

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 , $\alpha\text{-RhBi}_2$, 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 A-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} NiSbS ,⁶ AuSn_2 ⁷ ($\alpha\text{-NiAs}_2$ ⁸), Rh_3Se_3 ,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 pnictogen and/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 Buerger⁴ in 1936. It is, however, more convenient to regard CoSb_2 , which was shown by Zhdanov and Kuz'min⁵ some thirty years later to be isostructural with FeAsS, as the structural prototype for this class of compounds (*cf.* Pearson¹³). Complete structure determinations of binary com-

pounds with this structure type have been reported^{5,14} for CoAs_2 , CoSb_2 , RhSb_2 , $\alpha\text{-RhBi}_2$, and IrSb_2 , whereas only unit cell dimensions are available for RhP_2 , RhAs_2 , IrP_2 , IrAs_2 , and IrBi_2 .

The true symmetry of the CoSb_2 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 FeS_2 -*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 CoAs_2 ,¹⁷⁻¹⁹ CoSb_2 ,^{18,20} and $\alpha\text{-RhBi}_2$ ²¹ have been reported (before 1955) to crystallize orthorhombically with a subsequent erroneous classification among the compounds with the FeS_2 -*m* type structure.

Except for CoAs_2 which appears²² to be of stoichiometric composition without an appreciable range of homogeneity, and CoSb_2 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 CoSb_2 type structure are reported to exhibit semiconducting properties,²⁶⁻³³ with the possible exception of $\alpha\text{-RhBi}_2$ which is said to be metallic and superconducting³⁴⁻³⁶ at low temperatures. The electrical and structural data are accordingly consistent with the diamagnetic^{33,37} properties of RhP_2 , RhAs_2 , RhSb_2 , IrP_2 , and IrAs_2 , provided that the proposed bonding scheme is correct. For CoAs_2 and CoSb_2 , however, the observation of weak paramagnetism^{18,33,37} 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 CoSb_2 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 crushings) at 800°C over a period of 30 days. The temperature of the furnaces was kept constant to within $\pm 0.5^\circ\text{C}$, using Getrosist (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 $\text{CuK}\alpha_1$ -radiation ($\lambda = 1.54050 \text{ \AA}$) using KCl ($\alpha = 6.2919 \text{ \AA}^{38}$) 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 $\text{MoK}\alpha$ -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.*³⁹ The least squares refinements were carried out according to programmes by Dahl *et al.*⁴⁰ The agreement between F_o and F_c is expressed by the reliability factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. 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 O) using 40–130 mg samples.

RESULTS AND DISCUSSION

(i) *Identification of the phases.* Polycrystalline samples of the phases CoAs_2 , CoSb_2 , RhP_2 , RhAs_2 , RhSb_2 , $\alpha\text{-RhBi}_2$, IrP_2 , IrAs_2 , and IrSb_2 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 CoP_2 , CoBi_2 , and IrBi_2 . 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 IrBi_2 phase previously reported by Zhuravlev and Smirnova.⁴¹ 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 IrBi_2 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 CoP_2 and CoBi_2 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-

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,⁴² 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.^{5,14,22,26,30,33,37,43-48}

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_2 ($\text{CoSb}_{1.9}$ 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.⁴² Consistent with this, reaction kinetical experiments confirm that intended CoSb_2 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_2 , RhSb_2 , $\alpha\text{-RhBi}_2$, and IrSb_2 had recently been subjected to refinements on the basis of single crystal data. (The structural data for CoAs_2 by Darmon and Wintenberger¹⁴ 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_2 and IrP_2 . All crystals of RhAs_2 and IrAs_2 tested have invariably proved to be twins or multiple crystals, while the very first crystal of CoAs_2 to be mounted on the Weissenberg goniometer proved to be a true single crystal.

The systematic extinctions in the diffraction data of CoAs_2 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_2 type structure places $4T$, $4X_I$, and $4X_{II}$ atoms in position $4(e)$: $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$. 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 (*vide infra*) adds three further parameters.

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

Table 1. Structural data for binary compounds with the CoSb₂ type structure. The positional parameters for CoSb₂, RhSb₂, α-RhBi₂, and IrSb₂ are quoted from Zhdanov and Kuz'min.⁵ The dimensions (α', β', c', and β') of the pseudo-marcasite cells are given in the square brackets.

Compound	a [α'] in Å	b [β'] in Å	c [c'] in Å	β [β'] in °	Atom	x	y	z
CoAs ₂	5.9106(5)	5.8680(6)	5.9587(5)	116.432(8)	Co	0.2723(6)	0.0031(14)	0.2832(6)
	[5.0447(5)]	[5.8680(6)]	[3.1259(2)]	[90.519(2)]	As _I	0.3411(5)	0.3655(12)	0.1752(5)
					As _{II}	0.1555(5)	0.6344(12)	0.3642(5)
CoSb ₂	6.5077(3)	6.3879(4)	6.5430(3)	117.660(4)	Co	0.270	0.000	0.280
	[5.5833(3)]	[6.3879(4)]	[3.3774(1)]	[90.350(1)]	Sb _I	0.354	0.359	0.168
					Sb _{II}	0.162	0.638	0.368
RhP ₂	5.7417(9)	5.7951(7)	5.8389(7)	112.911(10)	Rh	0.284(3)	0.000(6)	0.297(3)
	[4.8260(9)]	[5.7951(7)]	[3.1998(3)]	[91.044(3)]	P _I	0.328(7)	0.374(9)	0.190(6)
					P _{II}	0.146(7)	0.619(10)	0.368(8)
RhAs ₂	6.0629(4)	6.0816(5)	6.1498(4)	114.707(6)	Rh	0.280(2)	0.000(5)	0.291(3)
	[5.1416(4)]	[6.0816(5)]	[3.2943(2)]	[90.398(2)]	As _I	0.339(3)	0.367(6)	0.182(3)
					As _{II}	0.153(3)	0.626(5)	0.372(4)
RhSb ₂	6.6156(4)	6.5596(4)	6.6858(3)	116.821(6)	Rh	0.277	0.000	0.288
	[5.6652(4)]	[6.5596(4)]	[3.4839(1)]	[90.678(2)]	Sb _I	0.350	0.360	0.173
					Sb _{II}	0.160	0.633	0.373
α-RhBi ₂	6.9207(5)	6.7945(4)	6.9613(4)	117.735(6)	Rh	0.270	0.000	0.280
	[5.9413(5)]	[6.7945(4)]	[3.5887(2)]	[90.379(2)]	Bi _I	0.354	0.359	0.168
					Bi _{II}	0.162	0.638	0.368
IrP ₂	5.7453(5)	5.7915(5)	5.8494(4)	111.575(6)	Ir	0.233(2)	0.000(5)	0.296(3)
	[4.7942(5)]	[5.7915(5)]	[3.2599(2)]	[91.106(2)]	P _I	0.328(8)	0.373(10)	0.190(7)
					P _{II}	0.144(9)	0.621(11)	0.366(8)
IrAs ₂	6.0549(5)	6.0717(4)	6.1587(4)	113.197(6)	Ir	0.282(2)	0.000(4)	0.293(2)
	[5.0982(5)]	[6.0717(4)]	[3.3620(2)]	[91.060(2)]	As _I	0.338(3)	0.366(5)	0.182(3)
					As _{II}	0.151(3)	0.625(6)	0.370(3)
IrSb ₂	6.5945(3)	6.5492(4)	6.6951(3)	115.158(4)	Ir	0.280	0.000	0.291
	[5.6091(3)]	[6.5492(4)]	[3.5627(1)]	[90.958(1)]	Sb _I	0.348	0.360	0.175
					Sb _{II}	0.157	0.629	0.374

Table 2. Observed and calculated densities (for compositions TX_2).

Phase	d_{pycn} (gcm^{-3})	$d_{\text{x-ray}}$ (gcm^{-3})	Phase	d_{pycn} (gcm^{-3})	$d_{\text{x-ray}}$ (gcm^{-3})
CoAs ₂	7.41	7.49	α -RhBi ₂	11.86	11.94
CoSb ₂	8.30	8.34	IrP ₂	9.25	9.33
RhP ₂	6.07	6.12	IrAs ₂	10.83	10.92
RhAs ₂	8.09	8.15	IrSb ₂	10.98	11.06
RhSb ₂	8.85	8.89			

The assignment of CoSb₂ type structure to CoAs₂ 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 Hamilton⁴⁹ 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) Å² 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_{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 RhP₂, RhAs₂, IrP₂, and IrAs₂ 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 CoSb₂ 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 RhP₂, RhAs₂, IrP₂, and IrAs₂ 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, RhP₃, RhAs₂, RhSb₂, α-RhBi₃, IrP₃, IrAs₂, and IrSb₂. (The standard deviations correspond to those in the positional parameters; cf. Table 1.)

Interatomic distances (Å)

Type	CoAs ₂	CoSb ₂	RhP ₃	RhAs ₂	RhSb ₂	α-RhBi ₃	IrP ₃	IrAs ₂	IrSb ₂	
Bonding interatomic distances	T-X _I	2.54	2.30(6)	2.40(4)	2.60	2.71	2.29(6)	2.39(4)	2.58	
	T-X _I	2.50	2.33(4)	2.42(3)	2.57	2.66	2.34(4)	2.42(2)	2.58	
	T-X _I	2.330(4)	2.32(3)	2.39(2)	2.53	2.64	2.33(4)	2.39(2)	2.53	
	T-X _{II}	2.385(10)	2.44(6)	2.52(4)	2.67	2.72	2.42(7)	2.52(4)	2.69	
	T-X _{II}	2.404(4)	2.66	2.38(3)	2.51(2)	2.73	2.39(4)	2.53(2)	2.74	
	T-X _{II}	2.414(5)	2.60	2.42(5)	2.48(3)	2.67	2.45(5)	2.52(2)	2.69	
	X _I -X _{II}	2.462(7)	2.82	2.24(6)	2.49(3)	2.84	2.25(7)	2.48(3)	2.81	
	T-T	2.780(4)	3.04	2.68(2)	2.83(2)	3.03	2.75(2)	2.86(2)	3.06	
	Shortest interatomic distances neglected as bonding	T-X _I	3.708(7)	4.01	3.67(5)	3.82(3)	4.26	3.62(3)	3.85(3)	4.11
		X _I -X _{II}	3.146(5)	3.55	3.00(5)	3.21(2)	3.77	2.99(6)	3.20(3)	3.54
T-T		3.476(4)	3.72	3.72(2)	3.77(2)	3.91	3.78(2)	3.87(2)	4.07	

Table 3. Continued.

Interatomic angles (°)

Type	CoAs ₂	CoSb ₂	RhP ₂	RhAs ₂	RhSb ₂	α -RhBi ₂	IrP ₂	IrAs ₂	IrSb ₂
X _I -T-X _I	79.0(2)	78.1	82.4(12)	80.7(7)	78.5	78.0	83.8(14)	82.4(7)	80.4
X _I -T-X _I	83.7(3)	85.9	79.8(17)	81.8(11)	84.1	85.9	79.5(18)	81.3(10)	83.4
X _I -T-X _I	86.0(3)	87.5	85.4(19)	86.5(12)	87.2	87.5	84.9(19)	85.9(11)	86.9
X _I -T-X _{II}	86.9(2)	86.9	90.3(14)	89.4(8)	88.1	86.9	91.4(15)	90.6(7)	90.0
X _I -T-X _{II}	87.7(1)	90.2	78.0(14)	82.0(8)	86.3	90.3	77.1(15)	79.9(7)	82.9
X _I -T-X _{II}	90.0(3)	89.6	89.5(19)	89.4(13)	89.7	89.6	89.3(19)	89.4(11)	89.8
X _I -T-X _{II}	90.7(2)	91.6	88.7(16)	90.0(8)	90.9	91.6	88.8(18)	89.5(9)	90.2
X _I -T-X _{II}	91.3(3)	89.9	94.7(18)	92.7(13)	90.8	89.9	94.6(19)	92.7(11)	91.1
X _I -T-X _{II}	91.4(2)	89.9	90.8(17)	90.9(10)	89.7	89.9	91.1(19)	90.4(9)	89.4
X _{II} -T-X _{II}	92.0(2)	92.9	92.0(17)	92.1(11)	92.9	92.9	92.4(18)	92.8(9)	93.2
X _{II} -T-X _{II}	93.6(2)	92.1	95.7(16)	94.7(10)	93.3	92.1	96.0(17)	95.4(9)	94.1
X _{II} -T-X _{II}	106.5(2)	104.8	109.4(12)	107.9(8)	107.0	104.8	107.9(14)	107.1(7)	106.7
T-X _I -T	73.5(2)	75.2	70.6(11)	72.1(7)	73.0	75.2	72.1(12)	72.9(6)	73.3
T-X _I -T	125.1(3)	128.2	119.6(19)	123.3(12)	127.0	128.3	119.5(20)	122.7(11)	126.0
T-X _I -T	127.8(3)	129.9	125.7(21)	127.7(14)	130.3	129.9	125.5(23)	127.9(12)	130.2
X _{II} -X _I -T	107.0(2)	103.6	110.5(19)	107.9(9)	104.6	103.6	111.1(21)	108.3(9)	105.1
X _{II} -X _I -T	109.5(3)	107.9	111.5(24)	110.3(15)	108.9	108.0	110.5(26)	109.7(13)	109.0
X _{II} -X _I -T	110.2(3)	109.2	113.6(24)	111.6(15)	109.9	109.2	113.0(26)	111.1(13)	110.0
T-X _{II} -T	92.3(2)	89.8	102.0(16)	99.0(8)	93.7	89.7	102.9(17)	100.1(8)	97.1
T-X _{II} -T	122.5(3)	124.7	116.0(21)	119.8(12)	122.7	124.7	115.5(21)	118.2(11)	120.9
T-X _{II} -T	124.7(3)	124.8	123.3(21)	123.6(12)	124.1	124.9	123.6(23)	123.5(12)	123.5
X _I -X _{II} -T	103.8(3)	104.0	103.1(23)	102.9(12)	103.1	104.0	102.6(24)	102.6(12)	102.8
X _I -X _{II} -T	105.1(2)	103.8	104.7(17)	104.0(9)	103.6	103.8	105.2(20)	104.5(8)	103.5
X _I -X _{II} -T	106.2(3)	107.5	106.0(23)	106.7(12)	107.5	107.6	104.9(24)	106.0(13)	107.3

the X atom in the sequence $P-As-Sb-Bi$ for a given metal atom. The unit cell dimensions (including β 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^5 configuration for T ^{16,56}), 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 4. Magnetic susceptibility data for binary compounds with the $CoSb_2$ type structure, and β - $RhBi_2$ (*cf.* Refs. 21, 35, 36, 58, 59).

Compound	$\chi_g \times 10^6$ in e.m.u./g; temperature range in °K
$CoAs_2$	-0.02; 80-900
$CoSb_2$	0.00; 80-900
RhP_2	-0.47; 80-1000
$RhAs_2$	-0.40 ₅ ; -0.00004 T ; 80-850
$RhSb_2$	-0.36; 80-750
α - $RhBi_2$	-0.29 ₅ ; -0.00005 T ; 80-650
β - $RhBi_2$	-0.17; 850-1000
IrP_2	-0.39 ₅ ; -0.00008 T ; 80-900
$IrAs_2$	-0.31 ₅ ; -0.00010 T ; 80-800
$IrSb_2$	-0.41; 80-1000

in some cases, it proved possible to express the χ 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,^{33,37} $CoAs_2$ was here found to be slightly diamagnetic, probably due to

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.^{33,37}

REFERENCES

1. Bragg, W. L. *Proc. Roy. Soc. (London)* **A 89** (1914) 468.
2. Ewald, P. P. and Friedrich, W. *Ann. Phys.* **44** (1914) 1183.
3. Buerger, M. J. *Am. Mineralogist* **16** (1931) 361.
4. Buerger, M. J. *Z. Krist.* **95** (1936) 83.
5. Zhdanov, G. S. and Kuz'min, R. N. *Soviet Phys. Cryst.* **6** (1962) 704.
6. Peacock, M. A. and Henry, W. G. *Univ. Toronto Studies Geol. Ser.* **52** (1948) 71; Takéuchi, Y. *Mineral. J.* **2** (1957) 90.
7. Schubert, K., Breimer, H. and Gohle, R. *Z. Metallk.* **50** (1959) 146.
8. Stassen, W. N. and Heyding, R. D. *Can. J. Chem.* **46** (1968) 2159.
9. Hohnke, D. and Parthé, E. *Z. Krist.* **127** (1968) 164.
10. Parthé, E. *Third International Conference on Solid Compounds of Transition Elements, Oslo 1969*, p. 151.
11. Grønvald, F. and Røst, E. *Acta Cryst.* **10** (1957) 329.
12. Barricelli, L. B. *Acta Cryst.* **11** (1958) 75.
13. Pearson, W. B. *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon, Oxford - London - Edinburgh - New York - Toronto - Sydney - Paris - Braunschweig 1967, Vol. II.
14. Darmon, R. and Wintenberger, M. *Bull. Soc. France Minér. Crist.* **89** (1966) 213.
15. Brostigen, G. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 2983.
16. Brostigen, G. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 2993.
17. Peacock, M. A. *Proc. Roy. Soc. Canada* **38** (1944) 155.
18. Rosenqvist, T. *Acta Met.* **1** (1953) 761; *N.T.H.-Trykk*, Trondheim 1953.
19. Heyding, R. D. and Calvert, L. D. *Can. J. Chem.* **38** (1960) 313.
20. Fürst, U. and Halla, F. *Z. physik. Chem. B* **40** (1938) 285.
21. Zhuravlev, N. N. and Zhdanov, G. S. *Soviet Phys. JETP* **1** (1955) 91.
22. Roseboom, E. H. *Am. Mineralogist* **48** (1963) 271.
23. Hulliger, F. and Mooser, E. *Progr. Solid State Chem.* **2** (1965) 330.
24. Hulliger, F. and Mooser, E. *J. Phys. Chem. Solids* **26** (1965) 429.
25. Pearson, W. B. *Z. Krist.* **121** (1965) 449.
26. Dudkin, L. D. and Abrikosov, N. Kh. *Zh. Neorg. Khim.* **1** (1965) 2096.
27. Dudkin, L. D. and Abrikosov, N. Kh. *Zh. Neorg. Khim.* **2** (1957) 212.
28. Dudkin, L. D. and Abrikosov, N. Kh. *Voprosy Met. i Fiz. Poluprovod. Akad. Nauk SSSR Trudy 3-go (Trei'ego) Soveshch. Moscow* 1957 94.
29. Abrikosov, N. Kh. *Izv. Akad. Nauk SSSR Ser. Fiz.* **21** (1957) 141.
30. Hulliger, F. *Helv. Phys. Acta* **32** (1959) 615.
31. Dudkin, L. D. *Soviet Phys. Solid State* **2** (1960) 371.
32. Dudkin, L. D. and Vaidanich, V. I. *Voprosy Met. i Fiz. Poluprovod. Akad. Nauk SSSR Trudy 4-go (Chetvertogo) Soveshch. Moscow* 1961 113.
33. Hulliger, F. *Phys. Letters* **4** (1963) 282.
34. Alekseevskii, N. E., Brandt, N. B. and Kostina, T. I. *Izv. Akad. Nauk SSSR Ser. Fiz.* **16** (1952) 233.
35. Alekseevskii, N. E., Zhdanov, G. S. and Zhuravlev, N. N. *Soviet Phys. JETP* **1** (1955) 99.
36. Zhuravlev, N. N. and Zhdanov, G. S. *Izv. Akad. Nauk SSSR Ser. Fiz.* **20** (1956) 708.
37. Bennett, S. L. and Heyding, R. D. *Can. J. Chem.* **44** (1966) 3017.
38. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
39. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
40. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
41. Zhuravlev, N. N. and Smirnova, E. M. *Soviet Phys. Cryst.* **10** (1966) 694.
42. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 3273.
43. Zhuravlev, N. N. *Kristallografija* **1** (1956) 506.

44. Zhdanov, G. S., Zhuravlev, N. N. and Kuz'min, R. N. *Zh. Neorg. Khim.* **3** (1958) 750.
45. Zhuravlev, N. N., Zhdanov, G. S. and Kuz'min, R. N. *Soviet Phys. Cryst.* **5** (1961) 532.
46. Swanson, H. E., Cook, M. I., Evans, E. H. and de Groot, H. J. *Natl. Bur. Std. (U.S.) Circ.* **539 X** (1960) p. 21.
47. Rundqvist, S. *Acta Chem. Scand.* **15** (1961) 451.
48. Quesnel, J. C. and Heyding, R. D. *Can. J. Chem.* **40** (1962) 814.
49. Hamilton, W. C. *Acta Cryst.* **18** (1965) 502.
50. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 3284.
51. Dahl, E. *Acta Chem. Scand.* **23** (1969) 2677.
52. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **23** (1969) 3043.
53. Brostigen, G. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 1925.
54. Furuseth, S., Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **19** (1965) 735.
55. Kjekshus, A. and Nicholson, D. G. *Acta Chem. Scand.* *In press.*
56. Bjerkelund, E. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 3317.
57. Kjekshus, A. *Acta Chem. Scand.* **18** (1964) 2379.
58. Kuz'min, R. N. and Zhuravlev, N. N. *Soviet Phys. Cryst.* **6** (1961) 209.
59. Ross, R. G. and Hume-Rothery, W. J. *Less-Common Metals* **4** (1962) 454.

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