Reports

Indium Telluride (II′): Transitory Intermediate Phase in the Transformation InTe(II) to InTe(I)

Abstract. *The high-pressure cubic metallic form of indium telluride, InTe(II), transforms at 1 atmosphere to a new transitory polymorph, designated InTe(II′), which, in turn, transforms to the stable tetragonal polymorph InTe(I). The new polymorph is apparently tetragonal with unit-cell dimensions* $a_0 = 6.06$ *Å,* $c_0 = 6.55$ *Å. The transformation rates of InTe(II) to InTe(II′) and of InTe(II′) to InTe(I) are dependent on both time and temperature; the former is very rapid above 60°C and the latter is very rapid above 125°C.*

The high-pressure metallic polymorph of indium telluride, InTe(II), discovered by Banus *et al.* (*1*), has been recovered for laboratory study at room temperature and 1 atmosphere by cooling under pressures of 30 to 50 kb from either above or below the liquidus to either room temperature (*1–3*) or liquid-nitrogen temperature (*4, 5*). Metallic InTe(II) has the NaCl (Type B1) structure (*1–3, 5*) with reported unit-cell dimensions at room temperature of 6.16 Å (*1–3*) and 6.18 Å (*5*). A series of defect NaCl structures over the composition range $In_{1-x}Te$ with $0 \leqq x \leqq 0.18$ has been synthesized under pressure (*3*). Measurements of the following physical properties of indium telluride have been reported: density of InTe(II) (*1, 2, 5*); compressibility of InTe(I) and InTe(II) to 30 kb at 25°C (*5*); pressure-temperature dependence of electrical resistance to 40 kb and 850°C (*1*), and temperature dependence of electrical resistance at 1 atmosphere of InTe(I) and InTe(II) (*5*); superconducting transition temperature (T_c) of InTe(II) (*1, 3, 5, 6*); magnetic susceptibility of InTe(I) (*5*) and InTe(II) (*5, 7*); In^{115} and Te^{125} nuclear magnetic Knight shift and line width in InTe(II) (*7*); and lattice parameters and superconducting transition temperatures for indium-deficient compositional variants of InTe(II) (*3*). The two polymorphs of InTe are related, at room temperature at 1 atmosphere, by a density increase of 8.7 percent relative to InTe(I) as based on a cell edge of 6.16 Å for cubic InTe(II) and the reported cell edges of tetragonal InTe(I) (*8*); our earlier statement (*2*) of a 15.6-percent increase in density relative to InTe(I) is incorrect. On the basis of the compressibility data of Darnell and Libby (*5*), the density increase relative to InTe(I) at the equilibrium pressure (∼ 30 kb) for the InTe(I) to InTe(II) transition at 25°C is about 6.7 percent.

The persistence of metallic InTe(II) in the metastable state as a function of the metastable state as a function of time and temperature at 1 atmosphere has been reported as follows: (i) above 125°C rapid transformation to InTe(I) (*1, 4*); (ii) at 100°C, 75-percent transformation to InTe(I) in 1 hour (*1*); (iii) after 3 days at room temperature (followed by grinding to minus-325 mesh) no transformation to InTe(I) detectable by x-ray diffraction (*2*); (iv) at room temperature 20-percent conversion to InTe(I) after 4 months (*1*); (v) at dry-ice temperature no transformation to InTe(I) detectable, presumably by x-ray diffraction, after 9 months (*1*).

We now present evidence for a third polymorph of indium telluride, designated InTe(II′), which occurs as a transitory intermediate phase in the transformation at atmospheric pressure of the metastable metallic high-pressure form to the stable tetragonal form. At room pressure, therefore, the transformation of InTe(II) appears to proceed as follows: InTe(II) to InTe(II′) to InTe(I).

InTe(I) was prepared by melting a 1:1 (atom) mixture of semiconductor-grade indium (99.999 percent) and tellurium (twice sublimed in hydrogen) at 800°C in a sealed evacuated silica tube; a rocking furnace was used to improve homogeneity. The InTe(II) was prepared by subjecting powdered InTe(I) to 50 kb and 300° to 500°C in a belt apparatus for 16 hours, and subsequent slow cooling under pressure over a 4-hour period to room temperature. The identity and single-phase character of both InTe(I) and InTe(II) were established by x-ray powder diffraction and incident light microscopy in polished section. The InTe(II) was crushed to minus-400 mesh and stored both at −15°C and at room temperature.

Within 60 days the x-ray powder pattern of the InTe(II) stored at room temperature shows an inversion of the relative intensities of the two strongest lines of the cubic pattern at 3.07 Å and 2.17 Å, the appearance of three extra low-angle lines not correlative with InTe(I), an apparent shift of the first line at 3.07 Å toward a higher angle (actually the result of an additional unresolved reflection at 3.03 Å), and the appearance of an additional strong line at 2.14 Å. Within 139 days at room temperature, InTe(II) has transformed completely to a new noncubic phase, designated InTe(II′), x-ray powder diffraction data for which are given in Table 1. The x-ray diffraction pattern of InTe(II′) can be indexed on a tetragonal cell with $c/a = 1.08$, $a_0 = 6.06$ Å, $c_0 = 6.55$ Å; the structure of InTe(II′), therefore, appears to be a distortion of the B1 structure. Inasmuch as the density of

Table 1. X-ray powder diffraction data for InTe(II′). Manganese-filtered FeK α_1 radiation, $\lambda = 1.93597$ Å; 57.3-mm camera; indexed on tetragonal cell with $c/a = 1.08$, $a_0 = 6.06$ Å, $c_0 = 6.55$ Å. I, relative intensity.

hkl	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	$I_{obs.}$
110	4.28	4.29	30
111	3.62	3.59	25
002	3.25	3.27	10
200	3.03	3.03	50
112	2.62	2.60	10
202	2.24	2.22	5
220	2.14	2.14	100
310	1.92	1.92	30
311	1.84	1.84	10
203	1.77	1.77	20
312	1.66	1.65	5
114, 400	1.52	1.52	20
204	1.45	1.44	5
402	1.38	1.38	30
005, 332	1.31	1.31	5
314, 403	1.24 B	1.24	25
430, 500, 205	1.20 B	1.20	5
334, 106	1.075 B	1.075	15
206	1.025 B	1.025	20

Table 2. Densities and unit-cell data for polymorphs of indium telluride.

Phase	Crystal system	Structure type	Unit-cell parameters			Z	Density (g/cm^3)
			a_0 (Å)	c_0 (Å)	Vol. (Å$_3$)		
InTe(II)	Cubic	B1	6.16		233.7	4	6.89
InTe(II')	Tetragonal		6.06	6.55	240.5	4	6.69
InTe(I)	Tetragonal	B37	8.44	7.14	508.2	8	6.34

InTe(II') should lie between the known densities of InTe(II) and InTe(I), the number of formula weights per unit cell (*Z*) based on this indexing must be 4 and the calculated density of InTe(II') is 6.69 (Table 2). The density decrease relative to InTe(II) associated with the tranformation InTe(II) to InTe(II') is 2.9 percent, whereas the density decrease relative to InTe(II') associated with the transformation InTe(II') to InTe(I) is 5.2 percent. The structure of InTe(II') is probably more closely related to that of InTe(II) than it is to InTe(I).

In a polished metallographic section in plane-polarized incident light, InTe(II') has a distinct tan or cream color and shows weak reflection pleochroism. It is strongly anisotropic with vivid polarization colors that are predominantly royal blue, yellow, and red-brown; it commonly appears mottled as the result of nonuniformly disseminated, barely resolvable, granular inclusions of a white phase. Blue isotropic InTe(II) and InTe(II') may be observed in intimate association in polished section, but there is no evidence for any simple crystallographic control of the newly developing InTe(II') by the older cubic phase. The minute inclusions in the InTe(II') are restricted to this phase and have never been observed in InTe(II). They almost certainly represent nucleation sites of InTe(I), which develop directly from InTe(II') and not from InTe(II). Resolvable grains of InTe(I) are invariably contiguous with InTe(II') and have not been observed in direct contact with InTe(II).

When InTe(II) is stored at −15°C, there is no detectable change in the x-ray powder pattern after 200 days, although InTe(II′) was detected by x-ray diffraction after an arbitrarily selected time period of 334 days. The microscope is a much more sensitive indicator of the presence of InTe(II') in InTe(II); for example, InTe(II) stored at −15°C for 108 days contained about 10 percent InTe(II') as revealed microscopically, whereas the x-ray powder pattern shows only the cubic phase. Correspondingly, the deterioration of the nuclear magnetic resonance signal amplitude in InTe(II) (*7*) was traced with the microscope to the development of small amounts of InTe(II') which were not detected by standard x-ray powder methods. It is more difficult to detect small amounts of InTe(I) in InTe(II') with the microscope because of the relative similarity in their optical properties. InTe(I), however, is not obviously colored in plane–polarized incident light, and, while distinctly anisotropic, it does not show the striking polarization colors exhibited by InTe(II').

The concept of InTe(II') as an intermediate phase in the transformation of InTe(II) to InTe(I) is also supported by both the sequential development and relative proportions of phases that occur in pure InTe(II) as a function of time and temperature. At 25°C and −15°C InTe(II) spontaneously transforms to InTe(II'), the rate of transformation being greater at the higher temperature. No evidence for the development of InTe(I) at 25°C and −15°C was observed by x-ray diffraction after 5 months and 11 months, respectively. At temperatures above about 60°C InTe(II) transforms rapidly to InTe(II') so that at 90°C InTe(II) is completely transformed to InTe(II') within 2 hours. Correspondingly, the rate of transformation of InTe(II') to InTe(I) increases rapidly above 125°C so that within 1 hour at 130°C about 25 percent of a sample of InTe(II') is transformed to InTe(I). Thus the sequence of phase transformation in metallic indium telluride at room pressure is: InTe(II) → InTe(II') → InTe(I).

At 20 kb and room temperature in an opposed-anvil device InTe(II') was transformed back to InTe(II) which was retained after pressure release; the minimum pressure at room temperature required for the transition InTe(II') to InTe(II) has not yet been determined.

Measurements made by R. S. Tucker on a sample of InTe(II') containing about 20 percent of InTe(I) indicate that InTe(II') does not have a superconducting transition at least as low as 1.5°K.

Note added in proof: When InTe(I) was subjected to 35kb at about 150°C and then quenched to the temperature of liquid nitrogen before the pressure was released, the resulting mixture was composed of InTe(I) and InTe(II), and the InTe(II) occurred as lamellae oriented parallel to a single crystallographic plane (probably 001) in the grains of residual untransformed InTe(I). This arrested state in the transformation of InTe(I) to InTe(II) provides further evidence that InTe(II′) is not an intermediate phase in the transformation of InTe(I) to InTe(II) under pressure but forms only from a precursor, namely InTe(II), in the transformation of InTe(II) to InTe(I) at 1 atmosphere.

When InTe was melted (>1000°C) at 35 kb in a boron nitride container and then quenched to the temperature of liquid nitrogen before the pressure was released, the InTe(II) had an abnormally small cell edge (6.12 Å), which is indicative of the composition $In_{1-x}Te$ where x is ~ 0.07 (*3*). Presumably the rejected indium migrated into the porous container. $In_{1-x}Te$(II) shows remarkable metastable persistence when heated in air at 1 atmosphere successively for 3-hour periods at 90°, 110°, and 140°C; when heated at 190°C for 3 hours it transforms completely to InTe(II′) with $a_0 = 6.06$ Å and $c_0 = 6.50$ Å (Table 2). When the latter is heated in air at 1 atmosphere for 3-hour periods at 240° and 300°C the products are composed of cubic In_2Te_3, InTe(I), and residual InTe(II′). The appearance of In_2Te_3 also indicates that InTe(II) disproportionates at or above the liquidus under pressure and becomes deficient in indium.

Although solid InTe at high pressure is reportedly inert to tantalum (*3*), we found that liquid InTe at 35 kb is not compatible with a tantalum container; reaction products consist of a mixture of InTe(II) with an abnormally large lattice parameter of 6.17 to 6.18 Å, $TaTe_{85}$ (*9*), and elemental indium.

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Electron Yield in the γ-Radiolysis of Water Vapor

Abstract. *Nitrous oxide at low concentrations reduces the high yield of hydrogen from γ-irradiated water vapor containing methanol from 8.9 per 100 electron volts absorbed to a plateau value of 5.9. This indicates that both electrons (yield 3.0) and hydrogen atoms (yield 5.4) are precursors to the hydrogen, the former being scavenged by nitrous oxide.*

The high yield of hydrogen, $G(H_2)$, produced when various additives are present during the γ-irradiation of water vapor has been interpreted (*1*) in terms of reactions of H atoms:

$$H_2O \rightarrow H, OH, H_2$$
$$H + CH_3OH \rightarrow H_2 + \dot{C}H_2OH$$

These H atoms are believed to originate from both the excitation and ionization of H_2O, and for the latter the reactions

$$H_2O \rightarrow H_2O^+ + e^- \quad (1)$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + HO \quad (2)$$
$$H_3O^+ + e^- \rightarrow 2H + OH \text{ or } H_2O + H \quad (3)$$

have been suggested.

Using experimental methods described (*1*) we have made observations which support the idea that two precursors to H atoms are present. The presence of 0.1 percent of nitrous oxide is sufficient to reduce $G(H_2)$ from a mixture of water vapor and methanol from 8.9 to a plateau value of 5.9, which remains constant over a fivefold increase of N_2O (Fig. 1). Nitrogen is also produced with $G(N_2) = 3.8$.

As in the case of aqueous systems (*2*) and gaseous propane (*3*), it seems probable that N_2O acts as an electron scavenger

$$N_2O + e^- \rightarrow N_2 + O^-$$

thus preventing reaction 3. If this is so, then a yield of electrons $G(e) = 3.0$ is produced, and, since the yield of hydrogen as molecules is 0.5, this would leave an H-atom yield $G(H) = 5.4$.

If H atoms arise entirely from excitation, then the extent is about twice that of ionization. However, H atoms may originate partly from the ultimate neutralization process. The following sequence seems feasible:

$$O^- + H_2O \rightarrow OH^- + OH$$
$$H_3O^+ + OH^- \rightarrow H_2O + H + OH$$

If this does occur, then the original neutralization, reaction 3, must produce two H atoms and there are about equal amounts of excitation and ionization.

We also find that in the absence of methanol the same range of N_2O concentration gives $G(N_2) = 3.0 \pm 0.4$ (10 experiments) in water vapor. This is essentially the same as the decrease in $G(H_2)$ when methanol is present, but less than $G(N_2)$ in these conditions. The higher $G(N_2)$ probably originates from the reaction

$$N_2O + \dot{C}H_2OH \rightarrow N_2 + OH + CH_2O \quad (4)$$

In support of this we have confirmed an earlier observation (*4*) that N_2O in pure methanol vapor gives rise to a chain reaction, since values of $G(N_2)$ are as high as 50.

However, with pure methanol N_2O does not affect $G(H_2)$, even though it would appear that the charge-neutralization process analogous to that in water occurs

$$CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$$

and will be prevented by N_2O. It would seem that the alternative neutralization also produces a hydrogen atom and might be

$$CH_3OH_2^+ + OH^- \rightarrow CH_3OH + H + OH$$

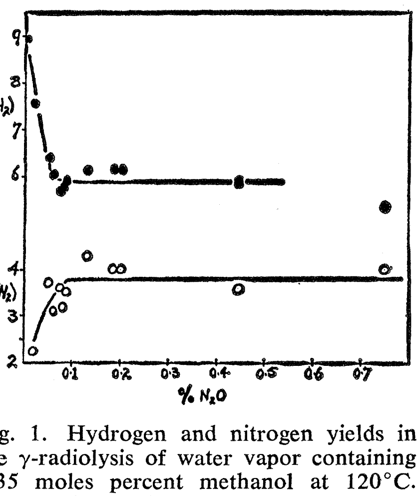

Fig. 1. Hydrogen and nitrogen yields in the γ-radiolysis of water vapor containing 2.35 moles percent methanol at 120°C. Dose: 10^{19} ev g^{-1}.

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Iron Accumulation in Cockerel Plasma after Estrogen: Relation to Induced Phosphoprotein Synthesis

Abstract. *In cockerels a single injection of estrogen causes a rise of several fold in the plasma iron. At 18 hours this response is proportional to the amount of diethylstilbestrol injected and may be used as a convenient measure of estrogen action. The phenomenon is probably related to the estrogen-induced synthesis of iron-binding phosphoproteins.*

The blood of laying hens contains a phosphoprotein fraction that can also appear in cockerels treated with estrogen (*1, 2*). Most of this phosphoprotein, in both laying hens (*3*) and estrogenized cockerels (*4*), is identical to the egg protein, phosvitin. Phosvitin has a high iron-binding potential (*5*) and such a complex may account for the total iron content of egg yolk (*6*). We now report on the possible correlation between the phosphoprotein and the iron content of plasma.

White Leghorn cockerels (100 to 150 g) and 3-month-old laying hens were used. The method for the estimation of plasma iron was based on that of Tompsett (*7*). This method gave the same values for total inorganic iron as those obtained with ashed samples of hemoglobin-free material. Plasma (0.5 ml) was heated in a boiling water