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On the MnP Type Structure of RuSb and RhSb

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The crystal structures of RuSb and RhSb have been determined from powder neutron diffraction data. The results are used in revaluation of a geometrical model for the relationship between the NiAs and MnP type structures.

Geometrical and bonding properties which affect the relation between the NiAs and MnP type crystal structures are discussed in Ref. 1 on the basis of structural data for phosphides and arsenides of the latter type. Hence, accurate structure determinations for the only hitherto known MnP type antimonides, RuSb [2] and RhSb,[3] are of considerable interest. (The abbreviations T = transition element and X = non-metal from groups IV B to VI B are used throughout this text.)

EXPERIMENTAL

RuSb and RhSb were prepared by heating equi-atomic quantities of the elements [99.99 % Ru and Rh (Johnson, Matthey & Co.) and 99.9995 % Sb (Koch-Light Laboratories)] in crucibles of alumina inside evacuated, sealed silica tubes. Three heat treatments of 10 – 14 d duration at 850 – 1200 °C, interrupted by intermediate crushings, were necessary to obtain homogeneous samples. The samples were finally cooled to 600 °C over 2 d and then air-quenched.

Experimental details concerning X-ray and neutron diffraction measurements have been reported in Ref. 4.

RESULTS AND DISCUSSION

The unit cell dimensions and positional parameters for RuSb and RhSb, as derived by least squares treatments of powder X-ray (Guinier) and neutron diffraction data, are listed in Table 1 together with the shortest interatomic distances. Both with respect to axial ratios and positional parameters, these compounds fall naturally in among the other compounds with MnP type structure listed in Refs. 1 and 5. As this result is not an *a priori* consequence of the geometrical model in Ref. 1, a critical reexamination of the model and its postulates is called for.

The main aspects of the model are recapitulated in Table 2, and only a few, particularly

Table 1. Unit cell dimensions, positional parameters, and shortest interatomic distances for RuSb and RhSb. [Space group *Pnma*, positions 4(*c*).]

Parameter	RuSb	RhSb
a (Å)	5.9608 (13)	5.9718 (7)
b (Å)	3.7023 (9)	3.8621 (7)
c (Å)	6.5797 (13)	6.3242 (9)
x_T	0.0053 (10)	0.0053 (19)
z_T	0.2037 (7)	0.1942 (12)
x_X	0.1992 (8)	0.1949 (15)
z_X	0.5808 (10)	0.5915 (14)
$T-X$(Å) × 1	2.614 (8)	2.589 (13)
$T-X$(Å) × 2	2.631 (6)	2.645 (9)
$T-X$(Å) × 2	2.680 (6)	2.712 (10)
$T-X$(Å) × 1	2.737 (8)	2.756 (12)
$(T-X)_{av.}$(Å)	2.662	2.677
$T-T$(Å) × 2	3.042 (8)	3.068 (16)
$T-T$(Å) × 2	3.258 (5)	3.125 (8)
$T-X$ (Å)	4.258 (8)	3.976 (12)
$T-T$ (Å)	3.702 (1)	3.862 (1)
$X-X$ (Å)	3.193 (6)	3.238 (10)

Table 2. Geometrical model for conversion from NiAs to MnP type structure. Postulates (including empirical constraints) and consequences outlined in Ref. 1. (Axes and positional parameters expressed in terms of MnP type cell of setting *Pnma*.)

Postulate No.	Cue for content	Application, specification, elaboration, *etc.*	Mathematical formulation [Formula No.]	Matching numerical value
1	Coordination symmetry essentially retained			
2	Approx. equal size for T and X			
3	2 and 4 $T-T$ contacts in NiAs and MnP type, respectively	Equal length of $T-T$ contacts in MnP type	$z_T=\frac{1}{4}-\frac{1}{8}\left(1+\frac{b^2}{c^2}-\frac{a^2}{c^2}\right)$ [I]	$0.181<z_T<0.195$
4	$(T-X)_{av.}$ bond length unchanged from NiAs to MnP type with min. scatter in latter type	$T-X$ bond lengths equalized two by two in MnP type	$x_X=\frac{1}{4}-\frac{1}{12}\left(-1+\frac{b^2}{a^2}+\frac{c^2}{a^2}\right)$ [II]	$0.194<x_X<0.206$
			$x_X=\frac{1}{4}-\frac{1}{8}\left(-1+3\frac{b^2}{a^2}+\frac{1c^2}{3a^2}\right)$ [III]	$0.152<x_X<0.202$
			$x_X=\frac{1}{4}-\frac{1}{8}\left(-1+\frac{b^2}{a^2}+\frac{5c^2}{3a^2}\right)$ [IV]	$0.065<x_X<0.077$
			$x_X=\frac{1}{4}-\frac{1}{6}\left(-1+\frac{b^2}{a^2}+\frac{c^2}{a^2}\right)$ [V]	$0.138<x_X<0.162$
		Scatter in $T-X$ bond lengths in MnP type minimized		Calc. for CoP $x_X=0.205$
5	T displaced mainly $\|\|\pm c$ in MnP type	$x_T\approx 0$, $z_T\neq\frac{1}{4}$		
6	X displaced mainly $\|\|\pm a$ in MnP type	$x_X\neq\frac{1}{4}$, $z_X\approx\frac{7}{12}$		
7	Limitations on axial proportions in MnP type	$\frac{c}{a}\approx 1.10$ $1.63<\frac{c}{b}<2.08$		
8	Negligible $X-X$ bonding interaction	Shortest $X-X$ distance ~20 % longer than bonding $X-X$	x_X defined by: $\frac{5}{2}x_X^2+\frac{3}{4}x_X\approx$ $\frac{3}{16}+\left(\frac{3}{2}z_T^2-\frac{3}{4}z_T+\frac{3}{20}\right)\frac{c^2}{a^2}$ [VI]	
9	"Idealized" MnP type	$\frac{c}{a}=1.10$, $\frac{c}{b}=\sqrt{3}$, $x_T=0$, $z_T=0.20$ $x_X=0.20$, $z_X=\frac{7}{12}$		
10	Volume per formula unit unchanged from NiAs to MnP type			

relevant points will be considered further in the text. Post. 1 appears to have a superior function and is implicitly included in most of the other postulates. It carries information about the nature of the NiAs → MnP type transition, which may be explored by means of group theory as has been done in Ref. 6. However, no quantitative deductions are made directly from this postulate in Ref. 1. The same applies to Post. 10 which merely states a particular requirement on second order phase transitions.

The contents of Posts. 3 and 8 are essential to the original quantitative development of the geometrical model.[1] Thus, "the strive" for establishing four $T-T$ contacts is considered as the initiator and driving force of the NiAs→ MnP type transition. Unfortunately, the understanding of the physical background for this statement has not proceeded beyond the rather vague indications in Ref. 1. In a similar manner the non-metal atoms may be regarded as the stoppers of the transformation process. In this case, however, the physical picture is more clear-cut since the size of X (*vide infra*) and the assumed non-bonding character of all $X-X$ distances will act as limitators for the deformation of the NiAs type atomic arrangement.

Formulae Nos. [II]–[V] in Table 2 (when combinations giving undetermined x_X are omitted) show that Post. 4 has much the same function as Post. 8, in that both provide mathematical expressions for the calculation of the parameter x_X. Granted that one is prepared to accept "the strive" for four $T-T$ contacts as a reasonable cause of the MnP type deformation, one may equally well accept that the X atoms adjust their positions to equalize the $T-X$ bond lengths. However, complete equalization of the four crystallographically independent $T-X$ distances is incompatible with T positions defined according to formula No. [I], and this constraint can only be achieved on returning to the NiAs type symmetry. The unattainableness of the requirement in Post. 4 is also reflected in formulae Nos. [II]–[V], which are obtained by equalizing the $T-X$ bond lengths two by two, resulting in different mathematical expressions and numerical values for the parameter x_X. On relinquishing the strict requirement for equal $T-X$ distances

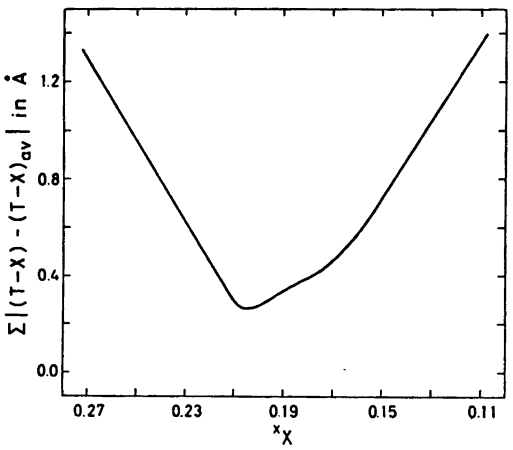

Fig. 1. Scatter in $T-X$ bond lengths as function of x_X for CoP. (Unit cell dimensions and other positional parameters from Refs. 7 and 8.)

in the MnP type structure, the physical basis for using Post. 4 to derive expressions for x_X is no longer present. On this background Post. 8 seems to be physically more attractive than the above version of Post. 4.

The scatter in the $T-X$ distances ($\sum|(T-X) - (T-X)_{av.}|$) can be expressed by x_X. Equated to zero, the differentiated expression will, in principle, give the x_X value corresponding to a minimum scatter in the $T-X$ distances. Unfortunately, the complexity of the expressions prevents a general mathematical solution according to this procedure. However, the problem can be solved numerically for a given set of values for all but x_X of the variables. As an illustration of a practical solution of this type, Fig. 1 presents the variation of $\sum|(T-X) - (T-X)_{av.}|$ with x_X for the almost "ideal" MnP type structure of CoP. In this case the scatter has a minimum at $x_X = 0.205$, which closely approaches the value given in Post. 9.

The conclusion is accordingly that the postulated minimum scatter in $T-X$ bond lengths is a satisfactory and operative principle for the fixing of x_X in the MnP type structure. Since there is only empirical correlation between bond lengths and energetic parameters for this type of solids, the physical nature of Post. 4 is still somewhat dubious.

Consultation of the structural data for MnP type compounds unveils that nature "mini-

mizes" the scatter in $T-X$ bond distances in an intuitively lucid way. In practice, the two pairs of two-fold degenerate $T-X$ bond distances are often found to be roughly equal (*cf.*, formula No. [II]) and the two remaining $T-X$ bond distances are almost symmetrically located on both sides of "this average". However, the arguments for raising the basis of formula No. [II] to a postulate of the model seem physically less clear-cut than maintaining the whole content of Post. 4.

Although only superficially discussed in Ref. 1, Post. 2 (which is a corollary to Post. 9) was considered a key postulate that, *inter alia*, quantified the parameter x_X from Post. 8. Unfortunately, the simple and intuitive concept of size is particularly ill-defined in rather low-symmetrical atomic arrangements like the MnP type, and the poor specification of this concept in Ref. 1 may have obscured the presentation. Thus, some clarifying comments are appropriate.

Consider the average $T-X$ bond length $(T-X)_{\text{av.}}=r_T+r_X$ as being composed of a bonding, average radius r_T for T and r_X for X. (The term radius is used here loosely as a measure of size, or rather as a simple model concept without referring to any specific scale.) If the magnitude of r_X (or r_T) dominates, a close-packed arrangement of X (or T) is expected, and an NiAs (or "anti-NiAs") type structure may emerge. In cases where $r_T \approx r_X$, the prediction of structure type from simple considerations becomes less clear-cut and more assumptions must be included in the model.

Let us assume $r_T \approx r_X$ as a starting point for an "idealized" MnP type structure. On this basis $(T-X)_{\text{av.}}$ would match a hypothetical $X-X$ bonding distance. Recalling the physical picture of "the strive" for four $T-T$ contacts as the *initiator* (Post. 3) and the non-bonding character of the shortest $X-X$ distances as the *limitator* (Post. 8) of the MnP type deformation, it seemed natural in Ref. 1 to introduce a 20 % increased radius for X (relative to the bonding r_X) to ensure no $X-X$ bonding. The use of $r_T \approx r_X$ and the 20 % criterion corresponds roughly to the expression $[(X-X)_{\text{shortest}}]^2=\frac{3}{2}[(T-X)_{\text{av.}}]^2$, which is equivalent to formula No. [VI] and on the introduction of Post. 7 gives $x_X \approx 0.20$, matching the experimental facts.

These considerations, of course, suffer from the weaknesses inherent in all oversimplified models. Using tabulated values for atomic radii, considerations of the MnP type series RuP – RuAs – RuSb would at first sight seem to suggest that the model is totally unrealistic. However, on introducing another simple concept, degree of ionicity, it is natural to claim that RuP is more ionic than RuSb.[9] On this basis, $r_{\text{Ru}}(\text{RuP}) < r_{\text{Ru}}(\text{RuSb})$ and $[r_{\text{P}}(\text{RuP}) - r_{\text{P}}(\text{neutral})]/r_{\text{P}}(\text{neutral}) > [r_{\text{Sb}}(\text{RuSb}) - r_{\text{Sb}}(\text{neutral})]/r_{\text{Sb}}(\text{neutral})$. This approach also serves to emphasize the limited value of tabulated atomic radii to define *individual* atomic sizes.

It should also be warned against the use of the model to make conclusions on fundamental bonding properties. The significance of the geometrical model lies in singling out Post. 3 as an initiator and Post. 8 as a limitator for the NiAs→MnP type deformation. The new data for RuSb and RhSb have not shaken this conclusion.

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