CRYSTAL CHEMISTRY AND SUPERCONDUCTIVITY
OF PRESSURE-INDUCED PHASES IN THE In–Te SYSTEM

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Abstract—In the In–Te system, a pressure-induced NaCl-type phase exists in the region $In_{0.80}Te$ to $In_{1.15}Te$. Superconductivity exists in the whole range, with the maximum transition temperature occurring for the stoichiometric InTe. A hypothesis previously given for the metallic behavior of this phase and the decrease of transition temperature on either side of the stoichiometric InTe is further elaborated. It is proposed that the transformation to the NaCl-type structure removes the structural constraint on electron transfer existing in the normal InTe. A method for calculating carrier concentration is given and it is shown that the superconducting transition temperature is a function of carrier concentration.

At least two other pressure-induced In–Te phases exist. One is In_3Te_4 which becomes superconducting at 1.25–$1.15°$K. In_3Te_4 has the anti-Sn_4As_3 structure with seven atoms in a rhombohedral unit cell, all lying on the threefold axis. The positional parameters of the atoms and interatomic distances are given and the coordination shown to be related to that found in the NaCl-type structure. Pressure–temperature experiments on normal In_2Te_3 indicate that a pressure-induced phase with this (or approximately this) composition cannot be obtained metastably without the presence of the In_3Te_4 and an unidentified phase. The pressure-induced In_2Te_3 phase has the well-known Bi_2Te_3 structure and is closely related to the In_3Te_4 structure. Superconductivity tests and X-ray diffraction investigation lead to the conclusion that the In_3Te_4 phases occurring with the In_2Te_3 phase are sometimes not stoichiometric and in such cases usually contain excess tellurium.

INTRODUCTION

IN A RECENT letter,[1] we reported the occurrence and superconducting behavior of pressure-induced vacancy structures of the NaCl-type in the In–Te system. It was proposed that the metallic behavior of the NaCl-type InTe resulted from the removal of the structurally imposed constraint in the normal phase, on electron transfer from In^+ to In^{3+} ions. This proposal has led to successful prediction[2] of other superconductors with NaCl-type and a related structure and of existence of solid solution regions in NaCl-type phases of binary systems.

The behavior of the In–Te system at high pressures is quite complex and we shall discuss in this paper only those aspects of it which are fairly clear.

EXPERIMENTAL

Appropriate amounts of the constituent elements in each case were melted together in an evacuated sealed

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fused silica tube. The resulting product was ground and mixed thoroughly to ensure homogeneity. X-ray powder photographs always showed the mixture of normal compounds expected from the phase diagram reported by KLEMM and VOGEL.[3] Specimens were packed into Ta containers and subjected to pressure and heating as described elsewhere.[4] The NaCl-type compounds were obtained usually by using 30 kbar and 400–500°C for various lengths of time not exceeding 4 hr. Pressures and temperatures for other phases will be given in later sections.

X-ray powder photographs (CuK radiation) were taken of all specimens subjected to high pressure and in some cases diffractometer patterns were obtained. Single crystal X-ray data were also obtained in some cases to be discussed later.

Superconductivity tests were made by the method of SCHAWLOW and DEVLIN.[5]

THE NaCl TYPE PHASES

Results

Since our earlier publication[1] on the Te-rich NaCl-type compounds, we have obtained In-rich pressure-induced NaCl-type phases to approximately $In_{1.15}Te$. It has also been possible to extend

the Te solubility to $In_{0.80}Te$; previously we reported that it extends to $In_{0.82}Te$. The results of superconductivity tests on these specimens are given in Table 1.

The lattice constants of all specimens are listed in Table 1 and plotted vs. composition in Fig. 1.* On the In-rich side, there is practically no change in lattice constant with change in In concentration; this was one of the reasons we thought earlier that solid solution on the In-rich side did not exist. Further, although excess Te enhances the odd-index X-ray reflections, excess In does not appear to do so. In fact, careful examination now shows that although we can just see the {111} reflection of stoichiometric InTe, it can no longer be seen in the photograph of $In_{1.15}Te$. Also, the stability at atmospheric pressure of these phases is greater, the greater the Te content; on the In-rich side, the stability is markedly less than that of stoichiometric InTe. Superconductivity tests on the In-rich specimens which had already begun to revert

indicate that the composition tends to move toward the stoichiometric InTe with exsolution of In possibly containing dissolved Te.

Table 1. *Superconducting transition temperatures,* T_c, *and lattice constants,* a, *and carrier concentrations,* n, *for* $In_{1-x}Te$ *and* $In_{1+x}Te$ *compounds with* NaCl-*type structure*

$1+x$	T_C (°K)	a (Å)	$n \times 10^{-22}/cm^3$
1·15	2·60–2·35	6·179 ± 0·005	1·34
1·10	2·80–2·55	6·182	1·45
1·05	3·41–2·95	6·181	1·58
1·015	3·51–3·25	6·178	1·67
1·00	3·45–3·20	6·177	1·71
$1-x$			
0·95	2·7 –2·5	6·14 ± 0·01	1·47
0·91	2·04–1·87	6·110 ± 0·003	1·28
0·87	1·55–1·40	6·081	1·09
0·83	1·15–1·09	6·055	0·88
0·82	1·06–1·02	6·052	0·83
0·80		6·040	

The X-ray data on the In-rich compounds indicate that the excess In atoms replace Te atoms. If Te vacancies were to occur, the intensity of the {111} reflection should first decrease and at about

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* A reconsideration of the plot of lattice constant vs. $1-x$ for the $In_{1-x}Te$ phases[1] indicated that a straight line could be passed through the points for $x \geqslant 0.05$. This line extrapolates to $a = 6.175$ Å for stoichiometric InTe (see Fig. 1). The back-reflection lines of the powder photograph of our original InTe were quite broad. We have since made a new specimen for which the back-reflection lines were much sharper and which gave $a = 6.177$ Å.
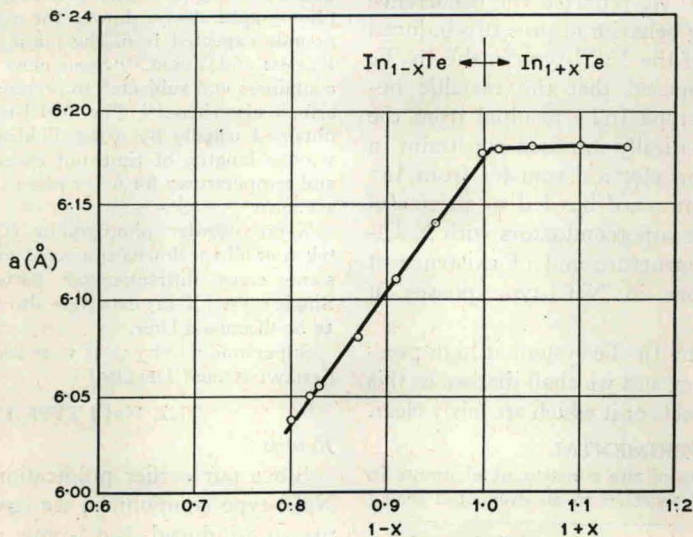

FIG. 1. Lattice constant vs. composition.