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Compounds with the Skutterudite Type Crystal Structure

I. On Oftedal's Relation

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The $CoAs_3$ (skutterudite) type crystal structure is examined and anisotropic interactions arising from the non-metal (X) sublattice are suggested as the principal cause of the rectangular distortion of the X_4 groups.

Cobalt triarsenide constitutes the prototype of an interesting class of transition metal pnictides. The most striking feature of the $CoAs_3$ type structure (in which the transition metal (T) and pnigogen (X) atoms are, respectively, octahedrally and tetrahedrally coordinated) is the collection of the pnigogens into planar X_4 groups.

The original crystal structure determination [1] of the mineral skutterudite ($CoAs_3$ with variable amounts of Fe and/or Ni substituted for Co; *cf.*, *e.g.*, Ref. 2) was based on the assumption of a postulated relation ($y+z=1/2$) between the variable parameters for the X atoms. Such a constraint, which has been termed "Oftedal's relation", implies that the X_4 groups are strictly square. Oftedal's relation was also assumed in subsequent determinations [3,4] of the isostructural compounds $CoSb_3$, $RhSb_3$, and $IrSb_3$ and in a redetermination [5] of skutterudite itself. The validity of this postulate was first explicitly questioned during X-ray powder studies [6,7] of RhP_3, $IrAs_3$, and $IrSb_3$. More recently, accurate structure determinations,[8] on CoP_3, RhP_3, IrP_3, and NiP_3 using X-ray powder diffraction methods and a single crystal study [9] on skutterudite show unequivocally that there are small, but significant deviations from Oftedal's relation, implying that the X_4 groups are rectangular rather than square. Rundqvist and Ersson [8] proposed a possible explanation as to the physical cause of this observation, an interpretation which has been accepted by Mandel and Donohue.[9]

We present here an alternative model which we believe provides a more realistic explanation for the rectangular arrangement of the X_4 groups.

ATOMIC ARRANGEMENT

In the $CoAs_3$ type structure the T atoms occupy the fixed coordinate position $8(e)$ and the X atoms the general position $24(g)$ of space group $Im3$. Hence, the atomic arrangement is completely specified by the two positional parameters y and z and the unit cell edge a. Given the composition TX_3 then, without any loss of generality, the positional parameters are assumed to be within the intervals

$$1/4 \leqq y < 1/2, \quad 0 < z \leqq 1/4 \qquad (1)$$

It is evident, however, that this neglects the finite size of the atoms and their mutual interactions which further restrict these permitted intervals for y and z (*vide infra*). It should also be noted that the combination

$$y = z = 1/4 \qquad (2)$$

converts the $CoAs_3$ type structure into the ReO_3 type structure (space group $Pm3m$ with only one TX_3 group per unit cell).

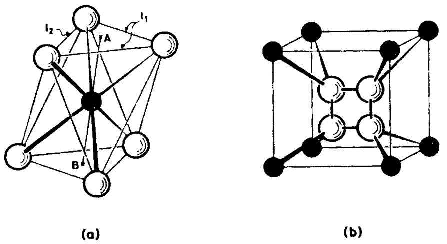

Fig. 1. Coordinations in the $CoAs_3$ type structure: (a) $6X$ atoms about T, and (b) $2X$ and $2T$ atoms about X.

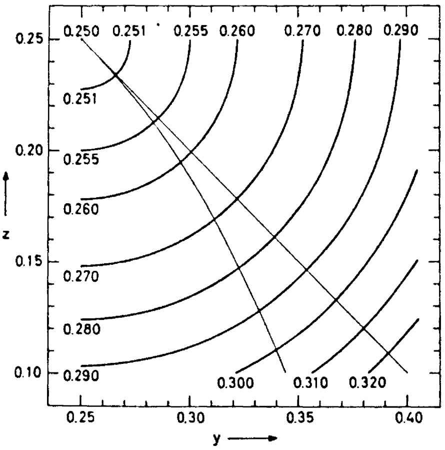

Fig. 2. Normalized $T-X$ distance (d/a) as functions of y and z. Oftedal's relation (eqn. 9) and the condition for perfect octahedral symmetry about T (eqn. 6) are shown by the thin lines.

The trigonal antiprismatic environment of the T atoms (Fig. 1a) is such that a straight line through T and the centres A and B of a pair of congruent, equilateral triangles intersects their planes at right angles. With this coordination symmetry the six $T-X$ distances d are equal

$$d = a[(1/4)^2 + (y - 1/4)^2 + (1/4 - z)^2]^{\frac{1}{2}} \qquad (3)$$

The dependence of the normalized $T-X$ distance d/a on y and z is, as shown in Fig. 2, a set of concentric circles around $y = z = 1/4$. The dimensions l_1 and l_2 of the triangle are given by

$$l_1 = a[(1/2 - y)^2 + (1/2 - z)^2 + (1/2 - y - z)^2]^{\frac{1}{2}} \tag{4}$$

$$l_2 = a[y^2 + z^2 + (y - z)^2]^{\frac{1}{2}} \tag{5}$$

Equating l_1 and l_2 places the restraint

$$2y(1/2 - z) = 3/8 - z \tag{6}$$

on the positional parameters and produces in this case perfect octahedral symmetry. The only permissible distortion from perfect octahedral symmetry within the $CoAs_3$ type structure follows from the condition $l_1 \neq l_2$ which gives rise to two sets (6+6) of mutually supplementary $X-T-X$ angles. Fig. 3 shows the dependence of one of these sets on y and z.

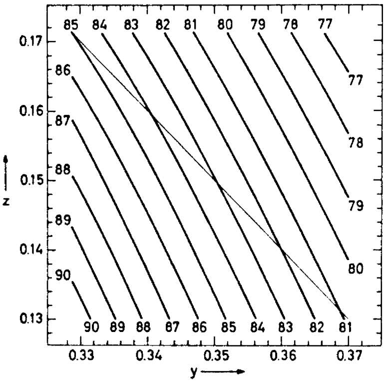

Fig. 3. $X-T-X$ bond angle *versus* y and z, the thin line showing Oftedal's relation.

Each X atom is surrounded by two X and two T atoms at the corners of a tetrahedron which is more severely distorted than the octahedron. The $X-X-X$ angle (within the planar X_4 groups, *cf.* Fig. 1b) is fixed at 90°,

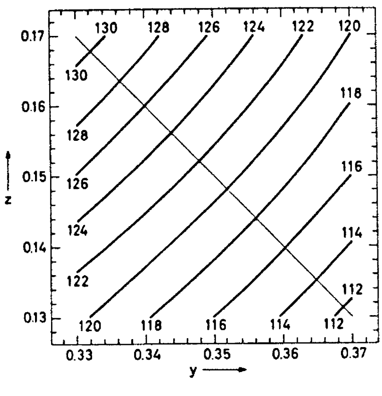

Fig. 4. Variation of $T-X-T$ bond angle with y and z, Oftedal's relation being shown by the thin line.

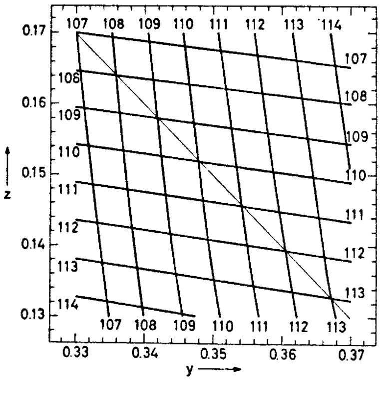

Fig. 5. $X-X-T$ bond angles *versus* y and z, Oftedal's relation being indicated.

whereas the $T-X-T$ and $X-X-T$ angles depend on the positional parameters as shown in Figs. 4 and 5, respectively. The interatomic distances

$$d_1 = 2az \tag{7}$$

$$d_2 = 2a(1/2 - y) \tag{8}$$

within the rectangular X_4 group reflect strong covalent interactions. The dependence of the ratio d_2/d_1 on y and z is shown in Fig. 6, Oftedal's relation

$$y+z=1/2 \tag{9}$$

being obtained for $d_1=d_2$.

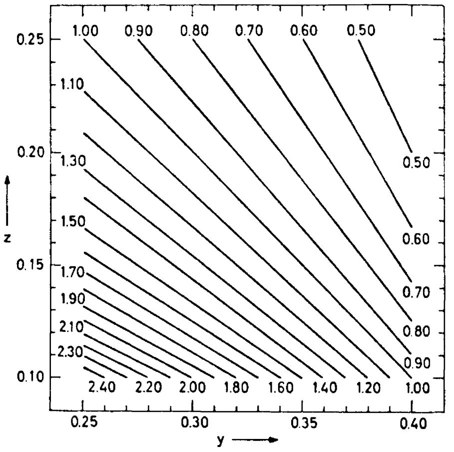

Fig. 6. Ratio of $X-X$ bond lengths (d_2/d_1) as functions of y and z.

Rundqvist and Ersson[8] have suggested that the distortion of the X_4 groups from square to rectangular is a compromise imposed by the competing tendency for T to attain regular octahedral coordination. The simultaneous fulfilment of eqns. 6 and 9 results in a reversion to the ReO_3 type structure with $d=a/4$ and $d_1=d_2=a/2$, the latter distance being too long for $X-X$ bonding. Hence, the following three features are together mutually incompatible:

(i) Regular octahedral symmetry around T (eqn. 6).
(ii) Square X_4 groups, *i.e.* $d_1=d_2$ (Oftedal's relation, eqn. 9).
(iii) $X-X$ distances (*i.e.* d_1 and/or d_2) within the range for bonding.

There are, however, no objections as far as the space group is concerned as to the compatibility of any two of these requirements. The supposition that point (iii) is essential * for the $CoAs_3$ type structure thus naturally raises the question of whether point (i) or (ii) is the most important factor in determining the structural stability. A quantitative criterion for judgements of this type is unfortunately not available.

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* This severely limits the permitted parameter ranges for y and z, and it is consistently observed[8,9] that $0.3431 \leqq y \leqq 0.3547$ and $0.1393 \leqq z \leqq 0.1503$.

As a specific example the data for the skutterudite mineral [9] give $d_1 = 2.464$ Å, $d_2 = 2.572$ Å, and $X-T-X = 84.6°$. It is possible to imagine a hypothetical $CoAs_3$ structure with $d_1' = d_2' = d_1$ giving an $X-T-X$ angle of 83.0°. Thus, the difference between the actual and hypothetical structure amounts to 1.6° in $X-T-X$ bond angle and 0.108 Å in $X-X$ bond length. It seems unlikely that the energy gain resulting from such a small variation in bond angle should be comparable to that involved in making d_1 and d_2 unequal by as much as 0.108 Å. On this basis it appears that the principal cause of the deviation from Oftedal's relation is not the competition between points (i) and (ii), but is to be sought elsewhere.

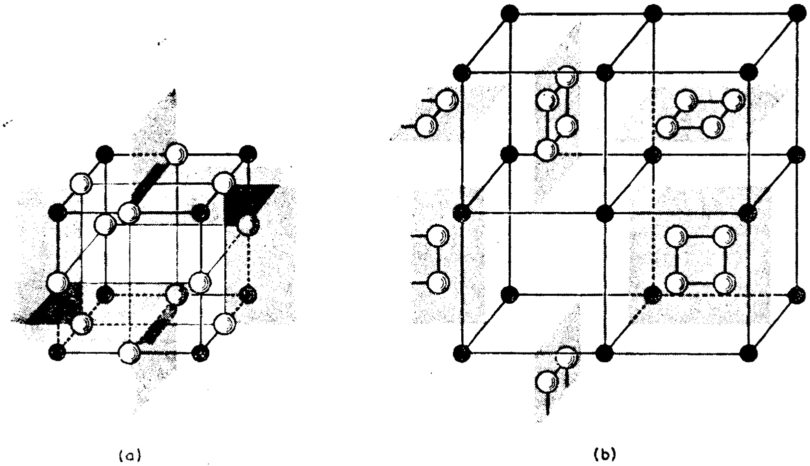
(a) (b)

Fig. 7. Relationship between the ReO_3 (a; one unit cell) and $CoAs_3$ (b; half a unit cell in which the origin is shifted to 1/4,1/4,1/4) type structures. The shading emphasizes the planes through the X_4 groups.

At this stage it is useful to take advantage of the similarities and differences between the $CoAs_3$ and ReO_3 type structures, which are brought out in Fig. 7. In a hypothetical transformation from the more symmetric ReO_3 type structure to the $CoAs_3$ type, the formerly square X_4 groups are drawn together by covalent $X-X$ interactions, thus leaving two cavities per $CoAs_3$ unit cell symmetrically arranged on opposite sides of the X_4 groups. It is to be noted that these cavities are consistently arranged with respect to the $X-X$ bond distance d_2, and it is accordingly suggested that the consequent anisotropic environment of the X_4 groups is primarily responsible for the observed inequality $d_1 < d_2$.

ATOMIC INTERACTIONS

Since the properties of these macromolecular TX_3 compounds strongly suggest [10] a high degree of covalency the subsequent description of the interatomic interactions may be divided into two parts. Firstly, there is the major effect due to covalent bonding between nearest neighbour atoms and secondly the perturbation from the remainder of the lattice. The lattice contribution arises as a consequence of the electronic distribution within the $T-X$ bonds. This effect should not be neglected, because, although individual contributions decrease with increasing distance R from any given atom, the number of atoms contained in a volume shell $\mathrm{d}R$ is proportional to R^2. The overall interaction experienced by a given atom is treated as follows.

The equilibrium distance (r_0) between two covalently bound atoms is due to a balance between shorter range internuclear and electronic core repulsions ($\mathbf{R}$) and the attractive force ($\mathbf{A}$) resulting from the interactions of their valence shells, *i.e.* $\mathbf{R}(r_0)+\mathbf{A}(r_0)=\mathbf{0}$ for an isolated, diatomic molecule. In a crystal structure, however, the lattice influences the interatomic distance (r) such that $\mathbf{R}(r)+\mathbf{A}(r)=\mathbf{G}(r)\neq\mathbf{0}$, and the net force ($\mathbf{F}$) resulting from the lattice is defined by

$$\mathbf{G}(r) + \mathbf{F} = \mathbf{0} \tag{10}$$

Consideration of the immediate environment about the X atoms in the $CoAs_3$ type structure (Fig. 1b) yields

$$\mathbf{G} = \mathbf{G}_1(d_1) + \mathbf{G}_2(d_2) + \mathbf{G}_3(d) + \mathbf{G}_4(d) \tag{11}$$

where the subscripts 1 and 2 refer to the two $X-X$ bonds and 3 and 4 to the two $X-T$ bonds. The components of the vector $\mathbf{G}$ in the three crystallographic directions a, b, and c are

$$\begin{aligned} G_a &= 0 \\ G_b &= -\,G_2(d_2) + \frac{2a(y-1/4)}{d}G_3(d) \\ G_c &= \quad G_1(d_1) - \frac{2a(1/4-z)}{d}G_3(d) \end{aligned} \tag{12}$$

where $|\mathbf{G}_3(d)|=|\mathbf{G}_4(d)|$ because the two $X-T$ bond lengths are equal.

The lattice interactions as defined by $\mathbf{F}$ (eqn. 10) are conveniently described in terms of the X and T atom sublattices, *i.e.* $\mathbf{F}=\mathbf{F}(X)+\mathbf{F}(T)$. The effective charges on the T and X atoms are denoted $3q$ and $-q$, respectively, although the sign and magnitude of q is unimportant for the present considerations.

Within a given unit cell $\mathbf{r}_n[0,0,0]$ represents the vector from atom X_n to the X atom with coordinates $1/2,1/2-y,1/2-z$, which is numbered as X_7 in Table 1 and arbitrarily chosen as the origin. The vector from atom X_n in another unit cell, specified by the integers i,j,k, to the origin is given by

$$\mathbf{r}_n[i,j,k] : (1/2 - u_n - i, 1/2 - y - v_n - j, 1/2 - z - w_n - k) \tag{13}$$

$$-\infty < i,j,k < \infty \tag{14}$$

The interaction of the X sublattice on $X_7[0,0,0]$ is expressed as

$$\mathbf{F}(X) = \left[\frac{q}{a}\right]^2 \sum_n \sum_{i,j,k} \mathbf{f}_n[i,j,k] \tag{15}$$

where $\mathbf{f}_n$ is the normalized contribution to the total Coulomb force from a general $X_n[i,j,k]$ acting on $X_7[0,0,0]$ and is given by

$$\mathbf{f}_n = \frac{\mathbf{r}[i,j,k]}{(r[i,j,k])^3} \tag{16}$$

Similarly, the influence of the T sublattice on $X_7[0,0,0]$ is

$$\mathbf{F}(T) = 3\left[\frac{q}{a}\right]^2 \sum_m \sum_{i,j,k} \mathbf{f}_m[i,j,k] \tag{17}$$

Table 1. Numbering of non-metal (X_n) and metal (T_m) atoms within the unit cell of the $CoAs_3$ type structure.

n	u_n	v_n	w_n	n	u_n	v_n	w_n
1	z	0	y	13	$1/2-z$	1/2	$1/2-y$
2	$\bar{z}$	0	y	14	$1/2+z$	1/2	$1/2-y$
3	z	0	$\bar{y}$	15	$1/2-z$	1/2	$1/2+y$
4	$\bar{z}$	0	$\bar{y}$	16	$1/2+z$	1/2	$1/2+y$
5	y	z	0	17	0	$\bar{y}$	z
6	$\bar{y}$	z	0	18	$1/2-y$	$1/2+z$	1/2
7	1/2	$1/2-y$	$1/2-z$	19	$1/2+y$	$1/2+z$	1/2
8	1/2	$1/2-y$	$1/2+z$	20	0	$\bar{y}$	$\bar{z}$
9	0	y	z	21	y	$\bar{z}$	0
10	$1/2-y$	$1/2-z$	1/2	22	$\bar{y}$	$\bar{z}$	0
11	$1/2+y$	$1/2-z$	1/2	23	1/2	$1/2+y$	$1/2-z$
12	0	y	$\bar{z}$	24	1/2	$1/2+y$	$1/2+z$

m	u_m	v_m	w_m	m	u_m	v_m	w_m
1	1/4	1/4	1/4	5	1/4	3/4	1/4
2	3/4	1/4	1/4	6	3/4	3/4	1/4
3	1/4	1/4	3/4	7	1/4	3/4	3/4
4	3/4	1/4	3/4	8	3/4	3/4	3/4

The components of $\mathbf{F}(X)$ and $\mathbf{F}(T)$ in the a direction fulfil the condition

$$F_a(X) \equiv F_a(T) \equiv 0 \tag{18}$$

whereas in the b and c directions this is generally not the case and the components must satisfy the conditions

$$G_b(X,T) + F_b(X) + F_b(T) = 0 \tag{19}$$

$$G_c(X,T) + F_c(X) + F_c(T) = 0 \tag{20}$$

Only the difference between the overall forces acting in the b and c directions is relevant to the discussion and this may be obtained by combination of eqns. 19 and 20. The assumption of Oftedal's relation (eqn. 9) considerably simplifies the resulting expression since both $X-X$ bonds are then equivalent and hence

$$G_b(X,T) + G_c(X,T) = 0 \tag{21}$$

Summing over those parts of the T sublattice with a fixed value for the summation index m (see Table 1) gives eight terms each in the b and c directions, which on substituting Oftedal's relation and rearranging yields

$$\sum_m \left\{ \sum_{i,j,k} f_m[i,j,k] \right\}_b + \sum_m \left\{ \sum_{i,j,k} f_m[i,j,k] \right\}_c = 0 \tag{22}$$

and therefore

$$F_b(T) + F_c(T) = 0 \tag{23}$$

Thus, it is seen that the total interaction of the T sublattice is equal in the two $X-X$ bond directions.

Repeating essentially the same procedure for the X sublattice interaction the twenty-four terms which are thereby obtained for the components in the b and c directions may be considerably simplified so that only those corresponding to the positions numbered $n=1$, 3, 5, 10, 13, 15, 18, and 21 in Table 1 need to be considered. Numerical computations based on Oftedal's relation show that

$$F_b(X) + F_c(X) \neq 0 \tag{24}$$

unless

$$y = z = 1/4 \text{ or } q = 0$$

The former condition gives rise to the ReO_3 type structure (*vide supra*) whereas the latter requirement would imply a non-existent lattice interaction.

The conclusion is accordingly that the assumption of Oftedal's relation is not consistent with the $CoAs_3$ type structure, and that the principal cause of the rectangular deviation lies in the X sublattice interactions and is not attributable to differences in covalency between the $T-X$ and $X-X$ bonds or to the T sublattice.

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