10. W. S. Broecker, J. L. Kulp, C. S. Tucek, *Science* **124**, 154 (1956).
11. R. Stuckenrath, Jr., *Am. J. Sci. Radiocarbon* **5**, 82 (1963).
12. S. Kusumgar, D. Lal, R. P. Sarna, *ibid.*, p. 273.
13. Unpublished dates of Tata Institute of Fundamental Research, Bombay.
14. E. J. Ralph, *Am. J. Sci. Radiocarbon Suppl.* **1**, 45 (1959).
15. I am grateful to D. Lal for his helpful discussions on the interpretation of dates, and to B. Peters for other stimulaitng discussions. I also thank R. P. Sarna for his assistance throughout this work.

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High-Pressure Phase Transition in Tin Telluride

Abstract. *At 18 kilobars, tin telluride transforms from a sodium chloride–type structure to an orthorhombic crystal structure (space group* Pnma*). This structural change is accompanied by a 360-percent increase in electrical resistivity.*

Tin telluride is an $A^{IV}B^{VI}$ compound analogous to PbS, PbSe, PbTe. At atmospheric pressure these four compounds have a cubic crystal structure (*1*) of the sodium chloride type. Tin telluride is a semiconductor with a very high apparent carrier concentration due primarily to the large number of tin vacancies in its crystal lattice (*2*).

The resistance of SnTe was measured as a function of pressure with a modified "belt" high-pressure apparatus similar to that described by Hall (*3*). The apparatus was calibrated with the following accepted transition pressures (*4*): bismuth I-II, 25 kb; thallium, 37 kb; and barium, 59 kb. Silver chloride was used as the pressure-transmitting medium, and the conical high-pressure gaskets were made of pyrophyllite. The specimens were cylindrical compacts of SnTe measuring 1.5 mm in diameter by 20 mm in length.

The effect of pressure on the electrical resistance of SnTe is shown on Fig. 1. The curve shows that the resistance of SnTe decreases gradually with increasing pressure. At 18 kb, however, there is a rapid, 360-percent increase in resistance, after which the resistance again drops smoothly with increasing pressure. The discontinuity in the resistivity curve at 18 kb indicates a first-order structural transformation, while the smooth drop in resistance beyond the maximum represents the effect of pressure on the resistivity of the high-pressure phase (phase 2). This transformation is completely reversible. The pressure was increased and decreased successively several times with each specimen and each cycle yielded the same resistivity curve.

The transformation at 18 kb was confirmed by x-ray diffraction patterns obtained with an opposed-diamond-anvil high-pressure x-ray camera similar to the unit described by Piermarini and Weir (*5*). Figure 2 is a photograph of the diffraction patterns of SnTe obtained at 1 atm and at 20 kb, and Table 1 is a summary of the x-ray data at 20 kb.

These data show that the high-pressure phase of SnTe has an orthorhombic structure (space group *Pnma*) analogous to the structure of the atmospheric-pressure phase of SnS and SnSe (*6*). The lattice parameters of the high-pressure phase of SnTe are $a = 11.59$ Å, $b = 4.37$ Å, and $c = 4.48$ Å, corresponding to a calculated density of 7.21 g/cm³ for four molecules per unit cell. This is an 11-percent increase in density over phase 1 at atmospheric pressure.

The average compressibility K, $(\Delta V/V_0\Delta P)$ of the low-pressure NaCl-type phase is 2.3×10^{-3} kb^{-1} between atmospheric pressure and 8.2 kb, determined from the lattice parameters at these pressures. By extrapolation, the density of this phase is 4 percent greater at 18 kb than at 1 atm. There is thus a net increase of 7 percent in density when the NaCl-type structure transforms to the orthorhombic structure at 18 kb.

Table 1. Analysis of the x-ray data obtained at 20 kbar; d is in Angstrom units.

d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}
3.54	3.54	2.01	20	8
3.08	3.13	011	40*	100*
	3.02	111		
2.91	2.93	301	100	45
	2.90	400		
2.68	(Tin)			
2.41	2.43	311	60	37
	2.43	410		
2.16	2.24	002	50	36
	2.19	020		
	2.12	411		
1.96	1.96	112	10	11
	1.94	302		
1.86	1.88	212	30	33
	1.86	511		
	1.86	221		
1.72	1.74	420	30	20
1.62	1.61	502	10	3
1.54	1.56	022	10	16
	1.55	701		
	1.55	122		
	1.51	512		
1.43	1.45	322	10	9
	1.45	800		
1.37	1.38	131	10	16
	1.38	422		
1.29	1.30	331	10	8
	1.30	522		

* Intensity calculations predict strongest reflection at 111. At elevated pressures, anisotropic bonding often leads to preferred orientation, which might explain the strongest reflection at 400.

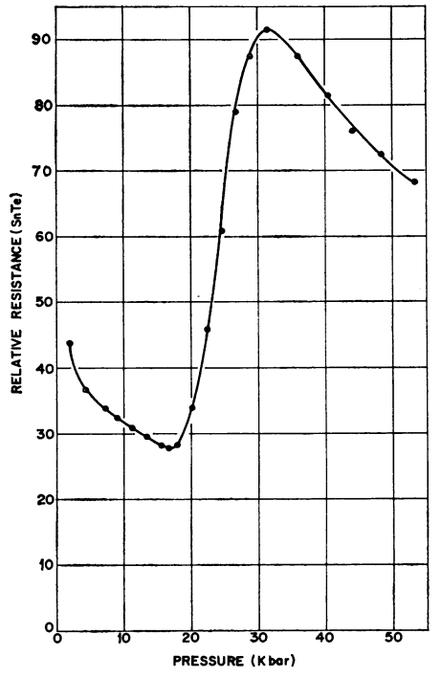

Fig. 1. The effect of pressure on the resistance of SnTe.

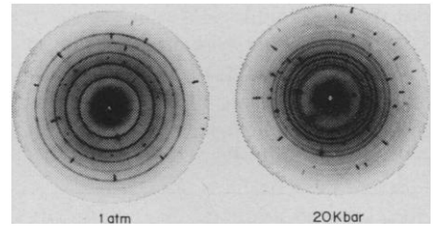

Fig. 2. X-ray diffraction patterns of SnTe obtained at 1 atm and 20 kb.

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References and Notes

1. M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), pp. 1099, 1105, 1111, 1210.
2. R. F. Brebrick, *Phys. Chem. Solids* **24**, 27 (1963).
3. H. T. Hall, *Rev. Sci. Instr.* **31**, 125 (1960).
4. R. H. Wentorf, Jr., *Modern Very High Pressure Techniques* (Butterworth, Washington, 1962), p. 229.
5. G. J. Piermarini and C. E. Weir, *J. Res. Natl. Bur. Stand.* **66A**, 325 (1962).
6. A. Okazaki and I. Ueda, *J. Phys. Soc. Japan* **11**, 470 (1956).
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