

libria in the complete absence of liquid "sorbent" of low volatility. In such cases, it is convenient to measure the retention volumes of all species. For each component i one has, according to Eq. 1

$$\bar{C}_i V_L = C_i (V_R')_i \quad (3)$$

for the amount of i in the liquid phase. Thus, from the retention volumes of all species the total amount of stationary liquid in the column is readily calculated. The relative volatility K_i of species i (defined as the ratio of the mole fractions y_i and x_i of i in the gas and liquid phases, respectively) in multi-component gas-liquid equilibria then is readily obtained from

$$K_i = \frac{y_i}{x_i} = \frac{\sum_{j=1}^n C_j (V_R')_j}{(V_R')_i \sum_{j=1}^n C_j} \quad (4)$$

where the summations are carried out over all n components. If the mixture is not too complex, the retention volumes of all components can be determined in one single experiment, with use of different isotopes or different relative amounts of tagged species to distinguish between the various components.

Compared to other chromatographic methods in which the sorption isotherm of a substance is obtained from the peak or band shape, the tracer-pulse method has the disadvantages of requiring a separate measurement for each point on the isotherm. The evaluation, however, is simpler and more rapid since the retention volume of each peak immediately gives an isotherm point, whereas in the other methods the evaluation of the peak or band shape requires, at each point, a graphical integration or slope construction. In view of their speed, the disadvantage of a larger number of chromatographic measurements is likely to weigh little against the gain in accuracy, reliability, and ease of evaluation. Furthermore, the tracer-pulse method also permits measurements of single-component gas sorption in the absence of a carrier gas, and of partition coefficients or relative volatilities of a number of components in multicomponent systems in one single experiment.

The tracer-pulse method is, of course, restricted to substances that can be tagged with detectable isotopes. For lack of a suitable isotope a modified "differential method", based on the same principle as the differential reactor

in heterogeneous catalysis, may be used. After the column is in equilibrium with solvent and solute at concentration C , this concentration is changed stepwise to a slightly higher or lower value and the retention volume of the concentration step (more accurately, of the center of gravity of the step) is measured. It is readily shown by a material balance written around the column that the adjusted retention volume of the step, V_R' , at sufficient dilution is related to the slope of the isotherm by

$$d\bar{C}/dC = V_R'/V_L \quad (5)$$

provided that the step has been made so small that the isotherm slope remains essentially unchanged by the concentration change. To verify that this condition is met, two measurements may be made by changing the concentration in the first from C to $C + \Delta C$ and in the second from C to $C - \Delta C$; both retention volumes should be the same within the tolerable error. The use of a concentration pulse instead of a step is possible and is experimentally more convenient, but has the disadvantage that, to obtain a detectable peak height $C + \Delta C$ in the effluent over the background of height C , the injected pulse must be of considerably higher concentration, a fact which puts more strain on the assumption of constant isotherm slope within the range of concentrations occurring in the column. Because it involves the more difficult detection of small concentration changes in the effluent, the assumption of invariant isotherm slope, and a slope construction in computing the isotherm from the retention volumes, the differential method is less accurate and more cumbersome than the tracer-pulse method. However, the advantage of invariance against extraneous peak or band-broadening effects is preserved.

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High-Pressure Transitions in $A^{(III)}B^{(VI)}$ Compounds: Indium Telluride

Abstract. *Metallic InTe(II) has a NaCl structure with $a_0 = 6.154 \text{ \AA}$ and becomes superconducting below 3.5°K . These results are substantially different from those previously reported. The pressure-temperature diagram to 850°C and 50 kb is presented.*

In a systematic study of the effects of high pressure on the $A^{(III)}B^{(VI)}$ compounds, a high pressure metallic phase of InTe has been discovered. The properties of this InTe(II) phase, preliminary measurements of which have been reported (1-3), differ in several essential respects from those observed independently and recently reported by Darnell, Libby, and co-workers (4, 5). Specifically, we find that InTe(II) has the NaCl (B1) structure rather than simple cubic (4); that its lattice constant is 6.154 \AA rather than 3.07 \AA (4); and that its superconducting transition temperature is 3.5° to 3.7°K rather than 2.18°K (5).

Initially InTe(II) was synthesized by fusion of the semiconductor grade elements at 40 to 50 kb and about 1000°C (1). It has also been obtained by transformation, at pressures above 28 kb and temperatures above 150°C , of the stoichiometric tetragonal InTe(I) phase prepared at 1 atm (2). When the samples are cooled to room temperature, the high-pressure phase is readily recovered at atmospheric pressure but slowly transforms (20 percent in 4 months) to InTe(I). Samples have been retained at dry-ice temperature for as long as 9 months without detectable transformation. At 100°C , the transformation to InTe(I) is 75 percent complete in 1 hour, and above 125°C InTe(II) has no appreciable stability at atmospheric pressure.

Darnell, Yencha, and Libby (4) proposed a simple cubic structure for InTe(II) with lattice spacing of 3.07 \AA . For a 1:1 binary compound, the indices which they assign to their d -spacings can only be those of a CsCl structure. Since this structure would have one atom each of In and Te per unit cell, the calculated density would be 13.8 g/cm^3 , not 6.69 as they report. Since the average density measured for several samples by liquid displacement is 6.82 g/cm^3 , a simple cubic structure is eliminated. We propose that InTe(II) has the NaCl structure with $a_0 = 6.154 \text{ \AA}$, corresponding to a theoretical den-

sity of 6.92 g/cm³. Our measured *d*-spacings are in good agreement with those of Darnell, Yench, and Libby, as shown in Table 1, which also gives the proposed lattice assignments.

The x-ray diffraction pattern for the NaCl structure normally includes lines with indices of 111, 311, and 331. When (*h* + *k* + *l*) is odd, however, the structure factor *F* is proportional to (*f*_{cation} − *f*_{anion}). Since *f* is proportional to the atomic number, in InTe(II) the *F* values for these three lines are too small for them to be observed. The diffraction pattern for SnTe (6), a well-known compound with NaCl structure, offers another example in which these lines are missing, as shown in Table 1.

Our first-reported lattice parameter of

Table 1. Comparison of lattice spacings for InTe(II) and SnTe.

InTe(II)				SnTe	
NaCl structure		Simple cubic (4)		NaCl (6)	
<i>hkl</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)
200	3.068	100	3.056	200	3.15
220	2.175	110	2.174	220	2.23
222	1.777	111	1.773	222	1.882
400	1.539	200	1.536	400	1.577
420	1.377	210	1.374	420	1.410
422	1.257	211	1.255	422	1.287
440	1.089			440	1.1147
<i>a</i> ₀ = 6.154		<i>a</i> ₀ = 3.07		<i>a</i> ₀ = 6.303	

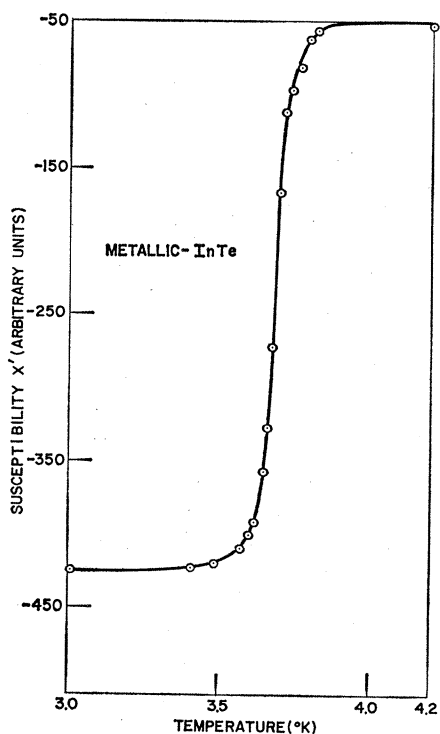


Fig. 1. Typical superconducting transition of InTe(II). The susceptibility, which depends on the coil and sample size, is in arbitrary units.

6.096 Å for the NaCl structure of InTe(II) (I), was measured on a directly synthesized sample which was subsequently found by analysis to be slightly indium-rich. The more recent samples were very nearly stoichiometric, In_{1.000}Te_{1.002}.

The metallic character of InTe(II) is demonstrated by the increase in its resistance with temperature up to 300°C at pressures above 30 kb; by its absolute thermoelectric power of −2.0 μV per degree C at 1 atm and room temperature; and its transition to a superconducting state at 3.5° to 3.7°K and 1 atm.

The superconducting transition temperature (*T*_c) was determined on three samples by measuring the complex alternating-current susceptibility (7) in a direct-current field of about 0.01 oersted. The alternating-current field, 18 cy/sec, ranged from 0.004 to 0.04 oersted. A representative transition is shown in Fig. 1. In any magnetic determination of superconductivity it is a problem to determine whether the bulk of the sample is superconducting. We have taken the imaginary part of the complex susceptibility, χ'', as our criterion of bulk superconductivity (7). We feel that the small size of the single χ'' peak (< 5 percent of Δχ') indicates that the transition is due primarily to superconductivity in the bulk of the specimen and not to a filamentary structure. A value of *T*_c of 3.5°K was also obtained for a fourth sample by using a self-inductance technique at 400 cy/sec (8). The superconductivity is not due to traces of In since neither InTe(I) prior to transformation nor InTe(I) obtained by heating InTe(II) at 130°C for 1 hour showed any evidence of a superconducting transition down to 1.6°K. The critical field of InTe(II) extrapolated to 0°K from measurements down to 1.6°K is about 1.2 kgauss, remarkably high for a bulk superconductor. The *T*_c of 2.18°K reported by Bömmel *et al.* (5) is identical to the λ point for liquid He. At this temperature the thermal conductivity of liquid He increases abruptly by several orders of magnitude. This may have obscured or influenced the measurement of *T*_c in their work.

When InTe(I) is transformed into InTe(II), the electrical resistance drops sharply. The pressure-temperature diagram for InTe obtained by observing resistance changes is shown in Fig. 2. This work was carried out in a tetrahedral hinge unit by a technique already described (9) and is limited to

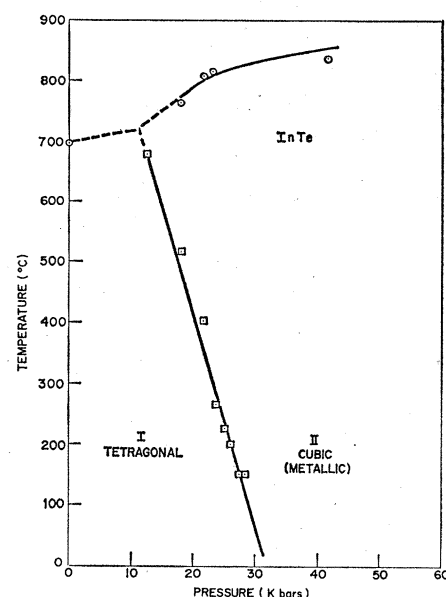


Fig. 2. Pressure-temperature phase diagram for InTe. Points on the I-II transformation line were obtained by experiments both at constant temperature and constant pressure. Sample resistance increases sharply on melting.

pressures above 10 kb. Therefore the triple point has not yet been clearly defined. Differential thermal analysis in low-pressure equipment is being used to fix this point. The room-temperature resistivity of InTe(II) measured with four leads to the sample at 40 kb is 6×10^{-5} ohm-cm. Resistivities measured with standard four-point probes at 1 atm varied from 4 to 14×10^{-5} ohm-cm depending on the method of sample preparation (10).

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