	3.533	5.3
100	3.2081	17.1	3.548	5.4
80	3.2094	17.2	3.562	5.3
60	3.2102	17.3	3.576	5.3
40	3.2106	17.3	3.586	5.5
20	3.2107	17.4	3.593	5.4
4.2	3.2107	17.4	3.593	5.6

Table III shows a comparison of the room temperature values with the ones shown in the references.[11–13]

One difference can be pointed out between the CaF_2 crystal and the face-centered cubic crystals of the alkali halides which we have studied in this laboratory.[1,2] For the alkali halides the constants $C_{12}=C_{44}$ at about $T=\theta_0$; for CaF_2 it appears that these constants would not be equal at $T=\theta_0$.

The Debye theta at 0°K (θ_0) has been calculated from the elastic constants. Using de Launey's tables,[14] a value of 513.6°K is obtained. The method of Bett's, Bhatia, and Wyman yields a value of 514.0°K. In order to estimate an error in θ_0 due to errors in the elastic constants, the latter method was used since a computing program for this already existed. All combinations of errors in the three constants were tried in the computation and the extreme values of θ_0 were 2.5°K above and below the value of 514.0°K. If it is assumed that the numerical method of de Launey is slightly more accurate and that the error due to errors in the constants are about the same in either case, then the best estimate of θ_0 from the elastic constants would be 513.6±2.5°K.

TABLE III. Comparison of elastic constant values at room temperature (units of 10^{11} dyne/cm^2).

	c_{11}	c_{12}	c_{44}
Present work	16.4	5.3	3.370
Values-Lehrbuch der Kristallphysik	16.4	4.47	3.38
Bhagavantam	16.44	5.02	3.47
Srinivasan (Theoretical)	16.8	4.8	4.0

DISCUSSION AND CONCLUSIONS

It is now evident that the T^3 law for specific heats resulting in a constant Debye theta is obeyed to an accuracy of 1% only below 15°K for CaF_2. This more nearly corresponds to the rough limit for the T^3 region observed in the alkali halides than did the former value $T=\theta_0/12$ indicated by earlier measurements on CaF_2. The former difference of 36°K between the θ_0 values determined by the two methods has now been resolved by the agreement within the estimated possible error of the two values

$$\theta_0(\text{elastic constants}) = 513.6\pm 2.5°\text{K},$$
$$\theta_0(\text{specific heat}) = 508\pm 5°\text{K}.$$

Although there is agreement within the combined error, the value derived from specific heat measurements is about 1% below the value derived from elastic constant measurements. This difference bears a noticeable resemblance to such a difference observed in measurements on LiF where the specific heat measurements[3] also yielded a slightly lower θ_0. This trend may be evidence of a general, small difference between θ_0 values determined by the two methods having a possible theoretical explanation.[15]

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