Thieno[2,3-b]thiophene. A mixture consisting of 9.2 g (0.050 mole) of crude 2-thieno[2,3-b]-thiophenecarboxylic acid, 5 g of copper powder, and 100 ml of freshly distilled quinoline was heated carefully and with efficient stirring to 180°. After being kept at that temperature for 2 h, the mixture was heated at 225–230° for 24 h, whereafter quinoline and liquid thiophthene were distilled off. The distillate was acidified with hydrochloric acid and the oil which separated was taken up in ether and dried. Fractionation yielded 5.4 g (78 %) of thieno[2,3-b]thiophene, b.p. 95°/10 mm Hg; picrate m.p. 135.5–136.5° after recrystallizations from methanol and ethanol. [Lit.[2], b.p. 98°/13 mm Hg, picrate m.p. 137–138°]. NMR (CCl_4): (Hard coupled AB-spectrum centered at 2.89 τ with a coupling of 5.4 c/s).

The NMR-spectra were obtained on a Varian A-60 NMR-spectrometer.

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Received February 8, 1967.

Ternary Transition Metal Arsenides with the *anti*-$PbCl_2$ Structure

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The occurrence of a number of ternary transition metal phosphides crystallizing with the *anti*-$PbCl_2$-type structure was recently reported.[1] Isostructural compounds also occur in ternary silicide and germanide systems, and the representatives for this class of compounds have been denoted by the name of *E*-phases.[2,3] As mentioned in Ref. 1, crystal-chemical considerations indicate, that *E*-phases should occur also in ternary transition metal-arsenic systems. The results of the present investigation prove the correctness of this prediction, and crystallographic data for eight ternary arsenides crystallizing with the *anti*-$PbCl_2$-type structure are given in Table 1.

The ternary arsenides were prepared by heating the component elements in evacuated and sealed silica tubes at 1000°C. Attempts to prepare *E*-phases containing zirconium and hafnium were not successful. Different synthetic techniques were tried, involving both heat-treatment of mixtures of the elements and arc-melting of mixtures of zirconium or hafnium with the mono-arsenides of the iron group metals. The resulting alloys gave rather line-rich powder patterns, which could not be easily interpreted.

The lattice parameters as given in Table 1 were in each instance determined accurately (estimated relative accuracy 0.04 %). However, appreciable homogeneity ranges were observed for some of the compounds. Since deviations from the ideal composition may have occurred during the synthesis of the samples, the values in Table 1 should be regarded with some caution.

The *E*-type structure appears to have a quite widespread occurrence in ternary systems, the number of known *E*-phases is now approaching fifty. As regards the conditions for the formation of *E*-phases, the importance of the size-factor principle has already been stressed in the crystal-

Table 1. Unit cell dimensions for some ternary arsenides crystallizing with the *anti*-$PbCl_2$-type structure. (Powder diffraction data taken with Guinier-Hägg cameras, $CrK\alpha_1$ radiation, internal calibration standard silicon, $a = 5.4305$ Å).

Compound	a (Å)	b (Å)	c (Å)	U (Å^3)	a/c
TiCoAs	6.221	3.696	7.084	162.9	0.878
TiNiAs	6.221	3.714	7.121	164.5	0.874
NbFeAs	6.258	3.734	7.181	167.8	0.871
NbCoAs	6.247	3.724	7.136	166.0	0.875
NbNiAs	6.242	3.721	7.190	167.0	0.868
TaFeAs	6.233	3.732	7.162	166.6	0.870
TaCoAs	6.211	3.706	7.116	163.8	0.873
TaNiAs	6.206	3.708	7.151	164.6	0.868

chemical discussions.[1,4] Although this principle gives a reasonable explanation for the ordering of the three component atoms at the different crystallographic positions in the structure, it cannot satisfactorily account for, *e.g.*, the non-occurrence of *E*-phases in some of the systems containing zirconium and hafnium. For a better understanding of this and other problems in the chemistry of *E*-phases, further studies of the physical and chemical properties seem very desirable.

Among the values in Table 1, one particular feature may finally be worth mentioning. The unit cell volumes for the nickel-containing compounds are in each instance larger than for the corresponding cobalt-containing compounds. In view of the uncertainties concerning the homogeneity ranges of the phases as mentioned above, this observation alone might not be very significant. However, the same volume effect is also observed for the *E*-type phosphides (see Table 3 in Ref. 1), and a reinterpretation of the powder diffraction data for the *E*-type silicides and germanides as given in Ref. 3 yields an analogous result. The consistency among all these values makes it safe to conclude that the nickel atoms take a larger volume in the structures of the *E* phases than do the cobalt atoms. This might at first sight seem somewhat surprising, since the normal metal radius for nickel is slightly smaller than the cobalt radius. In a more general comparison of isostructural nickel and cobalt alloy phases it is observed that the cobalt compounds have the largest cell volumes in a number of cobalt- and nickel-rich compounds with rare-earth metals as well as in the cobalt and nickel borides. On the other hand, the nickel compounds have the largest cell volumes in a number of other alloys and also in nickel and cobalt compounds with the V B and VI B sub-group elements. So far, no consistent explanation for this effect can be offered. It appears, however, that a more thorough analysis might reveal interesting information about the electronic structure of the cobalt and nickel atoms in different chemical environments. This problem will be further discussed in a forthcoming paper.

Acknowledgements. The work has been supported by grants from the *Swedish Natural Science Research Council.* One of the authors (P.T.) wishes to thank *The International Seminar in Physics*, Uppsala, and the *Swedish International Development Authority* for financial support.

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Received February 9, 1967.