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Elastic Constants, Thermal Expansion, and Debye Temperature of Lead Telluride

BLAND HOUSTON, R. E. STRAKNA,* AND HENRY S. BELSON
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
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Measurements of the elastic constants and thermal expansion of PbTe have been made from 4.2° to 303.2°K. The extrapolated 0°K values for C_{44}, $(C_{11}-C_{12})/2$, and $(C_{11}+2C_{12})/3$, respectively, are 1.514 ± 0.009, 6.184 ± 0.066, and $4.560\pm0.042\times10^{11}$ dyn/cm². At 303.2°K these values are 1.344 ± 0.008, 5.016 ± 0.057, and $4.107\pm0.037\times10^{11}$ dyn/cm². Intermediate values are presented graphically, as are the thermal-expansion data. The linear coefficient of thermal expansion is found to be $20.4\pm0.4\times10^{-6}$/°C at room temperature. The 0°K Debye temperature is calculated to be $176.7°\pm 0.5°$K.

I. INTRODUCTION

Lead telluride has been widely investigated both theoretically and experimentally,[1] largely because of its interesting electrical properties. In spite of this extensive investigation, certain fundamental parameters of this material are still in question at low temperatures, namely, the elastic constants and the thermal expansion; and no data were available for a direct computation of the 0°K Debye temperature. We have made measurements of the transverse and longitudinal ultrasonic velocities in the [100] direction and of the longitudinal ultrasonic velocity in the [111] direction from 4.2° to 303.2°K and have measured the thermal expansion over the same temperature range. From these measurements we have calculated the elastic constants and the 0°K Debye temperature using Kubic harmonic expansions to evaluate the integral involved.[2]

II. EXPERIMENTAL

A. Samples

The crystals were grown using a Czochralski technique in which slowly rotating crystals are pulled from the melt under an argon atmosphere. The starting materials were 99.999% pure lead and tellurium. Emission spectroscopy has shown the crystals to be at least as pure as the starting materials, but a mass spectrographic analysis performed on one of the crystals indicated the presence of carbon in amounts slightly larger than implied by the quoted purities. The crystals were cooled at about 100°C/h in the puller. They were all p type with a carrier concentration of about 3×10^{18} carriers/cm³. The crystals were grown in two orientations, [100] and [111]. Those grown in the [100] direction were good single crystals while those grown in the [111] direction contained a few small grains which were rotated 1° to 2° about the growth direction. The grains in the [111] crystals should not affect the ultrasonic measurements since the wave propagation was in the growth direction. The samples were oriented optically by the use of reflections from [100] and [111] facets which were developed by epitaxial growth from the vapor while the crystals were being pulled. This method of orientation was checked using Laue back-reflection photographs. The samples used for the ultrasonic measurements were prepared with two plane parallel surfaces, which were normal to the direction of the sound propagation. The normals to these surfaces coincided with the desired crystallographic axis to within $\frac{1}{2}°$ and the two surfaces were parallel to within 5″ of arc and flat within 0.1 μm. Since the thermal expansion in a cubic crystal is isotropic the sample used for the thermal-expansion measurement was not oriented.

B. Elastic Constants

The velocity measurements were taken using a conventional pulse-modulated MHz ultrasonic system.[3] The absolute values of the elastic constants were found at 303.2°K by measuring the shear and longitudinal velocities along the [100] and [111] directions. A pulse-time technique was used in which the transit time of a multiple path length was measured. The temperature dependences of the velocities were measured using a phase-interference technique in which the width of the pulse-modulated ultrasonic signal was lengthened until successive reflections overlapped. The frequency of the MHz signal was then varied until either maximum constructive or destructive interference occurred. The change of this critical frequency with temperature is proportional to the change of velocity with temperature. The thermal-expansion results were used to correct this temperature dependence for change in sample length with temperature.

The results of the velocity measurements are shown in Table I. The values appearing in Table I are read from smooth curves through the data. The lowest temperature at which data were taken was 4.2°K. The values quoted in Table I for 303.2°K correspond to values obtained from the absolute measurements referred to in the preceding paragraph. The [111] shear velocity at 303.2°K was found to be 2.150×10^5 cm/sec. We assign an accuracy of $\pm0.3\%$ to these velocity measurements.

*Present address: U.S. Navy Underwater Sound Laboratory, New London, Conn.

[1] For an extensive list of references on PbTe see J. R. Burke, Jr., Phys. Rev. **160**, 636 (1967).

[2] D. D. Betts, Can. J. Phys. **30**, 233 (1961).

[3] R. E. Strakna, Phys. Rev. **123**, 2020 (1961).

TABLE I. Longitudinal and shear velocities in PbTe as a function of temperature.

T (°K)	$V_{[100]}{}^{L}$	$V_{[100]}{}^{S}$	$V_{[111]}{}^{L}$
	(in units of 10^5 cm/sec)		
0	3.911	1.345	2.803
10	3.907	1.344	2.802
20	3.901	1.343	2.799
30	3.894	1.342	2.796
50	3.880	1.338	2.787
100	3.838	1.326	2.764
150	3.792	1.314	2.742
200	3.737	1.302	2.721
250	3.683	1.290	2.699
303.2	3.620	1.277	2.676

The four measurements at 303.2°K can be checked for internal consistency. For this check we make use of the fact that the square of the longitudinal velocity plus twice the square of the shear velocity in both directions in which measurements were made is equal to $(C_{11}+2C_{44})$/density. Using the velocities measured in each direction to evaluate this quantity, we find that the two values differ by only 0.25%. This is well within the experimental error assigned to the velocity measurements, since from those errors we calculate an error of ±0.6% for each of calculated values. The internal consistency also confirms the accuracy of the sample orientation, because of the high anisotropy of PbTe. The [111] shear velocities are especially sensitive to small misorientations.

From these velocities and the density one is able to calculate the elastic constants.[4] One of us (BH) has measured the density at 25°C to be 8.2405±0.001 g/cm³. The value calculated from the x-ray lattice parameter[5–7] is 8.248±0.002 g/cm³. Although these values do not agree within their assigned experimental errors, they differ from each other by only 0.1% which for present purposes is a negligible discrepancy. The measured value appropriately corrected for thermal expansion was used in the calculation of the elastic constants. Table II shows our values for C_{11}, C_{12}, and C_{44} along with those of Einspruch and Manning[8] (EM) and of Chudinov[9] (C) for comparison. The errors shown with our values are derived entirely from the errors assigned to the velocity measurements.

Some of the difference between our results and those of previous workers can be ascribed to the 1% higher value of density which we used. EM took their value from literature published prior to the growth of PbTe by the Czochralski technique. Chudinov's check of internal consistency was only within 6.5% after making an additional independent room-temperature velocity measurement.

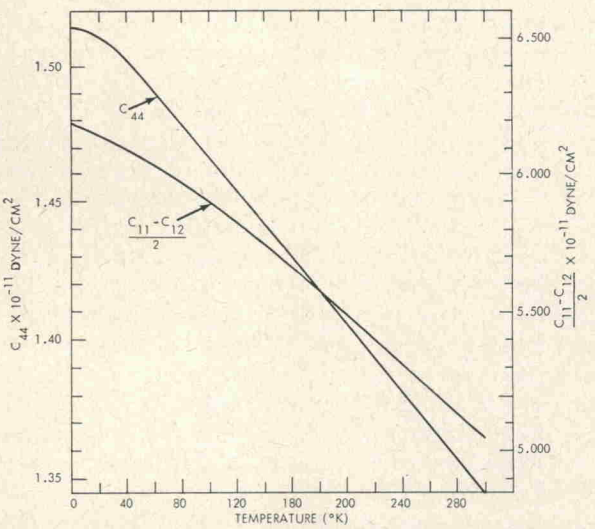

FIG. 1. Shear moduli of PbTe as a function of temperature. C_{44} is read on the left scale. $(C_{11}-C_{12})/2$ is read on the right scale.

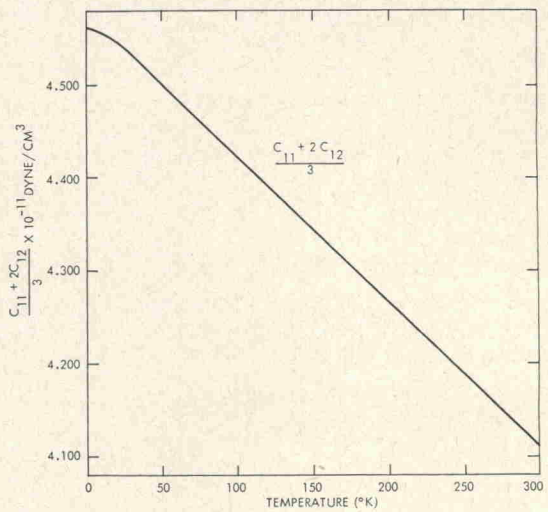

FIG. 2. Elastic constant $(C_{11}+2C_{12})/3$ as a function of temperature.

We present in Figs. 1 and 2 the values for C_{44}, $(C_{11}-C_{12})/2$, and $(C_{11}+2C_{12})/3$ as a function of temperature. This representation of the elastic constants has more physical significance and is frequently more useful than the one used in Table II. The errors in these elastic constants are assumed to come entirely from the errors in the velocity measurements. As an indication of the errors implied by this assumption we quote the following values with their probable errors for C_{44}, $(C_{11}-C_{12})/2$, and $(C_{11}+2C_{12})/3$: at 0°K (extrapolated), 1.514±0.009, 6.184±0.066, and 4.560±0.042; and at 303.2°K, 1.344±0.008, 5.016±0.057, and 4.107±

[4] See Warren P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Co., Inc., Princeton, N. J., 1958), Appendix p. 370.

[5] E. Miller, K. Komerek, and I. Cadoff, Trans. AIME **218**, 382 (1960).

[6] S. Strong (private communication).

[7] E. L. Brady, J. Electrochem. Soc. **101**, 466 (1954).

[8] N. G. Einspruch and R. J. Manning, J. Acoust. Soc. Am. **35**, 215 (1963).

[9] A. A. Chudinov, Sov. Phys.—Solid State **4**, 553 (1962).

TABLE II. Comparison of elastic-constant measurements on PbTe.

	C_{11}	C_{12}	C_{44}	T (°K)
	(in units of 10^{11} dyn cm^{-2})			
Present work	12.81±0.08	0.44±0.07	1.514±0.009	0
Present work	10.80±0.07	0.77±0.08	1.343±0.008	303.2
Einspruch and Manning[a]	10.72	0.768	1.300	302.2
Chudinov[b]	10.4	−0.437	1.30	293.2

[a] See Ref. 8. [b] See Ref. 9.

0.037, respectively in units of 10^{11} dyn/cm^2. EM does not give any temperature-dependent data. Chudinov gives three velocities (not those we measured) from 80° to 640°K, which were apparently not corrected for thermal expansion. Comparing a similar set of uncorrected velocities computed from our data we get agreement within about 1% in magnitude, and within about 0.5% for the temperature dependence.

C. Thermal Expansion

The thermal expansion was measured in a capacitative cell, the cell forming one element of a tank circuit which determined the frequency of a free-running Hartley oscillator. This frequency of about 3 MHz was measured using a digital counter. Any changes in capacitance were reflected in frequency changes. The cell itself was made of copper, one plate of which consisted of a cylinder with an axial hole closed at the bottom. The sample was inserted into this hole and covered with an insulating SiO_2 cap which protruded from the hole by about 50 μm. A plane copper cap extending over the cylinder formed the other plate of the capacitor and was spring loaded to remain in contact with the SiO_2. The system was calibrated using pure Al, Cu, and SiO_2 samples to measure the thermal expansion of the copper reference cylinder. When appropriate corrections for fringing and changes in dimension were made, the calibrations using the three different samples agreed within 2%, and we estimate the accuracy of the thermal-expansion data to be within this range. In Fig. 3 we show $\Delta l/l_0$ from room temperature to helium temperature where l_0 is the specimen length extrapolated to 0°K. In the vicinity of room temperature we measure α, the linear coefficient of expansion, to be 20.4×10^{-6}/°K. If we use only the two points at 77°K and 300°K we find α to be 19.7×10^{-6}/°K. This may be compared to the value obtained by Strong[6] who found α to be 16.3×10^{-6}/°K from x-ray lattice parameter measurements at these two temperatures. Novikova and Abrikosov[10] have measured the thermal expansion of PbTe from 20° to 340°K. A comparison of our results with theirs indicates their values for the thermal expansion are about 3% lower than ours over the entire range of temperatures where they can be compared. Moss[11] gives a value of 27×10^{-6}/°K at an unspecified temperature.

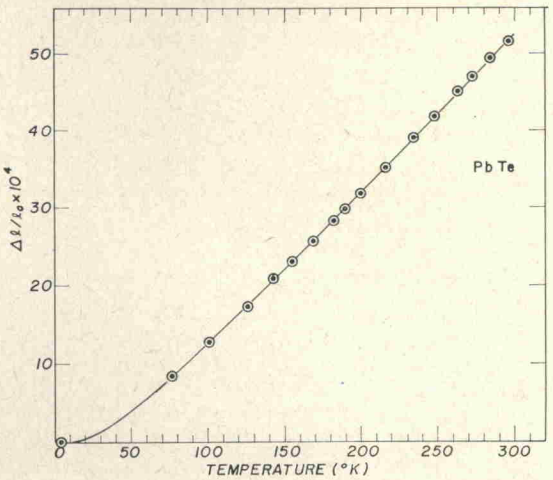

FIG. 3. Thermal expansion of PbTe as a function of temperature.

III. THE DEBYE TEMPERATURE

There are a number of methods by which the 0°K Debye temperature, θ_0, may be calculated from the elastic constants in the case of a cubic crystal.[12] In the case of extreme anisotropy $[\eta=2C_{44}/(C_{11}-C_{12})]$ the choice of methods is severely restricted. Since PbTe is extremely anisotropic ($\eta=0.245$), its parameters lie outside the range of the tables or graphs used in most of the simpler methods. One exception is the series-expansion method using a graph given by Leibfried.[13] The calculation requires values for C_{11}, C_{12}, C_{44}, the atomic density, and the mass density all extrapolated to 0°K. We used values of 12.81×10^{11} dyn/cm^2, 0.437×10^{11} dyn/cm^2, 1.514×10^{11} dyn/cm^2, 3.0143×10^{22} atoms/cm^3, and 8.3704 g/cm^3, respectively for these quantities. The value for the mass density used in the calculations of θ_0 is the same as was used in the calculation of the elastic constants from the velocities; therefore θ_0 is independent of the value used. The atomic density was computed using the x-ray lattice parameter[5] corrected for thermal expansion. With this method we found θ_0 to be 175.1°±3°K, where the error is calculated from an

[10] S. I. Novikova and N. Kh. Abrikosov, Sov. Phys.—Solid State **5**, 1397 (1964)

[11] T. S. Moss, *Photoconductivity in the Elements* (Butterworths Scientific Publications, London, 1952), p. 67.

[12] G. A. Alers, *Physical Acoustics*, W. P. Mason, Ed. (Academic Press Inc., New York, 1965), Vol. III, Pt. B, pp. 5–16, 37.

[13] G. Leibfried, in *Handbuch der Physik* VII, S. Flügge, Ed. (Springer-Verlag, Berlin, 1955), p. 252.

estimate of the error involved in reading the graph. The Kubic harmonic expansion method using the parameters given by Betts[2] was applied in an attempt to obtain more accurate results. We calculated θ_0 to four different degrees of approximation by truncating the expansion at the third-, sixth-, ninth-, and fifteenth-order terms. The results were 166.54, 174.93, 176.82, and 176.71°K, respectively. The convergence appears to be satisfactory and the values after the first are in agreement with the result obtained using Leibfried's graph. The error involved in the calculation is probably negligible compared to the errors due to the uncertainties in the experimentally measured quantities used in the calculation. These latter errors contribute less than 0.5°K using the errors quoted above and in the references. We, therefore, quote a value for θ_0 of $176.7°\pm0.5°$K.

Previous measurements of θ have been made by calorimetric means. Parkinson and Quarrington[14] have measured the molar heat of PbTe and compute θ for temperatures between 20°K and 160°K. They find values which range between 115°K and 140°K. Cochran *et al.*,[15] have made a calculation of θ as a function of temperature using the frequency distribution of normal modes of vibration obtained from an inelastic neutron scattering experiment. Choosing a particular model, they present results for θ which lie some 5% lower than the data of Parkinson and Quarrington. Extrapolating to 0°K, they predict θ to be about 166°K, about 5% lower than our value of 176.7°K.

[14] D. H. Parkinson and J. E. Quarrington, Proc. Phys. Soc. (London) **67A**, 41 (1954).

[15] W. Cochran, R. A. Cowley, G. Dolling, and M. M. Elcombe, Proc. Roy. Soc. (London) **293A**, 433 (1966).

ACKNOWLEDGMENTS

We would like to express our appreciation to Frank Bis for his assistance in the crystal growth and to Elmer Gubner for his assistance in the density measurements.

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Mercury-melting-line determination by latent heat method

James C. Houck

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234
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The equilibrium pressure for the melting and freezing of mercury was observed for the temperature range −38.834–0.023 °C by latent heat detection. The corresponding pressure range was 0.14–757.32 MPa (MPa = 10^6 N/m^2). The least-squares fit was obtained for this range of pressure with a standard deviation of the residuals of 0.055 MPa for pressure expressed as a third-order polynomial in temperature.

PACS numbers: 06.20.Hq, 07.35.+k, 64.70.Dv

I. INTRODUCTION

The mercury melting line was recommended as being a "fixed point" on the high-pressure scale by a committee of the Symposium on Accurate Characterization of the High-Pressure Environment.[1] The recommendation of this committee was that the best value of the mercury freezing pressure at 0 °C is 756.9 MPa with an estimated uncertainty of 0.2 MPa. It also suggested that the Simon equation of Bogdanov,[2,3] adjusted to agree with the value of 756.9 MPa at 0 °C, be used.

Since the Gaithersburg meeting, two additional determinations have been made yielding values of 757.1 [4] and 756.9 MPa,[5] respectively, both of which fall within the uncertainty of the recommended value.

Bogdanov[2] estimated the uncertainty of his pressure measurements to be 0.7 MPa at 500 MPa. We estimated that we could determine the melting line at this same pressure with a total systematic uncertainty of 0.1 MPa and with comparable uncertainties at other pressures. Since with these lesser uncertainties the melting line could be more satisfactorily used for calibration purposes, we have made measurements of the melting line in the region of our capabilities. A discussion of uncertainties appears in Sec. IV.

Various means of detecting the mercury melting transition have been used in the past: by volume change,[6] by change of resistance,[7] and by latent heat of fusion.[8] We made an attempt to detect the transition by observing the change in a 10-MHz ultrasonic pulse sent through the walls of a vessel containing the mercury but this method proved to be erratic. A reflected pulse sent in through a buffer rod closure was tried but this also lacked the desired dependability. In the process of these experiments, the magnitude of the change in temperature due to the latent heat became apparent. A vessel including sheathed thermocouples in addition to the platinum resistance thermometer was designed and the latent heat of fusion method became our method of detection.

II. APPARATUS AND TECHNIQUE

The apparatus employed in this work was comprised of a pressure vessel for holding the mercury, a system for subjecting the mercury to a suitable range of pressures, a Manganin resistance gauge for measuring the pressure of the mercury within the vessel, a platinum resistance thermometer for measuring the temperature of the vessel, a thermal control system for regulating the temperature of the pressure vessel, and a differential thermal sensor for detecting changes in temperature due to the latent heat of fusion of the mercury.

In order to minimize the uncertainty of the temperature measurement, a calibrated platinum resistance thermometer, meeting the defining standards of the International Practical Temperature Scale of 1968 (IPTS 1968), was used to measure the temperature. The resistance of the thermometer was read at the triple point of water and at the equilibrium temperatures of the experiments by a Mueller G-2 dc bridge. The unbalance of the bridge was amplified and fed to a dual-channel strip-chart recorder. The sensitivity of the system was such that resistance changes equivalent to 0.001 °C could be measured. The estimated systematic uncertainty of the temperature measurement was 0.002 °C. The pressure vessel shown in Fig. 1 was constructed of maraging steel with a well for the standard platinum resistance thermometer, a well for a sheathed chromel-alumel thermocouple, and a through hole for the mercury. The lower end of the through hole was closed with a solid plug and the upper end was connected to high-pressure tubing through which a sheathed thermocouple extended down into the mercury. A mixture of *n*-pentane and *i*-pentane was used as the pressure fluid. The high-pressure tubing supported the pressure vessel and thermometer in a temperature-controlled bath shown in Fig. 2. The high-pressure tubing extended above the bath to a tee through which the sheathed thermocouple exited the pressure system. The stainless-steel sheath of this thermocouple was

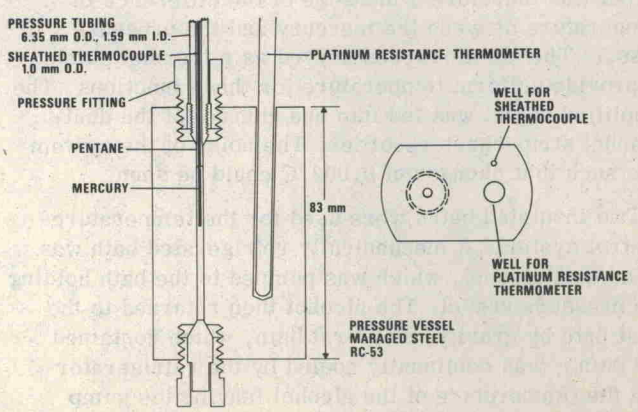

FIG. 1. Detailed drawing of pressure vessel, showing a vertical cross section and a top view.

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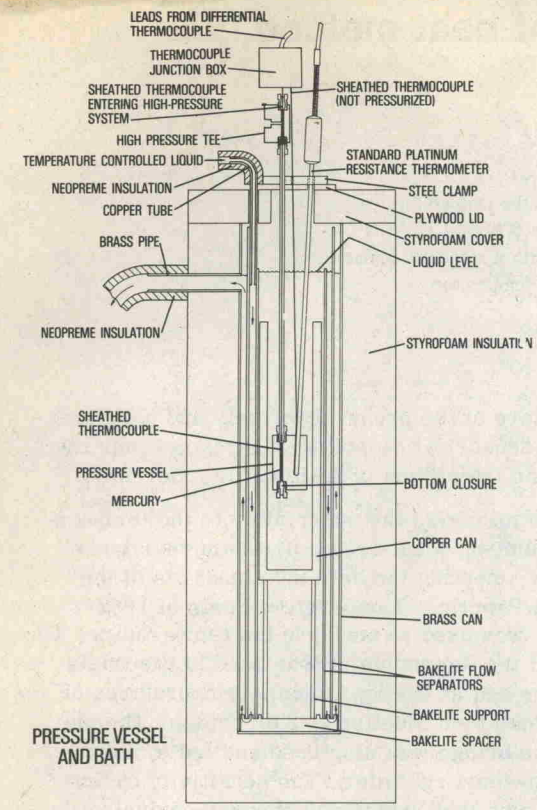

FIG. 2. Pressure vessel and bath.

silver soldered into a plug which sealed the top part of the tee. Pressure was applied through the side port of the tee. The pressure was generated by an intensifier with primary oil pressure supplied by an air-driven pump with a screw-driven hand generator in parallel for semifine adjustment. The high-pressure side of the intensifier was precharged with the pentane mixture by a hand pump, which was then valved off. Another valve in the high-pressure system was turned in and out to vary the volume and provided the fine pressure control. The two sheathed thermocouples, one from the mercury and the second from the well, entered an aluminum box mounted above the tee, where two similar wires were connected together, and leads attached to the other two wires were led out for connection to an amplifier. The output was therefore a measure of the difference in temperature between the mercury and the pressure vessel. The aluminum box served as a thermal shield to provide uniform temperature for these junctions. The amplified signal was fed into one channel of the dual-channel strip-chart recorder. The noise of the system was such that changes of 0.002 °C could be seen.

Two insulated baths were used for the temperature-control system. A mechanically refrigerated bath was filled with alcohol, which was pumped to the bath holding the pressure vessel. The alcohol then returned to the first bath by gravity. The first bath, which contained the pump, was continually cooled by the refrigerator and the temperature of the alcohol leaving the pump was monitored by the platinum resistance element of a controller which supplied electric power to a heater in this bath to maintain the set temperature. This fluid varied in temperature by up to 0.010 °C. The second bath was lagged to eliminate this variation by having the pressure vessel inside a heavy copper can filled with stagnant alcohol, which in turn was surrounded by two concentric Bakelite tubes, the inner one serving to further lag the temperature. The temperature-controlled alcohol, after flowing down around the outside of the inner tube and up around the outside of the second tube, was returned to the first bath. This lagging reduced the fluctuations and gave temperatures stable to 1 mdeg/h after equilibrium. The liquid mercury was usually superpressurized by between 55 and 100 MPa before it froze. When it freezes under these conditions, the pressure is valueless as a freezing point determination and the latent heat raises the temperature of the pressure vessel and the surrounding bath, requiring several hours to return to equilibrium conditions. Two different pressure vessels were used, the first with a bore of 4.8 mm for pressures to 420 MPa and the second with a bore of 2.3 mm for pressures to 757 MPa. The larger amount of mercury used in the first vessel caused a rise in the temperature of the vessel, from 0.125 to 0.160 °C on freezing, whereas the smaller amount in the second vessel caused the 0.060—0.075 °C rise. The second vessel was used to determine maximum temperature differences between the mercury and the vessel and showed brief differences of 0.8—1.8 °C on the freezing from the supercooled state and approximately a 0.4 °C difference on the melting due to a fairly large pressure decrease. Figure 3 shows a temporal trace from a dual-channel recorder of temperature changes on superpressurized freezing on complete rapid melting of the mercury sample and on superpressurized freezing. The right-hand trace shows the amplified unbalance form the Mueller bridge, normally balanced to determine the temperature of the vessel. This shows changes in temperature of 0.060 °C for both freezing and melting. The left-hand trace shows the amplified signal from the sheathed differential thermocouples, one junction in the mercury, the other in a well in the vessel. On freezing by superpressurization, the quick freezing results in an increase in the tem-

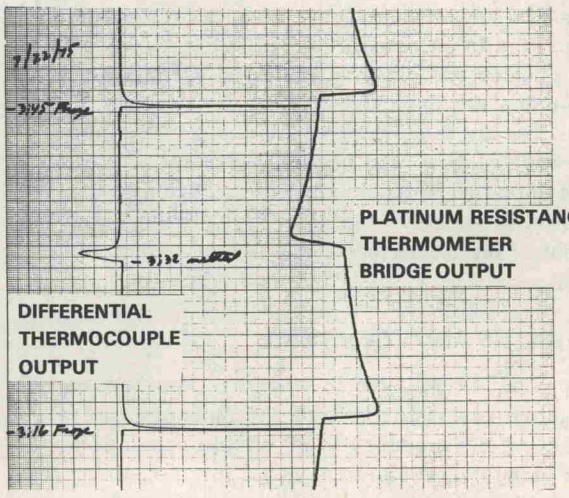

FIG. 3. Temperature changes on superpressurized freezing and on complete rapid melting of the mercury sample.

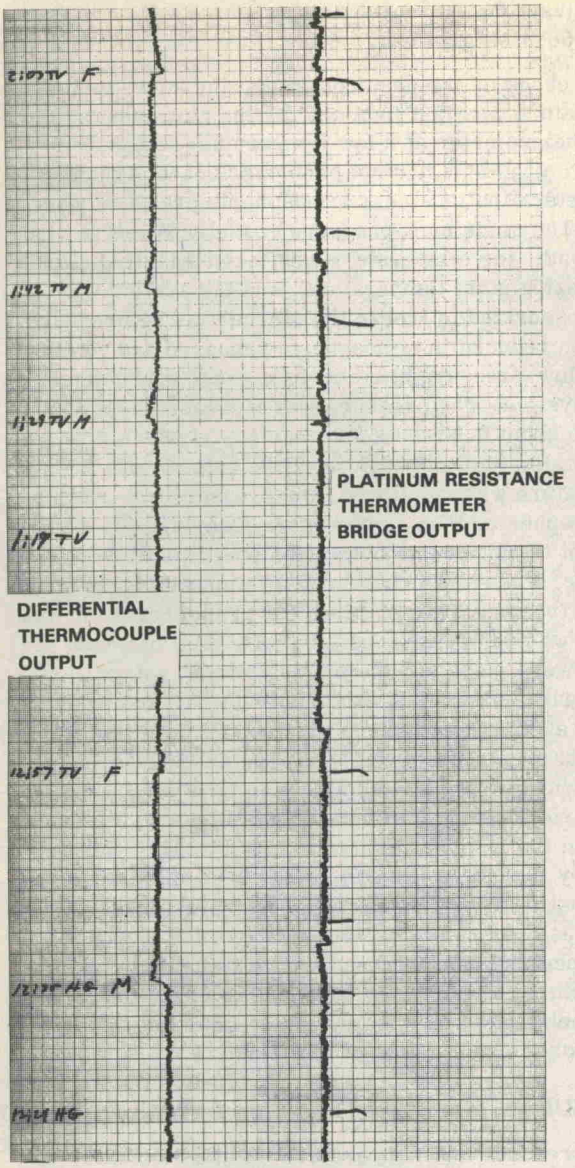

FIG. 4. Recordings of temperature changes during the melting-line determination.

perature of the mercury of 1.8 °C. On melting by reducing the pressure, a decrease in temperature of 0.4 °C is shown covering a longer period of time.

III. PROCEDURE

For detection of the phase transition, the bath is set for the desired temperature, the mercury is overpressurized to cause it to freeze, and sufficient time is allowed for the system to come to equilibrium. The recorder is set for greater sensitivity than that shown in Fig. 3. The recorder sensitivity for the bridge output is 4 mm/0.001 °C and the bridge is kept manually balanced to read temperatures of the vessel to 0.001 °C. The recorder sensitivity of the output from the differential thermocouple is 1 mm/0.001 °C and changes of approximately 0.002 °C can be seen above the noise level. The pressure is then decreased to near the expected pressure for phase transition, then it is further decreased by increments of about 0.1 MPa every 10 min.

Figure 4 shows the recorder traces for several pressure adjustments to cause melting and freezing during an elapsed time of almost 2 h. The left-hand trace (the differential thermocouple output) shows the melting (M) or freezing (F) occurring when the pressure is changed either by operating a hand generator (HG) on the low-pressure side of the intensifier for coarse pressure changes or by turning a valve (TV) in the high-pressure system which changed the pressure by changing the volume of the system by the travel of the valve. The right-hand trace was used to monitor the output of the bridge for measuring the resistance of the platinum resistance thermometer and the tick marks indicate places where the current was reversed after balancing the bridge.

The pressure was determined by measuring the resistance of a seasoned calibrated four-lead Manganin coil with a Mueller bridge. (This Manganin coil had been calibrated against a controlled clearance piston gauge which had an upper limt of 420 MPa and an estimated systematic uncertainty of 100 ppm. Thirty points were used in the calibration over the range of pressure 0—420 MPa and a least-squares fit was obtained for pressure as a second-order polynomial of resistance of the Manganin gauge with a residual standard deviation

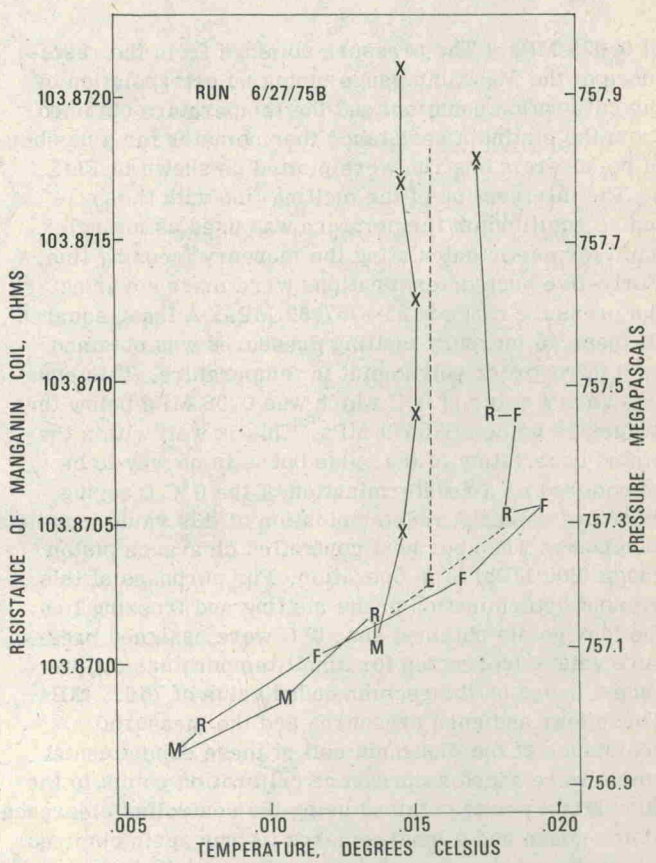

FIG. 5. Plot of melting and freezing to determine a single point on the melting line [temperature of pressure vessel after changes in pressure: X—change in pressure, no apparent melting or freezing; M(F)—melting (freezing) observed by differential thermocouple; R—recovery after melting or freezing; E—graphically estimated value for melting-freezing pressure at equilibrium temperature of the system].

TABLE I. Mercury-melting-line data in order of acquisition.

Pressure (MPa)	Temperature (K)	Pressure (MPa)	Temperature (K)
183.32	243.784	110.16	240.001
235.84	246.496	54.41	237.119
235.86	246.498	54.20	237.109
183.50	243.795	5.35	234.588
235.85	246.495	5.46	234.592
235.91	246.499	5.56	234.593
235.26	246.461	30.47	235.884
288.50	249.205	30.52	235.887
341.34	251.925	613.36	265.856
394.43	254.657	613.03	265.836
182.79	243.752	654.07	267.930
394.28	254.642	676.00	269.048
288.56	249.205	679.70	269.237
394.28	254.649	757.28	273.170
288.08	249.184	757.32	273.173
393.98	254.633	757.15	273.161
446.86	257.348	757.20	273.166
446.84	257.346	237.74	246.588
500.24	260.073	237.76	246.586
394.12	254.632	0.16	234.316
288.12	249.190	0.27	234.323
500.02	260.067	0.34	234.326
533.96	261.801	0.14	234.316
144.78	241.793	0.20	234.319
144.82	241.796	0.19	234.318
110.04	239.996	0.18	234.317

of 0.025 MPa.) The pressure obtained from the resistance of the Manganin gauge (using an extrapolation of the calibration equation) and the temperature obtained from the platinum resistance thermometer for a number of points from one run were plotted as shown in Fig. 5. The intersection of the melting line with the estimated equilibrium temperature was used as a single point for use in calculating the mercury freezing line. Forty-five such determinations were made covering the pressure range 5.35—757.32 MPa. A least-squares fit these 45 mercury melting pressures was obtained as a third-order polynomial in temperature. This equation gave a value at 0 °C which was 0.06 MPa below the suggested value of 756.9 MPa. This is well within the stated uncertainty of the value but is in no way to be considered as a redetermination of the 0 °C freezing pressure value. A redetermination of this value may be undertaken when our next controlled clearance piston gauge (800 MPa) is in operation. For purposes of this present determination of the melting and freezing line, the four points obtained near 0 °C were assigned pressure values (corrected for small temperature differences) based on the recommended value of 756.9 MPa. These four assigned pressures and the measured resistance of the Manganin coil at these experimental points were added as pressure calibration points to the 30 original points obtained using the controlled clearance piston gauge and a least-squares fit was again obtained for pressure as a second-order polynomial of resistance of the Manganin gauge. This fit had a residual standard deviation of 0.027 MPa. The pressure given by this equation at 420 MPa is 0.012 MPa above the original calibration equation. This calibration equation was then used to recalculate the pressures for the experimental points for the mercury melting lines and therefore adjusts the mercury-melting-line equation to the value 756.9 MPa at 0 °C.

As a check on the assumption that the equilibrium temperature was that indicated by the platinum resistance thermometer at a low temperature and that temperature gradients had not been overlooked, freezing point determinations near atmospheric pressure were made. The same high-pressure vessel was left in place in the bath, the temperature was taken slightly below the freezing point temperature, and the system was overpressurized to freeze the mercury. The pressure was then reduced to atmospheric pressure and a calibrated low-pressure bourdon-tube gauge was connected to the system. The pressure was increased by a hand pump to about 0.15 MPa and thermostat was set to slowly raise the temperature of the bath. While the temperature was monitored, the pressure was reduced to atmospheric, then raised again observing the differential thermocouple output to detect melting or freezing. Values of pressure and temperature for melting and freezing were obtained for pressures 0.14—0.34 MPa. Two such runs (consisting of a total of seven points) were made and the points obtained were fitted to a linear equation and extrapolated to atmospheric pressure. The temperature obtained for freezing at atmospheric pressure was −38.836 °C. This is in agreement with the same value −38.836 °C for the atmospheric freezing pressure of mercury calculated from the triple-point temperature −38.841 °C determined by Furukawa (Thermometry Section, Heat Division, Institute for Basic Standards). This agreement serves as a check on the calibration of the platinum resistance thermometer and the lack of gradients at equilibrium. These seven points were added to the 45 points obtained using the Manganin gauge to give 52 points for the calculation of the mercury melting line.

IV. RESULTS

The pressure and temperature for the 52 points, obtained as previously described, are given in Table I.

Bogdanov's Simon equation had been modified by the committee[1] to pass through 756.9 MPa at 0 °C. We further modified it by changing the coefficient again to still pass through 756.9 MPa at 0 °C for a triple-point temperature of 234.309 K for use with temperature measured on the IPTS 1968 scale. This modified equation

$$P = 3824.91\left[\left(\frac{T}{234.309}\right)^{1.1772} - 1\right], \tag{1}$$

where T is the Kelvin ($T = 273.15 + t\,^{\circ}\mathrm{C}$) and P is in MPa, was used to calculate the pressure from the temperature of each of the experimental points. The difference between these calculated pressures and the experimental pressures ranged from −0.030 to +0.757 MPa. This is close to the estimated uncertainty stated by Bogdanov[2] of 0.7 MPa at 500 MPa.

Since for this limited pressure range and with these arbitrary modifications this equation no longer appeared to be a good fit to the data, we determined a two-parameter Simon equation under the same constraints and obtained an exponent of 1.1346 by a least-

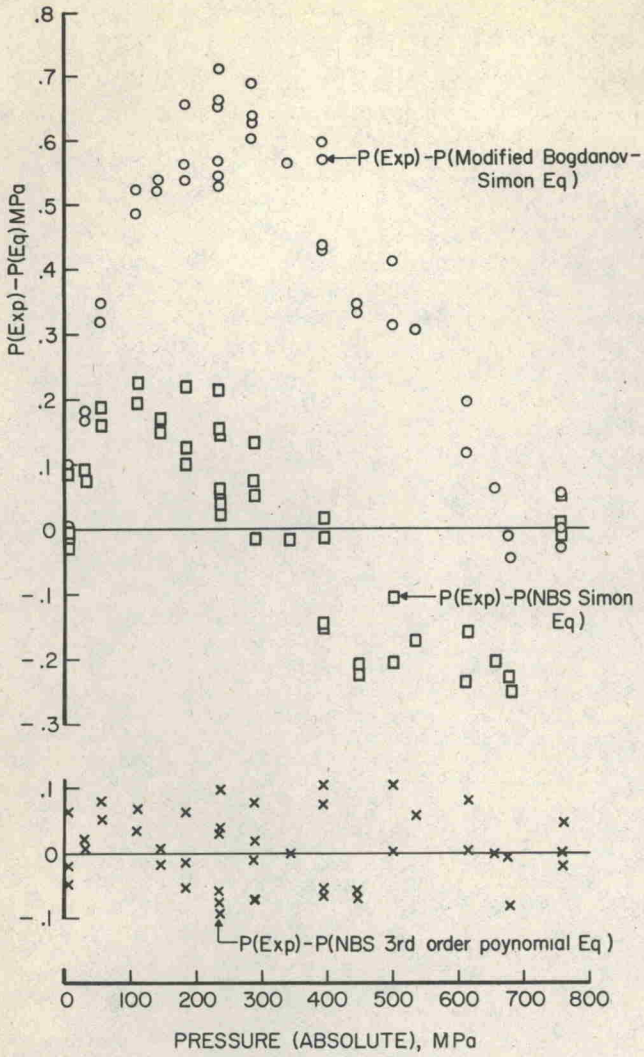

FIG. 6. Residuals from fitting three different functions of temperature to the data.

squares method to give

$$P = 3981.89\left[\left(\frac{T}{234.309}\right)^{1.1346} - 1\right], \qquad (2)$$

where T is in Kelvin and P is in MPa. The differences between pressures calculated from this equation and the experimental pressures ranged from -0.262 to 0.230 MPa. The residuals for both Eqs. (1) and (2) are plotted in Fig. 6. From this it is seen that there are systematic deviations for both equations. It appears that a two-parameter Simon equation is not the best choice for the mercury melting line. Hardy, Crawford, and Daniels[9] concluded that argon and mercury melting lines could not *both* be fitted by the two-parameter Simon equations.

We fitted a third-order polynomial to the data and obtained the following equation:

$$P = 19.33115d + 0.0014055d^2 + 0.000067028d^3, \qquad (3)$$

where P is in MPa and $d = T - 234.309$ K. The pressure at 234.309 K, the triple point of mercury, is approximately 0.0002 Pa, which is sufficiently close to zero to be set to zero in these equations. The deviations from this curve ranged from -0.096 to $+0.104$ MPa with the residual standard deviation from the curve equal to 0.055 MPa. These deviations are also shown in Fig. 6. There is no significant systematic variation of the residuals from Eq. (3). That fact and the smaller size of the deviations show this to be the most satisfactory equation to use over the range of pressure 0—757 MPa.

At 420 MPa (the highest pressure at which the controlled clearance piston gauge was used) the estimated systematic uncertainties total 0.09 MPa with 0.04 MPa from the original pressure calibration, 0.01 MPa from the small modification of the calibration due to including the 757-MPa points, and 0.04 MPa from the temperature uncertainty. The residual standard deviation from Eq. (3) is 0.055 MPa and σ (the standard deviation of the predicted value) at 420 MPa is 0.014 MPa; 3σ plus the estimated systematic uncertainties give a total uncertainty of 0.14 MPa. This total uncertainty would be slightly smaller below 420 MPa and increase at higher pressures. At 757 MPa, σ is 0.025 MPa, while the controlling uncertainty is the 0.2 MPa stated uncertainty.[1]

Equation (3) should serve as a calibration equation over the range 0—757 MPa until some new value of the freezing pressure of mercury at 0 °C is defined.

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