Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 37, No. 10, 3771–3774, September 1966

Thermodynamic Aspects of the Temperature–Pressure Phase Diagram of InTe

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(Received 8 April 1966)

The heat of transformation at one atmosphere from the metastable high-pressure phase of InTe to the low-pressure phase has been measured by metal solution calorimetry to be 0.44±0.01 kcal/g·atom and by differential scanning calorimetry to be 0.42±0.03 kcal/g·atom. These values are compared to the heat of transformation at 30 kbar obtained by applying the Clausius–Clapeyron equation to the temperature–pressure phase diagram of InTe.

The volume change on fusion of the low-pressure phase, InTe(I), at one atmosphere was measured to be 0.80 cc/mole. The initial slope of the liquidus in the phase diagram calculated using this value is in close agreement with the previously determined experimental slope. It is estimated that the triple point between the liquidus and the InTe(I)–InTe(II) phase boundary occurs at 718°C and 11 kbar.

INTRODUCTION

THE low-pressure and high-pressure phases of the compound InTe are attractive for thermodynamic studies since the temperature–pressure phase diagram has been established,[1] and the high-pressure phase can be retained at atmospheric pressure. In addition, there is some uncertainty in the initial slope of the liquidus with pressure which could be resolved by a determination of the volume change on fusion and the heat of fusion of the low-pressure phase, InTe(I).

Prediction of the volume change on fusion of binary intermetallic compounds is difficult since many, but not all, of the III–V and II–VI compounds are similar to Si and Ge in having a large negative volume change on fusion and, therefore, a strongly negative slope of the liquidus with pressure.[2] The compound InTe is similar to many of these intermetallic compounds in that the boundary between the low-pressure and high-pressure phases intersects the liquidus with a resulting triple point above atmospheric pressure. Since the slope of the liquidus for InTe(I) at the triple point appears to be zero or slightly positive, it is difficult to extrapolate between it and the melting point at 1 atm, further emphasizing the need for thermodynamic data at atmospheric pressure.

In this study, therefore, the volume change on fusion of InTe(I) at 1 atm was determined and used with the heat of fusion at 1 atm[3] to calculate the initial slope of the liquidus. In addition the heat of transformation of metastable phase InTe(II) to InTe(I) was determined at 1 atm by two calorimetric methods and is discussed

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in relation to the slope of the boundary between InTe(I) and (II) in the temperature–pressure phase diagram.

EXPERIMENTAL PROCEDURES AND RESULTS

Material

Samples of indium telluride were prepared by melting stoichiometric amounts of 99.999% indium (Cominco Products, Inc.) and 99.999% tellurium (Ohio Semiconductors) in evacuated, sealed, fused quartz tubes. Slow cooling from the melt gave large crystals which were analyzed by the method of Gardels and Cornwell.[4] The atomic ratio of indium to tellurium in the samples was 1.000 to 0.998–1.002. Mass spectrographic measurements showed total impurity levels to be below 0.1%.

The high-pressure phase, InTe(II), was prepared by pressing cylinders of the low-pressure phase, InTe(I), at 40–50 kbar in a 2000-ton tetrahedral-anvil high-pressure unit[5] and heating to 500°C for several hours. The InTe(II) phase was retained by cooling to room temperature before releasing the pressure. The metallic blue cylinders of InTe(II), 0.25–0.3 in. in diameter and 0.4 in. long, were stored at dry-ice temperature to prevent the slow transformation back to the low-pressure phase.[1,6] The lattice parameter of the rock-salt cubic InTe(II) phase was 6.177 Å, in agreement with earlier results[1] and those of subsequent workers.[7,8]

Volume Change on Melting InTe(I)

The difference in volume of the low-pressure phase, InTe(I), in liquid and solid states was determined by the method of fed and unfed castings as modified by Ball.[9] In this technique, the volume change on solidification, rather than that on melting, is measured. Two identical crucibles of a nonreactive material and a charge of the element or compound under investigation are sealed in an evacuated, fused silica capsule. The crucibles are fixed in position by dimples in the capsule wall. The upper crucible is positioned with its opening upwards and the lower crucible with its opening downwards. The capsule is suspended in the heating zone of a furnace at a temperature 10° to 25°C above the melting point of the material under test until the charge melts and fills the crucibles. The capsule is then lowered slowly out of the melting zone so that solidification starts at the bottom of the capsule. In this way, the opening of the lower, or unfed, crucible is closed before its contents solidify, sealing the liquid in the crucible. The trapped liquid then solidifies, isolated from the remaining liquid in the capsule. The liquid in the upper, or fed, crucible solidifies from the bottom of the crucible. Thus, liquid is added or lost through the top opening to compensate for the volume change on solidification.

In the present investigation, crucibles of 4.5 to 5.0 cc capacity were machined from rods of AUC grade graphite. The internal dimensions of the crucibles at room temperature were measured to 0.0001 in. The dimensions of the crucibles at the melting point of InTe(I) (696°C) were then calculated using thermal expansion coefficients of graphite of 1×10^{-6}/°C along the grain (axis of crucible) and 1.5×10^{-6}/°C across the grain (radius of crucible).[10] The densities and the molar volume V of the solid and the liquid were calculated from the crucible volumes corrected to 696°C and the weights of the ingots.

The principal experimental difficulty was the formation of voids in the fed ingot. All crucibles were cut along the vertical axis after weighing and the ingots inspected. The weight of the fed ingot was discarded if voids were observed in it. Voids were always found in the unfed ingots, indicating a decrease in volume of solidification.

The densities and molar volumes of the solid and the liquid are listed in Table I, together with the volume change on melting, ΔV, calculated both from the averaged molar volumes of solid and liquid InTe and from the five individual runs where the results for both solid and liquid could be accepted. The measurements of the density and of the molar volume of liquid InTe were more reproducible than those of solid InTe(I) (Table I). Sufficient runs were carried out to give reasonable confidence to the averaged value of the molar volume of the solid and, therefore, to the ΔV on melting calculated from the average.

The value of ΔV on melting of 0.80 cc/mole, calculated from the average values of the volumes of the solid and liquid, is preferred to that of 0.83±0.41 cc/mole determined from the individual runs since it is based on more data. The comparatively large error limits for the value obtained from individual runs are the result of

TABLE I. Densities and molar volumes of InTe(I) at its melting point (696±1°C).

	Solid$^{696°}$	Liquid$^{696°}$
Average density (g/cc)	5.845±0.081[6][a]	5.733±0.035[7][a]
Molar volume V (cc/mole)	41.48 ±0.44[6][a]	42.28 ±0.27[7][a]
ΔV =	0.80 cc/mole[b] 0.83±0.41 cc/mole[c]	

[a] Numbers in brackets indicate the number of runs used for the average.
[b] Based on the average V for solid InTe(I) and the liquid.
[c] Based on the five runs in which the V for both solid and liquid could be accepted.

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measuring small differences between two large numbers each of which has a certain variation. However, good agreement has been obtained for the ΔV on melting calculated in the two ways. If it is assumed that the expansion coefficient of InTe(I) is linear and that there are no phase changes between 25° and 696°C, the molar volume and the density at any temperature can be calculated from the molar volumes at 25°C and at the melting point.

Measurement of Heat Transformation from InTe(II) to InTe(I) using a Liquid-Metal Solution Calorimeter

The heat of transformation, ΔH_t, from InTe(II) to InTe(I) at 0°C was measured by metal solution calorimetry as the difference in the heat effects, at infinite dilution, on dissolution of the two phases added alternately to liquid bismuth from a reference temperature of 0°C. The experimental technique and method of calculation have been described in detail elsewhere.[11]

The heat effects on solution and consequently the heat of transformation depend on the thermodynamic data used in calculating the heat effects for the calibrating addition. In the present investigation the calorimeter was calibrated by adding bismuth at 0°C to the bismuth bath at 350°C. The reported results are based on a value of 4.96 kcal/g·atom for the difference in the heat contents of bismuth at 350°C and 0°C.[12] If a new value becomes available for this quantity, the results may be adjusted in direct proportion.

In a typical calorimetric run, three or four alternate additions each of the low- and high-pressure phases were made to the bismuth bath. Five calorimetric runs were carried out with one batch of the high-pressure phase. The samples of InTe(I) used in three of these runs were retransformed samples of InTe(II). The semiconductor grade of InTe(I) was used in the remaining two of the five runs. A sixth calorimetric run was carried out with a second batch of the InTe(II) and with samples of the InTe(I) which were obtained by retransforming part of this batch.

The results of a typical calorimetric run are shown in Fig. 1, where the measured heat effects on dissolution of the low- and high-pressure phases are plotted against the atomic fraction of indium telluride in the bath. At the end of a calorimetric run, the concentration of indium telluride in the bath was less than 2.0 at.%. In this concentration range, the heats of solution were a linear function of the concentration of solute in the bath. The heat of transformation (ΔH_t) from the high-pressure to low-pressure phase measured at 0°C and 1 atm was 0.44±0.01 kcal/g·atom; the stated limit of error is the maximum deviation from the mean value, based on the six runs.

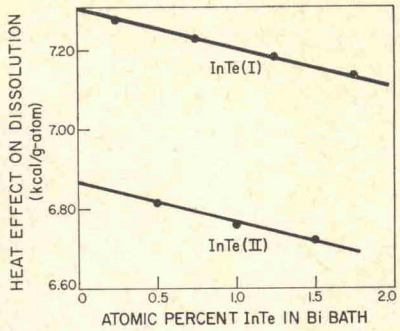

FIG. 1. The measured heat effect on dissolution in liquid bismuth of InTe(I) and InTe(II) as a function of the solute concentration.

Measurement of Heat of Transformation from InTe(II) to InTe(I) using a Scanning Calorimeter

The second technique used to determine the ΔH_t of the metastable phase InTe(II) to InTe(I) was differential scanning calorimetry using a Perkin–Elmer model DSC-1 calorimeter. In this apparatus, the sample and an inert standard are sealed into aluminum foil capsules and are heated at a constant rate by independent resistance heaters. The difference in heater power needed to keep the sample and standard temperatures equal throughout the run is recorded as a function of temperature. When one stable phase is transformed into another, a peak appears on the recorder chart at the transformation temperature and the area under the curve is proportional to ΔH_t. The areas are measured by a planimeter, using the average of five measurements. The calories per unit area are determined from the area of similar curves obtained during the melting of weighed samples of high-purity indium metal, adjusted for the span and chart speed, and the heat of fusion of indium (ΔH_f=0.78±0.02 kcal/g·atom, T_m=156.6°C).[12]

Although there is no thermodynamically defined temperature for the transformation of a metastable phase to its stable form, ΔH_t for such a transition can be measured by scanning calorimetry if the rate of transformation is strongly temperature-dependent. In this case, for sufficiently rapid heating rates, the transformation occurs predominantly within a narrow temperature range and produces a well-defined exothermic peak. For InTe(II), two such peaks were observed in each run, as seen in the typical recorder traces reproduced in Fig. 2. The baseline generally curved slightly after the first peak and strongly after the second due to the change in the heat capacity of the samples. Therefore the baseline during the transformation (as shown in Fig. 2 by the dotted lines) had to be approximated using techniques which proved satisfactory for standard samples.

The existence of two exothermic peaks indicated that the InTe(II) → InTe(I) transformation takes place in two steps, and therefore confirmed the findings of Sclar *et al.*[6] that at atmospheric pressure an inter-

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[12] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, New York, 1963).

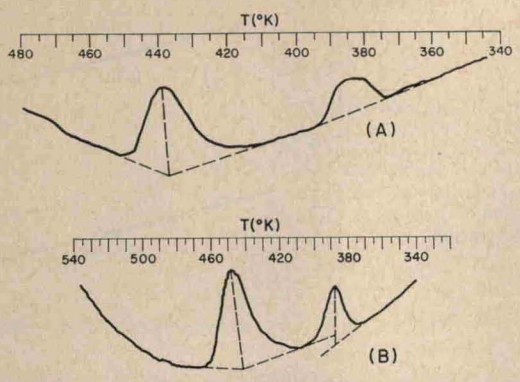

FIG. 2. Reproduction of recorder traces from DSC-1 scanning calorimeter. Dotted lines are the base lines under the peaks, extrapolated by accepted techniques for this equipment. Area calibration is 5.38 mcal/cm². Curve A: sample No. 13, 29.49 mg, total area 18.03 cm², 20°/min heating rate, degree marks printed by recorder. Curve B: sample No. 5, 23.88 mg, total area 14.56 cm², 40°/min heating rate.

mediate phase InTe(II′) is formed during the transformation. In eight runs, the temperature at which the evolution of heat was first detected was 94°±6°C for the first peak and 134°±6°C for the second. These values are consistent with the results of Sclar *et al.*[6] obtained in their x-ray and metallographic studies. [All of the samples used for the present study had been checked by x-ray powder patterns and metallographic examination to show the absence of any InTe(II′) or InTe(I) after storage at −78°C.] The relative quantities of heat liberated during the two steps varied considerably from run to run. The percentage of the total heat evolved during the first step ranged from 14% to 39%. However, the total heat liberated during the two steps was quite reproducible. The average value obtained for the ΔH_t is 0.42±0.03 kcal/g·atom.

DISCUSSION

The initial slope of the liquidus curve of InTe(I) in the pressure-vs-temperature diagram, dT/dp, can be calculated from the Clausius–Clapeyron equation in the form

$$dT/dp = T\Delta V/\Delta H,$$

where T is the temperature, ΔV the change in volume on melting, and ΔH the heat of fusion. Using the experimentally determined value of ΔV and the published value of ΔH (4.29 kcal/g·atom),[3] the value of dT/dp at the melting point at atmospheric pressure is 2.16°/kbar. This confirms the proposed initial slope in the phase diagram.[1] If this slope does not change with pressure up to the triple point, the InTe(I) melting curve intersects the InTe(I)–InTe(II) phase boundary at 11 kbar and 718°C. This location for the triple point is close to the one estimated previously.[1]

The values of the heat of transformation from InTe(II) to InTe(I) obtained by the two calorimetric methods are in close agreement. It should be noted that the value of 0.42±0.03 kcal/g·atom obtained using the differential scanning calorimeter refers to a temperature range of 90°–140°C while the value of 0.44 ±0.01 kcal/g·atom obtained using the metal solution calorimeter refers to a temperature of 0°C.

The heat of transformation from InTe(II) to InTe(I) can be calculated using the Clausius–Clapeyron equation. The factor dT/dp is the slope of the boundary between the two phases in the temperature-vs-pressure diagram and ΔV is the volume change on transformation.

The latter factor can be calculated from the lattice parameters of the two phases at a temperature and pressure corresponding to the phase boundary. It is difficult, however, to measure lattice parameters accurately under pressure. The volume change at the phase boundary, therefore, was calculated from the measured lattice parameters of the two phases at room temperature and atmospheric pressure and from the published values[8] of the compressibilities between 1 atm and 30 kbar. The volume change on transformation from the low-pressure to the high-pressure phase at 25°C and 30 kbar calculated on this basis was −0.97 cc/g·atom. The heat of transformation calculated using this value of ΔV and a value of dT/dp from the phase diagram of −33.3°C/kbar was 207 cal/g·atom. This is in agreement with a value of approximately 200 cal/g·atom obtained in the same manner by Darnell and Libby.[8]

The measured and the calculated values of the heat of transformation refer to 1 atm and 30 kbar, respectively, and cannot be compared directly as no data are available on the pressure dependence of the heat capacities of the two phases. The compressibilities of the two phases over this range of pressure indicate that the change in the heat capacity of the low-pressure phase with pressure may be expected to be larger than that of the high-pressure phase. The difference of ∼230 cal/g·atom between the heat of transformation at 1 atm and that at 30 kbar indicates that the average pressure coefficient of heat content is greater for InTe(I) than for InTe(II) by about 8×10^{-6} kcal/g·atom·atm between 1 atm and 30 kbar.

ACKNOWLEDGMENTS

The authors wish to thank Dr. A. J. Strauss and Professor M. B. Bever for stimulating discussions and helpful advice during this research. They also thank T. E. Stack and L. I. Sudenfield for assistance in the experimental work. We are also indebted to Professor W. R. Vieth, Department of Chemical Engineering, Massachusetts Institute of Technology, for the use of the Perkin–Elmer DSC-1 calorimeter. One of the authors (PMR) acknowledges the support of the Office of Naval Research under Contract ONR-3963-(19).