

Compounds with the Skutterudite Type Crystal Structure. III. Structural Data for Arsenides and Antimonides

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The crystal structures of CoAs_3 , CoSb_3 , $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$, RhAs_3 , RhSb_3 , IrAs_3 , and IrSb_3 with the CoAs_3 (skutterudite) type structure have been (re)determined by X-ray powder diffraction methods. The results are discussed in relation to those for the isostructural phosphides and the mineral itself.

Following the structure determination¹ of the cubic mineral skutterudite, mineralogical studies²⁻⁶ (by chemical analyses and syntheses, optical microscopy, and X-ray diffraction) have revealed that this is a triarsenide with a general formula $(\text{Fe}, \text{Co}, \text{Ni})\text{As}_3$. Since CoAs_3 is the only binary arsenide with 1:3 composition in this system, this compound is commonly associated with the mineralogical name skutterudite and constitutes the prototype for the structure type.

Over the years, a number of isostructural phases have been synthesized and studied by various methods.⁷⁻³⁵

Considering the structural properties in particular, among the binary compounds, only the phosphides CoP_3 , NiP_3 , RhP_3 , and IrP_3 have been subjected to structure determinations³¹ of sufficient accuracy for bonding considerations. In addition, there has also been a recent accurate redetermination of the mineral itself.³³ The accurate structure determinations have unequivocally demonstrated that the non-metal (X) atoms of the CoAs_3 type structure form a planar, rectangular rather than square arrangement. The latter aspect is a consequence of the failure of the variable positional parameters y and z for X to satisfy the so-called²⁴ Oftedal's relation $y+z=\frac{1}{2}$. Based on these sparse experimental evidences, we previously took the liberty of proposing a model³⁴ which accounts for

these observations. On this background we have felt a provocation to undertake correspondingly accurate (re)determinations of the other binary compounds. In addition, we conveniently included the ternary compound $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ which was prepared for ¹²¹Sb Mössbauer studies.³⁵

EXPERIMENTAL

Samples of CoSb_3 , $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$, RhSb_3 , and IrSb_3 were prepared earlier.³⁵ The triarsenides were prepared similarly by heating stoichiometric quantities of the elements (Co, Rh, and Ir from the same batches as before,³⁵ and 99.9999% As from Koch-Light Laboratories) in pure alumina crucibles placed inside evacuated, sealed quartz tubes. The samples were heated at 800 (CoAs_3) or 900°C (RhAs_3 and IrAs_3) for a period of three weeks. After intermediate crushing the samples were reannealed for a further week at the same temperatures, and finally cooled to room temperature over a period of two weeks.

The purities of the samples were ascertained from X-ray powder photographs taken in a Guinier type camera with monochromatized $\text{CuK}\alpha_1$ -radiation using KCl as internal standard. The unit cell dimensions were refined by applying the method of least squares.

Integrated X-ray intensities were obtained from 2θ counting scans by subtracting appropriate background counts. Three or more scans were taken of each compound. A General Electric wide angle powder diffractometer (calibrated with Si as standard) was employed using Ni-filtered $\text{CuK}\alpha$ -radiation and 1° slits.

The intensity data were corrected for the combined Lorentz and polarization factors. The determinations of the positional parameters followed the method described in Refs. 24 and 31. To perform the calculations, a special computer programme was written for the CD 3300 com-

puter. Atomic scattering factors used were taken from tables by Hanson *et al.*³⁸

RESULTS AND DISCUSSION

The unit cell dimensions of the various compounds subject to this study are listed in Table 1.

Table 1. Unit cell dimension (with standard deviation) and positional parameters for arsenides and antimonides with CoAs₃ type structure. Probable errors in y and z range from 0.0005 to 0.001.

Compound	a (Å)	y	z
CoAs ₃	8.2055(3)	0.344 ₂	0.151 ₄
RhAs ₃	8.4507(3)	0.348 ₃	0.145 ₉
IrAs ₃	8.4673(8)	0.347 ₇	0.145 ₄
CoSb ₃	9.0347(6)	0.335 ₁	0.160 ₂
Fe _{0.5} Ni _{0.5} Sb ₃	9.0904(5)	0.335	0.159
RhSb ₃	9.2322(6)	0.342 ₀	0.151 ₇
IrSb ₃	9.2533(5)	0.340 ₇	0.153 ₈

The space group, $Im\bar{3}$, attributed to skutterudite was very carefully determined in the original work of Oftedal,¹ and was recently confirmed by Mandel and Donohue.³³ All the structural evidences which have been accumulated^{11-15,20-24,29,31,32} hitherto, strongly suggest that this space group also applies to the isostructural compounds. Since the space group cannot be explicitly determined on the basis of powder diffraction data, $Im\bar{3}$ was postulated also for the present investigation.

In terms of $Im\bar{3}$, the CoAs₃ type structure places 8 T (metal atoms) in position (c) and 24 X in (g). The atomic arrangement is accordingly specified by the lattice constant a and two positional parameters y and z . In addition, there are two thermal parameters open to determination on the basis of powder diffraction data which permit only isotropic temperature factors.

The cubic $Im\bar{3}$ symmetry of the unit cell provides for the overlap of reflections with different structure factors $F(hkl)$. For this reason, the refinement procedure used in Refs. 24 and 31 was adopted. In brief outline, this method aims at minimizing the function $R(y_X, z_X, B_T, B_X) = \sum |jF_o^2 - jF_c^2| / \sum jF_o^2$. In order to simplify

the calculations and to facilitate the graphical representation of the results, the simplifying assumption of $B_T = B_X = 0.5 \text{ \AA}^2$ was introduced. The assumption of constant B values is not a serious limitation, however, since R generally is known to be a slowly varying function of the thermal parameters.

In accordance with considerations presented in Ref. 34, the variables y and z were varied in steps of 0.01 over the ranges $1/4 \leq y < 1/2$ and $0 < z \leq 1/4$. The resulting R maps revealed in all cases only one well defined minimum. The areas around these minima were explored in detail in order to determine them with the best possible accuracy. The positional parameters as defined by the location of these minima are given in Table 1, R factors between 0.056 and 0.113 being obtained. Judging from the curvatures of the $R(y, z)$ surfaces, the probable uncertainties in y and z are likely to be 0.0005 to 0.001. Since secondary minima previously were recorded²⁴ in corresponding R maps for IrAs₃ and IrSb₃, recalculations on the basis of these data were also performed as a part of this study. Contrary to the earlier findings, no secondary minima could be found this time. (The non-computerized work reported in Ref. 24 consumed about one man-year and the computational mistakes should be estimated on this background.) The location of the minima were found to be 0.349, 0.145 for IrAs₃ and 0.341, 0.154 for IrSb₃ in satisfactory agreement with the values given in Table 1.

The results of the present study together with those of Rundqvist and Ersson,³¹ and Mandel and Donohue,³³ are illustrated in Fig. 1. The diagram clearly shows that none of the compounds satisfy Oftedal's relation $y + z = 1/2$, the confirmation of this fact being the main object of the study. It is interesting to note that with the exception of NiP₃ which occupies a special position among these compounds (*vide infra*), the points define an approximately parallel line with that given by Oftedal's relation. A least squares fitted line on this basis would follow the equation $1/2 - (y + z) = 0.006$.

The bonding interatomic distances and angles are listed in Table 2. As a consequence mainly of the empirical relationship inferred above, the difference $d_2 - d_1$ between the 2 $X-X$ bond distances is constant to within $0.10 \pm 0.02 \text{ \AA}$ for all compounds except NiP₃.

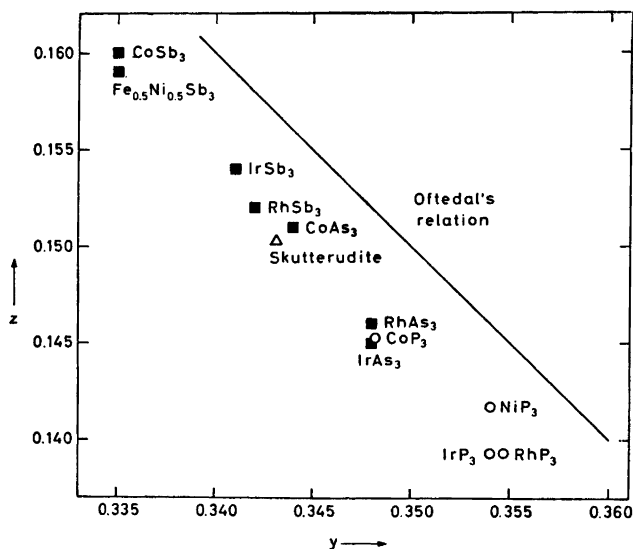


Fig. 1. Positional parameters for compounds with CoAs_3 type structure, Oftedal's relation being included for comparison. Points marked \circ quoted from Rundqvist and Ersson,³¹ \triangle from Mandel and Donohue.³³

Table 2. Interatomic distances (Å) and angles ($^\circ$) in compounds with CoAs_3 type structure. (Angle $X-X-X$ (1) is fixed at 90° .)

Compound	$T-X(6)$ (d)	$X-X(1)$ (d_1)	$X-X(1)$ (d_2)	$X-T-X$ (δ)	$X-T-X$ (δ)	$T-X-T$ (1)	$X-X-T$ (2)	$X-X-T$ (2)
CoP_3^a	2.222	2.240	2.340	84.0	96.0	120.3	109.9	111.3
NiP_3^a	2.280	2.216	2.283	83.1	96.9	118.0	110.9	111.8
RhP_3^a	2.341	2.227	2.323	83.2	96.8	117.3	111.0	112.2
IrP_3^a	2.345	2.233	2.340	83.4	96.6	117.4	110.8	112.2
Skutterudite ^b	2.334	2.464	2.572	84.6	95.4	122.8	109.1	110.5
CoAs_3	2.337	2.478	2.560	84.3	95.7	122.7	109.3	110.3
RhAs_3	2.434	2.468	2.569	84.0	96.0	120.5	109.9	111.2
IrAs_3	2.441	2.456	2.574	84.1	95.9	120.2	109.9	111.4
CoSb_3	2.520	2.891	2.982	85.3	94.7	127.3	107.7	108.8
$\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$	2.539	2.891	3.000	85.4	94.6	127.1	107.7	109.0
RhSb_3	2.621	2.807	2.917	84.6	95.4	123.5	108.9	110.2
IrSb_3	2.617	2.850	2.943	84.6	95.4	124.2	108.8	109.8

^a Calculated from data in Ref. 31. ^b Calculated from data in Ref. 33.

We have previously attributed³⁴ the rectangular distortion of the X_4 groups to anisotropic interactions arising from charges on the X sublattice. Thus, at first sight the approximate constancy of the distortion seemed somewhat surprising. However, d_2-d_1 is determined by a difference in force (acting in

mutually perpendicular directions) which in turn is proportional to square of charge and inversely proportional to square of distance, and a constant value for d_2-d_1 , may therefore simply imply that two effects are counterbalanced. The smaller value for d_2-d_1 in NiP_3 is consistent with the assumption²⁸ of delocali-

zation of one surplus electron over the lattice which thus would provide a shielding effect.

In accordance with the anisotropic interaction model,³⁴ $d_2 - d_1$ does not show any simple systematic correlation with bonding interatomic distances or angles. If, on the other hand, the rectangular distortion had been a consequence of competition between the X_4 group and the TX_6 octahedron,³¹ the $X-T-X$ angle is expected to show some relation to $d_2 - d_1$.

Important features of the bonding situation in these compounds are unquestionably reflected in the value of $d_2 - d_1$. Another parameter which reflects the inequality of the two $X-X$ bonds is the nuclear quadrupole interaction. Hence it seems natural that $d_2 - d_1$ versus $|eQV_{zz}|$ ³⁵ shows (Fig. 2) an approximately linear rela-

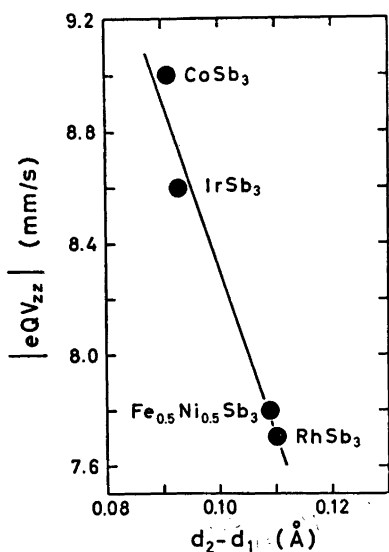


Fig. 2. ¹²¹Sb Mössbauer quadrupole interaction as a function of $d_2 - d_1$ for CoSb₃, Fe_{0.5}Ni_{0.5}Sb₃, RhSb₃, and IrSb₃.

tionship for the antimonides. It is not surprising that the electron imbalance reflected in the different bond lengths of d_1 and d_2 by far outweighs the minor variations in the average bond angle around X as opposed to the situation prevailing in compounds with pyrite, marcasite, and arsenopyrite type structures.³⁷

As expected (cf., e.g., Ref. 38) d_1 , d_2 , or their average shows approximately linear and mutually parallel dependences when plotted against

the $T-X$ bond distance d for the sequences CoP₃-CoAs₃-CoSb₃, RhP₃-RhAs₃-RhSb₃, and IrP₃-IrAs₃-IrSb₃.

A few comments concerning the work of Mandel and Donohue³⁸ seem appropriate. Their analytical composition indicating a 10% metal excess (or arsenic deficiency) as often found² by chemical analysis of natural skutterudites. The work of Roseboom⁶ on the arsenic content of synthetic CoAs₃ and X-ray investigations on mixtures of the minerals skutterudite and rammelsbergite (β -NiAs₂) indicate* that the formula given by Mandel and Donohue is not representative for the crystal used in the structure determination. Moreover, 10% deviation from stoichiometry is also expected to be reflected in y_X and z_X . Since skutterudite nicely follows the same trend as the other isostructural compounds (Fig. 1), a 1:3 ratio between metal and non-metal appears most probable. The only reasonable explanation of the analytical deficiency is therefore that the apparent metal-excess arises from impurities. The thermal parameters given by these authors are fully consistent with the anisotropic interaction model,³⁴ in that the relative difference between the root mean square vibration amplitudes equals the relative difference between the corresponding $X-X$ distances.

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* Roseboom observed no significant differences in the lattice constant on either side of the stoichiometric 1:3 ratio and he added as much as 7% by weight of rammelsbergite without being able to detect it by powder X-ray methods.

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