The elastic constants and thermal expansion of single-crystal CdTe

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Abstract. The elastic constants and thermal expansion of single-crystal CdTe have been measured in the temperature range 4·2–300 K. The values of elastic constants obtained at 298 K were $C_{11} = 5·38 \times 10^{10}$ N m^{-2}, $C_{12} = 3·74 \times 10^{10}$ N m^{-2} and $C_{44} = 2·018 \times 10^{10}$ N m^{-2}. Their temperature variation is in good agreement with Vekilov and Rusakov's (1971) values and the temperature dependence of the thermal expansion is similar to the other measurements in the literature. An anomaly in both parameters is observed, which has hitherto not been reported, and is tentatively attributed to a change in ionicity. The Debye temperature at 0 K is calculated from the elastic constants and a value of 162·7 K obtained.

1. Introduction

The single-crystal elastic constants and thermal expansion of the II–VI compounds, and their temperature dependence have been extensively investigated recently. In particular there have been three separate measurements of the elastic constants of single-crystal CdTe, which has a cubic zinc-blende structure, and hence three independent elastic constants C_{11}, C_{44} and C_{12}. McSkimin and Thomas (1962) reported some very precise measurements at room temperature, using an ultrasonic pulse-echo phase-comparison technique, while Berlincourt *et al* (1963) measured the elastic constants at 77 K with an ultrasonic resonance method. These separate measurements were largely incompatable in that they predicted a very large negative temperature dependence for C_{11} and C_{12} and a small positive temperature dependence for C_{44}, the latter conflicting with all other results on II–VI compounds. Recent work by Vekilov and Rusakov (1971) between 77 and 300 K is in reasonable agreement with McSkimin and Thomas's results at room temperature, and their elastic constants have a small linear negative temperature dependence down to 120 K.

The thermal expansion of polycrystalline CdTe has been measured by Novikova (1961) and Browder and Ballard (1969) in the temperature range 20–360 K. The temperature dependence of the linear expansion coefficient is well behaved except that it changes sign at 71·5 K (Novikova) and 60 K (Browder and Ballard).

In this paper we present further measurements of the single-crystal elastic constants of CdTe in the temperature range 4·2–300 K and the first measurements of the thermal expansion of CdTe single crystals. Small anomalies in the elastic constants are found at 79 K where there is a marked anomaly in the thermal expansion coefficient measured along a [100] direction.

2. Experimental details

The CdTe single crystals were grown in the Physics Department here using a modified Bridgman technique and were in the form of plates whose large faces were (110) planes. The orientation of all specimens were checked by Laue x-ray techniques, and these showed no signs of strain or twinning. Analysis has shown that the maximum possible deviation from equiatomic composition is about 0·01 %. For the elastic constant measurements the (110) faces were lapped flat and parallel to better than 0·5 μm.

The elastic constants were measured using a standard ultrasonic pulse-echo method with pulse duration of 0·5 μs at a frequency of 15 MHz. Various bonding materials were used including oil, polystyrene fluid 276-V9 and Armstrong epoxy resins with little change in the measured velocity of sound. Propagation of longitudinal and shear waves down the [110] direction yields combinations of the three elastic constants

$$v_{long} = \left(\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}\right)^{1/2}$$

$$v_{1\,shear} = \left(\frac{C_{44}}{\rho}\right)^{1/2}$$

$$v_{2\,shear} = \left(\frac{C_{11} - C_{12}}{\rho}\right)^{1/2}$$

where for v_1 the shear vibration is parallel to [001] and for v_2 the vibration is parallel to [1$\bar{1}$0]. In calculating the elastic constants an x-ray density of $5·854 \times 10^3$ kg m^{-3} at 298 K was used and its variation with temperature calculated from the available thermal expansion data. This correction was also applied to the measured specimen dimensions. The absolute error in the elastic constants is estimated to be $\pm 0·3$ % with relative errors of 0·05 %, although no corrections have been made for bond effects.

A strain-gauge technique was used to measure the linear coefficient of thermal expansion, α, comparing the expansion of the sample with that of quartz (Spectrosil B). Values of the fractional change in resistance of the strain gauge were taken at 0·3 K intervals, maintaining the temperature steady to $\pm 0·01$ K at each reading. Mean values of the linear expansion coefficient were computed for every five consecutive readings. This led to a slight loss of detail in the variation of the expansion coefficient with temperature but reduced relative errors in α to about 3 %.

Temperatures in both experiments were measured with a gold $+0·03$ % iron–chromel thermocouple, which had been previously calibrated against a platinum resistance thermometer and had an absolute accuracy of $\pm 0·25$ K. A computed least-squares curve fit enabled temperature intervals to be measured to $\pm 0·02$ K.

3. Results

The measured elastic constants are depicted in figures 1–3 and the room temperature values of C_{11}, C_{44} and C_{12} calculated from them are compared to those of other workers in table 1. The constants vary in the normal manner with temperature and the temperature gradients are very much in agreement with Vekilov's. However, a small anomaly was noted in all the measurements at 79 K. An accurate measurement of this anomaly proved to be difficult due to bond problems in this temperature range. The inset in the graph of

C_{44} against T shows evidence for the anomaly and the other two elastic constants have small discontinuities at the same temperature. No anomaly could be discerned in the ultrasonic attenuation but due to bond effects the accuracy of the measurement was not high.
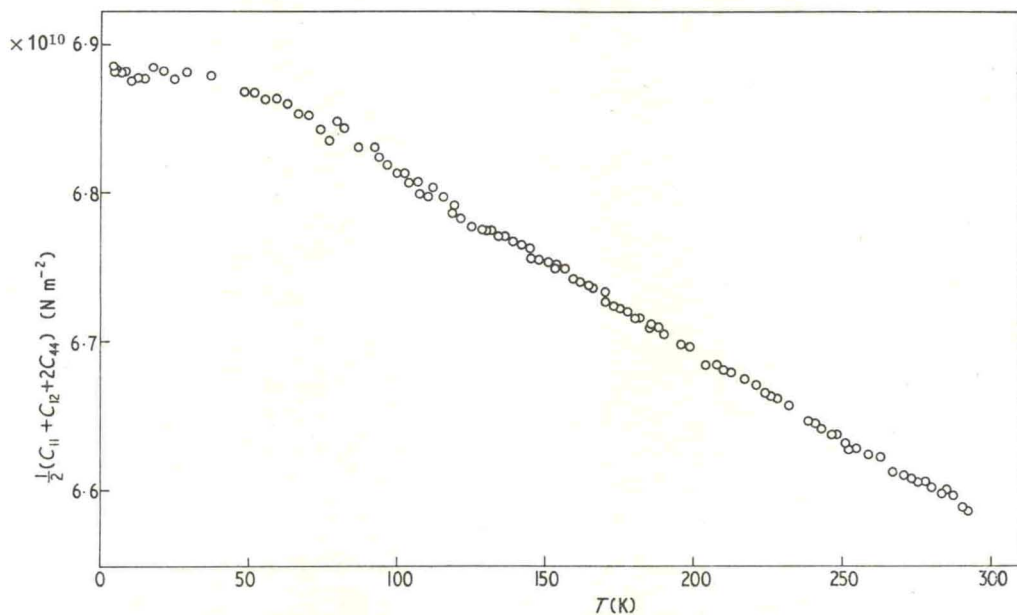

Figure 1. Variation of $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ with temperature.
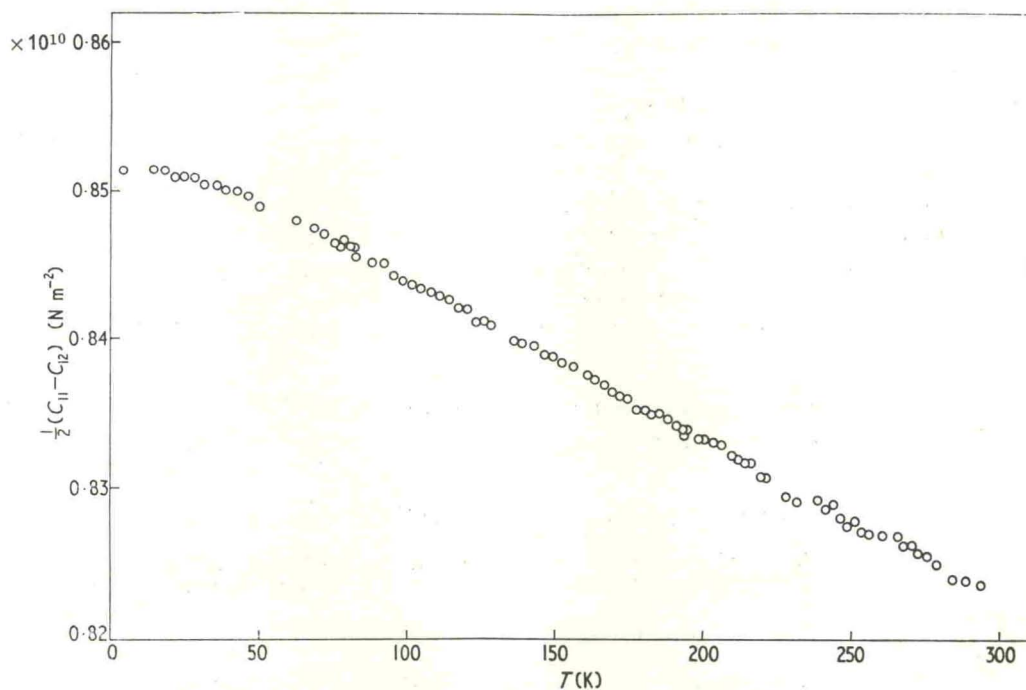

Figure 2. Variation of $\frac{1}{2}(C_{11} - C_{12})$ with temperature.
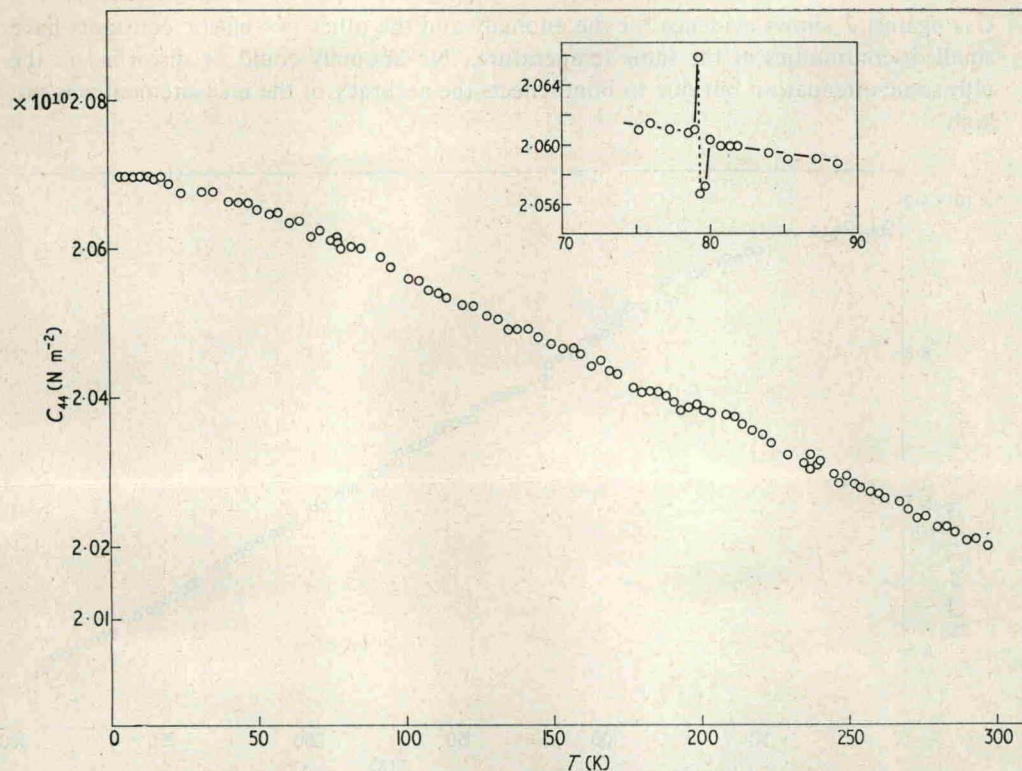
Figure 3. Variation of C_{44} with temperature. The inset shows the detail in a separate run through the anomaly with temperature decreasing.

The temperature variation of the linear expansion coefficient, measured along a [100] axis, is shown in figure 4. The fractional change in lattice parameter, relative to 90 K, is shown in figure 5. No thermal expansion coefficient has been measured previously for single-crystal CdTe, but measurements of Novikova (1961) and Browder and Ballard (1969) on polycrystalline CdTe are shown for comparison in figure 4. In the present work α passes through zero at 63·7 K, compared with 71·5 K and about 60 K in previous investigations. The peak in the expansion anomaly occurs at $79\cdot0 \pm 0\cdot1$ K.

Observations were made of the thermal expansion anomaly in another sample, cleaved from a different boule, on several occasions. The peak in α occurred at the same temperature, although data above and below this temperature sometimes displayed hysteresis.

Table 1. Elastic constants of CdTe in units of 10^{10} N m^{-2}

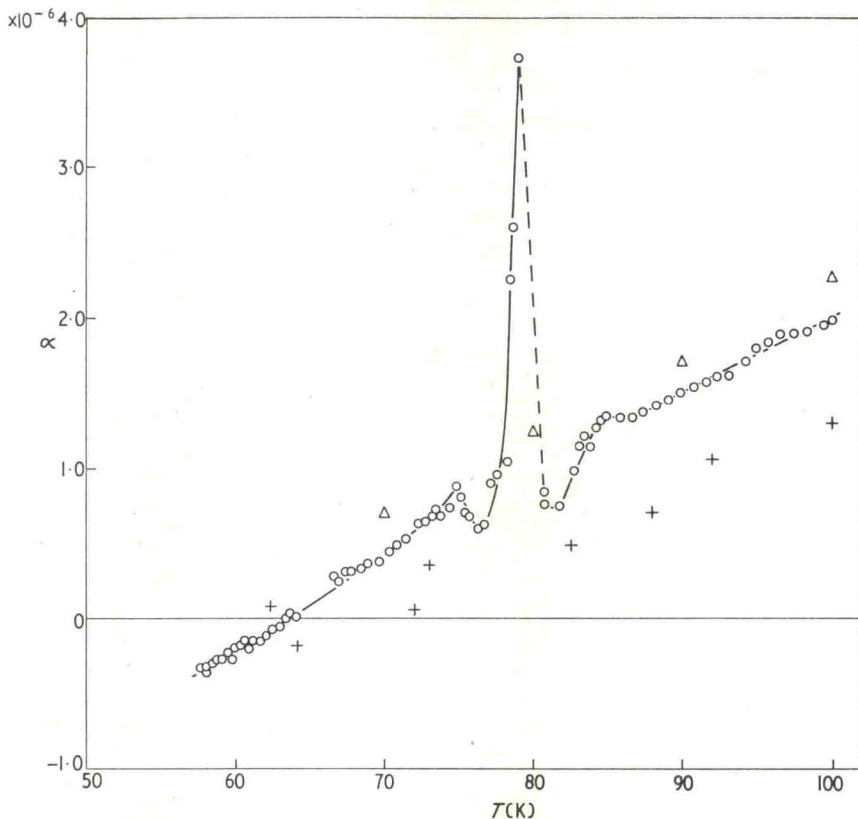| Experimenters	C_{11}	C_{44}	C_{12}	T (K)
McSkimin and Thomas (1962)	5·351	1·994	3·681	298
Vekilov and Rusakov (1971)	5·33	2·044	3·65	300
	5·57	2·095	3·84	77
Berlincour, *et al* (1963)	6·15	1·96	4·30	77
Present work	5·38	2·018	3·74	298
	5·62	2·061	3·93	77

Figure 4. Temperature variation of the linear thermal expansion coefficient α of single-crystal CdTe measured along the $\langle 100 \rangle$ axis ($\bigcirc$). The polycrystalline results of Browder and Ballard ($\triangle$) and Novikova ($+$) are shown for comparison.
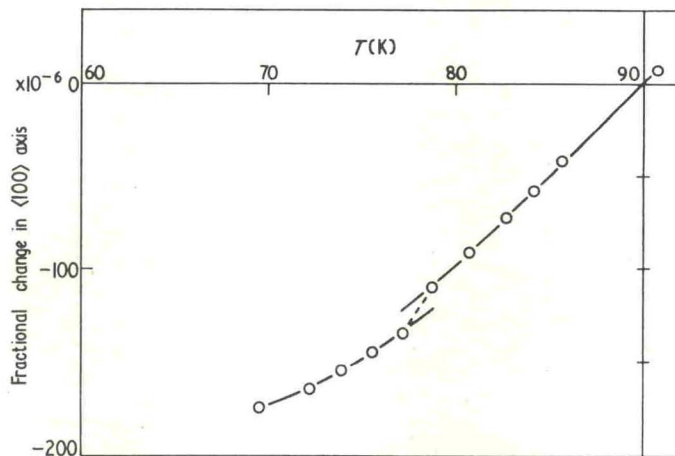

Figure 5. Fractional change in lattice parameter, in a $\langle 100 \rangle$ direction, relative to 90 K.

4. Conclusions

There is no evidence that any of the II–VI compounds show an anomaly in either the elastic constants or thermal expansion similar to that described here. The absence of any

anomaly in previous work on CdTe may, however, be easily explained. The elastic constant work of Vekilov and Rusakov (1971) was only taken down to 77 K, and results were reported at 20 K intervals. The thermal expansion work of Novikova was carried out on polycrystalline samples, which would tend to average out any anomaly if it was anisotropic in character. Browder and Ballard only reported work down to 70 K, with results taken at 10 K intervals. The specific heat data of Rusakov *et al* (1971), again on polycrystalline material, do not exhibit any anomalous behaviour. If one assumes that the effect on the elastic constants is only due to the lattice distortion, and assuming that the elastic constants vary as r^{-4}, where r is the interatomic distance (Huntingdon 1958), the change of about 1 part in 10^5 in the lattice parameter should produce a change of about 4 parts in 10^5 in the elastic constants. This would not be detectable with the present experimental arrangement.

It has been suggested by Berlincourt *et al* (1963) and Vekilov and Rusakov (1971) that the structure and elastic properties of II–VI compounds with the cubic sphalerite and hexagonal wurtzite structures are sensitive to the degree of ionic bonding. A decrease in temperature will cause a variation in the width of the forbidden energy gap in the valence electron gas and consequently change the degree of ionic bonding. One can only tentatively assume that the anomalous behaviour observed could be due to an abrupt change in ionicity.

More accurate measurements of the elastic constants using either the phase comparison or sing-around technique would be useful together with an x-ray investigation of the lattice parameters near 80 K. Detailed specific heat measurements on single-crystal samples and measurements of the dielectric constant d_{14} or the piezoelectric constant e_{14} would also be of interest. The change in ionicity could be directly monitored by resistivity measurements close to 80 K.

The elastic constants have been extrapolated to 0 K and used to calculate the Debye temperature θ_D of CdTe. The approximation due to Anderson (1963) was used and a value of 162·7 K obtained. This is in agreement with the value of 161 ± 4 K calculated from elastic constant measurements extrapolated from 77 K (Vekilov and Rusakov 1971) and 164 ± 5 K from specific heat measurements (Rusakov *et al* 1971).

Acknowledgments

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