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Molar heat capacity of GeTe, SnTe, and PbTe from 0.9 to 60 K†

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The molar heat capacity of GeTe, SnTe, and PbTe have been measured by the heat-pulse method from 0.9 to 60 K. No conclusive evidence was found for the effect of the soft TO phonon modes known to be present in these materials. An anomalous excess heat capacity previously reported near 3 K for GeTe was not confirmed. A detailed comparison of the calorimetric $\Theta_D(T)$ and that calculated from the phonon dispersion curves as measured by inelastic neutron scattering has been made for SnTe and PbTe, with the result that the lattice-dynamical model for PbTe has been verified but a minor refinement is indicated for SnTe. An attempt to explain an anomalous heat capacity for PbTe near 2 K based on the soft TO modes was unsuccessful and the effect remains unexplained. No superconductivity was found in PbTe above 0.9 K.

I. INTRODUCTION

Considerable interest has been generated in the metallurgical, electronic, and lattice-dynamical properties of the group-IV tellurides, GeTe, SnTe, and PbTe.[1,2] Both GeTe[3,4] and SnTe[3,5] exist over comparatively large homogeneity ranges (± 0.5 at.%) centered in the tellurium-rich side of the stoichiometric composition. The compound PbTe has a very narrow single-phase region (± 0.002 at.%) that does include the stoichiometric compound.[3,6] All three compounds are degenerate direct-gap narrow-band semiconductors.[2] In all three materials the Group-IV cations act as acceptors except for Pb-rich PbTe, where the excess Pb provides donor states.[2] As a result congruently grown GeTe (Ref. 7) (50.61-at.% Te) and SnTe (Ref. 8) (50.4 at.% Te) have hole concentrations near 10^{20} to $10^{21}/\text{cm}^3$, while[9] PbTe can be either n-type (Pb rich) or p-type (Te rich) but with carrier concentrations between 10^{17} and $10^{19}/\text{cm}^3$. Density measurements[2] have determined that GeTe and SnTe have cation vacancies rather than anion interstitials so that the correct chemical formulas for the congruently melting materials are $\text{Ge}_{0.976}\text{Te}_{1.000}$ and $\text{Sn}_{0.984}\text{Te}_{1.000}$. Both GeTe,[10] and SnTe,[11] are low-temperature superconductors ($T_c \leq 0.4$ K), while[12] PbTe has not yet been conclusively shown to be superconducting. Inelastic neutron scattering,[13-16] Raman spectroscopy,[17] and far-infrared absorption measurements[18] have confirmed the presence of a soft TO phonon mode in the three compounds. In congruently grown PbTe and SnTe the frequency of this soft mode does not go to zero at any finite temperature, that is, the compounds retain the cubic NaCl structure at all temperatures. Recent evidence[19] indicates that in SnTe the displacive phase transformation will occur at finite temperatures in samples with less than 1.5×10^{20} carriers/cm^3, that is, for noncongruently grown samples. In GeTe, Raman scattering[17] has verified the soft mode character of cubic to trigonal phase transformation[20] near 400 °C.

Despite extensive research on the basic properties of these materials and the considerable effort put into utilizing these materials and their pseudobinary alloys as tunable lasers and infrared detectors, very little has been reported on their low-temperature heat capacities. Until recently the only low-temperature heat-capacity C_p measurements on GeTe were either below 1 K[21,22] or above 53 K.[23] Finegold[21] and Goodman and Marcucci[22] confirmed the bulk nature of the superconductivity in GeTe using heat capacity measurements below 1 K. Finegold[21] found the electronic coefficient of the heat capacity $\gamma = 1.32 \pm 0.02$ mJ/mole K^2 and the Debye temperature at 0 K, $\Theta_D(0) = 166 \pm 3$ K for $\text{GeTe}_{1.05}$. Goodman and Marcucci[22] investigated three samples of GeTe_{1+x} with $x = 0.01$, 0.02, and 0.03 between 0.08 and 0.4 K and found γ between 1.13 and 1.34 mJ/mole K^2. They could not confirm Finegold's measurement of $\Theta_D(0)$ because in the temperature range they investigated the lattice heat capacity was too small. Recently, Lewis[24] measured heat capacity of $\text{GeTe}_{1.02}$ from 1.2 to 22 K and found an anomalous enhancement of the heat capacity near 3 K. As a result, he was unable to confirm the previous values of γ or $\Theta_D(0)$. To our knowledge neither the phonon dispersion curves nor the elastic constants of GeTe have been successfully measured. Our heat-capacity measurements on GeTe from 0.9 to 60 K do not exhibit the anomalous excess heat capacity reported by Lewis.[24] Although our results above 53 K agree very well with Zhdanova[23] we were unable to confirm Finegold's[21] value of $\Theta_D(0)$.

For SnTe_{1+x}, measurements have been made by Phillips *et al.*[25] and Mathur and coworkers.[26] Phillips *et al.*[25] measured several samples of SnTe_{1+x} from 0.1 to 2.0 K with $x = 0.005$, 0.025, 0.035, 0.030, and 0.010, and found that γ varied as the cube root of the carrier concentration with

TABLE I. Sample-preparation parameters; actual starting composition A, the soak temperature (°C) B, thermal gradient (°C/cm) C, and melting point (°C) MP.

	A	B	C	MP[a]
GeTe	$GeTe_{1.0061}$	741	30	725
SnTe	$SnTe_{1.004}$	852	23	806
PbTe	$Pb_{1.001}Te$	930	19	917

[a] Reference 3.

values of γ ranging from 0.75 to 1.27 mJ/mole K^2. They also determined that Θ_D seemed to be slightly dependent upon x and that the samples showed a deviation from the usual $\gamma T + \beta T^3$ dependence at temperatures below 2 K. Mathur *et al.*[26] measured C_p from 1.8 to 25 K and found good agreement with Phillips *et al.*[25] for Θ_D and γ. No comparison of the calorimetric $\Theta_D(T)$ with that calculated by Cowley *et al.*[13] from their phonon dispersion curves was attempted by Mathur and co-workers.[26] In general our heat-capacity measurements of SnTe are in good agreement with those previously reported. The calorimetric $\Theta_D(T)$ reported here are in good agreement with the $\Theta_D(T)$ calculated by Cowley *et al.*[13] from their neutron scattering experiments except for $T < 5$ K. The discrepancy is a minor one, most probably due to the lack of neutron data at the corresponding phonon frequencies and the unavailability of low-temperature elastic constants at the time of the experiments performed by Cowley *et al.*[13]

In the case of PbTe the only heat capacity measurements are those of Parkinson and Quarrington[27] from 20 to 300 K, which gave a $\Theta_D(T)$ varying only slightly with temperature. Agreement between their calorimetric $\Theta_D(T)$ and that calculated by Cochran, *et al.*[14] from their phonon dispersion curves was found to be fair above 20 K. The discrepancy was ascribed[13] to anharmonic effects. Our data above 25 K agree quite well with those of Parkinson and Quarrington.[27] We have verified the unusually rapid variations of $\Theta_D(t)$ below 20 K as calculated by Cochran *et al.*[14] and thereby confirmed their model for the lattice dynamics of PbTe.

One of the main purposes of this study was to determine if the effects of the soft TO mode could be observed in the heat-capacity measurements. An anomalous heat capacity was found for PbTe near 2 K, but a similar anomaly was not observed in either GeTe or SnTe. Quantitative analysis of the anomaly in PbTe indicated that it could not be ascribed to the soft TO mode and its existence remains unexplained.

II. EXPERIMENT

A. Sample preparation

Crystalline samples of GeTe, SnTe, and PbTe were prepared by the Bridgman method. The compound constituents in the ratios shown in Table I were sealed in quartz crucibles evacuated to 10^{-4} Torr or better. The samples were placed in the furnace and allowed to soak at a temperature above the melting point for at least 12 h. They were then lowered through the temperature gradient (see Table I) at a rate of 0.4 cm/h. The resulting ingots consisted of several large intergrown grains. The samples used for the electrical and thermal measurements were cut from the tapered end of the ingot which was the first portion of the charge to solidify. Typically, the heat-capacity samples had masses ranging from 5 to 12 g.

A complete mass spectrographic analysis of each of the samples was made and the results are shown in Table II. The dc measurements of electrical resistivity and Hall effect were made at 77 and 300 K. Ohmic contacts were made to the samples with indium. It was not possible with the available equipment to observe the Hall effect in SnTe and GeTe at 300 K because of their high carrier concentrations. All samples were p-type at 77 K. Values of carrier concentration, Hall mobility, and electrical resistivity are shown in Table III.

B. Heat-capacity measurements and thermometry

The heat-capacity apparatus used is similar to that described previously[28] in which the calorimeter is surrounded by a nearly isothermal shield.

TABLE II. Spark source mass spectrographic analysis in ppm atomic referred to the cation.[a]

	N	Na	Al	Si	K	Ca	Fe	Ni	Zn	Pd	Zr	Pb
GeTe	0.6	10	0.5	< 2	3	2	2	0.1	2	< 1	< 10	2
SnTe	< 4	20	22	ND[b]	60	< 0.4	< 5	ND	< 0.4	< 0.9	< 10	ND
PbTe	10	0.3	ND	10	70	1	< 10	1	< 5	2	2	⋯

[a] Other elements below detection limits.

[b] ND means not detected.

TABLE III. Electrical resistivity ρ, carrier concentration P, and Hall mobility μ_H at 300 and 77 K.

	300 K			77 K		
	ρ Ω cm	P cm^{-3}	μ_H cm^2/V sec	ρ Ω cm	P cm^{-3}	μ_H cm^2/V sec
GeTe	1.4×10^{-4}	...	...	5.3×10^{-5}	8.0×10^{19}	1.4×10^{3}
SnTe	6.6×10^{-5}	...	...	3.2×10^{-5}	8×10^{20}	2×10^{2}
PbTe	7.7×10^{-3}	1.7×10^{18}	4.8×10^{2}	9.4×10^{-4}	1.6×10^{18}	4.2×10^{3}

The data were taken from 0.9 to 60 K using the heat-pulse method. Two separate but overlapping sets of temperature calibrations were made of the germanium thermometer. The first set consisted of 65 temperature points spaced approximately logarithmically from 1.08 to 60 K. The temperatures were determined by comparison with another germanium thermometer whose calibration was based on the NBS 1955 temperature scale from 20 to 60 K and the paramagnetic salt temperature scale[29] from 1.08 to 20 K. The second set of calibration points from 0.85 to 1.33 K were obtained in a somewhat unusual manner. A large 30-g single crystal of thorium was placed in the calorimeter and the resistance R of the germanium thermometer was measured as the sample went superconducting in various applied magnetic fields ($0 \leq H_c \leq 85$ G). The $R(H_c)$ data were determined by noting the change in slope of the warming (and cooling) curve of the sample due to the large change in the total heat capacity of the thorium as it was driven from the superconducting to the normal state (and vice versa). The transition was sharp enough (≤ 0.5 mK) and the change in heat capacity large enough that an equivalent precision of ±0.5 mK could be easily achieved. The hysteresis between the warming and cooling curves was 1–2 mK and their average value was used. The 100 G incremental dial of a Varian Mark I Fieldial electromagnet was used to measure H_c. The vertical component of the earth's magnetic field was determined to be less than 0.15 G by a Gaussmeter. From the precise critical-field $H_c(T)$ measurements of Dekker and Finnemore[30] for thorium, we obtained the desired $R(T)$ calibration of the germanium thermometer from 0.85 to 1.33 K. Since this independent calibration overlapped that made above 1.08 K by the more common method, we could compare the relative agreement between the two sets of calibration points between 1.08 and 1.33 K. The thorium points were systematically 1.5 mK higher than the other points. Since the higher temperature calibration points were probably more accurate (± 1 mK), we adjusted the thorium data by lowering them 1.5 mK over the whole range from 0.85 to 1.33 K.

The $R(T)$ calibration data were fit using five polynomials ranging from the fifth to the eighth degree in $\ln(R/R_0)$. The absolute least-squares-fitting technique required that $\sum[\ln(T_{\text{obs}}/T_{\text{calc}})]^2$ be minimized over all the data points within the interval. To ensure uniform continuity of two adjacent polynomials at the knot point, their functional values and first derivatives were made equal at the knot point.

C. Precision, reproducibility, and accuracy

An indication of the precision and reproducibility of the heat-capacity measurements is obtained from the deviations of five separate sets of addenda measurements from a relative least-squares fit of the data. Although each set of data varied somewhat systematically from each other, when they were fitted as a whole the resultant deviations were apparently random. A convenient measure of of the reproducibility of the heat-capacity measurements is the relative rms deviation of all the five addenda measurements, which for 0.876 to 1.00 K is ±0.65%, for 1 to 3 K is ±0.3%, and from 3 to 60 K is ±0.20%. The relative rms deviation of a single set of heat-capacity data from a polynomial fit has values of 50 to 80% of those just given for the reproducibility. The overall accuracy was tested by measurements of several vacuum annealed pure ASARCO (American Smelting and Refining Co.) copper samples.[31] The deviation of our copper measurements from those of the copper reference equation[32] (CRE) and Holste, Cestes, and Swenson[33] (HCS) are shown in Fig. 1(a) ($0 < T \leq 5$ K) and Fig. 1(b) ($5 < T < 30$ K). From 30 to 60 K our copper data were compared to the NBS compilation[34] and it was found to agree at 30 K within 0.3% but at 60 K our data are about 0.6% too high. Between 3.5 and 20 K, [see Fig. 1(a) and 1(b)] our data lie within 0.4% of either CRE or HCS. Between 20 and 25 K our data agree within 0.2% with those of HCS (and Martin[35] as well), while a 0.6% deviation exists with respect to the CRE at 25 K. Our results, although less precise than those of HCS or Martin,[35] lend sup-

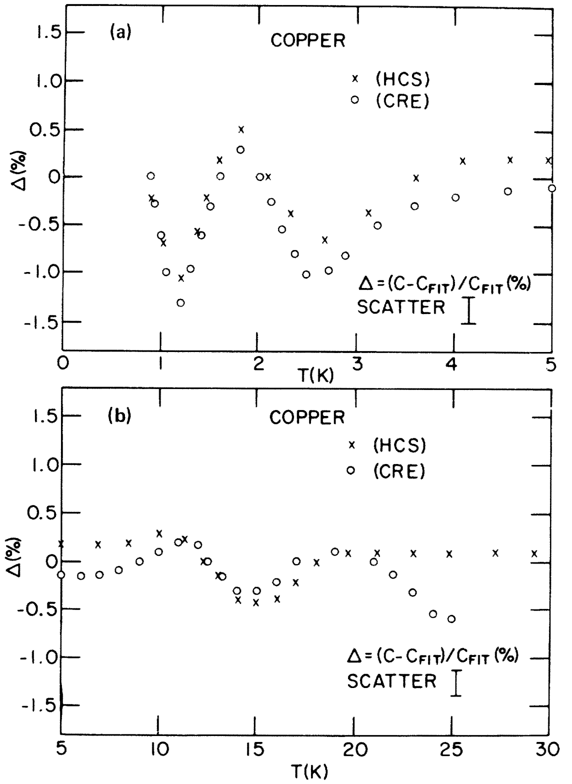

FIG. 1. Deviation of our heat-capacity measurements of copper from these of Holste, Cetas, and Swenson (Ref. 33) (HCS) and the copper reference equation (CRE) of Osbourne *et al.* (Ref. 32). Figure 1(a) shows the presence of systematic errors below 3.5 K. Figure 1(b) shows an agreement with both HCS and CRE except for $T > 20$ K where our data agree more closely with those of HCS. C_{FIT} represents the polynomials given in Refs. 32 and 33.

port to the suggestion that the CRE is in error between 20 and 25 K by approximately 0.5 to 0.9%.

Below 3.5 K our copper data vary systematically when compared to either HCS or CRE. Figure 2 shows the deviation of the data for our Group IV telluride samples when they are compared to the best polynomial fit, as described below. The close similarity of the deviations of the telluride samples and the copper samples implies that the deviations are reproducible and therefore inherent in our experimental apparatus. The origins of these systematic errors are not clear, except we note that there is no correlation with the deviations of the thermometer calibration points from their least-squares fit. Data for the telluride samples below 4 K were corrected for these deviations before values of γ and $\Theta_D(T)$ were extracted.

III. RESULTS

Usually the low-temperature heat capacity can be represented by an odd power series expansion in the temperature T of the form

$$C=\gamma T+\beta T^3+\sum_{i=1}^{n}\delta_i T^{2i+3}\ , \tag{1}$$

where C is the molar heat capacity in units of mJ/mole K, γ the electronic coefficient of the heat capacity, is in units of mJ/mole K^2, β is the lowest-order lattice contribution (Debye term) in units of mJ/mole K^4, and the δ_i are the coefficients of the higher-order lattice terms arising from the dispersion of the low-frequency phonon modes. For a Debye solid (no phonon dispersion) with infinite cutoff frequency $\delta_i=0$ for all i and the Debye temperature is a constant given by

$$\Theta_D=(1944r/\beta)^{1/3}\ , \tag{2}$$

where r is the number of atoms per molecule. For congruently grown samples of GeTe, SnTe, and PbTe, $r=1.976$, 1.984, and 2.000, respectively. For most materials at sufficiently low temperatures, Eq. (1) reduces to

$$C=\gamma T+\beta T^3\ , \tag{3}$$

so that a plot of C/T vs T^2 would yield a straight line with slope β and intercept γ. The Debye temperature obtained from the value of β is $\Theta_D(0)$, the Debye temperature at 0 K.

Another representation of the low-temperature heat capacity of a material is to absorb the T^5 and high powers of T into a temperature dependent Debye temperature $\Theta_D(T)$ so that Eq. (1) can be rewritten

$$C=\gamma T+[1944r/\Theta_D(T)]T^3 \quad \text{for } T\le\tfrac{1}{20}\Theta_D\ . \tag{4}$$

For $T\ge\frac{1}{20}\Theta_D$, one must use the Debye heat-capacity function

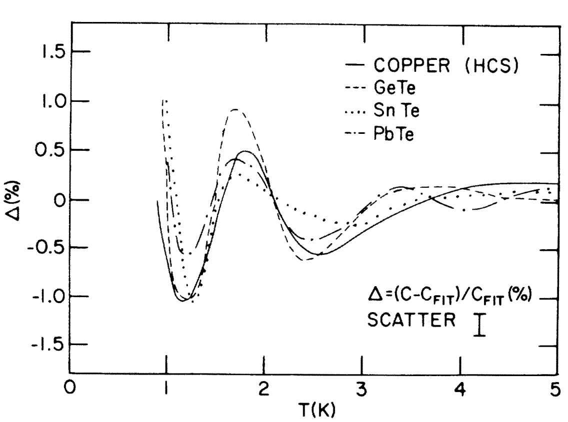

FIG. 2. Deviations of our heat capacity measurements for GeTe, SnTe, and PbTe from the best polynomial fit, C_{FIT}. Comparison to the copper deviations clearly shows the inherent nature of the systematic errors present in our measurements.

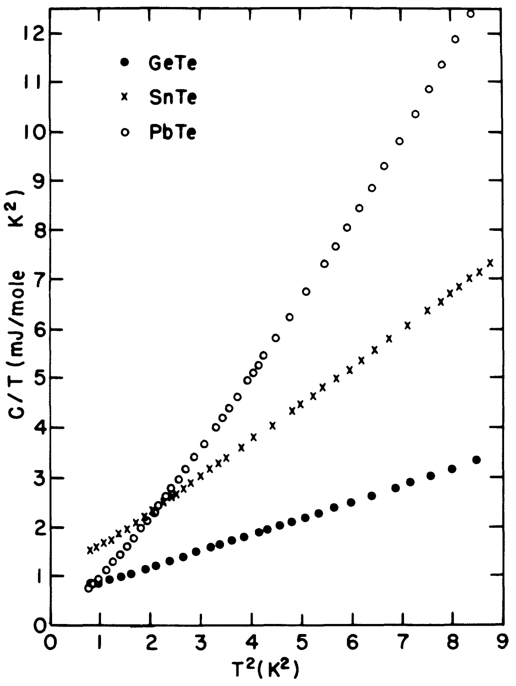

FIG. 3. Heat capacity of GeTe, SnTe, and PbTe plotted as C/T vs T^2 for $0 < T \leq 3$ K. The nonzero γ for SnTe and GeTe confirms the high carrier concentration for these materials in constrast to PbTe, which has a very small and not readily determined value of γ. Also the slope of these curves for a given T shows that the Debye temperature increases with decreasing mass of the cation. Finally, the general curvature in these data is more pronounced with increasing mass of the cation.

$$C_D = 3Rr \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\, dx \qquad (5)$$

to obtain $\Theta_D(T)$ from the lattice heat capacity. In this work we shall use both methods of analyzing the heat-capacity results.

Data for GeTe, SnTe, and PbTe for $0 < T < 3$ K are plotted in Fig. 3 as C/T vs T^2. None of the three curves can be fit to a straight line over the entire temperature range, which implies that the δ_i are not zero and must be taken into account at even the lowest temperature range. It should be noted that the data for GeTe and SnTe appear to have nonzero intercepts (γ) while PbTe has a zero or a very small intercept. This is consistent with the carrier concentrations of the three samples. At a given temperature, the slope of the data increases as one goes from GeTe to SnTe to PbTe, which indicates a decreasing $\Theta_D(T)$ for the same sequence. Also it is noted that the curvature of the plots increases with the mass of the cation. For example, the curvature for GeTe is very small while that for PbTe is noticeable even at the lowest temperatures.

Because of the systematic errors inherent in the telluride data below 3.5 K (see Fig. 2), some care was required in the analysis of this data. The general strategy was to least-square fit the data using a polynomial of the form given by Eq. (1). The lowest degree polynomial that gave deviations similar to those obtained for copper was considered to be the best fit. For all three materials such a polynomial could be found. The best polynomial fit then represents the heat capacity of the sample within the precision of our data which is of the order of 0.2%. Data for both GeTe and SnTe could be fit to a fifth-degree trinomial in T for $0.9 \leq T \leq 5$ K. The resultant deviations are shown in Fig. 2. The values of γ, β, δ_1, and $\Theta_D(0)$ for GeTe and SnTe are given in Table IV, where $\Theta_D(0)$ was calculated from β and the congruent values of r using Eq. (2). Attempts to fit the data for PbTe over the same temperature range with a fifth-degree binomial (γ assumed to be zero) were unsuccessful, in the sense that the deviations (as large as 4%) did not reproduce those of the copper measurements. Including a nonzero γ did not improve the fit. This result suggested the presence of an anomalous heat capacity below 5 K. The temperature range of the fit was expanded to 8 K, until finally the copper deviations could be reproduced with an eleven-term polynomial with powers of T ranging from 3 to 23. For comparison, over the same temperature range from 0.9 to 8 K the GeTe data could be fit with a three-term polynomial while that for SnTe required a five-term polynomial.

Clearly PbTe has an anomalous lattice heat

TABLE IV. Coefficients of best polynomial fit using Eq. (1) for the molar heat capacity of GeTe and SnTe which is valid from 0.90 to 5.0 K. Values of $\Theta_D(0)$, r, and the gram molecular weight m are also given.

	γ (mJ/mole K^2)	β (mJ/mole K^4)	δ_1 (mJ/mole K^6)	$\theta_D(0)$ (K)	r (atoms/formula)	m (g/mole)
GeTe	0.5543 ±0.0030	0.3069 ±0.0010	0.002257 $\pm 20\times10^{-6}$	232.2 ±0.4	1.976	198.45
SnTe	0.9394 ±0.0040	0.6669 ±0.0015	0.006844 $\pm 30\times10^{-6}$	179.5 ±0.3	1.984	244.39

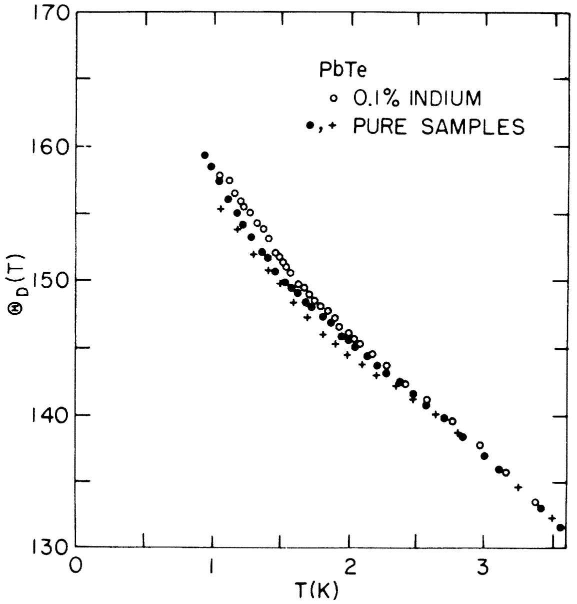

FIG. 4. Debye temperature $\Theta_D(T)$ plotted vs temperature for three PbTe samples showing the existence and variability of the anomalous dip in $\Theta_D(T)$.

capacity. The anomaly is evident in Fig. 4 where $\Theta_D(T)$ (corrected for the expected systematic errors below 3.5 K and assuming $\gamma = 0$) for three different PbTe samples is plotted from 0.9 to 3.6 K. Two of the samples were undoped and prepared in essentially the same manner while the third sample was doped with 0.1% indium. The dopant level was verified by mass spectrographic analysis. All three samples show nearly identical heat capacities above 3 k whereas below 3 K they all exhibit a shallow minimum in $\Theta_D(T)$ centered at approximately 1.8 K. A plot of $\Theta_D(T)$ for PbTe (undoped) from 0 to 12 K is shown in Fig. 5 which again illustrates the presence and extent of the anomalous behavior of $\Theta_D(T)$ near 2 K. For comparison the $\Theta_D(T)$ calculated by Cochran *et al.*[14] from the phonon dispersion curves measured at 296 K are shown by the solid line and the value of $\Theta_D(0) = 176.7$ K calculated by Houston *et al.*[36] from the temperature dependence of the elastic constants is also plotted. The discrepancy in $\Theta_D(0)$ between the elastic constants and the neutron results is probably due to the fact that the latter measurements were not made to low enough phonon frequencies considering the fact that some dispersion of the acoustic modes is still evident at the lowest frequencies. Although this discrepancy casts some doubt on the accuracy of the neutron based $\Theta_D(T)$ our purpose was to contrast its smooth behavior with the $\Theta_D(T)$ derived from the heat-capacity measurements. No such anomalous behavior was evident in the $\Theta_D(T)$ for SnTe or GeTe. Attempts to smooth the calorimetric $\Theta_D(T)$ near 2 K required changes in the heat capacity of 3–4%. Such an error is well beyond any expected measurement errors as evidenced by the deviation of our copper data [see Fig. 1(a)]. Since the measurements of PbTe and copper were performed with several samples and reported more than once, an accidental error seems very unlikely.

The molar heat capacities for all three compounds from 0.9 to 60 K are given at appropriate temperatures in Table V. Figures 6, 7, and 8 show $\Theta_D(T)$ vs T for GeTe, SnTe, and PbTe calculated from Eq. (5) using values of $\gamma = 1.976$, 1.984, and 2.000, respectively. Below 5 K the molar heat capacity and $\Theta_D(T)$ for GeTe and SnTe were obtained from the best polynomial fit with the coefficients given in Table IV. The molar heat capacity and $\Theta_D(T)$ below 3.5 K for PbTe have also been corrected for the expected systematic errors.

IV. DISCUSSION

A. GeTe

Comparison of our heat-capacity results for GeTe with those of other workers shows rather poor agreement except above 53 K (Zhdanova[23]). Our value of $\Theta_D(0)$ is some 10% higher than that of Finegold[21] which is well outside the combined errors. In addition, our value of γ is a factor of two smaller than that reported by Goodman and Marcucci[22] and Finegold.[21] The latter result suggests that the carrier concentration of our sample may be lower than those of these other workers. To our knowledge there has been no determination of the carrier concentration as a function of stoichiome-

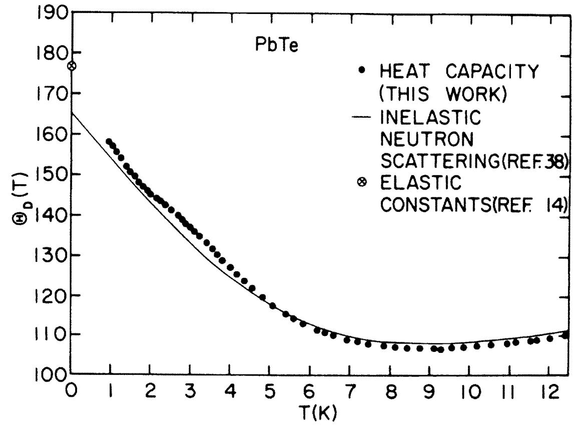

FIG. 5. Plot of $\Theta_D(T)$ vs T for $T < 12$ K for PbTe compared to that calculated from the phonon dispersion curves. Note the anomalous inflection in the calorimetric $\Theta_D(T)$ or compare to the smooth behavior for the neutron $\Theta_D(T)$. The value of $\Theta_D(0)$ as calculated by Houston *et al.* (Ref. 38) from elastic constant measurements is shown for comparison.

TABLE V. Molar heat capacity C (mJ/mole K) for GeTe, SnTe, and PbTe.

T (K)	GeTe	SnTe	PbTe	T (K)	GeTe	SnTe	PbTe
0.9	0.724	1.336	0.713	21	5590	9970	14320
1.0	0.863	1.613	0.995	22	6265	10735	15345
1.5	1.884	3.712	3.828	23	6950	11740	16420
2.0	3.636	7.433	10.23	24	7640	12700	17500
2.5	6.401	13.44	21.61	25	8355	13660	18500
3.0	10.50	22.49	40.84	26	9075	14650	19520
3.5	16.28	35.47	72.45	27	9810	15640	20470
4.0	24.17	53.44	121.1	28	10550	16690	21420
4.5	34.52	77.62	194.4	29	11260	17670	22400
5.0	48.35	110.5	294.5	30	12020	18570	23290
6	86.52	206.6	594.7	32	13060	20390	24970
7	145.3	359.6	1037	34	14940	22160	26620
8	232.4	583.2	1617	36	16320	23760	28200
9	356.6	887.6	2315	38	17700	25270	29490
10	525.0	1276	3111	40	19040	26730	30850
11	742.0	1746	3984	42	19910	28090	32000
12	1008	2295	4905	44	21640	29340	33130
13	1332	2900	5850	46	22840	30530	34160
14	1706	3590	6835	48	24010	31580	35170
15	2136	4330	7890	50	25040	32600	35950
16	2624	5145	8960	52	26120	33580	36710
17	3154	6005	10015	54	27140	34470	37530
18	3709	6825	11090	56	28190	35280	38330
19	4310	7775	12170	58	29130	···	39020
20	4935	8785	13230	60	29950	···	39620

try at 77 K for GeTe. However, the similarity in the electrical properties between SnTe and GeTe permits an approximate comparison of the room temperature and the 77 K values for the carrier concentration. Based on Berbrick,[8] the difference in the carrier concentration at the two temperatures for SnTe is approximately $1\times10^{20}/\text{cm}^3$ over the whole single phase region. Adjusting our 77 K value for GeTe by this amount leaves our carrier concentration at least a factor of ten below that of Goodman and Marcucci.[22] A source of this difference may be the presence of compensating impurities in our samples, although the required concentration of such impurities does not seem evident in the mass spectrographic analysis of our samples. It is possible that the Ge/Te ratio for our sam-

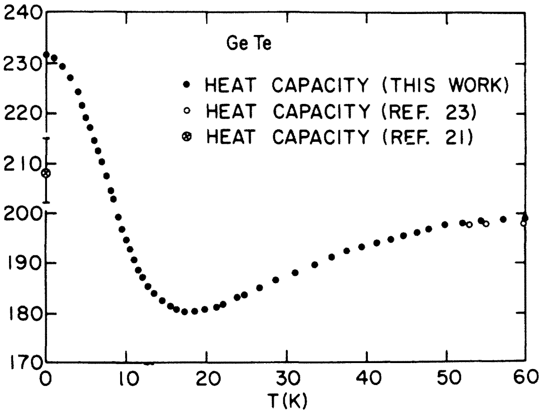

FIG. 6. Plot of $\Theta_D(T)$ for GeTe vs T from 0.9 to 60 K as compared to previously determined values for $\Theta_D(T)$.

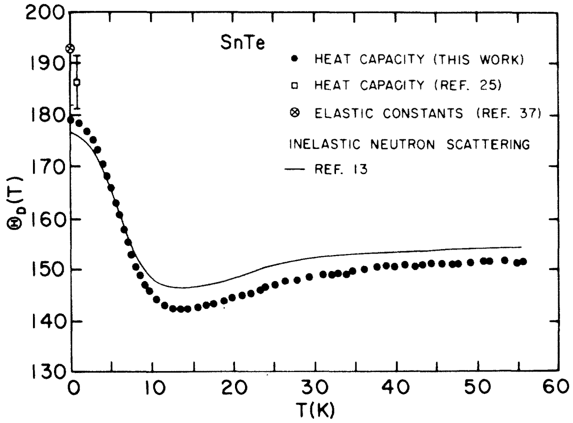

FIG. 7. Plot of $\Theta_D(T)$ vs T from 0.9 to 60 K for SnTe, as determined from a variety of measurements. The solid line denotes the neutron $\Theta_D(T)$ which was calculated from a model of the phonon dispersion curves measured by neutron scattering experiments performed in Ref. 13 at 100 K. The agreement between the two $\Theta_D(T)$ curves is within 5%. It is noted that the depth of the minimum in $\Theta_D(T)$ is somewhat larger for the calorimetric data than that calculated from the neutron measurements.

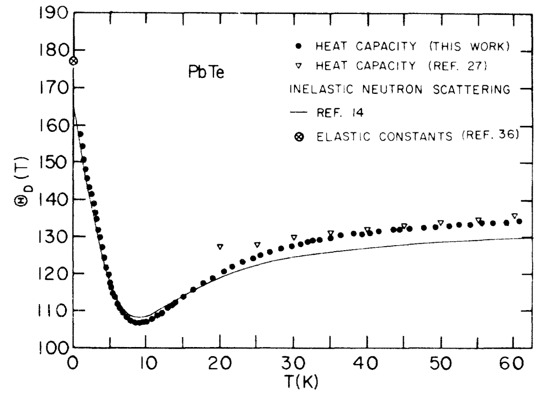

FIG. 8. Plot of $\Theta_D(T)$ vs T for PbTe from 0.9 to 60 K. Comparison to the heat-capacity data of Ref. 27 indicates good agreement. The overall behavior of $\Theta_D(T)$ derived from the neutron measurement is very well reproduced by our heat-capacity measurements.

ple is higher than those reported by other workers. However, a quantitative analysis[7] of high Ge/Te samples suggests that the minimum carrier concentration ($2\times10^{20}/\text{cm}^3$) is still higher than that of our samples. It is difficult to explain the 10% variance in $\Theta_D(0)$ between our value and that of Finegold,[21] even assuming a 0.5% shift in the Ge/Te ratio. According to Phillips *et al.*[25] a similar variation in the Sn/Te ratio for SnTe produces only a 3% change in $\Theta_D(0)$.

In Fig. 9 our results on GeTe and those of Lewis[24] are compared in a plot of C_L/T^3 vs $\log_{10}T$. For normal materials such a plot has a straight-line section of zero slope at low temperatures (constant Θ_D region), followed by a peak at higher temperatures due to the increased phonon density of states produced by dispersion at higher frequencies. The anomalous increase in lattice heat capacity near 2.5 K found by Lewis is not present in our data. In addition our maximum in C_L/T^3 is smaller and displaced to a higher temperature than the analogous peak in Lewis's data. It is difficult to understand the discrepancy between our results and those of Lewis since both samples have nearly the same Ge/Te ratio (1.020 for Lewis and 1.024 for our sample) and annealing treatment.

B. SnTe

Detailed measurements have been made by Berbrick[8] on the electrical properties of SnTe versus stoichiometry at 77 and 300 K. Our value for the carrier concentration at 77 K ($8\times10^{20}/\text{cm}^3$) and Hall mobility (200 cm^2/V sec) correspond, within ± 0.03-at.% Te, to the congruent composition of SnTe (50.4 at.% Te). Our values of γ and carrier concentration are in good agreement with those of Phillips *et al.*[25] Both measurements lead to values of γ near 1 mJ/mole K^2 for $8\times10^{20}/\text{cm}^3$. The heat-capacity results of Mathur and co-workers[26] on SnTe from 1 to 20 K are in graphical form and, within the allowed precision of reading points from their graphs [(5–10)%], our data agree with theirs. The $\Theta_D(0)$ values calculated by Phillips *et al.*[25] for several Sn/Te ratios are somewhat higher than that found from our data (see Fig. 7). The calorimetric determinations of $\Theta_D(0)$ by Phillips *et al.*[25] are 3% lower and our results are 6% lower than the value of $\Theta_D(0)$ reported by Beattie[37] from measurements of the elastic constants. The samples used by Beattie[37] had a room-temperature resistivity of 1.25×10^{-4} Ω cm (twice our value) and a carrier concentration of $6\times10^{20}/\text{cm}^3$. Extrapolating our carrier concentration at 77 and 300 K, assuming the relation found by Berbrick,[8] gives $6.5\times10^{20}/\text{cm}^3$ in good agreement with Beattie.[37]

Our value for $\Theta_D(0)$ and the elastic constant value lie outside the variation in $\Theta_D(0)$ due to a change in the Sn/Te ratio as measured by Phillips *et al.*[25] (see Fig. 7). This suggests that slight variations in the Sn/Te ratio (hence a change in carrier concentration) are not responsible for the different values of $\Theta_D(0)$. Inspection of Fig. 3 shows that near 1 K the heat capacity of SnTe is dominated by the electronic contribution [(60–70)%], which makes the determination of $\Theta_D(0)$ less precise. This, coupled with the fact that deviations from the T^3 behavior occur at very low temperatures, probably accounts for the discrepancy among the various values of $\Theta_D(0)$. For those materials which show deviations from the T^3 law at very low temperatures the calorimetric determination of $\Theta_D(0)$ actually gives a $\Theta_D(T)$ with T slightly above 0 K. For most materials $\Theta_D(T) < \Theta_D(0)$ so that what is called $\Theta_D(0)$ will be somewhat less than the actual $\Theta_D(0)$. If this is so, then the calorimetric $\Theta_D(0)$

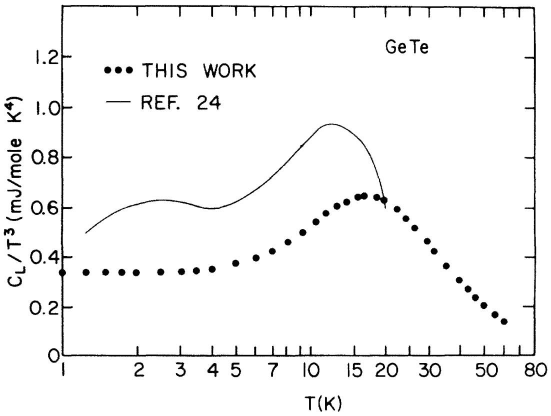

FIG. 9. Comparison of our measurement of the lattice heat capacity of GeTe C_L with those of Lewis, (Ref. 24) where C_L/T^3 is plotted vs the logarithm of T. The most important feature is the absence of the anomalous excess heat capacity near 2.5 K in our data.

will approach the elastic constants value of $\Theta_D(0)$ as the temperature range of the heat-capacity experiments approach 0 K. Since the measurements of Phillips *et al.*[25] extend to 0.3 K (compared to our 0.9 K), the relative disagreement among the various values of $\Theta_D(0)$ is understandable. With this in mind the best value for $\Theta_D(0)$ is most probably that determined by Beattie[37] from the elastic constants, i.e., 192.2 ± 0.4 K.

The $\Theta_D(T)$ calculated by Cowley *et al.*[13] for SnTe, based on a model derived from their inelastic-neutron-scattering studies at 100 K, is also plotted in Fig. 7. The overall agreement between our $\Theta_D(T)$ and that calculated by Cowley *et al.*[13] is within 5%. Above 10 K the neutron $\Theta_D(T)$ is only (2–3)% above our values and they seem to be converging slightly. This suggests that the difference may be due to the fact that the neutron data were taken at 100 K. Below 10 K the relative position of the two $\Theta_D(T)$ curves changes suggests a different source of error. Both $\Theta_D(T)$ curves are in error as $T \rightarrow 0$ as measured by their deviation from the elastic constant value of $\Theta_D(0)$. We have already commented on the possible source of error in the calorimetric $\Theta_D(T)$ (T is not low enough to extrapolate to 0 K). The deviation of the neutron $\Theta_D(T)$ at the very low temperatures probably reflects the absence of neutron data at frequencies below 0.5 THz and the lack of elastic constants data at the time the neutron experiments were performed. It is believed that incorporation of the available elastic constants data[37] into a lattice-dynamical model for SnTe would improve the calculated $\Theta_D(T)$ below 5 K.

C. PbTe

Referring to Figs. 4 and 5 it is clear that no precise value of $\Theta_D(0)$ for PbTe can be calculated from our heat-capacity data, because of its rapid variation below 4 K and the presence of the anomalous inflection near 2 K. However, using the best polynomial fit from 0.9 to 8 K (an eleven-term odd power series in T with exponents from 3 to 23), we obtained $\Theta_D(0) = 168$ K which is 10 K below the elastic constant value[36] of 176.6 ± 0.5 K. The fact that at a temperature of 1% of the elastic $\Theta_D(0)$, namely, 1.77 K, the Debye temperature is only 148 K [some 16% below the elastic $\Theta_D(0)$] indicates that this material is quite unusual, since most crystalline substances have a Θ_D at a temperature of 1% of the elastic $\Theta_D(0)$ within a few percent of the limiting value, i.e., the elastic $\Theta_D(0)$. For instance GeTe (SnTe) has its Θ_D [at a temperature of 1% of the best value of $\Theta_D(0)$] within 1% (1.5%) of $\Theta_D(0)$. Qualitatively, the neutron-determined $\Theta_D(T)$ and our $\Theta_D(T)$ agree quite well. In Fig. 8 our $\Theta_D(T)$ for PbTe is compared to that calculated from the neutron scattering[14] and to that obtained by Parkinson and Quarrington[27] from their heat-capacity data. The agreement between the two calorimetric $\Theta_D(T)$ is excellent above 30 K and good from 20 to 30 K. Below 20 K, the rapid variation in the neutron $\Theta_D(T)$ is qualitatively reproduced by the calorimetric $\Theta_D(T)$. This variation arises from the presence of very low-frequency TA phonon modes which produce a peak in the phonon density of states $g(\nu)$ near 0.75 THz. It is these states that are primarily responsible for the deep, sharp minimum in $\Theta_D(T)$ near 10 K. Quantitatively, the minimum in $\Theta_D(T)$ is somewhat more pronounced in the calorimetric $\Theta_D(T)$, suggesting the presence of a slight increase in the phonon density of states $g(\nu)$ over that predicted by the inelastic-neutron-scattering data. A possible source of these extra phonon modes is the fact that the TO modes are known to soften considerably as the temperature is lowered towards 0 K. At the zone center, along the $[00\xi]$ directions, the TO modes soften from 1.0 THz to 0.57 THz as the temperature is lowered from 300 to 1.2 K according to the far-infrared measurements of Kinch and Buss.[14] Also Alperin *et al.*[38] have found by neutron scattering that this same TO mode softens considerably along the $[\xi\xi\xi]$ direction for small reduced wave-vector q. At $q = 0$ the mode frequency drops from 0.87 THz at 293 K to 0.48 THz at 4 K. Although the total contribution of these low frequency soft modes to $g(\nu)$ is not known, they may be responsible for the generally lower calorimetric $\Theta_D(T)$ at low temperatures. A similar effect may be present in SnTe where the calorimetric $\Theta_D(T)$ is lower than the neutron evaluated $\Theta_D(T)$ since Pawley *et al.*[15] have observed a very similar softening of the TO mode in SnTe.

It is tempting to associate these soft TO modes in PbTe with the anomalous inflection of $\Theta_D(T)$ near 1.8 K observed in our samples of PbTe. Closer examination makes this an unlikely hypothesis. The absence of the inflection in the calorimetric $\Theta_D(T)$ for SnTe (any inflection of even 25% of that found in PbTe could have been observed), which also has these soft modes, strongly suggests that they are not the source of this anomaly. Furthermore, a quantitative estimate can be made of the temperature at which these modes would be expected to have their maximum effect on $\Theta_D(T)$. Following Katz,[39] a peak in the phonon density of states at ν_p will result in a depression of $\Theta_D(T)$ at $T = \frac{1}{5}(h/k)\nu_p$, where h is Planck's constant and k is Boltzmann's constant. Since 1 THz is approximately equal to 50 K, a peak in the $g(\nu)$ at 0.5 THz (such as that expected from the mode in PbTe) would produce a depression in $\Theta_D(T)$ at $\frac{1}{5}(25\text{ K}) = 5$ K. This is the correct order of magnitude for the generally lower $\Theta_D(T)$ below 10 K, but is higher than that of the anomaly at 1.8 K. The absence of the anomaly in SnTe,

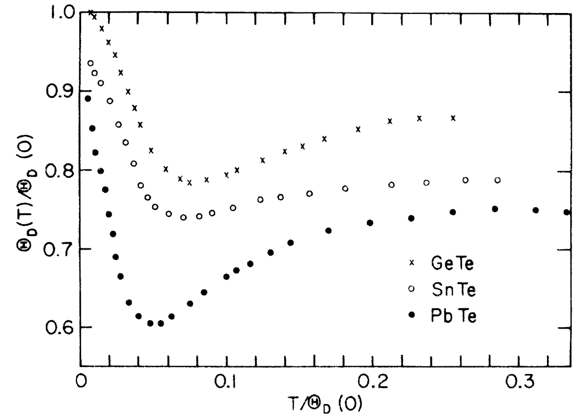

FIG. 10. Plot of $\Theta_D(T)$ vs T [both normalized to $\Theta_D(0)$] for GeTe, SnTe, and PbTe showing the systematic shift in the temperature and magnitude of the minimum in $\Theta_D(T)$ with the mass of the cation. In the case of SnTe and PbTe the best values of $\Theta_D(0)$ were taken to be those obtained from the elastic constant measurements, (Refs. 36 and 37) while that for GeTe was taken to be our calorimetric value for $\Theta_D(0)$ (see Table IV).

and the temperature at which is expected to occur in PbTe, rules out the soft TO modes as a source of the anomaly in PbTe and the anomaly remains unexplained.

It is noted that no evidence of superconductivity has been found above 0.9 K in any of our PbTe samples. This result confirms those of previous investigators[12] that superconductivity in PbTe, when it occurs, is probably due to Pb filaments in samples grown in the Pb-rich side on the phase diagram.

Finally in Fig. 10 the $\Theta_D(T)$ for GeTe, SnTe, and PbTe are compared in a normalized manner. The depth of the $\Theta_D(T)$ minimum increases with increasing mass of the cation while the temperature at which the dip in $\Theta_D(T)$ occurs decreases with increasing mass of the cation. The latter effect is qualitatively understandable if the TA phonon frequencies responsible for the minimum in $\Theta_D(T)$ depend primarily on the mass of the cation instead of changes in the force constants. The ratio of the minimum temperature for $\Theta_D(T)$ (0.66) and frequency of the $\Sigma_3(A)$ modes near the zone edge (0.64) for PbTe and SnTe are smaller than that calculated for an equal force constant model (0.86). This calculation shows that the primary effect is due to the mass change, which is consistent with the shifts in the minimum $\Theta_D(T)$ observed for GeTe.

V. CONCLUSION

The heat capacity of GeTe, SnTe, and PbTe have been measured from 0.9 to 60 K. Our results for GeTe differ in several respects with those of previous workers, although our high temperature measurements are in good agreement with the Zhdanova.[23] The low value of γ for our samples suggests a possible shift toward the Ge-rich side of the congruent composition or may represent the presence of compensating closer impurities. Although our values of Θ_D near 0 K are higher than those of Finegold[21] they are based on data over a wide temperature range where the lattice heat capacity is a significant portion of the total heat capacity. No anomalous excess heat capacity near 3 K such as that reported by Lewis[24] has been found. Values of carrier concentration and Hall coefficient verify the congruent composition of our SnTe sample. In general our data, where applicable, agree with the previous results of Phillips *et al.*[25] (below 2 K) and Mathur and co-workers[26] (1–25 K). We have verified the general features of the $\Theta_D(T)$ calculated by Cowley *et al.*[13] from their inelastic neutron data although a minor refinement of their model is indicated. The generally lower values of our $\Theta_D(T)$ may be due to softened TO modes not present at the temperature (100 K) at which the neutron data were taken. Our value for $\Theta_D(0)$ and those of Phillips *et al.*[25] are somewhat below that calculated by Beattie[37] from his elastic constant measurements. Our data from 0.9 to 20 K represent first determination of the heat capacity of PbTe in this temperature range. Above 25 K our data and those of Parkinson and Quarrington[27] are in very good agreement. The rapid variation of $\Theta_D(T)$ predicted by Cochran *et al.*[14] from their neutron data has been verified, although below 10 K the heat capacity indicates a slightly large phonon density of states that may be associated with the soft TO modes. An anomalous inflection in $\Theta_D(T)$ near 2 K observed only in our PbTe samples could not be accounted for in the basis of softened TO modes and the effect remains unexplained. The rapid variation of $\Theta_D(T)$ below 5 K and the presence of the anomalous behavior near 2 K prevented an accurate comparison of $\Theta_D(0)$ with the elastic constant value of $\Theta_D(0)$ = 177.6 K. No superconductivity was detected in any PbTe samples above 0.9 K.

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