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Heat capacities of ZnS, ZnSe and CdTe below 25 K

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Abstract. Heat capacities have been measured from 2 to 12 K for ZnS and up to 25 K for ZnSe and CdTe. Limiting values of the Debye temperature are $\theta_{\omega} = 339$ K for ZnS, 271 K for ZnSe and 161 K for CdTe which agree, within experimental error, with those calculated from elastic moduli.

1. Introduction

Linear thermal expansion coefficients α have been measured in this laboratory for a number of diamond-structure solids (Smith and White 1975) to investigate further the temperature dependence of the Grüneisen parameter γ . This parameter, defined by

$$\gamma = 3\alpha V B_{\rm s}/C_{\rm p},$$

where C_p is the heat capacity at constant pressure, B_s is the adiabatic bulk modulus and V is the molar volume, is negative over part of the low-temperature range for these solids (Carr *et al* 1965, Sparks and Swenson 1967) and appears to have a minimum value in the vicinity of $T \simeq \theta_0/15$, where θ_0 is the limiting value of the Debye characteristic temperature θ_p determined from measurements of C_p .

In the case of ZnS, ZnSe and CdTe, the published heat capacity data were insufficient for calculating values of γ and θ_0 so measurements were made from 2 K to 25 K and are reported in this paper. Some previous measurements are discussed below along with the present results.

2. Experimental details

Heat capacity measurements were carried out over the temperature range 2–25 K in the cryostat shown schematically in figure 1. The sample (C) was suspended in the vacuum space (D) by nylon threads (G) from the end of the push rod (H). A 4500 Ω manganin heater (E) and a germanium thermometer (F) were mounted in a MgO cylinder glued to the top of the sample.

The outer can (N) was immersed in liquid helium and the intermediate shield (J) cooled to 1.4 K by admitting liquid helium into the pumping chamber (L).

The inner shield (B) was cooled using the condensation pot (I). The sample was then

cooled by lowering it to press against the gold-plated copper bottom of the inner shield (B). When the sample temperature was below 2 K, the sample was isolated by raising it and allowing it to hang freely, suspended by the nylon threads. The heat leak did not exceed 1 erg s^{-1} .



Figure 1. Schematic diagram of cryostat.

Heat capacity measurements were carried out in the usual way by following the natural warm-up of the specimen on a chart recorder to determine the drift rate. Known heat inputs were then applied and a further drift rate determined. Heat inputs were adjusted to cause changes of 3% in the absolute temperature of the sample.

Energy for the heater circuit was provided by a constant current supply with a shortterm stability of better than 1 part in 10⁴. The supply was short-circuited by a reed relay contact which could be opened for a pre-set time. The time interval was controlled by a simple crystal oscillator stable to two parts per million followed by standard TTL circuits. A similar current supply was used for the germanium thermometer.

The temperature of the inner shield (B) was monitored by the germanium thermometer (O) and adjusted to the temperature of the sample by the heater (P) before each measurement.

The germanium thermometer (F) attached to the sample was calibrated by the thermometry section of the National Measurement Laboratory over the range 1.7-30 K against the $T_{x, 68}$ magnetic scale of Cetas and Swenson (1972). The calibration was fitted by a least-squares polynomial of degree 13 of the form

$$\log T = \sum_{n=0}^{13} C_n (\log R)^n.$$

The RMS error of calibration was 0.62 mK.

The heat capacity of the addenda (heater, thermometer and MgO cylinder) was measured independently with an uncertainty of $\pm 3\%$. The relative size of addenda heat

capacity was greatest at the lowest temperatures; for CdTe and ZnS samples, the addenda heat capacity was 15% and for ZnSe 30% of that of the sample.

3. Samples

The ZnS sample, mass 58 g, was a fine-grained polycrystalline block of Kodak Irtran 2 which the manufacturers state has a phase composition of approximately 95% sphalerite and 5% wurtzite. The ZnS and CdTe samples from Metals Research Ltd had masses of 23.3 g and 21.85 g, respectively.

4. Experimental results

The measured values of heat capacity are listed in table 1 and the values of the Debye temperatures θ_D calculated from these results are shown in figure 2 as a function of temperature.

T (K)	C,	T (K)	C _n	T (K)	C _n
CdTe		ZnS		ZnSe	
1.748	5.43	2.452	1.459	2.782	4.34
2.111	9.81	2.837	2.303	2.997	5.45
2.439	15.30	3.836	5.57	3.605	9.60
2.961	29.15	4.310	7.92	3.790	11.34
3.104	34.7	5.139	13.50	4.218	15.61
4.042	84.2	5.687	18.43	5.479	35.13
4.347	111.1	6.001	21.76	5.985	46.90
4.926	187.0	6.533	28.93	6.493	61.46
5.916	401	7.148	37.46	8.748	185.6
6.984	797	7.586	46.92	10.04	315.4
7.632	1077	8.047	57.09	12.44	724.3
8.272	1431	9.041	83.87	14.95	1421
9.098	1960	9.22	89.6	18.26	2635
10.14	2670	9.42	100.9	20.00	3360
11.10	3460	9.86	120.0	21.73	4090
12.49	4570	10.36	139.4	23.15	4745
14.22	5900	11.44	203.3	24.49	5420
15.33	6600				
16.45	7540				
18.82	9170				
20.66	10 300				
22.27	11140				
24.82	12460				

Table 1. Observed values of heat capacity, C_p . Units are mJ mol⁻¹ K⁻¹.

The limiting value, $\theta_0 = 339 \pm 2$ K, for pure ZnS extrapolated from C_p values is in good agreement with the value of 334 ± 6 K calculated from elastic constants measured by Vekilov and Rusakov (1971).

The heat capacity of ZnS has previously been measured by Martin (1955) over the range 2 K to 30 K. Below 20 K, the value of θ_D calculated by Martin rises to a maximum value of 315 K at 8 K. Martin's sample was a natural crystal of ZnS from Santander, N Spain. Measurements of C_p (and α) were made in this laboratory (Sheard *et al* 1975) on a similar crystal from Santander, which we believe to contain approximately 0.1% Fe (G A Slack private communication, Slack *et al* 1966) and results were in reasonable agreement with those of Martin. The discrepancy with the pure ZnS is attributed to the iron impurities in the natural crystal.



Figure 2. Debye temperature, θ_D , as a function of temperature, *T*, for ZnS, ZnSe and CdTe. Values of the Debye temperature calculated from elastic moduli are indicated by θ_{el} . The experimental points \bigcirc in all three sets of curves are from this work. For ZnS, the points \times are taken from Martin (1955) and the broken curve from Sheard *et al* (1975). For ZnSe, the points \times and \triangle are both taken from Irwin and LaCombe (1974), the \times being experimental and the \triangle calculated using the SNI model.

The limiting value θ_0 of 271 \pm 2 K for ZnSe is in reasonable agreement with the value 275 \pm 2 K calculated by Collins (1974 private communication) from the elastic moduli measured by Lee (1970).

The heat capacity of ZnSe has previously been measured by Irwin and La Combe (1974) over the temperature range 20 K to 140 K. The present results give a value for C_p that is 25% smaller at 20 K. This discrepancy, which is well outside the experimental accuracies, could have resulted from the smallness of Irwin and La Combe's sample, only 1.659 g, or from uncertainties in their thermometry at the lowest temperatures. The present results give very good agreement in the temperature range 15 K to 25 K with the values of θ_D calculated by Irwin and La Combe (1974) using a second-neighbour ionic (SNI) model.

The value of $\theta_0 = 160 \pm 2$ K for CdTe, from C_p values, agrees well with the value of 164 ± 5 K calculated from elastic constants by Vekilov and Rusakov (1971).

The heat capacity of CdTe has previously been measured by Rusakov *et al* (1971) over the temperature range 3 K to 4.5 K and 10 K to 300 K. However, the presentation

of their results for C_p and θ_D on a small graph does not allow the low-temperature values to be extracted with sufficient accuracy to make a meaningful comparison with the present measurements.

5. Conclusions

Experimental values of the heat capacity of tetrahedrally-bonded solids have been previously reported and discussed in detail; for example, for silicon and germanium by Flubacher *et al* (1959) and for III-V compounds by Cetas *et al* (1968). Present materials behave in a similar fashion to those measured earlier: $\theta_{\rm D}$ reaches a minimum at about $\theta_0/15$, and $\theta_{\rm min}/\theta_0$ is between 0.7 and 0.8. Limiting values of θ_0 from $C_{\rm p}$ agree with experimental error with those calculated from elastic data.

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