Cu(bpy)(dbm)$^+$(aq), 58918-83-5; Cu(bpy)(dpm)$^+$(aq), 58918-84-6; Cu(pbi)(bzac)$^+$(aq), 58918-85-7; Cu(pi)(bzac)$^+$(aq), 58918-86-8; Cu(en)(bzac)$^+$(aq), 58918-87-9; Ni(acac)$^+$(aq), 58918-88-0; Ni(bzac)$^+$(aq), 58918-89-1; Ni(dbm)$^+$(aq), 58918-90-4; Ni(bpy)(acac)$^+$(aq), 58918-91-5; Ni(bpy)(bzac)$^+$(aq), 58918-92-6; Ni(bpy)(dbm)$^+$(aq), 58918-93-7; Co(acac)$^+$(aq), 58918-94-8; Co(bzac)$^+$(aq), 58918-95-9; Co(dbm)$^+$(aq), 58918-96-0; Co(bpy)(acac)$^+$(aq), 58918-97-1; Co(bpy)(bzac)$^+$(aq), 58918-98-2; Co(bpy)(dbm)$^+$(aq), 58918-99-3.

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Crystallization of Amorphous GeTe under Pressure

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Two phases of GeTe were crystallized from amorphous thick films of 1:1 composition prepared by cathode vapor deposition.[2a] The crystallization was initiated in an opposed-anvils, high-pressure apparatus.[2b] Special care was taken to conform with the recommended sample thickness-to-diameter ratio so as to ensure uniform pressure distribution.[3] A graphical summary is presented in Figure 1.

It will be noted that at temperatures below 300 °C no crystallization resulted at pressures up to 120 kbars and for times up to 51 h at conditions as shown in Table I. However, from about 300 °C and above, the known rhombic phase (GeTe-I) and a new, orthorhombic phase of GeTe (GeTe-II) were quenched from the indicated experimental conditions.

The x-ray *d* spacings (Cu Kα) of GeTe-I agree well with the data of Schubert and Fricke,[4] who described the phase as having a trigonally distorted sodium chloride structure. The *d* spacings for GeTe-II may be indexed on the basis of an orthorhombic unit cell, type *Pnma*, with $a = 10.95$, $b = 4.03$, and $c = 4.45$ Å (Table II).

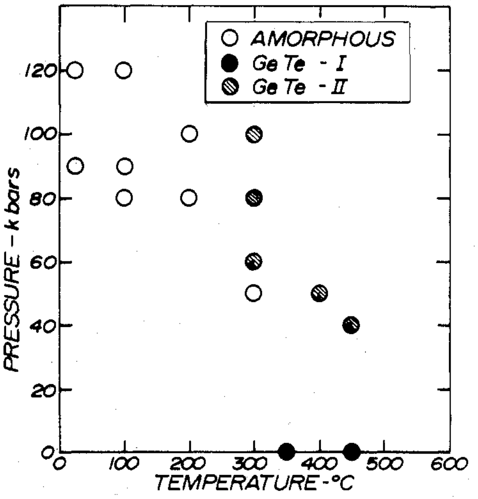

Figure 1. Results after quenching samples of amorphous 1:1 Ge:Te composition held at the *P–T* conditions as plotted.

Table I. Experimental Conditions

Pressure, kbars	Temp, °C	Time, h	Result
			Amorphous Thick Film
100	300	19	100% GeTe-II
90	25	19	Noncrystallized
100	200	20	Noncrystallized
90	100	20	Noncrystallized
80	300	26	100% GeTe-II
80	100	26	Noncrystallized
120	100	51	Noncrystallized
120	25	51	Noncrystallized
60	300	31	90% GeTe-II, 10% GeTe-I
50	300	31	Noncrystallized
50	400	15	95% GeTe-II, 5% GeTe-I
40	450	15	80% GeTe-II, 20% GeTe-I
0	350	24	100% GeTe-I
0	450	24	100% GeTe-I
			Powder of Amorphous Film
120	100	15	Noncrystallized
120	25	15	Noncrystallized
80	200	15	Noncrystallized

Table II. X-Ray *d* Spacings for GeTe-II[a]

hkl	d_{obsd}	d_{calcd}	*I*
201 (011)	3.15	3.18	60
111	2.90	2.89	100
400	2.730	2.740	20
211	2.589	2.601	20
311	2.433	2.423	20
112 (302)	1.924	1.924	20
220	1.870	1.885	60
600	1.824	1.830	20
511	1.767	1.770	80
312	1.720	1.721	20
701	1.481	1.480	40
113	1.383	1.384	40

[a] $a = 10.95$ Å, $b = 4.03$ Å, $c = 4.45$ Å, and $V = 1.96.4$ Å^3 (orthorhombic *Pnma*).

Discussion

One reason for starting with an amorphous material in studies of this type is that an intermediate or metastable phase might be encountered that would be of theoretical interest with respect to kinetics, free energy of formation, topotaxy, and other features. However, in the case of GeTe-II we believe that the phase may be stable in the *P–T* region in which it was found. This conclusion is not based on the rigorous criteria of reversibility because the experiments were not of sufficient number and design to permit a close determination of phase boundaries. Rather, it is based on the general concurrence of behavior of the series GeS, GeSe, and GeTe-II with the series SnS, SnSe, and SnTe, all of which are of the orthorhombic structure type *Pnma*. The systematic relationships of the cell parameters of the two series are shown in Figures 2 and 3. The volume of the rhombic GeTe-I (*Z* also 4) is shown in Figure 3 for comparison as being the less dense, low-pressure phase and not consistent with the series of orthorhombic phases.

In a study[5] of the system SnTe–GeTe, lattice parameters, obtained by x-ray diffraction of samples under high pressure, are given for compositions from 0 to 35 mol % GeTe. The phases were all isostructural with our GeTe-II. By extrap-

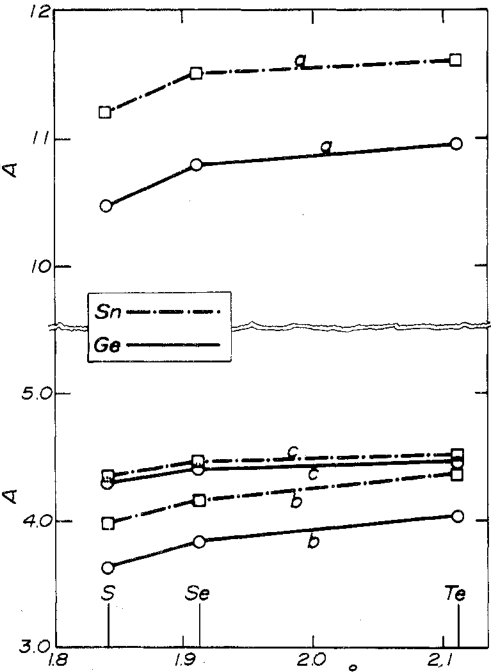

Figure 2. Lattice parameters of the S-Se-Te series of Sn and Ge; the phases are all of the SnS (or GeTe-II) structure. The unit axes are all referred to those of GeTe-II.

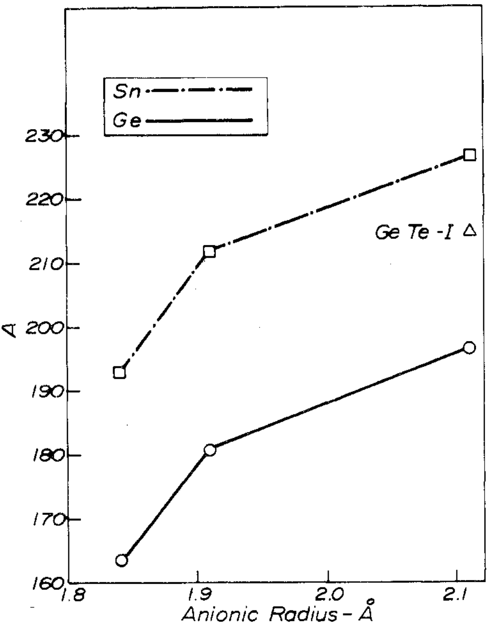

Figure 3. Unit cell volumes of the S-Se-Te series of Sn and Ge. The value for the rhombic phase, GeTe-I, not belonging to the isostructural orthorhombic series, is plotted for comparison.

olating these results to 100% GeTe we find the lattice parameters (under pressure) would be $a = 10.82$, $b = 4.04$, and $c = 4.10$ Å with $V = 179.5$ Å^3. The values are in good agreement with those of GeTe-II as quenched to 1 atm.

Attention is called both to an important difference and an important similarity between GeTe-II and the corresponding SnTe.[6] In the series GeS, GeSe, and GeTe-II, the sulfide and selenide are stable at atmospheric pressure, and GeTe-II must be formed at high pressures but can be quenched to room conditions. In the Sn series, however, although the sulfide and selenide are also stable at atmospheric pressure, SnTe (as indicated above[5,6]) may be observed only under high pressures using x-ray diffraction techniques and thus appears not to be quenchable. The ionic radius ratios of SnTe and GeTe are 0.44 and 0.34, respectively. These values indicate that the bonding character of SnTe is more metallic than that of GeTe. This focuses attention on a possible relationship between quenchability and degree of metallicity of similar, closely related phases.

In other work[7] on the SnTe–GeTe system, the high-pressure phase formed by compositions containing up to 35 mol % GeTe could not be retained or quenched even on cooling to 100 K before removing pressure. However, on diluting the same mixtures with boron, the pressure and cooling procedures are successful in retaining about 50% of the high-pressure phase at atmospheric pressure and 100 K for compositions containing up to 20 mol % GeTe. Thus with the system of SnTe–GeTe, differences in quenching behavior are beginning to fall within a framework of ionic parameters, temperature, pressure, and friction effects that may lend themselves to more than qualitative treatment.

Figure 1 summarizes results obtained with a 1:1 amorphous GeTe composition. It is evident that high pressures alone are not sufficient to produce noticeable crystallinity, at least to the experimental limit of 120 kbars. Complete conversion to GeTe-II occurred only at 80–100 kbars at 300°C, with mixtures of I and II forming at lower pressures.

A few runs made with a limited supply of amorphous films of 70:30 Ge:Te composition showed the formation of mixtures of I and II near 400 °C and 10 kbars. Much more work with other compositions and forms of starting materials will be necessary to detail phase relations in the system Ge–Te.

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Metal Atom Evaporation Synthesis and Intramolecular Exchange: (1,3-COD)FeL$_3$ Complexes from 1,5-COD

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In recent years, metal atom evaporation has emerged as a valuable technique for the synthesis of gram quantities of organometallic complexes, some of which cannot be readily obtained by conventional methods.[1-6] Following the report of Timms[7] on the preparation of Fe(1,5-COD)$_2$ (COD = cyclooctadiene), we thought its reaction with phosphites would provide an easy route to FeL$_5$ complexes. [1,5-COD is rapidly