

Specific Heats of Cu, GaAs, GaSb, InAs, and InSb from 1 to 30°K*

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The specific heats of Cu, GaAs, GaSb, InAs, and InSb have been measured over the temperature range from 1 to 30°K with an accuracy of 0.5%. A comparison of the copper data with other published data verifies this estimate of the accuracy. The analysis of all four III-V compounds requires the inclusion of a free-carrier term linear in the temperature ($c_{fc}/T \sim 5 \mu\text{J}/\text{K}^2 \text{g at.}$) to explain the low-temperature data. The inclusion of this term results in excellent agreement between calorimetric and elastic-constant values of Θ_0 . A reduced plot of Θ/Θ_0 versus T/Θ_0 shows a minimum (0.7 at approximately $T/\Theta_0=0.05$) which varies with average mass in both depth and location. The reduced Θ/Θ_0 curves for Ge and Si show qualitatively the same relative mass dependence but do not fall quantitatively into the pattern established by the compounds. The curve for GaAs ($\Theta_0=347^\circ\text{K}$, $M=72.32$) coincides with that of Si ($\Theta_0=645^\circ\text{K}$, $M=28.086$) instead of Ge ($\Theta_0=374^\circ\text{K}$, $M=72.59$), as might be expected. These heat-capacity data are used to recalculate temperature-dependent Grüneisen parameters from previous thermal-expansion data.

INTRODUCTION

GERMANIUM, silicon, and a number of the III-V compounds form a class of solids which have a common tetrahedrally-bonded zinc-blende structure. Because these solids have basically the same covalent binding, a relatively smooth, primarily mass-dependent relationship should exist between their thermodynamic properties. Indeed, inelastic neutron scattering experiments on diamond, silicon, germanium, and gallium arsenide show very similar phonon dispersion relations which can be understood in terms of a shell-model calculation.¹ Similar correlations are observed in low-temperature thermal expansion measurements for Si, Ge, GaAs, GaSb, InAs, and InSb.² Each of these solids shows a positive thermal expansion (proportional to T^3) for temperatures above 2°K, then a negative expansion region, and finally a positive expansion region at higher temperatures. Various features of these curves appear to scale with the low-temperature Debye Θ 's, showing a form of mass dependence.

Heat-capacity data exist to liquid-helium temperatures only for Ge and Si.³⁻⁵ Piesbergen has reported heat-capacity measurements for a number of III-V compounds down to 12°K,⁶ and Ohmura has published data for InSb for temperatures above 6°K.⁷ The Ge and Si data show a rapid decrease of the equivalent Debye temperature Θ with increasing temperature to a minimum value of $\Theta/\Theta_0 \sim 0.7$ at $T/\Theta_0 \sim 0.05$.³ The specific heats show a T^3 dependence to 2% only for temperatures $T/\Theta_0 \leq 0.007$, and specific differences appear to exist between Ge and Si at higher temperatures on the reduced plots of Θ/Θ_0 versus T/Θ_0 .

The lack of specific-heat data for the III-V compounds caused some uncertainty in the analysis of the thermal expansion results.² As a first approximation, the higher-temperature data (which in every case terminated near the minimum in the reduced Θ plot) were extrapolated to low temperatures by assuming low-temperature elastic-constant values of Θ_0 when available and by assuming a similarity between the reduced Θ versus T curves for these solids and those for Ge and Si. The measurements reported in this paper were undertaken to provide relatively precise heat-capacity data from 1 to 30°K for comparison with the existing data for Si and Ge and for use in the evaluation of the Grüneisen constants for the thermal-expansion data.

The accuracy and reliability of the present, relatively conventional measurements are compared with those of other workers using measurements on a high-purity copper sample. All of the data, including the copper measurements, are taken on a well-documented constant-volume gas thermometer temperature scale which is based on the NBS platinum resistance thermometer scale from 16 to 30°K.⁸ In particular, this temperature scale (called RTAS in the following) confirms other suggestions that the liquid-helium vapor pressure scale⁹ T_{58} could be too low on the Kelvin scale by as much as 9 mdeg near 4°K. The reflection of temperature scale uncertainties on heat-capacity measurements is discussed.

EXPERIMENTAL DETAILS

Samples

The data which are discussed below were taken on a high-purity copper sample and on the same III-V compound samples which were used for the thermal-expansion measurements of Sparks and Swenson.² The

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¹ G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) **88**, 463 (1966).

² P. W. Sparks and C. A. Swenson, Phys. Rev. **163**, 779 (1967).

³ P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).

⁴ P. H. Keesom and G. Seidel, Phys. Rev. **113**, 33 (1959).

⁵ C. A. Bryant and P. H. Keesom, Phys. Rev. **124**, 698 (1961).

⁶ U. Piesbergen, Z. Naturforsch. **18A**, 141 (1963).

⁷ Y. Ohmura, J. Phys. Soc. Japan **20**, 350 (1965).

⁸ J. S. Rogers, R. J. Tainsh, M. S. Anderson, and C. A. Swenson, Metrologia **4**, 47 (1968).

⁹ F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).

characteristics of the samples are given in Table I. The short length of the GaSb sample is due to an accident which occurred after the thermal-expansion measurements had been completed. The 1965 Calorimetry Conference copper standard¹⁰ is made from similar copper from the same source, but the small size of our addenda (see below) precluded our use of a portion of this standard.

Basic Cryogenics

The apparatus used for these experiments is identical to that described by Sample and Swenson¹¹ (without the capability for adiabatic demagnetization), and the actual calorimeter insert for the stationary metal Dewar system was constructed by Stevens.¹² The top of the insert has room-temperature vacuum and electrical connections, while the bottom consists of a vacuum jacket which is immersed in 4°K liquid helium. A second quantity of liquid helium which is condensed into a 50-cm³ pot inside the vacuum jacket can be pumped to approximately 0.9°K using a high-speed oil diffusion pump. All electrical leads (which come from the 4°K bath), a heat switch, and the frame (50 cm long, 3-cm diam) which supports the calorimeter are attached to the helium pot. After a sample is loaded into the calorimeter, a copper-plated heat shield is slid over the frame and anchored to the pot. Nitrogen is used as an exchange gas above 77°K, but no exchange gas is used below this temperature. When data are taken, the vacuum jacket is sealed off, and small leaks in the system are immediately apparent in both the vacuum system pressure and in the sample drift rates.

Calorimetry

The reason for the long, thin shape of the insert (and, hence, the calorimeter) is historical,¹¹ but this geometry is useful for measurements on our thermal-expansion samples which are long and thin (Table I). The calorimeter design allows a rapid interchange of these samples with a minimum effect on the heat capacity of the addenda.

The sample (which has one smooth, flat end) is placed on end in a small tray (15-mm diam, 5-mm-high walls, from 0.1-mm-thick high-purity copper sheet). Three wires (No. 22 bare copper), silver-soldered to the tray, extend upwards to support and give thermal contact to the sample. One of these wires extends to the jaws of a mechanical heat switch.¹¹ The tray is suspended from the frame using six spring-loaded nylon threads (0.1-mm diam, 4 cm long).

The sample is tied to the wire supports with a nylon thread, and thermal contact is made to the tray (mostly

at the base) with 35 mg of Dow Corning silicone vacuum grease. Samples are weighed to 0.1 mg initially and again after removal from the calorimeter. Any increase in weight is presumed to be due to the grease, which adheres to the sample, so an identical amount (to 0.1 mg) is added to the next sample before it is loaded onto the tray. The possible errors introduced in this procedure will be considered in the section on the addenda heat capacity.

The calorimeter heater (3340 Ω , about 6 ft, of Sigmund Cohn alloy No. 479, 92% Pt-8% W potentiometer wire, 9×10^{-4} -in. diam) is wound directly around the base of the tray and is anchored with epoxy adhesive. This wire is similar to that described by Ho and Phillips,¹³ and is useful because of its low temperature coefficient of resistivity (constant resistance 1 to 18°K, 0.3% increase 18 to 30°K), its small low-temperature heat capacity, and its strength. One heater potential lead is attached to a current lead at the tray, the other to the second current lead at the helium-pot anchor point.

The thermometer is a previously calibrated Honeywell Series IV germanium resistor (designated GR622) with a 4°K resistance of 500 Ω . The calibration of this thermometer will be discussed in a later section. It is attached to the bottom of the tray with copper foil and G.E. 7031 varnish, and its leads are electrically isolated and thermally anchored to the tray with pieces of nylon hosiery which have been saturated with the varnish.

The heater current is continuously adjustable from 10 μ A (0.33 μ W) to 3 mA (30 mW), and it is determined by measuring potentiometrically the voltage drop across a 500- Ω secondary standard resistor using an L & N Type K-3 potentiometer. The heat pulse is initiated by switching the current from a dummy heater to the sample heater, and the current is monitored continuously before, during, and after a heat pulse by one pen of a two-pen recorder. The potential leads from the heater (which measure e_h) are connected to the input of an integrating digital voltmeter (Vidar, Model 520) which is operating in the "time-integration" mode to obtain $\int_0^t e_h dt$. The total heat input to the sample then is given by the current times this quantity. The actual heat-pulse time also is measured using a conventional electronic timer, so that an average heater resistance can be calculated for each point from the current and the time interval. Various other checks were made to verify that this procedure is indeed valid (such as a direct heater-resistance measurement versus temperature, variation of heat-pulse times, etc.), and no systematic errors were found. The Vidar does appear to introduce some sample-heating, which is observable as a slight increase in the drift rate at the lowest temperatures. This is of the order of a few ergs per minute, and is assumed to be constant.

¹⁰ D. W. Osborne, H. E. Flotow, and F. Schreiner, *Rev. Sci. Instr.* **38**, 159 (1967).

¹¹ H. H. Sample and C. A. Swenson, *Phys. Rev.* **158**, 188 (1967).

¹² W. N. R. Stevens (to be published).

¹³ J. C. Ho and N. E. Phillips, *Rev. Sci. Instr.* **36**, 1382 (1965).

TABLE I. Summary of the electrical and physical characteristics of the samples which were used in this investigation, together with the source of the crystal.

Sample	Length (cm)	Mean diameter (cm)	Mass (g)	Average g at. wt.	Number of g atoms	Resistivity at 300°K ^a (Ω cm)	Net carrier concentration ^a (cm ⁻³)	Source
InSb	10.1	1.0	90.731	118.29	0.7669	0.024	$<2 \times 10^{16}$	Ohio Semiconductors
InAs	10.0	0.6	62.638	94.87	0.6602	0.012	$\sim 2 \times 10^{16}$	Texas Instruments
GaSb	4.5	0.6	15.640	95.47	0.1634	0.68	$\sim 10^{17}$	Texas Instruments
GaAs	8.3	0.6	27.004	72.32	0.3734	0.002	$\sim 2 \times 10^{18}$	Texas Instruments
Cu ^b	10.0	0.9 ^b	60.005	63.54	0.9444	ASARCO (99.999%)

^a The various uncompensated impurity concentrations were determined by comparing the observed resistivities with those of doped samples. Data for GaSb and InSb were obtained from N. B. Hannay, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), while the information for GaAs and InAs was obtained from unpublished literature supplied by Texas Instruments. The sample purity for InSb was substantiated by helicon dispersion relations which were observed in a piece of this sample by J. L. Stanford of this laboratory.

^b The resistivity ratio, $R_{300}/R_{4.2}$, of this sample as vacuum annealed is 550.

The thermometer resistances are measured potentiometrically also (using current-reversal techniques) by comparison with either a 1000-Ω or a 100-Ω standard resistor. The high-impedance current source uses a 45-V dry cell, and initial observations of large apparent thermal emf's were eliminated by using circuit-guarding techniques. Thermometer currents vary from 0.5 μA at the lowest temperatures (0.9°K, 10 000 Ω) to 100 μA above 25°K (25 Ω). In all cases the thermometer produces negligible heating and shows no current effect on the resistance. The various voltages are measured using a Guildline Type 9180 potentiometer. A Keithley 150A microvoltmeter (with an output to the second recorder pen) is used as a null detector for this system and also as a means for interpolation to 0.01 μV between the least count settings (0.1 μV) of the potentiometer. The choice of currents used results in a relatively constant value of $\delta T/T \sim 5 \times 10^{-6}$, where δT is the minimum detectable temperature change.

The sample temperature drifts are linear in time (for 5 min or so) both before and after a heat pulse. These correspond to heat leaks (+ or -) which vary from a few ergs per minute near 1°K to 10³ erg/min near 20°K. No attempt is made to control or monitor the temperature of the thermal shield, which surrounds the calorimeter and is attached to the helium pot. This shield is held at its lowest temperature (0.9°K) when taking data below 4°K, but it is free to drift upwards slowly in temperature for all other cases. One problem with the calorimeter involves the close proximity of the heater and the thermometer which causes a considerable "overshoot" of the thermometer temperature after a heat pulse. This gives ambiguous temperature increments only at the highest temperatures.

The long-term linear drift rates are used in the conventional manner to determine the temperature change ΔT of the sample at the midpoint of the heat pulse. This midpoint is unambiguous since both the heater current and the thermometer voltage traces appear on the recorder chart. The thermometer voltage change due to the heat pulse invariably spans ten or more equivalent chart widths, except for the small samples at the lowest temperatures, so the recorder

traces are used primarily for interpolation. In general, the temperature increments ΔT were chosen to be of the order of 0.05T to make errors due to the temperature variation of the heat capacity less than those involved in the determination of ΔT (0.1%).

Thermometry

The thermometer, GR622, is calibrated directly between 3.56 and 40°K by comparison with the two standard thermometers (GR618 and GR803) and the platinum resistance thermometer scale described in RTAS.⁸ The precision is 2 mdeg. This constant volume gas thermometer-based scale will be called T_{618} in the following. As is done in RTAS, the logarithm of the temperature ($\ln T$) is expressed analytically as a power series in $\ln R$, and the data are fitted to this expression using least-squares-fitting techniques which minimize $(T - T_{\text{calc}})^2$. The data from 3.56 to 30°K are fitted by an eleven-term series ($N=10$), while the data from 20 to 40°K require a five term series ($N=4$). In each case, the calibration data scatter randomly from the equations with an rms deviation of 2 mdeg. The transition between the two fits of the data is made at 28°K in the data analysis. At this temperature, the temperatures and dR/dT values as calculated from the two expressions agree to 1 mdeg and 0.1%, respectively.

The temperature scale as defined by RTAS does not agree with the liquid-helium vapor pressure scale T_{58} but lies roughly 8 mdeg higher from 3 to 5°K. The deviations are not well defined below this temperature. Since our data extended down to 1°K, we chose the rather awkward expedient of using T_{58} for temperatures from 1 to 4°K, and T_{618} for all higher temperatures, with some overlap near 4°K. This allows us to compare our results directly with other work (on copper, for instance) in the liquid-helium region where a well-defined and easily reproducible temperature scale exists. Such comparisons are not practical for temperatures between 4 and 20°K. If the RTAS conclusions are correct, all previous gas thermometer scales inadvertently or intentionally have been forced to blend smoothly into T_{58} near 4°K, and hence should show systematic differences from our data in this region.

The differences which can be expected to occur near 4°K for results calculated on the two scales can be estimated as follows: For a given thermometer resistance, heat capacities calculated on the two scales should be identical, since the two scales differ by a constant $\Delta T = 8$ mdeg.⁸ However, this value of the resistance corresponds to a T_{58} temperature near 4°K which is 0.2% less than that given by T_{618} . Hence, if the specific heat varies as T^3 , the value of C_v as calculated for 4.0000°K should be 0.6% larger for the T_{58} calibration than for the T_{618} calibration. If C_v were to vary linearly with temperature (as for a metal), the corresponding difference would be only 0.2%.

We are somewhat uncertain of the accuracy of our T_{58} calibration for GR622 below 2°K, so that one purpose of the measurement of the specific heat of copper was to check this calibration. These data give the expected temperature dependence, $C = AT + BT^3$, to 0.1% between 1.6 and 4.2°K, but show significant deviations at lower temperatures (up to 1% at 1°K). We use the higher-temperature data to extrapolate the copper data from 1.6 to 1°K and assume that the discrepancies which result are due to errors in the temperature scale or dR/dT . Rather than correct the temperature scale (by a total of 5 mdeg in this region), we choose to assume that all heat-capacity measurements will be in error by the same fractional amount as the copper data, and hence apply a temperature-dependent multiplicative correction (1% maximum value) to all of our data below 1.6°K.

Addenda Heat Capacity

The addenda heat capacity is determined with the original quantity of Dow Corning vacuum grease in the empty tray and with the nylon thread sample ties in contact with the vertical wire sample supports. Three separate addenda runs were made which were

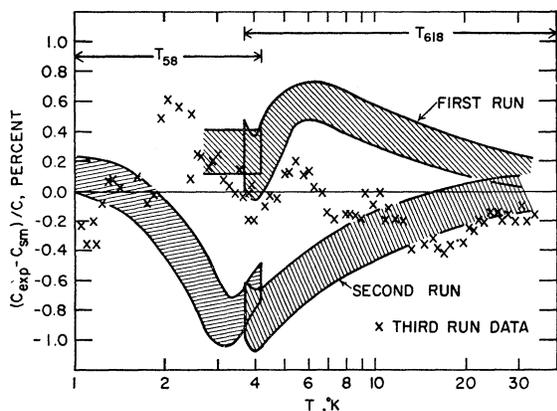


FIG. 1. Deviations of the addenda heat capacity from a smooth representation of the data. The cross-hatched areas represent the data from runs 1 and 2. The data for run 3 (x) were used as the addenda correction in the final data analysis.

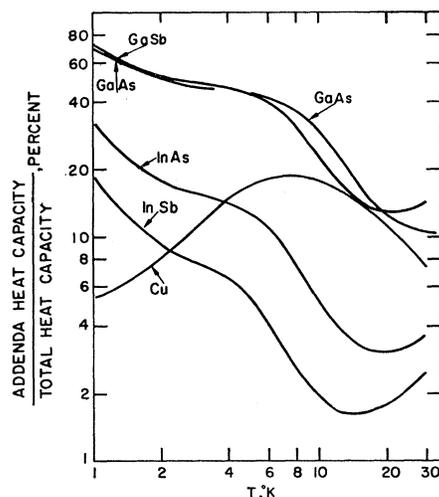


FIG. 2. The ratio (in percent) of the addenda heat capacity to the total measured heat capacity for each sample.

separated by measurements on various samples. The sequence of the various measurements is detailed in the following paragraph for future reference.

The first addenda run was made at the beginning of these heat-capacity measurements, and for various reasons the data below 2.8°K were discarded. Measurements then were made on Cu (as received), GaAs, GaSb, InAs, and the addenda, in that order. Between the second and third addenda runs, heat-capacity measurements were made on InSb and three hexagonal metals (Y, Sn, and Zn). After the third addenda run, data were taken for Bi, the Cu sample (after outgassing), Cd, and after a two-week delay, InSb again. The results of the heat-capacity measurements on the anisotropic metals will be presented elsewhere, and only the data on copper and the III-V compounds will be given in this paper.

The data for all three addenda runs were treated as equivalent and were least-squares-fitted to two power series, one for temperatures below 4.2°K (the T_{58} region), and one for higher temperatures (the T_{618} region). The deviations of the data from these power series are shown in Fig. 1, where an overlap of the two fits is shown at 4.2°K. The scatter of the data for an individual run (of the order of $\pm 0.2\%$) is shown explicitly only for the third run, and is indicated by the shading for the others. This scatter is clearly less than the systematic differences between runs, which can be as large as 1.5%. The reason for these differences is not clear. The random nature of the deviations between runs makes it unlikely that they are due to the loss (or gain) of grease. The heat capacity of Apeizon T grease has been measured,¹⁴ and if our grease has roughly the same characteristics, the loss of 1 mg (3%) should cause a maximum effect of 0.3% on the addenda

¹⁴ E. F. Westrum, Jr., Chien Chou, D. W. Osborne, and H. E. Flotow, *Cryogenics* 7, 43 (1967).

heat capacity at 5°K. The adsorption of air or moisture on the grease, if it has been exposed to the atmosphere when cool, possibly could have the random effect which we observe.

The results for the third run are chosen arbitrarily for the analysis of the heat-capacity data, since these data appear to represent an "average" (in some sense) of the other two runs. The uncertainties in the addenda correction ($\pm 1\%$ at worst) are not important for Cu, InAs, or InSb, but they do introduce significant uncertainties into the low-temperature results for GaSb and GaAs. Figure 2 gives the temperature dependence of the fraction of the total measured heat capacity which is contributed by the addenda for each sample.

Experimental Accuracy

The precision of an individual heat-capacity measurement is estimated to be of the order of 0.2%, with the major uncertainty arising from the determination of the ΔT of the heat pulse. The data usually scatter randomly from a smooth curve by about this amount (Fig. 1). The scatter of the data for the smallest heat-capacity samples (GaAs and GaSb) is larger than this below 2°K (1%), and more especially below 1.5°K, for unknown reasons, since the addenda runs show no such increased scatter. Periodic systematic checks were made to ascertain the effects of varying the heating times and the size of temperature increment, but no observable effects were found (to 0.2%). Each set of data was repeated with no intermediate warm-up to room temperature, and the data usually were taken the second time by a different person. Again, different sets of data agree well.

The data which were obtained for the InSb sample may be considered as typical to illustrate some of these

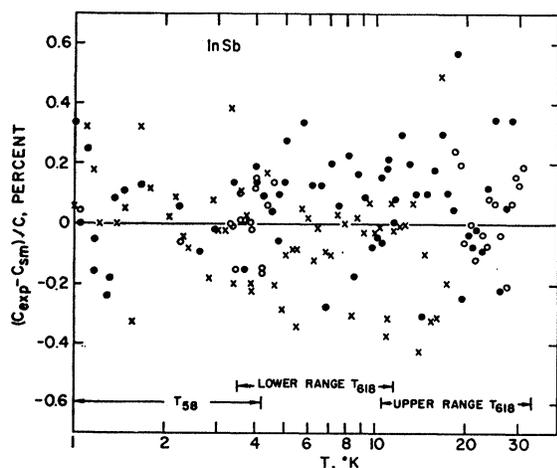


FIG. 3. Deviations of the data for InSb from a smooth representation (which required the three ranges indicated) of the total data. ● and × are data points for run 1 and were taken by two different persons; ○ are the data points taken in run 2, two months later.

points, since these data were obtained in two distinct runs which were separated by a considerable interval of time. All of the data were fitted by least-squares techniques to a power series in T^{2n-1} in three temperature regions, with Fig. 3 showing the deviations of the data from the resulting fit. The closed circles and crosses represent the original data as taken by two different persons on different nights. The open circles represent data taken in a single run two months later. The same addenda correction has been used for all data, and as can be deduced from Fig. 2 the effect of the addenda uncertainties is negligible.

We conclude that the precision of our data is of the order of 0.2 to 0.3%. An additional systematic uncertainty exists due to the temperature scale. If two temperature scales (T_1 and T_2) deviate from each other by 5 mdeg in a 1° temperature interval [i.e., $d(T_1 - T_2)dT = 5 \times 10^{-3}$], the individual heat-capacity determinations in that temperature interval will differ by 0.5%. An additional error (which is described in the thermometry section) could arise from the fact that identical values of T_1 and T_2 correspond to different values of the true thermodynamic temperature. Independent measurements of the heat capacity of copper made in different laboratories and with different temperature scales differ from each other by anywhere from 0.5 to 1%,¹⁰ although they can be internally smooth and consistent to 0.1%. If we choose to accept the estimates of RTAS as to the possible deviations of their temperature scale from the true thermodynamic scale (3 to 5 mdeg),⁸ we can conclude that the accuracy of the present data in general should be of the order of $\pm 0.5\%$ except below 2°K for GaAs and GaSb where the uncertainty (mostly due to the addenda) rises to 2%.

RESULTS AND DISCUSSION

In general, the low-temperature specific heat of a solid can be expanded in a power series in the temperature as¹⁵

$$C_v = \sum a_n T^n, \quad (n = 1, 3, 5, 7, \dots). \quad (1)$$

For a metal, $a_1 = \gamma$, the electronic specific-heat coefficient, while for a dielectric solid $a_1 = 0$. Free-carrier effects due to impurities can be of importance for a semiconductor at low temperatures, and these are reflected in nonzero values of a_1 .^{4,5} In all cases, $a_3 = 233.78R \Theta_0^{-3}$, where R is the gas constant and Θ_0 is the limiting continuum value of the Debye temperature. The higher-order terms, a_5, a_6 , etc., have no simple interpretation although a_5 is usually positive.

The various coefficients can be determined by least-squares procedures with proper weighting. For a metal, where the linear term is important, it is customary to fit the low-temperature data as

$$C_v/T = \sum a_n T^{n-1}, \quad (n = 1, 3, 5, \dots) \quad (2)$$

¹⁵ T. H. K. Barron and J. A. Morrison, Can. J. Phys. 35, 799 (1957).

TABLE II. Summary of the low-temperature results, T_{58} region.

	Cu	InSb	InAs	GaSb	GaAs
Average g at. weight	63.54	118.29	94.87	95.47	72.32
Fit region ($^{\circ}\text{K}$)	1.6-4.2	0.93-3.0	0.93-4.2	0.95-4.2	1.4-4.2
Maximum value of T/Θ_0 in fit	0.012	0.015	0.02	0.0165	0.015
Fit constants for Eq. (1) ^a					
(units are μJ , $^{\circ}\text{K}$, and g at.)					
a_1	693.2 ± 4	7.54 ± 0.8	(7.54)	4.8 ± 0.4	5.77 ± 1.0
a_3	47.88 ± 0.4	220.36 ± 2.0	220.17	123.02 ± 1	98.63 ± 2
a_5	...	3.045	3.285	0.987	0.720
a_7	-0.0753
a_9	0.00614
Θ_0^{cal} , ($^{\circ}\text{K}$), present values ^b	343.7 ± 1	206.6 ± 0.6	206.7	250.9 ± 0.7	270 ± 2
Martin ¹	345.8 ± 1.2				
Θ_0^{el} ($^{\circ}\text{K}$)	345.2 ± 1.0^j	205 ± 2^e		249 ^e	266 ^e
		205.8 ± 1^d		234 ^f	345 ± 3^h

^a Use of these constants reproduces the data to within 0.3% with all deviations completely random. The error limits, where shown, are the estimated accuracy of the coefficients.

^b Calculated from $\Theta_0^{\text{cal}} = (1.94436 \times 10^6 \text{ mJ}/^{\circ}\text{K g at.})/a_3$.

^c Slutsky and Garland (Ref. 23). Calculated from 4.2 $^{\circ}\text{K}$ ultrasonic data.

^d Alers (Ref. 24). Calculated by numerical integration on a computer, using data from Ref. 23.

^e Gerlich (Ref. 25). Calculated from 300 $^{\circ}\text{K}$ ultrasonic data.

^f Gerlich (Ref. 26). Calculated from 4.2 $^{\circ}\text{K}$ ultrasonic data.

^g Piesbergen (Ref. 27). Calculated from 300 $^{\circ}\text{K}$ ultrasonic data.

^h Garland and Park (Ref. 28). Calculated for 0 $^{\circ}\text{K}$ from ultrasonic data extrapolated from 77 and 300 $^{\circ}\text{K}$.

ⁱ Martin (Ref. 18), also gives a value of $a_1 = 165.2 \pm 0.8 \mu\text{cal}/^{\circ}\text{K}^2 \text{ g at.}$, which is to be compared with the present value of $165.6 \pm 1.0 \mu\text{cal}/^{\circ}\text{K}^2 \text{ g at.}$

^j Alers (Ref. 24). The uncertainty for Θ_0^{el} is 0.25% as quoted by Martin (Ref. 17).

to obtain a_1 or γ . Once a_1 has been obtained, the lattice terms may be calculated from

$$(C_v - a_1 T)/T^3 = \sum a_n T^{n-3}, \quad (n=3, 5, 7, \dots). \quad (3)$$

We have used these expressions to analyze our experimental specific-heat data in both the T_{58} and T_{618} regions. The following discussion will involve first the copper results, since these relate our accuracy and results directly to other precision calorimetry, and then the results on the III-V compounds. Both the tabulations and the graphical representations of the data will show differences near 4 $^{\circ}\text{K}$, where our T_{58} and T_{618} analyses overlap. We have made no effort to smooth the data in the region where these scales can be compared directly.

Copper

The copper sample is described in Table I. Our initial runs were made with the copper in the "as received" condition. Later, as suggested by Martin,¹⁶ the sample

was vacuum-outgassed for 8h at 900 $^{\circ}\text{C}$ and 10^{-6} Torr and then remeasured. In each case, the data scattered about smooth computer fits [Eq. (2)] by from 0.1 to 0.2%. The only systematic differences between the two sets of data occur below 6 $^{\circ}\text{K}$, where C_v for the annealed state is 0.3% below that of the original state. This agrees qualitatively with Martin's observations.¹⁶

The values which we obtain for a_1 and a_3 for the T_{58} data for the annealed copper are given in Table II, together with calorimetric and elastic-constant values for Θ_0 . A smoothed compilation of our copper data is given in Table III (for the T_{58} range) and Table IV (for the T_{618} range). These are obtained from computer fits of the data (in three ranges), which represent the data with a random deviation of 0.1%. The equivalent $\Theta_D(T)$ values are calculated from lattice heat capacities ($C^{\text{lat}} = C_v - a_1 T$) using the tabulated C_v values and a_1 from Table II.

The values of a_1 (or γ) and a_3 (or Θ_0) given in Table II reproduce our data to within the experimental

TABLE III. Smoothed values for the specific heats and the equivalent Debye Θ 's for the measured samples in the T_{58} region. Units are mJ/K g at. for C_v and K for Θ .

T_{58}	Cu		InSb		InAs		GaSb		GaAs	
	C_v^a	Θ^b	C_v^a	Θ^b	C_v^a	Θ^b	C_v^a	Θ^b	C_v^a	Θ^b
1.0	0.7411 ^c	343.7	0.2309	205.7	0.1288	250.3	0.1051	269.5	0.04935	346.2
1.5	1.201 ^c	343.7	0.7783	204.5	0.4299	249.5	0.3470	268.7	0.1625	345.7
2.0	1.769	343.7	1.875	203.0	1.025	248.3	0.8236	267.6	0.3834	345.1
2.5	2.481	343.7	3.757	201.1	2.031	246.9	1.626	266.2	0.7503	344.4
3.0	3.372	343.7	6.722	198.6	3.576	245.2	2.855	264.5	1.304	343.4
3.5	4.479	343.7	11.19	195.5	5.810	243.2	4.627	262.5	2.087	342.3
3.8	5.261	343.7	14.87	193.0	7.551	242.0	6.004	261.3	2.687	341.6
4.0	5.837	343.7	17.86	191.1	8.903	241.1	7.072	260.4	3.147	341.1
4.2	6.459	343.7	21.40	188.9	10.42	240.1	8.272	259.5	3.659	340.5

^a C_v is the total specific heat as measured, and includes the free-carrier contribution.

^b $\Theta(T)$ is obtained from $C_v - a_1 T = D(T/\Theta)$, where $D(T/\Theta)$ is the Debye specific-heat function and a_1 is as listed in Table II.

^c Extrapolated from data between 1.6 and 4.2 $^{\circ}\text{K}$.

¹⁶ D. L. Martin, Rev. Sci. Instr. 38, 1738 (1967).

TABLE IV. Smoothed values for the specific heats and the equivalent Debye Θ 's for the measured samples above 3.8°K calculated using the RTAS (T_{618}) temperature scale. Units are mJ/°K g at. for C_v and °K for Θ .

T_{618}	Cu		InSb		InAs		GaSb		GaAs	
	C_v^a	Θ^b	C_v^c	Θ^c	C_v^c	Θ^c	C_v^c	Θ^c	C_v^c	Θ^c
3.8	5.246	344.4	14.76	193.3	7.494	242.4	5.967	261.5	2.669	341.9
4.0	5.812	344.7	17.74	191.4	8.849	241.4	7.034	260.6	3.129	341.4
4.2	6.427	344.8	21.25	189.3	10.39	240.3	8.241	259.5	3.641	340.8
5.0	9.410	344.5	42.37	179.0	18.88	234.4	14.80	254.2	6.287	338.1
6.0	14.42	344.6	92.70	165.5	37.26	224.2	28.62	244.8	11.29	333.8
7.0	21.15	344.6	182.2	154.1	69.67	212.3	52.52	233.3	18.96	327.7
8.0	30.07	343.7	320.3	146.0	123.2	200.7	91.86	221.3	30.53	319.5
9.0	41.43	342.8	509.1	140.7	204.2	190.8	152.1	210.4	47.74	309.7
10.0	55.59	341.9	743.5	137.7	316.1	183.2	237.1	201.7	72.62	299.2
11.0	72.82	341.1	1015	136.4	458.6	178.0	348.2	195.1	107.2	289.0
12.0	93.59	340.3	1312	136.3	629.9	174.7	485.1	190.6	153.4	279.8
13.0	118.5	339.2	1628	137.0	827.5	172.7	646.7	187.6	212.6	271.9
14.0	148.2	337.7	1956	138.4	1047	171.8	830.7	185.7	286.1	265.2
15.0	183.3	336.0	2286	140.1	1285	171.6	1033	184.9	374.7	259.7
16.0	224.6	334.1	2617	142.3	1537	172.1	1253	184.6	478.4	255.3
17.0	272.6	332.1	2945	144.6	1798	173.1	1487	185.0	596.4	252.0
18.0	327.9	330.0	3271	147.0	2065	174.5	1730	185.8	728.2	249.6
19.0	391.1	328.0	3592	149.6	2333	176.2	1978	187.0	871.5	248.0
20.0	462.4	326.1	3906	152.2	2601	178.2	2228	188.6	1025	247.1
21.0	542.4	324.3	4206	155.0	2865	180.5	2480	190.5	1187	246.9
22.0	631.4	322.6	4493	157.9	3126	182.9	2731	192.5	1356	247.1
23.0	729.7	321.0	4765	161.0	3382	185.4	2981	194.7	1532	247.6
24.0	837.6	319.6	5031	164.0	3633	188.0	3230	197.0	1714	248.5
25.0	955.3	318.3	5297	166.9	3879	190.8	3477	199.3	1899	249.7
26.0	1083	317.1	5564	169.7	4121	193.5	3721	201.8	2087	251.1
27.0	1220	316.1	5824	172.5	4358	196.3	3960	204.3	2276	252.7
28.0	1367	315.1	6066	175.5	4590	199.1	4194	206.9	2466	254.5
29.0	1523	314.4	6301	178.4	4818	202.0	4427	209.5	2657	256.4
30.0	1688	313.7	6560	180.9	5041	204.8	4660	212.0	2848	258.4
31.0	1861	313.1	5258	207.7	4894	214.4	3041	260.4
32.0	2044	312.5	5473	210.5	5123	216.9	3235	262.5
33.0	2236	312.0	5689	213.2	5338	219.6	3428	264.6
34.0	5890	216.1	5572	221.8	3620	266.8

^a See footnote a, Table III.

^b See footnote b, Table III.

^c For the III-V compounds, the electronic effect was negligible in the T_{618} region, and C_v is regarded as due to the lattice only. Θ is calculated as in footnote b, Table III, where $\alpha_1=0$.

precision (0.1%), and agree with the range of values that appear in the literature.^{10,16-18} The most valid comparison of various data, however, is through the actual C_v values and this can be done most conveniently by making use of the reference equation of Osborne *et al.*,¹⁰ which represents an average of published C_v data for copper. This comparison is made in the deviation plot of Fig. 4. The abscissa represents the ISU data, so the discontinuities in the various curves at 4°K are due to the discontinuities introduced by our two temperature scales.

The scatter of our outgassed-copper data from a smooth relationship (0.1%, not shown) is less than or of the same order of magnitude as the systematic deviations of our data from the reference equation except near 7°K and above 22°K, and is comparable with the deviations of other data from this equation as reported in Osborne *et al.*¹⁰ Since the reference equation is based solely on Martin's work above 20°K, we also have plotted in Fig. 4 the deviation of Martin's smoothed data¹⁷ from the smoothed ISU data. Martin's data deviate appreciably from both our data and the

reference equation near 4°K, as is evident in the original compilation.¹⁰ An additional comparison between our results and Martin's can be made using common measurements of the specific heat of zinc. Our data (unpublished), taken in this series of measurements, are compared with Martin's published results¹⁹ in Fig. 4 also.

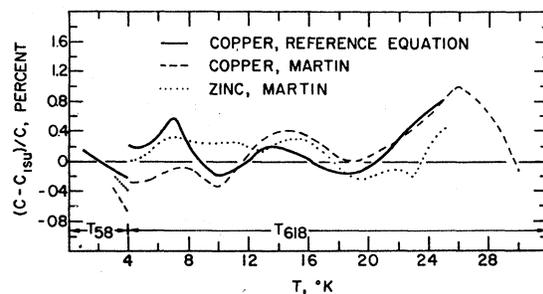


FIG. 4. A comparison of the present (ISU) data for copper and zinc with other published results, as is discussed in the text. The discontinuities at 4°K are due to the use of two different temperature scales (indicated as T_{58} and T_{618} in the figure) in the analysis of the ISU data.

¹⁷ D. L. Martin, Phys. Rev. **141**, 576 (1966).

¹⁸ D. L. Martin, Phys. Rev. **170**, 650 (1968).

¹⁹ D. L. Martin, Phys. Rev. **167**, 640 (1968).

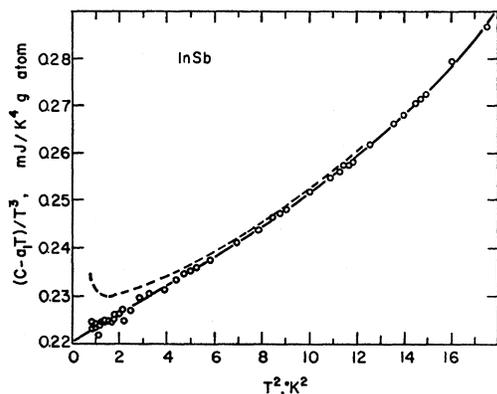


FIG. 5. A plot of the T_{58} -region data for InSb. The dashed line indicates the smoothed plot of the data which would result if a_1 were assumed to be zero. The points were plotted assuming the value of a_1 given in Table II. The solid line is given by the coefficients a_3 , a_5 , etc., of Table II.

These copper and zinc data comparisons suggest that except near 26°K our data agree with other data to within our estimated experimental accuracy of 0.5%. Indeed, at most temperatures below 22°K the agreement is at least a factor of 2 better than this. This is remarkable, in view of the ambiguities involved in experimental temperature scales in what we call the T_{618} region.⁸ The indication of a 1% difference between our data and Martin's at 26°K exists for both the zinc and copper data. This is puzzling, since both experiments are based directly on the platinum resistance thermometer scale in this temperature region.

III-V Compounds, General

Table II contains the value of the a_n [Eq. (3)] which are required to fit our III-V compound data in the T_{58} region. Tables III and IV are smooth, computer-calculated [using Eq. (3)] compilations of the total C_v data and the equivalent values of the Debye temperature Θ_D for the lattice contributions. This lattice contribution is obtained by subtracting the free-carrier contribution from the measured and tabulated values of C_v .

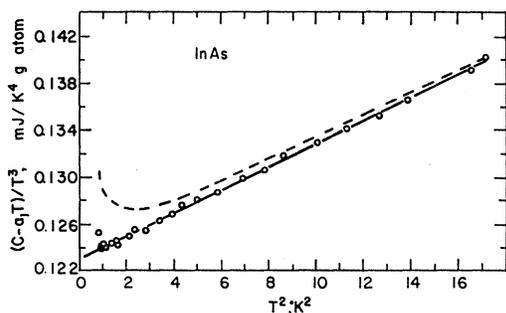


FIG. 6. A plot of the T_{58} data for InAs. See the caption of Fig. 5 for description.

Figures 5–8 give plots of the T_{58} data as suggested by Eq. (3). Initially, we assumed $a_1=0$ (no free-carrier contribution to C_v), and the dashed lines in these figures represent best curves drawn through the data points which were plotted with this assumption. The excess curvature, especially at low temperatures, was disturbing, so the data were refitted to include an a_1 contribution [Eq. (2)]. The data points and solid curves shown in these figures show the much simpler behavior which results when the values of a_1 given in Table II are assumed. These values of a_1 are approximately a factor of 5 less than those reported for germanium and silicon^{4,5} which were doped to obtain 10^{18} carriers/cm³. However, the characteristics of our samples (Table I) offer no *a priori* reason for deciding on the reasonableness of these a_1 values.

The precision to which a_3 (or Θ_0) can be obtained is limited by the nonideal behavior of the lattice heat capacity at the lowest temperatures. An inspection of Figs. 5–8 will show that C_v is given by its limiting continuum expression (proportional to T^3) to an accuracy of 2% only for $T/\Theta_0 \leq 0.007$ (from 1.4°K for InSb to 2.5°K for GaAs). Hence, with some deterioration of the experimental precision at the lowest temperatures, it is difficult to establish a_3 with an accuracy of greater than 0.5 to 1%. The good agreement which we show between elastic constant and calorimetric values of Θ_0 may be fortuitous, since free carriers can have a significant effect on the elastic constants of a semiconductor.^{4,5,20–22} No specific data exist for ascertaining the magnitude of this effect for the III-V's although the indications from the work on germanium and silicon are that it will be within our stated experimental accuracy.^{4,5}

Piesbergen⁶ has reported C_v measurements on a number of III-V compounds (including the four reported here) over the temperature range from 12 to 300°K. In general, his data agree with ours to within 2% (his stated accuracy) above 18°K. Below 18°K, his data for all four compounds give values of C_v which are much (up to 10%) higher than ours. This presumably is due to the falling off in sensitivity of his lead thermometer. Ohmura⁷ has reported data on InSb which differ from ours by average of 3% (his stated accuracy) in the range from 8 to 30°K. Because our data are roughly an order of magnitude more precise than these earlier data, no explicit comparisons will be made in the following specific discussions of the data.

Indium Antimonide

This sample has the largest heat capacity (due both to its physical size and low values of Θ) of any of the

²⁰ L. J. Brunner and R. W. Keyes, Phys. Rev. Letters **7**, 55 (1961).

²¹ A. E. Kadshevich, V. M. Beilin, Yu. Kh. Vekilov, O. M. Krasil'nikov, and V. N. Podd'yakov, Fiz.Tverd. Tela **9**, 1861 (1968) [English transl.: Soviet Phys.—Solid State **9**, 1467 (1968)].

²² R. W. Keyes, Solid State Phys. **20**, 37 (1967).

samples we measured. It was run twice (Fig. 3) with good agreement between the runs. The only difficulty in the data taking arose above 25°K where, because of the large heat capacity, relaxation times became large. The values of Θ_0 obtained from fits in two different ranges (Table II) are in excellent agreement with each other and with the elastic-constant value.^{23,24}

Indium Arsenide

The data for this sample are of the same general quality as for InSb. Gerlich has reported both room-temperature²⁵ and liquid-helium-temperature²⁶ elastic-constant measurements and corresponding values for Θ_0 . Our calorimetric value (250.9°K) agrees better with his room-temperature calculation (249°K) than with his low-temperature calculation (234°K).

Gallium Antimonide

This sample was our smallest both physically and in terms of heat capacity. As can be seen in Fig. 7, the lowest-temperature data (below 1.5°K) appear to be in

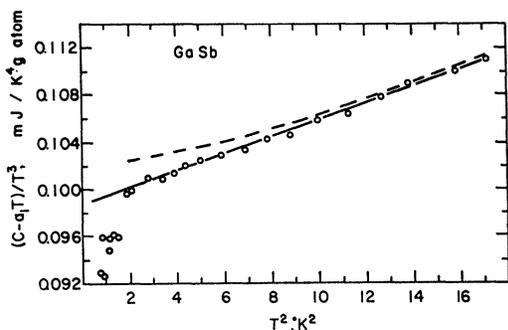


FIG. 7. A plot of the T_{58} data for GaSb. See the caption of Fig. 5 for description. The data below $T^2=2^\circ\text{K}^2$ were eliminated in calculating the coefficients a_3 , a_5 .

error. This is obvious from the recorder traces also, and these data have been ignored in the calculation of Θ_0 . The only elastic-constant data for GaSb are for room temperature and the elastic-constant value of Θ_0 has been calculated from these by Piesbergen.²⁷

Gallium Arsenide

The electronic term a_1 appears to be largest for this sample (Fig. 8), since the lattice heat capacity is so small, although a_1 actually is the smallest in absolute terms. The uncertainty in the extrapolation to obtain a_3 (Fig. 8) caused by the data scatter is compensated

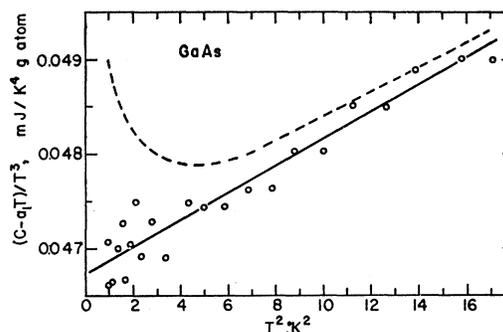


FIG. 8. A plot of the T_{58} data for GaAs. See the caption of Fig. 5 for description.

in part by the relatively small interval over which the extrapolation must be made. The calorimetric and elastic constant values of Θ_0 ²⁸ again are in good agreement.

CONCLUSIONS

The comparison of our copper data with other copper data suggests an accuracy of our data of the order of 0.5% except at the lowest temperatures. We find that a specific-heat contribution linear in the temperature must be included in the analysis of the III-V compound results. This presumably is due to free-carrier effects which arise because of our relatively impure samples. The specific-heat values for the limiting Debye temperature Θ_0 agree within experimental error with those calculated from elastic-constant measurements. The insensitivity of these calculations to the choice of the

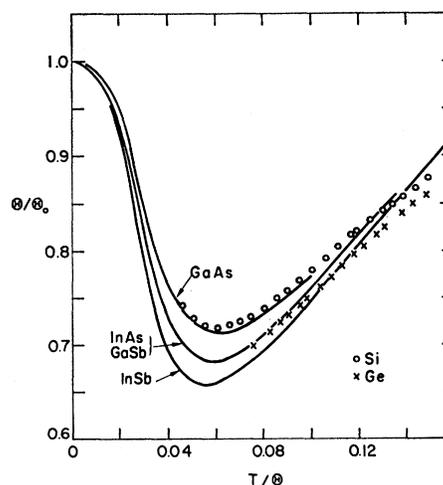


FIG. 9. A plot of the reduced Debye Θ_0 's against reduced temperature for the present heat-capacity data for the III-V compounds (Table IV) and for the data of Flubacher, *et al.*³ for Ge and Si. The curve for GaSb falls below the plotted curve for $T/\Theta_0 \geq 0.09$ and approaches the curve for InSb at the highest temperatures.

²³ L. J. Slutsky and C. W. Garland, *Phys. Rev.* **113**, 167 (1959).

²⁴ G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1965), Vol. IIIB, Chap. 1.

²⁵ D. Gerlich, *J. Appl. Phys.* **34**, 2915 (1963).

²⁶ D. Gerlich, *J. Appl. Phys.* **35**, 3062 (1964).

²⁷ U. Piesbergen, in *Physics of III-V Compounds*, edited by R. K. Willardson and A. C. Beer, (Academic Press Inc., New York, 1966), Vol. 2, p. 49.

²⁸ C. W. Garland and K. C. Park, *J. Appl. Phys.* **33**, 759 (1962).

TABLE V. Smoothed values of the Grüneisen parameters for the III-V compounds recalculated from the data of Sparks and Swenson^a using the present heat-capacity data. See the text.

T (°K)	γ			
	GaAs	GaSb	InAs	InSb
0	0.598	0.311	0.321	0.215
2	0.579	0.298	0.262	0.00
4	0.565	0.278	0.082	-0.537
6	0.532	0.231	-0.195	-0.869
8	0.468	-0.032	-0.378	-0.956
10	0.199	-0.321	-0.533	-0.978
12	0.021	-0.42	-0.577	-0.985
14	-0.107	-0.440	-0.611	-0.985
16	-0.185	-0.427	-0.637	-0.978
18	-0.216	-0.409	-0.633	-0.933
20	-0.235	-0.381	-0.620	-0.884
22	-0.237	-0.345	-0.604	-0.836
24	-0.234	-0.306	-0.584	-0.765
26	-0.222	-0.269	-0.557	-0.689
28	-0.211	-0.234	-0.529	-0.610
30	-0.200	-0.198	-0.496	-0.53
32	-0.176	-0.163	-0.465	-0.46
34	-0.148	...	-0.437	...
36	-0.114	...	-0.409	...
38	-0.090	...	-0.374	...
40	-0.071	...	-0.340	...
42	-0.306	...

^a Reference 2.

low-temperature or the high-temperature elastic constants is due presumably to the small total thermal expansion of these solids.

One of our initial concerns was to investigate systematic variations of thermodynamic properties of these solids from those of germanium and silicon on appropriate reduced plots. One such plot, which involves Θ/Θ_0 versus T/Θ_0 , is given in Fig. 9. The four III-V compounds show a regular change in the depth of the minimum and in the location of the minimum with average mass (or value of Θ_0). InAs and GaSb, which have the same average gram atomic weight, behave very much the same at low temperatures, with the data for GaSb (not shown) falling away slightly from the curve as plotted and approaching InSb above $T/\Theta_0 = 0.09$. The Ge and Si data, from Flubacher *et al.*,³

can be seen to deviate appreciably from the picture suggested by the III-V's. In particular, GaAs behaves much like Si, while on the basis of average atomic mass and approximate Θ values one would expect GaAs and Ge to behave similarly. The Ge data are identical with our InAs and GaSb curves for $T/\Theta_0 \leq 0.08$. The thermal-expansion results suggest similar differences between the reduced properties of the pure elements on one hand and the compounds on the other.² These differences, which in reality are quite small, probably will be understood only through a detailed calculation.

One objective of the present work was to provide data for the accurate calculation of the Grüneisen parameters for the III-V compounds. The values which we have recalculated from the thermal-expansion data of Sparks and Swenson² are given in Table V. The qualitative conclusions reached in the earlier paper are not changed. The major correction occurs for InAs where an incorrect value for Θ_0 (based on low-temperature elastic-constant data) was assumed in estimating the heat capacity. The present heat-capacity data suggest that the value of Θ_0 as calculated from the room-temperature elastic constants is more nearly correct, so that to be consistent we have used the high-temperature value of the bulk modulus ($B_T = 580$ kbar)²⁵ instead of the low-temperature value (634 kbar)²⁶ in the calculations for Table V. All other data which were used (except for the heat capacities) are identical with those given by Sparks and Swenson.²

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