On the Properties of Binary Compounds with the CoSb$_2$
Type Crystal Structure

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The compositions of the compounds CoAs$_2$, CoSb$_2$, RhP$_2$, RhAs$_2$, RhSb$_2$, α-RhBi$_2$, IrP$_2$, IrAs$_2$, and IrSb$_2$ are shown to be 1:2.00 by means of X-ray diffraction and density measurements. None of the compounds has an appreciable range of homogeneity. The CoSb$_2$ type crystal structure has been verified in these phases, and new positional parameters are given for CoAs$_2$, RhP$_2$, RhAs$_2$, IrP$_2$, and IrAs$_2$. The compounds have diamagnetic susceptibilities.

Associated with the pnictides and chalcogenides of Fe, Co, Ni, and other group VIII elements, there is a family of closely interrelated structure types which are characterized by distinct pairs of non-metal atoms in the crystal lattices and by (more or less distorted) octahedral and tetrahedral coordinations of near neighbours around the metal and non-metal atoms, respectively. Well established structure types included in this family are FeS$_2$-p (p = pyrite),$^{1,2}$ FeS$_2$-m (m = marcasite),$^3$ CoSb$_2$ (FeAsS-arsenopyrite),$^4,5$ NiSb$_2$,$^6$ AuSb$_2$, $^7$ (α-NiAs$_2$)$^8$, Rh$_3$Se$_6$, $^9$ IrSe$_3$, $^{10}$ PdS$_2$, $^{11}$ and IrSe$_2$, $^{12}$ of which the three first mentioned types dominate among the binary compounds with a frequency of occurrence in the given order. In contrast with earlier expectations, the structure types FeS$_2$-p and FeS$_2$-m appear to have a widespread occurrence, and are not restricted to transition metals in combination with pnigen or chalcogen elements. Although the CoSb$_2$ type structure is in fact more common than has perhaps been generally appreciated, the occurrence of binary compounds with this structure type is limited to combinations of Co, Rh, and Ir with P, As, Sb, and Bi. Of the twelve possible binary combinations of these elements, the existence of ten compounds with the CoSb$_2$ type structure has been recorded in the literature, those lacking being the hypothetical compounds CoP$_2$ and CoBi$_2$.

The CoSb$_2$ type structure was first discovered for the mineral arsenopyrite (FeAsS) by Buerger$^4$ in 1936. It is, however, more convenient to regard CoSb$_2$, which was shown by Zhdanov and Kuz'min$^5$ some thirty years later to be isostructural with FeAsS, as the structural prototype for this class of compounds (cf. Pearson$^{13}$). Complete structure determinations of binary com-

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pounds with this structure type have been reported for CoAs₂, CoSb₂, RhSb₂, α-RhBi₂, and IrSb₂, whereas only unit cell dimensions are available for RnP₂, RhAs₂, IrP₂, IrAs₂, and IrBi₂.

The true symmetry of the CoSb₂ type structure is monoclinic, but a suitable choice of axes leads to pseudo-orthorhombic symmetry of the unit cell with dimensions which are easily comparable with those found among the compounds with the FeS₂-m type structure (cf. Refs. 15, 16). The difference between the orthorhombic pseudo-cell and the monoclinic cell in the latter setting is so slight that the use of powder X-ray equipment of fairly high resolution or single crystal data is necessary to determine the true symmetry. Owing to this fact it is therefore not surprising to find that CoAs₂,₁⁷⁻⁻₂⁰ CoSb₂,₁⁵,²⁰ and α-RhBi₂²¹ have been reported (before 1955) to crystallize orthorhombically with a subsequent erroneous classification among the compounds with the FeS₂-m type structure.

Except for CoAs₂ which appears²² to be of stoichiometric composition without an appreciable range of homogeneity, and CoSb₂ for which there have been indications¹⁸ of a departure from stoichiometry, the remaining compounds of the above group have hitherto been neglected in relation to the details of their composition. Composition is, however, an important parameter in appraising the correctness of the bonding scheme proposed (cf. Refs. 16, 23–25) for these compounds.

All binary compounds with the CoSb₂ type structure are reported to exhibit semiconducting properties,²⁶⁻⁻³³ with the possible exception of α-RhBi₂ which is said to be metallic and superconducting³⁴⁻⁻³⁶ at low temperatures. The electrical and structural data are accordingly consistent with the diamagnetic³⁸,³⁷ properties of RhP₂, RhAs₂, RhSb₂, IrP₂, and IrAs₂, provided that the proposed bonding scheme is correct. For CoAs₂ and CoSb₂, however, the observation of weak paramagnetism¹⁸,³³,³⁷ is anomalous in relation to the assumption of the same bonding scheme as for the former compounds.

The object of the present paper is to report some new data on the composition, and structural and magnetic properties of the binary compounds with the CoSb₂ type structure.

**EXPERIMENTAL**

The pure elements used in this study were 99.999% Co (turnings from rods), Rh, and Ir (Johnson, Matthey & Co.), 99.999% red P (Koch-Light Laboratories), 99.999+ % As and Sb (Johnson, Matthey & Co.), and 99.99+ % Bi (American Smelting and Refining Co.). The samples were prepared by heating weighed quantities of the components in evacuated and sealed silica tubes. Several samples with different initial compositions were made of each phase, on both sides of the stoichiometric 1:2 ratio. During the syntheses the temperature was slowly increased to 800°C, the samples were kept at this temperature for 7 days, and then cooled slowly to room temperature. The samples were afterwards subjected to crushing and three further reannealings (with intermediate crushing) at 800°C over a period of 30 days. The temperature of the furnaces was kept constant to within ±0.5°C, using Getrostat (Philips) regulators in combination with a Frigistor reference chamber for the cold points of the Pt/Pt–Rh thermocouples. In order to minimize the effect of thermal gradients in the furnaces, the silica capsules were kept as short as possible and surrounded by quartz sand.

The preparation of single crystals was attempted by means of chemical transport reactions, using traces of chlorine, bromine, or iodine as transport agent. A variety of different thermal conditions were tried during these syntheses.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized CuKα1-radiation (λ=1.54050 Å) using KCl (α = 6.2919 Å) as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data. Integrated intensities were measured photometrically on the Guinier photographs.

Single crystal X-ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with MoKα-radiation using the multiple-film technique. The intensity measurements were carried out microphotometrically except for the weakest reflections which were estimated visually.

The observed intensities were corrected for the combined Lorentz and polarization factors, and for absorption and secondary extinction, the latter correction being applied only on the single crystal data. The atomic scattering factors used in the calculations of $F_c$-values were taken from Hanson et al. The least squares refinements were carried out according to programmes by Dahl et al. The agreement between $F_o$ and $F_c$ is expressed by the reliability factor $R = \frac{\sum||F_o|| - |F_c||}{\sum|F_o|}$. Throughout this paper the calculated standard deviations are appended in brackets after the corresponding parameter values, only the last digit(s) being given in each case.

The density measurements were made pycnometrically at 25.00°C with kerosene as displacement liquid. To remove gases adsorbed by the samples (weighing ~2 g) the pycnometer was filled with kerosene under vacuum.

Magnetic susceptibilities were measured between 90 and 1000 K by the Faraday method (maximum field ~8000 Oe) using 40–150 mg samples.

RESULTS AND DISCUSSION

(i) Identification of the phases. Polycrystalline samples of the phases CoAs₂, CoSb₂, RhP₂, RhAs₂, RhSb₂, α-RhBi₂, IrP₂, IrAs₂, and IrSb₂ are easily synthesized by direct reactions from the elements at 800°C. Most (if not all) of these phases are formed peritectically, and the opening of the capsules for crushing of the samples during the annealing processes is accordingly essential in order to ascertain that true thermodynamic equilibrium is obtained in each case. The existence of the phases is verified by the Guinier photographic data which furthermore serve to confirm identities with most of the corresponding phases reported in the literature.

Despite numerous attempts, it proved impossible to prepare phases corresponding to the formulae CoP₂, CoBi₂, and IrBi₂. Ordinary syntheses from the elements or several modified versions thereof as well as chemical transport reactions were tried over a wide range of thermal conditions, but all endeavours failed. Particular attention was paid to the attempted preparation of the IrBi₂ phase previously reported by Zhuravlev and Smirnova. However, none of many experiments carried out exactly according to their (somewhat unusual) procedure has confirmed the existence of this phase, Ir and Bi invariably being obtained as the only reaction products. If one therefore accepts the correctness of the evidence published by Zhuravlev and Smirnova, it must be concluded that the preparational conditions of IrBi₂ are highly irreproducible. However, its probable existence must be subjected to further examination. Comparatively little importance should also be attached to the apparent non-existence of CoP₂ and CoBi₂ since it is likely that they may be synthesized by a hitherto unattempted method, e.g. application of the combined high pressure-high temperature technique.

(ii) Homogeneity ranges and compositions. An extended range of homogeneity of a crystalline phase is usually accompanied by a variation in lattice dimen-

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sions with compositions, and this fact was utilized in seeking possible solid solubility ranges of the investigated phases. The unit cell dimensions for the various samples containing these $TX_2$ phases were extracted from the Guinier photographic data by application of the method of least squares. Following the statistical approach used earlier by Holseth and Kjekshus, the lattice parameters for each phase were found to be independent of the initial proportions of the components. It is therefore concluded that the phases concerned must be regarded as having well defined compositions, within the present detection limits.

The resulting mean values of the lattice dimensions and associated standard deviations are given in Table 1, these data being reasonably consistent with those reported in the literature.\textsuperscript{5,14,23,26,30,32,37,43-48}

The disappearing phase principle, applied by means of visual inspection of the samples and of the Guinier photographic data, showed the compounds to be stoichiometric within the limits defined by the formula $TX_{2.00 \pm 0.04}$. These findings were confirmed, and the degree of precision improved on the basis of comparisons (Table 2) of the pycnometrically determined densities with those calculated from the structural data (Table 1) on the assumption of 4 $TX_2$-groups per unit cell. The reported departure from stoichiometry of CoSb\textsubscript{3} (CoSb\textsubscript{1.9})\textsuperscript{18} reflects almost certainly therefore effects associated with the kinetics of its formation. The fundamental importance of the nature of the starting material of the metal component on the course of analogous reactions has been discussed by Holseth and Kjekshus. Consistent with this, reaction kinetical experiments confirm that intended CoSb\textsubscript{3} samples failed to reach equilibrium when coarse-grained (sheets, wires, or turnings from rods) Co was used as starting material and the intermediate crushings were neglected during the annealing process.

(iii) Refinement of the structures. When this work was initiated (in 1966) the structures of CoSb\textsubscript{3}, RhSb\textsubscript{3}, $\alpha$-RhBi\textsubscript{3}, and IrSb\textsubscript{3} had recently been subjected to refinements on the basis of single crystal data. (The structural data for CoAs\textsubscript{3} by Darmon and Wintenberger \textsuperscript{14} came to hand after the completion of the relevant part of the present work.) These compounds were therefore conveniently omitted from the present programme for crystal growth by chemical transport reactions. Of the other compounds, apparently single crystals of the arsenides were easily prepared by this technique whereas suitable transport conditions have not been found hitherto for RhP\textsubscript{3} and IrP\textsubscript{3}. All crystals of RhAs\textsubscript{3} and IrAs\textsubscript{3} tested have invariably proved to be twins or multiple crystals, while the very first crystal of CoAs\textsubscript{3} to be mounted on the Weissenberg goniometer proved to be a true single crystal.

The systematic extinctions in the diffraction data of CoAs\textsubscript{3} are of the type $h0l$ absent when $l = 2n + 1$, and $0k0$ absent when $k = 2n + 1$, which unequivocally determine the space group to be $P2_1/c$.

In terms of space group $P2_1/c$ the CoSb\textsubscript{3} type structure places 4$T$, 4$X_1$, and 4$X_{11}$ atoms in position 4(e): $\pm (x,y,z; x, 1-y, 1+z)$. Nine positional parameters are accordingly necessary in order to specify the location of all atoms within the unit cell (cf. Table 1), and the assumption of isotropic temperature factors (\emph{vide infra}) adds three further parameters.

* The symbols $T$ and $X$ are used to denote the metal and non-metal components, respectively.

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Table 1. Structural data for binary compounds with the CoSb₃ type structure. The positional parameters for CoSb₃, RhSb₃, α-RhBi₃, and IrSb₃ are quoted from Zhdanov and Kuz'min. The dimensions (a', b', c', and β') of the pseudo-marcsite cells are given in the square brackets.

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<th>Compound</th>
<th>(a') in Å</th>
<th>(b') in Å</th>
<th>(c') in Å</th>
<th>(β) in °</th>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
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Table 2. Observed and calculated densities (for compositions $TX_2$).

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<th>Phase</th>
<th>$d_{\text{pycn}}$ (g/cm$^3$)</th>
<th>$d_{\text{x-ray}}$ (g/cm$^3$)</th>
<th>Phase</th>
<th>$d_{\text{pycn}}$ (g/cm$^3$)</th>
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<td>CoSb$_2$</td>
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The assignment of CoSb$_2$ type structure to CoAs$_2$ is obviously correct, and least squares refinements could accordingly be started at once. The allowance for anisotropic temperature factors in the first refinement cycles led to standard deviations in these parameters, which exceeded the deviations from isotropy and gave moreover only insignificant improvement in $R$ compared with the isotropic case. This possibility is, for example, strongly rejected by application of the Hamilton $^{40}$ test, and isotropic temperature factors were therefore used in the final calculations. (It should be emphasized, however, that this limitation may prove to be an inadequate approximation in dealing with improved data.) There was no other problem associated with these calculations which were terminated at $R = 0.085$, the final positional parameters being as listed in Table 1, and the corresponding $B$-values were 0.16(4), 0.22(4), and 0.21(4) Å$^2$ for Co, As$_I$, and As$_II$, respectively. These positional parameters are in good agreement with those reported by Darmon and Wintenberger, $^{14}$ except in the case of $y_{\text{co}}$. However, judging from the standard deviations (0.003 compared with the present values given in Table 1), a substantial improvement in accuracy has been gained in this investigation. This improvement is also indicated by the fact that Darmon and Wintenberger terminated refinements at the considerably higher $R$-value of 0.21.

In the absence of single crystal data, refinements of the structures of RhP$_2$, RhAs$_2$, IrP$_2$, and IrAs$_2$ were attempted on the basis of powder X-ray data. In view of previous (bad) experience of this type of calculation, diminishing returns were expected from the endeavour. However, careful attention was paid to the correction of the various sets of data, and to the choice of input parameters, in order to avoid false solutions or divergence in the calculations. The calculations then took a fairly normal course, and gave very likely values for the positional parameters (cf. Table 1). Reasonable confidence in the results arises also from the fact that these sets of parameters are consistent with those obtained for the isostructural compounds, as may be seen from the trends within the data of Table 1. There is also a degree of correlation between the positional parameters of the compounds with the CoSb$_2$ type structure and the corresponding parameters of related compounds in the class A and B marcasites. $^{50-52}$

The inherent limitations on the positional parameters of RhP$_2$, RhAs$_2$, IrP$_2$, and IrAs$_2$ should be appreciated, and ideally would be confirmed using single crystal data.

Table 3. Interatomic distances and angles in the crystal structures of CoAs₂, CoSb₂, RhP₂, RhAs₂, RhSb₂, α-RhBi₂, IrP₂, IrAs₂, and IrSb₂.
(The standard deviations correspond to those in the positional parameters; cf. Table 1.)

<table>
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<th>Type</th>
<th>CoAs₂</th>
<th>CoSb₂</th>
<th>RhP₂</th>
<th>RhAs₂</th>
<th>RhSb₂</th>
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<th>RhSb₂</th>
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(iv) Interatomic distances and angles. The atomic arrangement of the CoSb₂ type structure is as shown in Fig. 1. Some important interatomic distances and angles calculated from the structural data in Table 1 are listed in Table 3. Each T atom is surrounded by six near X (three X₁ and three X₁₁) atoms at the corners of a distorted octahedron. The CoSb₂ type structure can be looked upon as being built up by these TX₆ octahedra, coupled together via common edges and corners. The T atoms are shifted from the centres of the X₆ octahedra in a manner producing alternately shorter and longer T–T distances which are aligned approximately parallel to [101] (cf. Fig. 1). Each X atom (X₁ and X₁₁ have very nearly the same configuration of nearest neighbours) is coordinated to one X and three T atoms, tetrahedrally arranged. The coordination octahedra and tetrahedra of the compounds with the CoSb₂ type structure are not of regular shapes (see Table 3), their irregularities being somewhat greater than for the related compounds with the FeS₂·m type structure.  

Circumstantial evidence suggests that it is impossible to obtain completely regular coordination polyhedra in the structure types FeSe₂·P, FeS₂·m, and CoSb₂, while retaining their composition, coordination numbers, and pairing of the X atoms.  

The lengths of the shortest interatomic T–X (X–T), and X–X distances listed in Table 3 are consistent with these being bonding distances. The shortest X₁–X₁₁ distances are in good agreement with the expectation values for the corresponding single bond X–X distances suggested by Furuhashi et al.  

The shortest T–X distances can also be interpreted as corresponding to (virtually) single bonds.  

The situation with respect to the shortest T–T distances is at first sight somewhat less clear. All of these T–T distances (Table 3) exceed the corresponding distances in the pure metals.  

As seen from the table, the latter distances show, furthermore, a systematic increase with increasing diameter of  

the $X$ atom in the sequence $\text{P} - \text{As} - \text{Sb} - \text{Bi}$ for a given metal atom. The unit cell dimensions (including $\beta$ and the volume) also exhibit monotonic (and almost linear) increases with increasing diameter of the non-metal component within the same sequence. However, despite these findings, the evidence which points in favour of the presence of $T - T$ bonding is in fact much stronger. The crystallographic support comes in the first place from the distinct difference in lengths between the shortest and next shortest $T - T$ distances (Table 3). Secondly, the CoSb$_2$ type structure can be considered as a distorted form of the FeS$_2$-m type structure, the distortion being a necessary consequence of the pairing of the $T$ atoms (cf., e.g., Refs. 15, 56). The most convincing support for the existence of a general $T - T$ bonding in these compounds comes from the restricted occurrence of the CoSb$_2$ type structure (which depends on a formal $d^9$ configuration for $T^{16,59}$), given that the compounds are diamagnetic semiconductors. The correctness of this interpretation follows from the fulfilment of the generalized (8 - N) rule (cf., e.g., Ref. 57):

$$n + P - Q = 8 \cdot a$$

where, per formula unit, $n (= 15)$ is the total number of electrons involved in bonding, $P (= 2)$ and $Q (= 1)$ are the number of electrons in $X - X$ and $T - T$ bonds, respectively, and $a (= 2)$ is the number of $X$ atoms. In view of the fact that there are $X - X$ and $T - T$ bonding in these compounds, they may be classified as being polyanionic-polycationic.

(v) Magnetic properties. The results of the magnetic susceptibility measurements are presented in Table 4. By the introduction of slight approximations

<table>
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<th>Compound</th>
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<td>CoSb$_2$</td>
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<tr>
<td>RhP$_2$</td>
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in some cases, it proved possible to express the $\chi$ versus $T$ relationships in analytical form for all compounds. The data are uncorrected for induced diamagnetism since reliable corrections are not easily estimated. With the exception of CoSb$_2$, which was found to have a constant susceptibility of zero value, all the listed compounds are diamagnetic. In contrast with earlier results,$^{35,57}$ CoAs$_2$ was here found to be slightly diamagnetic, probably due to

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a higher degree of purity of the present sample. For the remaining compounds
the present susceptibilities agree in sign, but differ somewhat in magnitude,
from those previously obtained. 26, 27

REFERENCES

10. Parthé, E. Third International Conference on Solid Compounds of Transition Elements,
    Oslo 1969, p. 151.
13. Pearson, W. B. A Handbook of Lattice Spacings and Structures of Metals and Alloys,
    Braunschweig 1967, Vol. II.
    SSSR Trudy 3-go (Chetvertogo) Soveshch. Moscov 1957 94.
    SSSR Trudy 4-go (Chetvertogo) Soveshch. Moscov 1961 113.
    Fiz. 16 (1952) 233.
35. Alekseevkii, N. E., Zhdanov, G. S. and Zhuravlev, N. N. Soviet Phys. JETP 1
    (1955) 99.

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Received June 10, 1970.

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