fore be an indication that such a process did indeed operate on a planetary scale in the early solar system, as proposed by Urey. Thus I suggest that Earth accreted from reduced iron and a silicate portion enriched in Ca, Al, Sr, Ba, U, Th, and rare earths and depleted in K, Rb, Cs, and other volatile elements.

PAUL W. GAST

Department of Geology and Geophysics, University of Minnesota, Minneapolis

References and Notes

1. P. W. Gast, *J. Geophys. Res.* **65**, 1287 (1960).
2. G. J. Wasserburg, G. J. F. MacDonald, F. Hoyle, W. Fowler, *Science* **143**, 465 (1964).
3. G. Edwards, *Geochim. Cosmochim. Acta* **8**, 284 (1955); P. W. Gast, *ibid.* **19**, 1 (1960).
4. L. H. Ahrens, W. H. Pinson, M. M. Kearns, *ibid.* **2**, 229 (1952); K. Heier and S. R. Taylor, in *Physics and Chemistry of the Earth V*, F. Press, L. H. Ahrens, S. K. Runcorn, Eds. (Macmillan, New York, 1964).
5. P. Lessing, R. W. Becker, R. C. Reynolds, *J. Geophys. Res.* **68**, 5851 (1963).
6. A. E. J. Engel and C. G. Engel, *Science* **144**, 1330 (1964); *ibid.* **146**, 477 (1964).
7. The cooperation of A. Poldervaart and B. Heezen, Columbia University, and of A. E. J. Engel and G. Goles, University of California at San Diego, in obtaining the dredge samples is gratefully acknowledged.
8. A. A. Smales, T. C. Hughes, B. Mapper, C. McInnes, R. K. Webster, *Geochim. Cosmochim. Acta* **28**, 209 (1964); P. W. Gast, *ibid.* **26**, 927 (1962).
9. B. Mason, *Meteorites* (Wiley, New York, 1962).
10. R. A. Schmitt, D. A. Olehy, R. H. Smith, *Geochim. Cosmochim. Acta* **28**, 28 (1964).
11. H. C. Urey, *The Planets* (Yale Univ. Press, New Haven, 1952).
12. H. Konig and H. Wanke, *Z. Naturforsch.* **14a**, 866 (1959).
13. G. W. Reed, K. Kigoshi, A. Turkevich, *Geochim. Cosmochim. Acta* **20**, 122 (1960).
14. D. Carr and J. L. Kulp, *Bull. Geol. Soc. Amer.* **64**, 253 (1953).
15. Supported by a National Science Foundation grant.

16 November 1964

High-Pressure Transitions of Germanium and a New High-Pressure Form of Germanium

Abstract. *Some transitions in germanium and other semiconductor systems have been detected after very long exposure to high pressures followed by various quenching techniques. In the case of Ge, a new high-pressure polymorph, Ge-IV, has been synthesized above 110 kilobars with a body-centered-cubic structure. The pressure for the Ge-I ⇌ Ge-III (body-centered-tetragonal structure) transition has been revised from about 120 to 25 kilobars at 30°C. The transition from the Ge-I (diamond structure) to the Ge-II (white tin structure) is metastable up to 140 kilobars. Thus some phase diagrams based on discontinuities observed in essentially dynamic systems may be inaccurate.*

Investigations of phase transitions in germanium under high pressures have revealed (i) that the melting point decreases with increasing pressure (*1*); (ii) that resistivity methods (*2*) detect a reversible, nonquenchable transition which high-pressure x-ray methods (*3*) indicate are related to the $\alpha \rightleftharpoons \beta$-tin transition [Ge-I$_{\text{(diamond)}}$ $\rightleftharpoons$ Ge-II$_{(\beta\text{-tin})}$] at about 120 kb; (iii) that the shift of absorption edge with pressure goes through a maximum at about 45 kb (*4*); (iv) that a crystalline phase designated as Ge-III can be formed at pressures "exceeding 120 kb" (*5*) and "quenched" to ambient conditions.

We report on our intensive study of the relationships existing in the high-pressure crystalline phases of Ge under conditions designed to approach equilibrium. Another crystalline form has now been found, and this phase (Ge-IV) is the analog of the quenchable high-pressure body-centered-cubic (bcc) phase reported for silicon (*6*).

In order that the germanium might approach equilibrium between 35 to 140 kb and −78° to 450°C, "long-run" experiments were undertaken with opposed anvil apparatus (*7–9*).

Our Bridgman compound anvils were of tungsten carbide (type 886 or K96) force-fitted into thick right cylinders of Rene 41 alloy (*8*). The familiar configuration for the sample was used for most of the runs at lower pressures, the anvils having working faces of 6.35 mm and 4.76 mm diameter; the sample (99.999 percent Ge) was contained in a nickel ring 0.25 mm thick and was covered with discs of foil (0.025 mm thick and made of platinum containing 10 percent rhodium). For runs above about 80 kb the nickel retaining ring was omitted because of "blowouts," and a packed sample 0.50 mm thick was sandwiched between the aforementioned foil discs. Owing to extrusion of sample under pressure, the thickness of this wafer was decreased to 0.23 mm for a 4.76-mm diameter anvil face and to 0.178 mm for a 3.17-mm face, the ratio of diameter to thickness comparing favorably with the ideal ratios of 15 to 20 reported by Myers *et al.* (*9*).

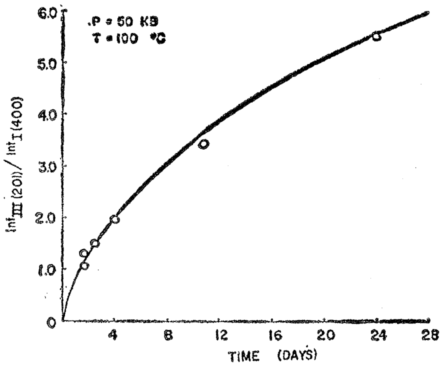

Fig. 1. X-ray diffraction intensity (*Int*) ratio of the Ge-III$_{(201)}$ and Ge-I$_{(400)}$ as a function of time at a fixed pressure and temperature, illustrating the sluggishness of the transition.

Actual pressures on the samples were probably not higher than we report. In assigning the pressure values we have considered diameter-to-thickness ratios (*9*) and results of varying such ratios in many runs with Ge. Furthermore, since the metallic sample assembly flows easily on the application of pressure, inhomogeneities of packing conducive to intensification of local pressure must tend to diminish with time.

Thus our achieving the transition at lower pressures cannot be attributed either to intense local shear on first raising the pressure or to hypothetical large pressure inhomogeneities; first raising the pressure up to 140 kb produced no quenchable transitions, and it was only after 10 hours at a stable configuration of the sample assembly that the dense phases were detectable by x-ray methods. The addition of continuous displacive shearing of small amplitude (*10*) did not change the transition pressures or the interval required for conversion.

Our investigation of the pressure-temperature phase relations of the Ge-I ⇌ Ge-III transition reported by Bundy and Kasper (*5*) to take place at pressures in excess of 120 kb indicated that the transition could be obtained at pressures as low as 25 kb at room temperature. However, at such low pressures, runs several days long were required to obtain an appreciable amount of Ge-III phase (see Fig. 1). The data shows that the "working" time required for an appreciable amount of GE-III to form is 4 to 5 days. Short runs (minute) would not reveal the equilibrium transition pressure.

The time required for 100-percent conversion of Ge-I → Ge-III at room temperature varied considerably with the pressure applied; at 75 to 90 kb, 3 weeks were required, whereas at 100 to 110 kb 1 to 2 days were sufficient. Hence, in the region of the univariant equilibrium boundary (Fig. 2), 4- to 5-day runs were always made to ensure that the Ge-III, if formed, would be detected. From the slope of this univariant line, 118.8 ± 7.2 atm/°C, and the volume change calculated from cell volumes at 1 bar, the enthalpy change, ΔH, of the transition at room temperature for Ge-I$\rightleftharpoons$Ge-III is 1.15 ±.07 kcal/mole, the usual approximations with the Clapeyron-Clausius relations being made.

As a check on the reversibility of the transition, samples of Ge-III were held in the Ge-I phase field just below the equilibrium curve. The Ge-III does revert back to Ge-I although the reverse reaction is also very sluggish, and long runs are again required in order to obtain significant change.

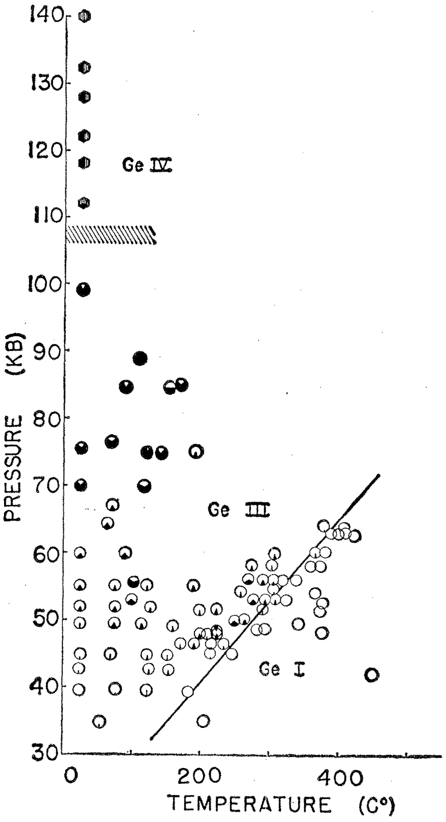

Fig. 2. Pressure-temperature equilibrium data for Ge-I, Ge-III, and Ge-IV. Dark filling and vertical line filling indicate the relative amounts of Ge-III and Ge-IV present after each run. The hexagonal points represent results of runs of 10 to 40 hours' duration.

If our data are extrapolated to atmospheric pressure, then Ge-III should be stable below −135°C (Fig. 3). However, for support of this extrapolation, runs under shear conditions of 10 to 20 kb at dry-ice temperatures failed to reveal Ge-III. Extrapolation to higher pressure, combined with Hall's original melting-point curve of Ge (*1*), places a triple point close to 615°C and 92 kb, which, however, is subject to the current revisions of high-pressure calibration points.

The x-ray reflections of Ge-III (Table 1) have been indexed on a tetragonal cell with our values, a_0 = 5.93 Å and c_0 = 6.98 Å, agreeing with those of Bundy and Kasper. The theoretical density, calculated on the basis of this unit cell, is 5.89 g/cm³ compared to the theoretical density of Ge-I of 5.325. The calculated density increase is therefore 10.7 percent.

Resistivity and x-ray studies established the occurrence of Ge-II (white tin structure) at high pressures only (*2, 3, 6*). Other evidence for the stability field of this phase was sought by us in our opposed anvil apparatus. Our usual long runs in the 120 kb region, where Ge-II was expected to form, resulted in Ge-III (with little or no Ge-I) after pressure release. Runs also were made with rapid application of pressure and with rapid or slow release of pressure, and there was no difference in the results. If we assume that the Ge-II→Ge-I transition is rapid, as demonstrated for the analogous Si transition (*3*), and if the Ge were brought into the Ge-II stability field quickly, then, irrespective of the holding time, on release of pressure only or mainly the Ge-I phase should be observed. This was not the case. It is improbable that well-crystallized Ge-III could form in a few seconds from Ge-II. Moreover, Fig. 1 shows how slowly Ge-III forms, while the I→II transition is known to be very rapid.

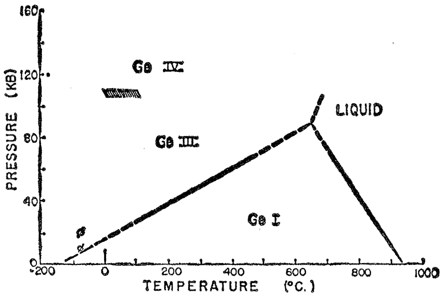

Fig. 3. The equilibrium phase diagram of germanium incorporating Hall's (*1*) melting point data and the present results. The univariant boundary between Ge-III and Ge-IV cannot be better defined as yet. The barred-circle symbols represent regions in which displacive shearing was used to try to effect the Ge-I → Ge-III transition at low temperatures.

Our data up to this point may be explained in two ways: (i) Ge-I transforms to Ge-II very sluggishly in the low-pressure region (30 to 90 kb), and the Ge-II, on removal of pressure, reverts completely in a few seconds to well-crystallized Ge-III; or (ii) Ge-I converts directly to Ge-III at equilibrium at the lower pressures, and only by overriding this transition at pressures near 120 kb can one favor the Ge-I to Ge-II metastable transition. Other data, however, establish the latter as the more probable explanation. Thus, Jamieson found that Ge-I could be converted completely to Ge-II in a short time at about 120 kb as observed *in situ* in his x-ray device (*3*). On release of the pressure the II phase completely disappeared, most of it reverting to I. A little III phase was also observed (this amount of III could have been missed in the high-pressure photograph). Thus, we have prima-facie evidence in Ge, and analogical evidence in Si, of the relatively rapid and reversible nature at high pressures of the diamond$\rightleftharpoons$white tin transition (equivalent to Ge-I→Ge-II). Hence it appears unlikely that Ge-III is formed by a metastable reaction

Table 1. X-ray *d*-spacings* for GE-III (body-centered-tetragonal). $a_0 = 5.93$ Å; $c_0 = 6.98$ Å; $z = 12$; density (calc.) = 5.89.

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
4.518	4.5199	101	5
3.593	3.5938	111	14
3.005	3.0079	012	39
2.728	2.7290	201	100
2.681	2.6827	112	22
2.478	2.4804	211	15
2.166	2.1683	103	5
2.032	2.0346	113	8
1.900	1.9040	301	12
1.8733	1.8768	310	20
1.8290	1.8306	203	20
1.8091	1.8135	311	22
1.7961	1.7989	222	29
1.7445	1.7490	004	13
1.5430	1.6447	320	6
1.5042	1.5066	204	5
1.4828	1.4826	400	5
1.4575	1.4612	313	5

* Obtained from x-ray powder diffraction with diffractometer scanning speeds of ⅛° and ¼° 2θ (CuKα) per minute. Indexing based on unit cell first reported by Bundy and Kasper (*5*). See also Kasper and Richards for data obtained by film techniques on a small polycrystalline chip (*11*).

Table 2. Comparison of data (Å) for bcc silicon and germanium-IV.

	Si		Ge:
hkl	J*	K & R†	this work
200		3.318	3.49
121	2.613	2.709	2.821
123	1.713	1.773	1.853
400		1.659	1.737
a_0	6.40	6.64	6.92

* The a_0 is calculated from the d spacings marked X by Jamieson (*3*) derived from x-ray diffraction at about 120-150 kb. † The *d* spacings are as given by Kasper and Richards (*11*) for the high-pressure silicon x-rayed at atmospheric pressure.

Ge-II$\rightleftharpoons$Ge-III on release of pressure; it appears instead to be formed by a very slow reconstructive transformation directly from I or II. In any case, it is also certain that even if the III form always results from II, the I→II transition cannot be any higher than about 30 kb at 100°C. The preferred interpretation of these relations is given in Fig. 4.

Examination of x-ray diffraction patterns of samples held at 110 to 130 kb at room temperature for 10 to 40 hours and then quenched disclosed two weak reflections which could not be accounted for. Furthermore, they disappeared at room temperature and pressure within a few hours. More experiments were made in which the samples were cooled to dry-ice temperatures at the end of long runs before release of the pressure. From then on, the samples were stored, ground, and x-rayed at dry-ice temperatures. With such handling, samples from runs at 140 kb and room temperature gave only these two, now very well-resolved reflections: at 31.71° and 49.17°C, 2θ (CuKα); and reflections at 25.5° and 52.7°C, 2θ. The reflections were much better defined than those we had obtained for the bcc high-pressure phase of silicon (*6*); more important, they were indexable on the same bcc cell of proportionately larger dimension. Furthermore, our x-ray data on Ge-IV to some extent are parallel to those of Jamieson on silicon (*3*). He reported two diffraction lines from silicon kept at high pressures for 3 days (and x-rayed at pressure), and these lines persisted at lower pressures. Our calculations show that these two reflections can result from the (121) and (123) planes of the bcc high-pressure phase of silicon, if one allows for a reasonable volume compressibility of about 10 percent owing to the 120- to 150-kb applied pressure. The two strongest lines of Ge-IV may also be indexed as (121) and (123), and the weaker ones as (200) and (400) (Table 2). Taken together, these data are evidence for a new Ge phase, Ge-IV.

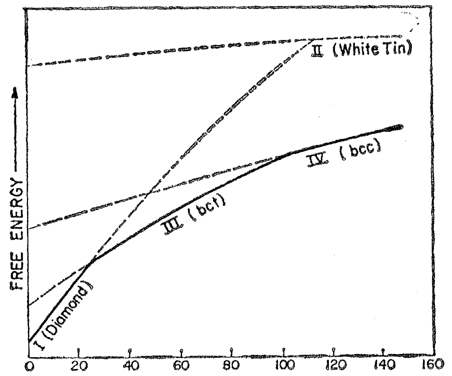

Fig. 4. Schematic free energy–pressure diagram drawn to emphasize qualitative stable and metastable relationships of the four crystalline phases of germanium at about 50° to 100°C.

The a_0 calculated from the (121) and (123) reflections is 6.92±0.01 Å, for which the theoretical density is 5.83 g/cm^3. This value is 9.5 percent greater than that of Ge-I but 1 percent less than that of Ge-III, all at 1 atm.

The Ge-IV may be stored indefinitely at dry-ice temperatures and atmospheric pressure; at 30°C approximately 90 percent disappears in 3 hours with the appearance of some Ge-III. On the other hand, Ge-III will persist at 100°C for several days and at room temperature indefinitely.

We believe our data have bearing on the interpretation of high-pressure work on semiconductor elements, Group III-V, and Group II-VI compounds. Thus, we and most workers in the field have erroneously assumed that phase transitions in semiconductors and metals would be too rapid to quench. We now find that these transitions are in the same general range of activation energy and rate as the sluggish phase transitions in typical oxide systems. It is therefore likely that pressures reported for certain transitions in similar systems are not equilibrium values. Further, the overlap of stable and metastable transitions makes difficult the interpretation of optical and electrical data under pressure in that these measurements are made under what are essentially dynamic conditions.

Our interpretation of the Ge equilibrium phase diagram (Fig. 3) does not show a firm phase boundary for the Ge-III$\rightleftharpoons$Ge-IV transition. Our data are not sufficient to establish it and an extension of the 1-percent volume differences (observed at 1 bar) to 110 kb is too uncertain to indicate the sign of the slope. Likewise the true slope for the Ge-III$\rightleftharpoons$liquid transformation is unknown.

CARL H. BATES
FRANK DACHILLE
RUSTUM ROY

Materials Research Laboratory,
Pennsylvania State University,
University Park

References and Notes

1. H. T. Hall, *J. Phys. Chem.* **59**, 1144 (1955).
2. S. Minomura and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 451 (1962).
3. J. C. Jamieson, *Science* **139**, 762 (1963).
4. H. G. Drickamer, in *Progress in Very High Pressure Research*, E. D. Bundy, W. R. Hibbard, Jr., H. M. Strong, Eds. (Wiley, New York, 1961), p. 16.
5. F. P. Bundy and J. S. Kasper, *Science* **139**, 340 (1963).
6. R. H. Wentorf and J. S. Kasper, *ibid.*, p. 338.
7. F. Dachille and R. Roy, *Z. Krist.* **111**, 451 (1959).
8. ———, in *Physics and Chemistry of High Pressures*, International Congress of European Federation of Chemical Engineering, 3rd Congress, London, June 1962 (Gordon and Breach, New York, 1963), p. 77.
9. M. B. Myers, F. Dachille, R. Roy, *Rev. Sci. Instr.* **34**, 401 (1963).
10. F. Dachille and R. Roy, in *Reactivity of Solids*, Proceedings, 4th International Symposium, Amsterdam, 1959, J. H. de Boer, Ed. (Elsevier, Amsterdam, 1960), p. 502.
11. J. S. Kasper and S. M. Richard, *Acta Cryst.* **17**, 752 (1964).
12. Supported by ONR, contract No. Nonr-656(20), Metallurgy Branch.

5 January 1965

Stratosphere and Troposphere: Transport of Material between Them

Abstract: *Data from two almost simultaneous balloon soundings show that ozone and dust in combination are transported from their stratospheric reservoirs into the troposphere by way of thin laminae measuring about 1 kilometer vertically by at least 480 kilometers horizontally. Transport in this layer occurs across the top of the jet stream in a region of very great vertical wind shear. Stratospheric aerosol may be an important instrument for the destruction of ozone within the stratosphere.*

Recent intensive study of the exchange of material between stratosphere and troposphere has been provoked by the fallout of radioactive debris injected into the stratosphere. The transport processes are undoubtedly important in determining the residence-time of all stratospheric materials: ozone, aerosols, water vapor, and others. All the mechanisms which exchange air