

also indicate the existence of a new phase. The long annealing produces specimens with fairly large grains, possibly of preferred orientations, and the beam does not encounter a random distribution of orientations. Therefore, the intensities of the reflections can vary markedly from sample to sample, and more data are necessary for statistical treatment before acceptable definition of the structure is possible. However, the results do show that the phase does not have the orthorhombic structure. The x-ray data do not agree with the body-centered cubic symmetry suggested by Martin and Smith¹⁷ for a possible new phase observed in their x-ray studies at about 200 kbar.

The results obtained in the high-pressure, high-temperature x-ray camera show that at about 60 kbar average pressure, the diffraction pattern at room temperature agrees with the reported line positions for the orthorhombic structure. However, on heating the InSb-II phase obtained at 40–50 kbar and room temperature, a new phase is detected at about 200°C. Unfortunately, the diffraction patterns obtained at these temperatures are diffuse and a definitive assignment of structure has not been possible in this case either. However, all the lines appearing on these films appear in the diffractometer tracings of the retained InSb-III phase. It was also found that after the specimen had been heated at 50 kbar to give the InSb-III phase, this phase was retained on cooling under pressure to room temperature. No change in diffraction pattern could be detected during a period of 10 days at room temperature and 50 kbar, in agreement with the results on the samples retained after preparation at 65 kbar as described above.

DISCUSSION

The phase stability on cooling, the difference in superconducting transition temperature, and the x-ray results lead us to conclude that InSb-III is a new phase, different from the orthorhombic phase. Referring to the partial P - T diagram given in Fig. 3, the boundaries between InSb-II and the orthorhombic phase and between InSb-III and the orthorhombic phase are indefinite. The shallow slope of the phase boundary between 37 and 52 kbar and the small positive value of the heat of transformation indicate that the difference in molar volumes between phases II and III is small. McWhan and Marezio¹⁶ have found that the orthorhombic phase is about 4% more dense than the β -Sn phase at 40 kbar, comparable to the magnitude we would expect for a difference between phases II and III.

Comparison of the estimated pressures between our experiments and those of McWhan and Marezio is made difficult because of the difference in equipment. It is further complicated by the orientation of the

TABLE I. Data on samples prepared at 65 kbar.

Sample	Pre-treatment	Anneal temp. (°C)	Anneal time (days)	T_c (°K)	Phase (x-ray)
(A) Equilibrium samples					
AQ	Melted	400	1	3.97	...
BH	None	250	4	3.87	...
BG	None	225	10	3.85	Phase III
BI	Melted	225	4	3.89	Phase III
BF	None	175	11	3.45	Ortho
BA	None	150	4	3.39	Ortho
AY	None	100–105	7	3.55	...
(B) Non-equilibrium samples					
BS	None	175	4	3.71	...
AO	Melted	150	2	3.98	...
AP	Melted	125	4	4.02	...
AR	Melted	100	4	4.01	Contains Phase III

incident x-ray beam; in their experiments the x-ray beam is normal to the pressure axis. Thus the large discrepancies in pressure for the x-ray results may be due entirely to the geometry of the systems and the difficulty in pressure measurements in these very small high-pressure units.

Filaments have been shown to have an effect on the superconducting transition temperature of some materials. The higher T_c of the specimens of InSb-III might possibly be caused by the presence of filaments of the orthorhombic phase in an InSb-II matrix. If this were the case, isolating the grains of InSb from each other by an inert material could reduce the opportunity for filaments to form and might cause a reduction in T_c . Vitreous silica was selected as the inert material since it showed no tendency to crystallize under the annealing conditions. When a sample consisting of a 50% by volume mixture of InSb and vitreous silica was pressed to 37 kbar and annealed at 350°C for 24 h, the T_c of the mixture was 3.95°K, very close to the value of 4.1°K for pure InSb-III samples prepared under the same conditions. This result does not support the explanation in terms of filaments. The lower T_c value may be the result of dilution by the silica. X-ray diffraction data also show no evidence of the two phases.

Resistivities on all specimens of InSb-II and InSb-III had a random variation of 1×10^{-5} to $7 \times 10^{-5} \Omega \cdot \text{cm}$, and showed no correlation with phase and anneal temperature. This suggests that the resistivities of these two metallic phases are not significantly different. This is probably the reason that the phase boundary between InSb-II and InSb-III was not detected in the previous studies^{2,3} in which the liquidus under high pressure was determined by measuring the resistance vs temperature at fixed pressures. The heat of transformation¹² is also too small to have been observed in the differential thermal analysis experiments by which Jayaraman *et al.*^{1,18} determined the liquidus up to 65

¹⁷ J. E. Martin and P. L. Smith, *Brit. J. Appl. Phys.* **16**, 495 (1965).

¹⁸ A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **130**, 540 (1963).