

Compounds with the Marcasite Type Crystal Structure

VII.* On the Phases $\text{Cr}_{1-u}\text{Fe}_u\text{Sb}_2$, $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$,
 $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$, and $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$

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The ternary solid solution series CrSb_2 – FeSb_2 – CoSb_2 – NiSb_2 and FeSb_2 – NiSb_2 have been investigated by the X-ray powder method, and the results are discussed in relation to the corresponding data for the analogous series containing arsenic. $\text{Cr}_{1-u}\text{Fe}_u\text{Sb}_2$ and $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ exhibit continuous regions of solid solubility ($0.00 \leq u \leq 1.00$), $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ shows a limited homogeneity range ($\sim 0.50 \leq u \leq 1.00$), and $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$ has a negligible solid solubility. The crystal structures of these phases are of the FeS_2 - m type, except for the region $\sim 0.75 < u \leq 1.00$ of $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$, where the CoSb_2 type structure prevails. The occurrence of the CoSb_2 type structure generally requires a formal low-spin d^5 configuration on the metal atoms. However, simple statistical considerations show that up to ~ 27.5 atomic % of the metal atoms in a binary compound with this structure type may be substituted by another metal of equal nominal valence, without destroying the basic stability of the CoSb_2 type atomic arrangement, which is dependent on the intrinsic metal-metal pairs.

A new phase $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_2$ with CoAs_2 type structure has also been identified: $a = 9.0902 \pm 0.0005$ Å; $d_{\text{pycn.}} = 7.411$ gcm $^{-3}$.

The closely related crystal structures of FeS_2 - p ($p = \text{pyrite}$),^{1,2} FeS_2 - m ($m = \text{marcasite}$),³ and CoSb_2 (FeAsS -arsenopyrite)^{4,5} constitute the prototypes for a considerable number of binary and ternary transition metal pnictides and chalcogenides. The physical and chemical properties of these phases have been extensively studied during the last 50 years, and the literature covering the field has become rather voluminous.

Along with the acquisition of experimental data there has been an almost continuous discussion (*cf.*, *e.g.*, Refs. 6–17) concerning the nature of the chemical bonding in these phases. A number of the hitherto most pertinent questions in this connection have been discussed in two recent communications from this Institute.^{16,17} In these papers, the two classes (A and B) of

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binary compounds with the FeS_2 - m type structure (which had previously been defined according to the axial proportions of the unit cell and denoted by a variety of terms^{8,11-13}) were shown to be related to the spatial orientation, mutual energy splitting, and filling of the essentially non-bonding d orbitals of the metal atoms. Class A was shown to comprise compounds with $0 \leq j \leq 4$ in the localized d^j configuration on the metal atoms, whereas class B corresponds to $6 \leq j \leq 10$. In addition, there is a third transitional class A/B of isostructural phases, defined by $4 < j < 6$, which covers the ranges of axial proportions between the virtually fixed values of the members of the classes A and B. The d^j configuration furthermore contributes in determining the occurrence of the structure types FeS_2 - p and CoSb_2 and their stability relative to that of FeS_2 - m .

Consideration of the pseudo-marcasite cell (Fig. 1 and *vide infra*) of the compounds with the CoSb_2 type structure shows that so far as the axial proportions are concerned, these compounds belong to the class A/B. However, the atomic arrangement within the true monoclinic unit cell (see Fig. 1)

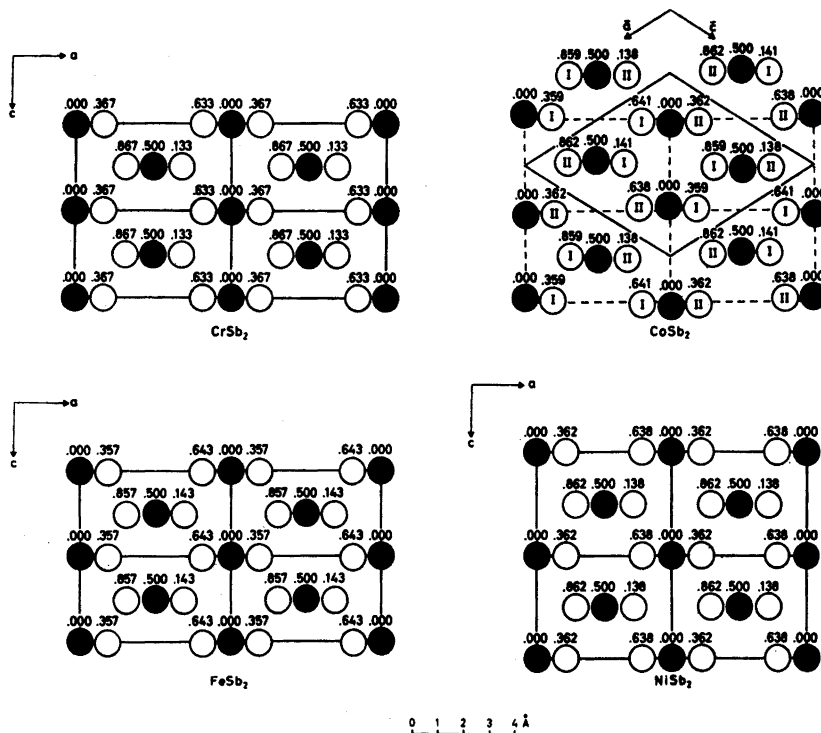


Fig. 1. Structural relationships within the series CrSb_2 - FeSb_2 - CoSb_2 - NiSb_2 . Filled and open circles represent the metal and non-metal atoms, respectively. The numbers give fractions of the projection axes which are parallel to $[010]$ in all cases. (For the lengths of the projection axes see Fig. 2.) The true unit cells are shown by full lines, whereas broken lines indicate the pseudo-marcasite cell of the CoSb_2 type structure.

differs from that in the FeS_2 - m type structure, in that the coordination polyhedra in the CoSb_2 type are somewhat more deformed and include characteristic pairs of metal atoms. Apart from the crystallographic distinction, an interesting feature of the CoSb_2 type structure is, that it appears to occur exclusively with a formal low-spin d^5 configuration for the metal atoms, and only when these are of one kind. In order to gain insight into the significance of the latter factors determining the occurrence of the CoSb_2 type structure, an investigation of the ternary solid solution series CrSb_2 - FeSb_2 - CoSb_2 - NiSb_2 and FeSb_2 - NiSb_2 has been undertaken. Due to the close structural resemblance of the binary compounds (*cf.* Fig. 1 and Refs. 5, 18-22), it is to be expected that a continuous transition between the classes A and B, through class A/B, should be possible within these series. The results of Roseboom²³ for a corresponding study of the analogous series containing arsenic support the above expectation of a virtually continuous range of solid solubility.

EXPERIMENTAL

The pure elements used in this study were 99.999 % Cr (Koch-Light Laboratories, Ltd.), 99.99+ % Fe, 99.999 % Co, and 99.995 % Ni (Johnson, Matthey & Co., Ltd.; turnings from rods), and 99.999+ % Sb (Johnson, Matthey & Co., Ltd.). In initial experiments, samples were made by heating weighed quantities of the components in evacuated and sealed silica tubes. Despite a number of attempts to vary the experimental conditions, this method failed to give homogeneous samples of the ternary phases. An alternative procedure was accordingly adopted, in which the first step consisted of the preparation of the binary compounds. CrSb_2 , FeSb_2 , CoSb_2 , and NiSb_2 were obtained by means of a sequence of crushing and reannealing processes which have been described in earlier papers,^{18,22} and their homogeneity ascertained from X-ray powder photographs. The binary di-antimonides produced in this way were mixed in proportions appropriate to the desired ternary compositions and subjected to a first annealing at 600°C for one month. All samples were crushed and reannealed for an additional period of four months at the same temperature. The samples were then crushed and reannealed at the same temperature, using two-week intervals until X-ray powder photographs showed no further detectable changes in the composition equilibrium.

The samples of $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_2$ were prepared from the elements by successive annealings at 600°C and finally quenched in water without shattering the enclosing silica capsules.

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 ($a = 6.2919 \text{ \AA}$ ²⁴) as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data. The probable errors in these determinations are assumed to correspond to twice the calculated standard deviations, and amount to $\sim \pm 0.03 \%$ in axes, and $\sim \pm 0.02 \%$ in angles.

RESULTS

The Guinier photographs of all samples which had achieved equilibrium showed sharp reflections. Indexing was possible on the assumption that these samples contained one or two phases with orthorhombic or monoclinic symmetries. The deduced unit cell dimensions (Fig. 2) resemble those found for the corresponding binary compounds. The observed intensities of the reflections on the Guinier photographs confirm that the atomic arrangement is either that of the FeS_2 - m or CoSb_2 type, within the ranges of solid solution,

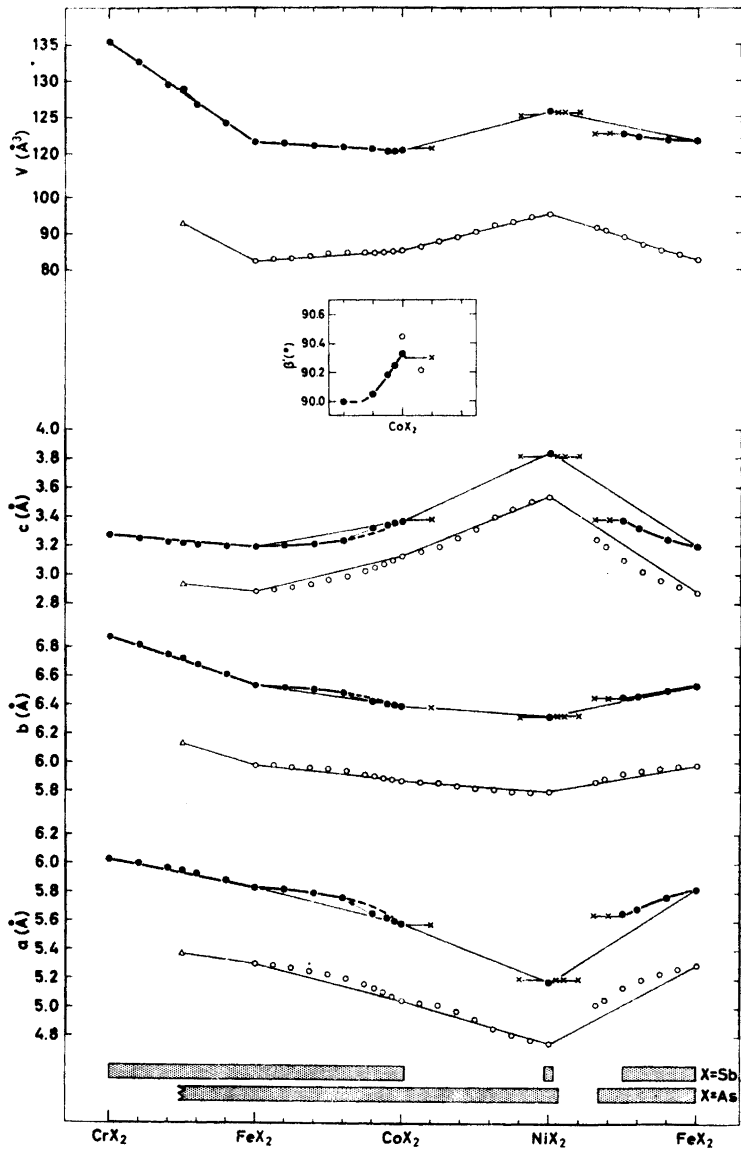


Fig. 2. Unit cell dimensions of the ternary solid solution series CrSb_2 – FeSb_2 – CoSb_2 – NiSb_2 and FeSb_2 – NiSb_2 as functions of composition, where filled circles represent single-phase samples, and crosses represent two-phase samples. The corresponding data (taken from Roseboom²³ (O) and Hulliger²⁵ (Δ)) for the analogous series containing arsenic are included for comparison.

the positional parameters having values close to those of the corresponding binary compounds. The quality of the intensity data does not permit a refinement of the positional parameters. The lack of additional superstructure reflections on the Guinier photographs definitely shows the substituted atoms to be arranged at random in the metal sublattice(s).

The results presented in Fig. 2 show examples of continuous, and more or less limited ranges of solid solubility. For the phases $\text{Cr}_{1-u}\text{Fe}_u\text{Sb}_2$ and $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ there occur the continuous regions of solid solubility shown at the base of Fig. 2, *i.e.* possible values of u cover the entire range $0.00 \leq u \leq 1.00$. CoSb_2 and NiSb_2 show only slight mutual solubility, permitted values of u being $0.00 \leq u < \sim 0.02$ and $\sim 0.97 < u \leq 1.00$ in the formula $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$. The homogeneity ranges of the $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ phase are specified by the conditions $0.00 \leq u < \sim 0.03$ and $\sim 0.50 < u \leq 1.00$, thus showing there to be little interchangeability of Ni with Fe in NiSb_2 whereas that of Fe with Ni in FeSb_2 is appreciable. With reference to those parts of the systems $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$ and $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$, where no solid solubility is observed, variations in the preparation temperature between 350 and 850°C showed the above results to be reasonably comprehensive.

As may be seen from Fig. 2, a substantially linear dependence on u is found for the unit cell dimensions of the $\text{Cr}_{1-u}\text{Fe}_u\text{Sb}_2$ phase. Except for the limited monoclinic region, the a , b , and c axes of the $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ phase show departures from linearity, while the unit cell volume varies linearly with u . This is also true for the $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ phase ($\sim 0.50 < u \leq 1.00$).

The results presented in Fig. 2 for the monoclinic region ($\sim 0.75 < u \leq 1.00$) of the $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ phase refer to the pseudo-marcasite cell (specified by a' , b' , c' , and β'), which is related to the true unit cell of the CoSb_2 type structure by the vectorial equations: $\mathbf{a}' = \frac{1}{2}(\mathbf{a} - \mathbf{c})$, $\mathbf{b}' = \mathbf{b}$, and $\mathbf{c}' = -\frac{1}{2}(\mathbf{a} + \mathbf{c})$; where \mathbf{a} , \mathbf{b} , and \mathbf{c} are as specified in Fig. 1. The incidence of monoclinic symmetry produces an easily observed splitting of a number of reflections in the Guinier photographs, in spite of the fact that β' of the pseudo-cell does not exceed 90.34°. Fig. 2 shows that although the axes of the pseudo-cell in the monoclinic interval depart from extrapolations from values for the orthorhombic region, the corresponding volumes are collinear.

The above results refer exclusively to samples which had attained an apparent thermodynamical equilibrium. However, non-equilibrium conditions were encountered in a number of samples belonging to the systems $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ ($\sim 0.80 < u \leq 1.00$), $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$ ($0.00 \leq u < \sim 0.20$), and $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ ($0.00 < u < 0.50$). In the systems $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ and $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$ such samples proved to contain the CoSb_3 ^{10,26} and probably CoSb ²⁷ phases in admixture with the di-antimonide phase(s), while the $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ and NiSb ²⁷ phases constituted contaminations in the case of $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$. Since these additional phases can be avoided by appropriate annealing (see Experimental), their temporary presence in the samples must consequently be attributed to reaction kinetical factors which clearly favour the formation of the tri-antimonide phases.

The unit cell dimension of the CoSb_3 phase was found to be invariant for samples with different nominal compositions. The present value of $a = 9.037 \pm 0.001$ Å agrees well with those reported earlier^{10,26} for the pure CoSb_3 phase. Neglecting the non-equilibrium status of the samples, these findings suggest

very strongly that there is no appreciable substitution of Co by Fe or Ni in CoSb_3 .

The previously unknown phase $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ was prepared in a pure state, and its composition was determined by application of the disappearing phase principle to the Guinier photographs of samples with different initial proportions of Fe and Ni. The dimension $a = 9.0902 \pm 0.0005$ Å of the cubic unit cell was found to be invariant for these samples, thus confirming that the $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ phase exhibits no appreciable range of homogeneity. The observed density, $d_{\text{pycn.}} = 7.411$ gcm⁻³ at 25.00°C, shows that the unit cell contains 8 $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ -groups ($Z_c = 7.94$). Obvious relationships in composition, dimension and content of the unit cells, and possible space groups, suggested at once that the $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ phase is isostructural with CoSb_3 and hence also with the prototype CoAs_3 -skutterudite.²⁸ This was ascertained by the reasonable agreement between observed and calculated X-ray intensities which was obtained on the basis of an assumed CoAs_3 type structure with $y = 0.35$ and $z = 0.15$ for the positional parameters of Sb. (Refinement of the structural parameters was not attempted.) It should be noted that $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ and CoSb_3 are not only isostructural, but in fact also iso-electronic compounds. The stoichiometric composition of $\text{Fe}_{0.50}\text{Ni}_{0.50}\text{Sb}_3$ also serves to distinguish this compound from the analogous phase $\text{Fe}_{1-u}\text{Ni}_u\text{As}_3$ which is found^{29,30} to exist over a broad solid solubility range.

DISCUSSION

It is appropriate to compare the present results with those obtained from the literature for the corresponding di-arsenide phases, which are also included in Fig. 2.

Judging from the interatomic distances found^{5,19,20,22} in the binary compounds under consideration, the radii of Fe, Co, and Ni are virtually identical (~ 1.15 Å), whereas Cr has a significantly larger radius (~ 1.29 Å). Hume-Rothery's³¹ necessary, but insufficient condition, governing the possible substitution of one kind of atom for another in a crystalline phase, requires that the radii of the atoms concerned should be within about 15 % of each other. This requirement is clearly satisfied in the ternary phases in question, where the metal atoms have, furthermore, identical valences¹⁷ and almost equal electronegativities.³² The most conspicuous feature of the results depicted in Fig. 2 is the almost complete absence of solid solubility in the system $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$. Neither of the above mentioned controlling factors necessitates this negative result, a conclusion which is, furthermore, emphasized by the continuous range of solid solubility which is found in the analogous $\text{Co}_{1-u}\text{Ni}_u\text{As}_2$ phase ($0.00 \leq u \leq 1.00$).

It appears, that in line with an earlier suggestion by Furuseth *et al.*,³³ the degree of mutual solid solubility is partially controlled by the compatibility or otherwise of the electronic band structures for the solvent and solute phases. This compatibility is to some extent evinced by the electrical conduction properties of the phases concerned. In this context, the binary compounds considered here are all semiconducting, with the exception of NiSb_2 which

exhibits a metallic type of conductivity (*cf.*, *e.g.*, Ref. 17). Hence, consistent with the incompatibility of the electrical characteristics of CoSb_2 and NiSb_2 , the $\text{Co}_{1-u}\text{Ni}_u\text{Sb}_2$ system shows no extensive solid solubility. The appreciable range of homogeneity exhibited by the $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ phase ($\sim 0.50 < u \leq 1.00$) demonstrates, on the other hand, that electrical parameters have only a limited applicability in deciding the compatibility of electronic band structures. In addition, it should be noted, that similarity of electrical conduction properties in the solvent and solute phases is not in itself a sufficient guarantee of compatibility of their band structures. This is demonstrated by the miscibility gap which is found in the case of $\text{Ni}_{1-u}\text{Fe}_u\text{As}_2$ (see Fig. 2) where the binary compounds are both semiconductors.

Fig. 2 shows departures from Vegard's law^{34,35} in respect of the axes a , b , and c for all phases except $\text{Cr}_{1-u}\text{Fe}_u\text{Sb}_2$. The deviation from the Vegard law relationship is of a similar character for the arsenide and antimonide phases, in that the a and b axes show positive, and the c axis negative deviations from linearity. The curves for corresponding pairs of phases are furthermore of a similar shape for a given axis. The origin of these findings is probably associated with the systematic variations of the positional parameters which are likely to occur as functions of composition within the homogeneity ranges. An approach based on the crystallographic additivity rule and the additional assumptions of linear dependences of positional parameters and radii on composition, was applied successfully in the case of ternary phases with the FeS_2 - p type structure by Furuseth *et al.*³³ The larger number of variables and their functional relationships in the FeS_2 - m and CoSb_2 type structures prevent the development of an analogous model for the present phases. However, trends which are seen in the structures of the binary compounds^{5,18-22} indicate that an approach of this kind may be qualitatively correct.

The axial proportions of the unit cells of the phases included in Fig. 2 have previously been used to test the so-called expansion model,¹⁷ which *inter alia* relates the classes A, A/B, and B of the FeS_2 - m type structure to the localized d^7 configuration on the metal atoms (see the introduction). A further development of the model provides insight into the factors which govern the occurrence of the CoSb_2 type structure.

Among the binary compounds, the CoSb_2 type structure is found exclusively for a formal low-spin d^5 configuration on the metal atoms. This applies also to the ternary phases which contain two different kinds of non-metal atom. In fact, with a formal low-spin d^5 configuration and only one kind of metal atom there is no example of a compound having the FeS_2 - m type structure. At first sight, the situation seems to be somewhat more complex for the isostructural ternary phases containing two kinds of metal atom.

The fact that the phases $\text{Ni}_{1-u}\text{Fe}_u\text{As}_2$ and $\text{Ni}_{1-u}\text{Fe}_u\text{Sb}_2$ with mixed configurations d^4/d^6 have the FeS_2 - m rather than the CoSb_2 type structure shows that an average d^5 configuration is an insufficient condition for the formation of the CoSb_2 type structure. Consideration of all known phases with the CoSb_2 type structure discloses that at least one of the component metal atoms must have a formal low-spin d^5 configuration for this structure to occur. This raises the question of what proportion of the constituent metal atoms must have this configuration. The observations on the $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ phase in this con-

nection show that the monoclinic region with the CoSb_2 type structure has an appreciable extension (*i.e.* $\sim 0.75 < u \leq 1.00$). The phases $\text{Fe}_{1-u}\text{Co}_u\text{As}_2$ and $\text{Co}_{1-u}\text{Ni}_u\text{As}_2$ also exhibit ranges with monoclinic symmetry, but the extension of these was not fully determined by Roseboom.²⁸ This prevents a quantitative testing of the latter phases, and $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ will be employed as a specific example.

In $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ the Fe and Co atoms adopt the d^4 and (formal) d^5 configurations, respectively, the structure of the phase passing continuously between an FeS_2 - m type at $u = 0$ and a CoSb_2 type at $u = 1$. The only important distinction between the FeS_2 - m and CoSb_2 type structures concerns the alternately longer and shorter metal-metal distances along the c' direction of the latter type (*cf.*, *e.g.*, Fig. 1). The metal-metal pairs so produced have each an internal bonding which is interpreted^{11-13,17} as changing the configuration of localized electrons on the metal atoms from a formal d^5 to an apparent d^6 . The supposed stability of such an apparent d^6 configuration provides a possible explanation of the restricted occurrence of the CoSb_2 type structure.

In these circumstances it is natural to take as a starting point a consideration of the metal-metal pairs. Assuming that Fe and Co are statistically distributed in the $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ phase, their frequencies of occurrence along the linear chains in the $c(c')$ direction are in proportion to their mole-fractions. Clearly, four or more consecutive Co atoms (*i.e.* two or more consecutive Co-Co pairs) within these chains must be regarded as favouring the formation of the CoSb_2 structure. Conversely, the presence of each Fe atom is unfavourable, while a neutral situation may be conceived as one in which there are one, two, or three consecutive Co atoms. Assuming that there is an equally probable incidence of the various favourable configurations, so that their contributions to the formation of the CoSb_2 structure are to be equally weighted, the total probability of obtaining favourable configurations is $p_1 = u^4$. Similarly, the probabilities for the unfavourable and neutral configurations are, respectively, $p_2 = 1 - u$ and $p_3 = u - u^4$. These probability functions are illustrated in Fig. 3.

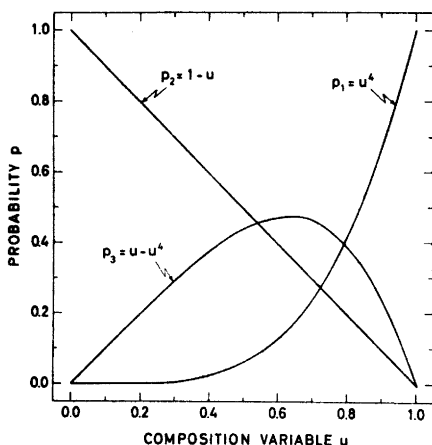


Fig. 3. Probability p of finding the atomic configurations: (i) 4 or more consecutive Co ($p_1 = u^4$), (ii) 1 or more consecutive Fe ($p_2 = 1 - u$), and (iii) 1, 2, or 3 consecutive Co *in toto* ($p_3 = u - u^4$) along the $c(c')$ direction. u refers to the composition of the $\text{Fe}_{1-u}\text{Co}_u\text{Sb}_2$ phase.

When the overall situation is sufficiently favourable, *i.e.* when $p_1 > p_2$, the CoSb_2 structure is to be expected, while $p_1 < p_2$ leads one to expect the FeS_2 -*m* type structure. As may be seen in Fig. 3, the critical equality of $p_1 = p_2$ leads to $u = 0.7245$ for the composition parameter. This value is in remarkably close agreement with the experimental value $u \approx 0.75$, considering the many simplifying assumptions which enter into the theoretical model (*vide supra*).

It thus appears that an amount of up to ~ 27.5 atomic % of the metal atom in a binary compound with the CoSb_2 type structure may be substituted by another metal of equal nominal valence. These findings are not to imply any loss of validity of the general requirement of a formal low-spin d^5 configuration on the metal atoms for the formation of the CoSb_2 type structure. They indicate, however, the limits to which metal atoms of an incompatible d^j configuration may be tolerated in the structure without destroying its basic stability, which is dependent on the intrinsic metal-metal pairs.

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