

each for the other two compounds.

The ionic model proposed for the NaCl-type intermetallic compounds allows one to predict when solid solutions will exist and in which of the elements they will be rich. In the Sn-Te system, NaCl-type compounds rich in Te should be expected because in  $\text{Sn}_{1-x}\text{Te}$  the valency of Te may be balanced by both  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  ions. It is unlikely, however, that NaCl-type Sn-Te compounds rich in Sn will exist. Similarly compounds of PbS, PbSe, and PbTe rich in the Group-VI element should be attainable, but not those rich in Pb. The high-pressure NaCl-type CdSe and CdTe phases<sup>12</sup> should not have solid solution ranges because of the single stable valences of the atoms involved. In the Sn-Sb system, solid solutions rich in either constituent should occur as has been reported.<sup>8</sup> Similarly, in the Sn-As system solid solutions rich in either constituent are to be expected. Although Hägg and Hybinette<sup>8</sup> did not observe this at atmospheric pressure, we have found that compounds  $\text{Sn}_{1+x}\text{As}$  and  $\text{Sn}_{1-x}\text{As}$  can be made at high pressures and retained metastably at atmospheric pressure. However, they begin to revert to the  $\text{Sn}_4\text{As}_3 + \text{SnAs}$  and  $\text{SnAs} + \text{As}$  phases, respectively, within a few hours after release of pressure. A test for superconductivity on what was later realized to be a partially reverted specimen indicated that again in this system a decrease in  $n$  results in decrease in  $T_c$ .

The NaCl-type phases in the In-Te system must therefore also have In-rich phases.<sup>6</sup> Despite our earlier conclusion<sup>1</sup> to the contrary, such phases, to about  $\text{In}_{1.15}\text{Te}$ , do exist; they cannot be retained metastably very long, but<sup>6</sup> again for these,  $T_c$  decreases with decreasing  $n$ .

Finally, it is worth emphasizing that the NaCl-type structure has now been shown to be favorable to both semiconductivity and superconductivity. If

the carrier concentration is high enough, the compound will be a superconductor. This should be true also for the compounds with the  $\text{Sn}_4\text{As}_3$  structure and for another related structure, the  $\text{Bi}_2\text{Te}_3$  structure. If it were possible to obtain, for example, a  $\text{Ge}_2\text{Te}_3$  with the  $\text{Bi}_2\text{Te}_3$  structure, it would be a superconductor and have a higher transition temperature than that of  $\text{Ge}_3\text{Te}_4$ .

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<sup>1</sup>S. Geller, A. Jayaraman, and G. W. Hull, Jr., *Appl. Phys. Letters* **4**, 35 (1964).

<sup>2</sup>B. B. Goodman, *Nature* **167**, 111 (1951).

<sup>3</sup>Marvin L. Cohen, *Phys. Rev.* **134**, A511 (1964).

<sup>4</sup>J. F. Schooley, W. R. Hosler, and Marvin L. Cohen, *Phys. Rev. Letters* **12**, 474 (1964).

<sup>5</sup>R. A. Hein, J. W. Gibson, R. Mazelsky, R. C. Miller, and J. K. Hulm, *Phys. Rev. Letters* **12**, 320 (1964).

<sup>6</sup>S. Geller, A. Jayaraman, and G. W. Hull, Jr., to be published.

<sup>7</sup>C. H. L. Goodman, *J. Phys. Chem. Solids* **6**, 305 (1958).

<sup>8</sup>G. H. Hägg and A. G. Hybinette, *Phil. Mag.* **20**, 913 (1953).

<sup>9</sup>A. L. Schawlow and G. E. Devlin, *Phys. Rev.* **113**, 120 (1959).

<sup>10</sup>Hägg and Hybinette (reference 8) reported that the compound  $\text{Sn}_3\text{As}_2$  was actually the one that existed but had the  $\text{Sn}_4\text{As}_3$  structure. We have found that " $\text{Sn}_3\text{As}_2$ " has two  $T_c$ 's,  $\sim \frac{1}{3}$  of the specimen at 3.6-3.5°K,  $\sim \frac{2}{3}$  at 1.21-1.17°K. The powder photograph indicates that free Sn is present and the  $T_c$ 's confirm the presence of Sn and  $\text{Sn}_4\text{As}_3$  in the right proportions.

<sup>11</sup>For a discussion of the calculation of these  $n$ 's, see reference 6.

<sup>12</sup>C. J. M. Rooymans, *Phys. Letters* **4**, 186 (1963); A. N. Mariano and E. P. Warekois, *Science* **142**, 672 (1963).