High Temperature Studies of Marcasite and Arsenopyrite Type Compounds

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High temperature investigations by X-ray diffraction, DTA, and quenching experiments have been carried out on FeAs₂, FeSb₂, CoAs₃, CoSb₂, RhAs₂, RhSb₂, RhBi₂, IrAs₂, IrSb₂, Fe₀.₅Ni₀.₅As₂, Fe₀.₅Ni₀.₅Sb₂, NiAs₂, and NiSb₂. The thermal properties of these compounds are discussed in relation to the arsenopyrite versus marcasite type structure.

Some two hundred binary and ternary transition metal (T) compounds of the main group V and VI elements (X) take the structure types FeSₙ₋ₚ (ₚ=pyrite), FeSₙ₋ₚ (ₚ=marcasite) and/or FeAsS (arsenopyrite; binary prototype CoSb₂). A substantial amount of the literature on the subject covers geological aspects or deals with various properties of individual compounds. However, an additional interest stems from their apparent suitability as model substances for bonding considerations. This interest may be based on several motives, their simplicity in atomic architecture and mutual structural resemblance (cf., e.g., Refs. 1, 2, and references therein) being probably the most important.

Features of the relations between the FeSₙ₋ₚ and FeSₙ₋ₚ types are presented in recent communications.³,⁴ The structural resemblance between the CoSb₂ and FeSₙ₋ₚ types is even more pronounced, and the former can be regarded as a slightly distorted variant of the latter. For the translational symmetry of the lattice the actual deformations are so small that prior to 1955, binary representatives of the CoSb₂ type were erroneously classified among the FeSₙ₋ₚ type compounds. The atomic arrangements correspond similarly and transitions between the two structure types may accordingly be expected as functions of composition, temperature, and/or pressure. In fact, gradual transitions from the CoSb₂ to the FeSₙ₋ₚ type have been accomplished in ternary series TₙCo₁₋ₙX₂ (T = Fe, Ni; X = As, Sb)⁵,⁶ as a function of the compositional parameter t.

At normal temperatures and pressures, binary CoSb₂ type compounds have exclusively been found for Co, Rh, and Ir in combination with P, As, Sb, or Bi. This apparent constraint on the CoSb₂ type structure compared with the widespread occurrence (in relation to the Periodic System) of compounds with the FeSₙ₋ₚ and FeSₙ₋ₚ types, provokes the question of what happens to the CoSb₂ type at higher temperatures. An answer to this question could also provide further insight into the occurrence of the various classes A, A/B, and B (vide infra) of the FeSₙ₋ₚ type. Elaboration of the latter point has led to a parallel study of representative FeSₙ₋ₚ type compounds. Thus, the compounds subject to this study are:

A(FeSₙ₋ₚ): FeAs₂, FeSb₂
B(FeSₙ₋ₚ): NiAs₂, NiSb₂
A/B(FeSₙ₋ₚ): Fe₉.₅Ni₉.₅As₂, Fe₉.₅Ni₉.₅Sb₂
A/B(CoSb₂): CoAs₂, CoSb₂, RhAs₂, RhSb₂, RhBi₂, IrAs₂, IrSb₂

where the assigned classifications (see Ref. 7) relate to the room temperature, unit cell proportions.

EXPERIMENTAL

The first preparational step consisted in heating appropriate amounts of the respective elements [turnings from 99.99 % Fe, 99.999 % Co, and 99.995 % Ni rods, 99.99 % Rh and 99.99 % Ir powders (all from Johnson, Matthey & Co.), 99.999 % As and 99.9995 % Sb (Koch-Light Laboratories), and 99.99 + % Bi (American Smelting and Refining Co.)] in evacuated, sealed silica tubes. The FeAs₂ and NiAs₂ (viz. β-NiAs₂) samples were treated as described previously [the "low temperature" modification, α-NiAs₂, was readily made by a 2 × 14 days reaction period (intervening crushing) from NiAs + As at 855 °C], but for the preparations of the other compounds, some modifications of earlier procedures were adopted.

The alterations introduced for FeSb₂, CoSb₂, and NiSb₂ consisted in the initial preparations of the phases FeSb₂, CoSb₂, and NiSb₂ by high temperature (1200 – 1000 °C) treatments. The samples were ground to fine powders, appropriate amounts of Sb added, and subsequently annealed once (CoSb₂) or twice (intervening crushing) at 700 °C (FeSb₂), 900 °C (CoSb₂), or 600 °C (NiSb₂). The FeSb₂ and CoSb₂ samples were slowly cooled to 600 °C. These simple alterations have thus eliminated the rather time-consuming grinding and annealing cycles earlier used.⁴³ CoAs₂, RhAs₂, RhSb₂, IrAs₂, and IrSb₂ were made essentially as described in Ref. 4. On turning to higher maximum temperatures, viz. 1000 °C (CoAs₂) or 1200 °C, the overall annealing periods and number of intervening crushings could be reduced appreciably (to 2 × 2 days). All samples were slowly cooled to 600 °C.

RhBi₁₄ was obtained after reaction at 750 °C (2 days), followed by grinding and annealing at 400 °C (1 month). Renewed attempts to prepare CoBi₄ and IrBi₄ (cf. Ref. 10) were in vain as also reported in, e.g., Ref. 4.

The ternary samples, Fe₆₋₄Ni₆₋₄As₂ and Fe₆₋₄Ni₆₋₄Sb₂, were made from the binary end members. Fe₆₋₄Ni₆₋₄As₂ is readily made by two successive annealings at 740 °C, followed by slow cooling to 600 °C. Fe₆₋₄Ni₆₋₄Sb₂ is, however, somewhat more difficult to make. The maximum temperature in the annealing process must not exceed 640 °C (vide infra) and equilibrium is attained rather slowly below this temperature. Of the numerous attempts to prepare pure Fe₆₋₄Ni₆₋₄Sb₂, none of the samples could be handled identically with respect to annealing time and number of intervening crushings. Further work on the synthetic and other properties of the Fe–Ni–Sb system is in progress.

The temperature of the furnaces surrounding the specimens was kept constant to within ±0.5 °C during the annealing processes, using Getrostist (Philips) temperature regulators and Frigistor reference chambers for the cold points of the Pt/Pt-Rh thermocouples. The recorded annealing and quenching temperatures were measured separately with calibrated Pt/Pt-Rh thermocouples. The silica capsules were made as short as possible in order to minimize effects of thermal gradients in the furnaces, and thin-walled ampoules were utilized for quenching experiments in order to ensure fast cooling rates. The quenching experiments were performed with or without shattering the silica ampoules (depending on the quenching rate required) when brought into contact with ice-water.

Room temperature X-ray powder diffraction data were obtained in a Guinier camera (CuKα₁ radiation, KCl as internal standard) and unit cell dimensions derived by applying the method of least squares. All samples were also examined by metallographic methods.

DTA data were collected with a Mettler Recording Vacuum Thermoanalyzer, using ~60 mg samples in sealed silica crucibles (Pd powder as reference). High temperature X-ray powder photographs were obtained in a Unicam camera (CuKα radiation) with the samples sealed in thin-walled silica capillaries. The temperature of the furnace surrounding the specimen was kept constant to within ±5 °C during the exposures. The Pt/Pt-Rh thermocouples of the furnace were calibrated with a standard sample (Ag) in the range 22 to 900 °C. The Guinier data were used to correct the Unicam photographs and least squares refinements were subsequently applied.

A General Electric powder X-ray diffractometer (CuKα₁ radiation, diamond powder as internal standard) with cryostat attachment was used to collect X-ray powder data below room temperature.

RESULTS AND DISCUSSION

(i). FeAs₂, FeSb₂, NiAs₂, and NiSb₂. The high temperature X-ray diffraction data (Fig. 1) show that the FeSb₂–m type structures of FeAs₂, FeSb₂, β-NiAs₂, and NiSb₂ persist until the samples decompose peritectically according to TX₁→TX + liq., where TX represents phases with NiAs/MnP type structure. The actual temperatures for these reactions are 1014 ± 7, 745 ± 4, 852 ± 5, and 620 ± 2 °C for FeAs₂, FeSb₂, NiAs₂, and NiSb₂, respectively, as determined by DTA and quenching experiments.

For FeSb₂ and NiSb₂ these results are in agreement with those reported in Refs. 11, 12. (Redetermined values for the temperature of the eutectic between TSb₂ and Sb are 628 ± 2 and 616 ± 2 °C for T = Fe and Ni, respectively.) The results for FeAs₂ and NiAs₂ are, on the
Fig. 1. Thermal expansion of: (a) FeAs$_2$, (b) FeSb$_2$, (c) $\beta$-NiAs$_2$ and (d) NiSb$_2$.

other hand, at variance. The reported temperature for the decomposition of FeAs₂ is in agreement with the present determination, but the interpretation differs: melting versus peritectic reaction. As a support for peritectic reaction, FeAs is detectable on the high temperature X-ray diagrams taken above 1014 °C. For Ni₃As₄ the temperature 852 °C is interpreted in Ref. 12 as representing an eutectic between NiAs and NiAs₂, and it is also reported that Ni₃As₄ decomposes (melts) above 1040 °C. According to the present results, Ni₃As₄ disappears at 852 °C, leaving NiAs and liquid. The equilibrium vapour pressures at these high temperatures disturb the sensitivity of the methods and further investigations are needed to find the cause of the discrepancy between Ref. 12 and the present results.

The only minor thermal effect on the c axes for the two class B type compounds, β-Ni₃As₂ and NiSb₂, is notable. The fact that the thermal expansion of c is considerably less than for a and b has also been observed for other class B, Fe₅S₇-m type compounds (particularly for FeSe₂ and FeTe₂). The class A compounds exhibit, on the other hand, comparable thermal expansions for all axes.

Quenching experiments (followed by room temperature X-ray analyses) from selected temperatures on samples with different nominal compositions, show that the unit cell dimensions are invariant both with respect to temperature and compositions. Hence (using also inferences from Ref. 9), we conclude that the compounds exhibit no appreciable ranges of homogeneity on either side of the TX₂ composition.

Below the temperatures of decomposition (see above), quenched samples demonstrated various degrees of "partial decompositions" TX₂(s) ⇌ TX(s) + X(g). This is particularly noticeable for Ni₃As₂ which, moreover, also exhibits an α⇌β transition (cf. Refs. 13, 14;

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**Fig. 2.** Unit cell dimensions of: (a) FeₓNi₉₋ₓAs₂ and (b) FeₓNi₉₋ₓSb₂ as functions of temperature.

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A third, high pressure-high temperature induced, modification with the FeS$_2$-P type structure is also known [14,15]. The reaction $\beta \rightarrow \alpha$ is so slow even at 560 °C that, once $\beta$-NiAs$_2$ is formed it persists with no detectable changes (at 560°C) up to ~60 days before the first traces of $\alpha$-NiAs$_2$ (orthorhombic; $a = 5.772(2)$, $b = 5.834(2)$, and $c = 11.420(7)$ Å) are detectable. Conversely, the reaction $\alpha \rightarrow \beta$ is also kinetically hampered below 600 °C, whereas complete conversion is rapidly attained above 640 °C. A number of quenching experiments on $\alpha$- and $\beta$-NiAs$_2$ between 560 and 590 °C establish the transformation temperature as 580 ± 4 °C. (The conversion rate for $\beta \rightarrow \alpha$ can be accelerated by adding excess As to $\beta$-NiAs$_2$, thus suggesting that the reaction is not of the solid state type but involves the vapour phase, cf. Ref. 3.)

Inspired by the existence of $\alpha$-NiAs$_2$, long term syntheses of NiSb$_2$ (from NiSb + Sb) at selected temperatures down to 300 °C were performed with no success in detecting a corresponding modification for NiSb$_2$.

(ii). Fe$_{8.5}$Ni$_{1.5}$As$_2$ and Fe$_{8.5}$Ni$_{1.5}$Sb$_2$. Data for the class A/B, FeS$_2$-m type representatives Fe$_{8.5}$Ni$_{1.5}$As$_2$ and Fe$_{8.5}$Ni$_{1.5}$Sb$_2$ are presented in Fig. 2, which show that their c axes (like for class B) expand only slightly below 775 and 642 °C, respectively. Above these temperatures, changes of composition occur according to Fe$_{8.5}$Ni$_{1.5}$X$_2$ → Fe$_{1-x}$Ni$_x$X$_4$ + “NiX” + liq. The notation “NiX” refers to an Ni-rich phase with NiAs like structure, whose composition (judged from data for quenched samples) changes with temperature. There may be a variable Fe content and/or a variable T to X ratio for “NiX”, but studies of the FeAs–NiAs and FeSb–NiSb series are needed to resolve this question.

The compositional changes for Fe$_{8.5}$Ni$_{1.5}$X$_2$ are, on the other hand, comparatively easy to follow as a function of temperature. Fig. 3 shows the unit cell dimensions of these phases in the samples quenched from various temperatures $T_q$. By comparison with unit cell dimensions for the Fe$_{1-x}$Ni$_x$X$_2$ phases, it is evident that a gradual decrease of Ni-content occurs with increasing $T_q$ (no indications of non-stoichiometry of these ternary phases being found; suggesting that the problem may be regarded as “pseudo-binary”). The complete disappearance (as judged from X-ray diffraction and metallographic examinations of quenched samples, high temperature X-ray diffraction and DTA) of the FeS$_2$-m type phases occurs at 1014 and 745 °C for $X = $As and Sb, respectively. (Due to the disturbingly high As pressure, the uncertainty is larger for Fe$_{1-x}$Ni$_x$As$_2$ than for Fe$_{1-x}$Ni$_x$Sb$_2$.) This fact and the trends for the unit cell dimensions (Fig. 3) strongly suggest that just before the final decomposition, the approximately pure FeX$_4$ remains.

The mutual substitution of one kind of atom for another is usually expected to increase with increasing temperature and this has also been suggested for Fe$_{1-x}$Ni$_x$As$_2$. Our results show that this cannot be the case and a more detailed reexamination of the phase relation-
Fig. 4. Pseudo FeS$_2$-m type unit cell dimensions versus temperature for (a) CoAs$_2$, (b) CoSb$_2$, (c) RhAs$_2$, (d) RhSb$_2$, (e) IrAs$_2$, and (f) IrSb$_2$.

ships (as a function of temperature) for Fe$_{1-x}$Ni$_x$X$_2$ (X = As, Sb) is called for.

(iii). CoAs$_2$, CoSb$_2$, RhAs$_2$, RhSb$_2$, IrAs$_2$, and IrSb$_2$. The scope of the present high temperature X-ray study included, originally, all binary compounds with the CoSb$_2$ type structure. Preliminary attempts showed that the samples of RnP$_2$ and IrP$_2$ were difficult to load into the silica capillaries, and examination of these compounds was postponed towards the end of the programme. For reasons given in section v they were, however, finally dismissed.

The indexing and reduction of the X-ray diffraction data for CoSb$_2$ type compounds were performed in terms of their true monoclinic unit cells \([a_{AP}, b_{AP}, c_{AP}; (\beta_{AP})]\), but in order to facilitate comparison with the FeS$_2$-m type compounds, their pseudo FeS$_2$-m type cells \([a' = (a_{AP} - c_{AP})/2, b' = b_{AP}, c' = (a_{AP} + c_{AP})/2; (\beta')]\) are conveniently used in the following presentation.

As evident from Fig. 4, CoAs$_2$, CoSb$_2$, and RhSb$_2$ apparently exhibit transformations from monoclinic to orthorhombic symmetry at 870, 650, and 1070 K, respectively; uncertainties being difficult to estimate (vide infra). RhAs$_2$, IrAs$_2$, and IrSb$_2$ maintain the monoclinic symmetry up to the maximum temperature (~1300 K) of examination. The peritectic decomposition of CoSb$_2$ at 931 ± 5 °C is significantly higher in temperature than reported in Ref. 17. This is also the case for CoSb$_3$ which undergoes the peritectic decomposition at 876 ± 5 °C according to the present finding.

The gradual structural changes as a function of temperature for the compounds under consideration are completely reproducible and do not vary, e.g., with the heating procedure of the samples in the X-ray equipment. Quenching experiments confirm that no appreciable ranges of homogeneity can exist for these TX$_2$ compounds. The crystalline perfection of samples quenched from temperatures where the high temperature X-ray data show that the orthorhombic symmetry prevails, is compatible with data for samples quenched from the monoclinic temperature region. (The orthorhombic state of these samples is not quenchable.) Hence, non-equilibrium crystal imperfections cannot be the cause of the observed gradual changes for CoAs$_2$, CoSb$_2$, and RhSb$_2$. The results in Fig. 4 must therefore imply that these compounds undergo phase transitions of second or higher order (see v). An anomaly in the thermal expansion curves of c is a common feature for all these transitions.

* Attempted syntheses of CoP$_3$ failed, the reaction product being invariably CoP and CoP$_3$.

dimensions reported in Refs. 18, 19. Since \( \beta \)-RbBi\(_2\) is quenchable, we intend to give the problem continued attention.

(iii) \( \text{CoSb}_2 \leftrightarrow \text{FeS}_2-m \) type transformations. The transformations referred to in section iii almost certainly reflect transitions between the CoSb\(_2\) and FeS\(_2\)-m type structures. Unequivocal confirmation of crystallographic changes is difficult in these cases due to the close structural relationship. The angle \( \beta' \) of the pseudo-cell gradually approaches 90\(^\circ\) and ultimately, the exact fulfillment of \( \beta' = 90^\circ \) becomes virtually indistinguishable from the approximate satisfaction of this condition. Apart from the splitting of certain reflections when \( \beta' \neq 90^\circ \), the CoSb\(_2\) type diffraction pattern differs from that of FeS\(_2\)-m also by additional reflections. The intensity of these reflections diminishes rapidly when \( \beta' \) becomes nearly 90\(^\circ\), and their possible presence or absence are even more difficult to detect than the degree of overlap between reflections. The somewhat low quality of the high temperature X-ray powder intensity data prevented clarification of this question through structural refinements. However, semi-quantitative calculations and comparison with relative intensities for CoAs\(_2\) versus Fe\(_{0.5}\)Ni\(_{0.5}\)As\(_2\) and CoSb\(_2\) versus Fe\(_{0.5}\)Ni\(_{0.5}\)Sb\(_2\) show that the FeS\(_2\)-m type is at least a very good approximation to the high temperature structures of CoAs\(_2\) and CoSb\(_2\). We believe that the same applies to RhSb\(_2\).

The CoSb\(_2\) \( \leftrightarrow \) FeS\(_2\)-m type transition may accordingly be regarded as experimentally well established for CoAs\(_2\), CoSb\(_2\), and RhSb\(_2\). The fact that these transitions are of second or higher order contradicts the prediction of Goodenough and emphasizes an important distinction between the CoSb\(_2\) \( \leftrightarrow \) FeS\(_2\)-m and VO\(_2\) \( \leftrightarrow \) TiO\(_2\)-\( r \) (\( r \)=rutile) type transitions.

It appears appropriate to ask why RhAs\(_2\), (\( \alpha \)-RbBi\(_2\)), IrAs\(_2\), and IrSb\(_2\) do not show corresponding CoSb\(_2\) \( \leftrightarrow \) FeS\(_2\)-m type transitions. The answer to this question is clearly hidden in the parameters (including those specifying the thermal movements of the atoms) which describe the distortion of the CoSb\(_2\) type relative to the FeS\(_2\)-m type structure. Since both structure types comprise a number of parameters (see vi), it is difficult to find a satisfactory, general approach to this problem. However, \( \beta' \) can probably be regarded as a parameter.
Fig. 6. Room temperature values $\beta'_0$ versus CoSb$_2$=FeS$_2$.m type transition temperature $T_I$ for CoAs$_2$, CoSb$_2$, and RhSb$_2$.

Describing the average degree of distortion between the CoSb$_2$ and FeS$_2$.m type structures. In line with this, Fig. 6 shows a linear empirical correlation between the CoSb$_2$=FeS$_2$.m type transition temperature $T_I$ (for CoAs$_2$, CoSb$_2$, and RhSb$_2$) and the room temperature values $\beta'_0$ of $\beta'$. Assuming that this correlation applies to all compounds with the CoSb$_2$ type structure, \textit{a}-RhBi$_2$ should undergo the CoSb$_2$=FeS$_2$.m type transition at about 700 K (i.e. very nearly at the same temperature as found for the \textit{a}=\beta transition). According to the same correlation, the remaining CoSb$_2$ type compounds should transform to the FeS$_2$.m type above 1300 K. This was, in fact, the reason why RhP$_2$ and IrP$_2$ were finally dismissed from the high temperature X-ray programme (\textit{vide supra}.

In the same way that compounds possessing the CoSb$_2$ type structure at room temperature convert to the FeS$_2$.m type at higher temperatures, it is feasible (but less likely) that those of the latter type could show the opposite transition at lower temperatures. Thus, FeAs$_2$, NiAs$_2$, NiSb$_2$, Fe$_{0.3}$Ni$_{0.7}$As$_2$, and Fe$_{0.3}$Ni$_{0.7}$Sb$_2$ were examined by X-ray diffraction down to 4 K. None of the X-ray diagrams gave, however, indication of (partial or complete) FeS$_2$.m$\rightarrow$CoSb$_2$ type transformation. This finding concurs with previous results for CrSb$_2$ and FeSb$_2$.\textsuperscript{21} Again the somewhat unique character (\textit{viz.} in relation to the Periodic System) of CoSb$_2$ type compounds is evident.

\textit{(vi). The CoSb$_2$ versus the FeS$_2$.m type structure.} A complete structural description of a crystalline solid involves specification of positions and movements of the atoms relative to each other. Although this problem can be approached in several ways, the conventional crystallographic scheme entirely dominates the field. (A discussion of the CoSb$_2$ and FeS$_2$.m type geometry in terms of alternative variables will be presented in a forthcoming paper.) Following the traditional scheme, a geometrical description of the FeS$_2$.m type structure [space group Pnmm; $T$ in 2(4), $X$ in 4 (4)] requires the knowledge of three axes $(a, b, c)$ and two positional parameters $(x, y)$, whereas the CoSb$_2$ type [space group $P2_1/c$; 4$T$, 4$X_I$, and 4$X_{II}$ in 4 (e)] demands three axes $(a_{AP}, b_{AP}, c_{AP})$, one angle $(\beta_{AP})$, and nine positional parameters $(x_T, y_T, z_T, x_1, y_1, z_1, x_{II}, y_{II}, z_{II})$.

Since the space group of the CoSb$_2$ type is a subgroup of that for the FeS$_2$.m type, the latter can be converted to a CoSb$_2$ type setting with $a_{AP} (=c_{AP})$, $b_{AP}$, and $c_{AP}$ specifying the unit cell, and $x_T = 1/4, y_T = 0, z_T = 1/4, x_1 = 1/4 + x/2, y_1 = y, z_1 = 1/4 - x/2, x_{II} = 1/4 - x/2, y_{II} = 1 - y$, and $z_{II} = 1/4 + x/2$ for the positional parameters. Hence, the CoSb$_2$ versus FeS$_2$.m type coordinate relationship can, in terms of the distortion parameters $\Delta x_T$, $\Delta y_T$, etc., be expressed as

$T$: $x_T = 1/4 + \Delta x_T, y_T = \Delta y_T, z_T = 1/4 + \Delta z_T$

$X_I$: $x_1 = 1/4 + x/2 + \Delta x_1, y_1 = y + \Delta y_1, z_1 = 1/4 - x/2 + \Delta z_1$

$X_{II}$: $x_{II} = 1/4 - x/2 + \Delta x_{II}, y_{II} = 1 - y + \Delta y_{II}$,

$z_{II} = 1/4 + x/2 + \Delta z_{II}$.

In order to judge the magnitude of these distortion parameters, sufficiently accurate values for the positional parameters of class A/B, FeS$_2$.m and CoSb$_2$ type compounds are
required. According to Ref. 22, x and y vary systematically within the FeS\textsubscript{3}-m type family. The natural class A/B, FeS\textsubscript{3}-m type candidates for such a comparison would be Fe\textsubscript{0.8}Ni\textsubscript{0.2}As\textsubscript{2} and Fe\textsubscript{0.8}Ni\textsubscript{0.2}Sb\textsubscript{2} (not yet structurally refined), or the Ru-Pd and Os-Pt analogues (could apparently not be prepared\textsuperscript{44}). In the lack of experimental data, it may be argued that average values for FeAs\textsubscript{4} versus NiAs\textsubscript{4} and FeSb\textsubscript{4} versus NiSb\textsubscript{4} will provide useful approximations. (Some support for this assumption is to be found in the approximately linear relationships between x, y and the compositional parameter t in the series Cr\textsubscript{0.75}Fe\textsubscript{0.25}As\textsubscript{4} and Cr\textsubscript{0.75}Fe\textsubscript{0.25}Sb\textsubscript{4}\textsuperscript{43}).

The degree of reliability of the structure determinations for the CoSb\textsubscript{4} type compounds represents another concern. The large number of positional parameters to be determined makes the results\textsuperscript{4} from powder diffraction data unreliable for RhP\textsubscript{3}, RhAs\textsubscript{3}, IrP\textsubscript{3}, and IrAs\textsubscript{3}. The structural data for CoSb\textsubscript{4}, RhSb\textsubscript{4}, α-RhBi\textsubscript{4}, and IrSb\textsubscript{4} are indeed obtained by single crystal methods\textsuperscript{46} but the results are apparently not of sufficient quality to justify comparative analyses. One is therefore left with CoAs\textsubscript{4} as the only suitable candidate.

A schematic presentation of the relationship between the FeS\textsubscript{3}-m and CoSb\textsubscript{4} type structures is shown in Fig. 7. The projection shows the positions of the T and X atoms in the FeS\textsubscript{3}-m type arrangement (assumed for Fe\textsubscript{0.8}Ni\textsubscript{0.2}As\textsubscript{4}, vide supra), whereas the lengths and directions of the arrows give their main displacements in the CoSb\textsubscript{4} type cell of CoAs\textsubscript{4} (displacements along the projection axis are negligible). The illustration shows that the X atoms are shifted mainly along ±(a−c), whereas the T atoms approximately along ±(a/5−c). The magnitude of each T displacement is about twice that of each X. (For CoAs\textsubscript{4} versus Fe\textsubscript{0.8}Ni\textsubscript{0.2}As\textsubscript{4}, \(\Delta x_{T} = 0.02\), \(\Delta y_{T} = 0.00\), \(\Delta z_{T} = 0.03\), \(\Delta x_{II} = 0.00\), \(\Delta y_{II} = 0.00\), \(\Delta z_{II} = 0.02\).) Similar relations appear to apply to the CoSb\textsubscript{4} type

\[\text{Fig. 7. Relationship between the FeS}_3\text{-m and CoSb}_4\text{ type structures. Filled and open circles represent } T \text{ and } X \text{ atoms, respectively, in class A/B, FeS}_3\text{-m type arrangement. Lengths and directions of arrows give displacements in order to obtain CoSb}_4\text{ type atomic arrangement.}\]

antimonides versus Fe\(_{0.5}\)Ni\(_{0.5}\)Sb\(_2\). The net effect of the displacements is that the average \(T-X\) distance is kept approximately constant during the transition. A consistent trend is, however, observed in the shifts such that the six approximately equal \(T-X\) distances in the FeS\(_4\)-\(m\) type structure are split into three shorter \((T-X_1)\) and three longer \((T-X_{11})\) distances in the CoSb\(_4\) type (see viii).

The FeS\(_4\)-\(m\)=CoSb\(_4\) type transition (and possibly other transitions originating from the FeS\(_4\)-\(m\) type structure) can be described in terms of the Landau theory.\(^{25}\) However, a general treatment of this problem is more complicated than for the NiAs=\(\approx\)MnP or NiAs=\(\approx\)NbS type transitions,\(^{26}\) due to the variable positional parameters of the FeS\(_4\)-\(m\) type as opposed to the variable-free NiAs type (in this respect).

(viii). Axial ratios. Due to differences in absolute dimensions, thermal expansion data are often difficult to compare. In order to facilitate comparison, axial ratios are frequently consulted. For compounds with the FeS\(_4\)-\(m\)

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Fig. 8. Axial ratios \(c/a, c/b\) and \(c'/a', c'/b'\) versus temperature for FeS\(_4\)-\(m\) and CoSb\(_4\) type compounds, respectively. Broken and solid curves correspond to CoSb\(_4\) and FeS\(_4\)-\(m\) type regions, respectively.

(and CoSb₃) type structure(s), axial ratios have an additional important function in providing the basis for division of the compounds into the classes A, B, and A/B (vide supra).

Fig. 8 shows the temperature variation in axial ratios c/a (c'/a') and c/b (c'/b') for the compounds under investigation. Evidently, the class A representatives FeAs₂ and FeSb₂, exhibit increasing c/a and c/b with increasing temperature, whereas the opposite trend prevails for the class B members β-NiAs₂ and NiSb₂ (cf. also the results for class B, FeS₂-m type chalcogenides in Ref. 3). The class A/B, FeS₂-m type compounds Fe₄Ni₈As₁₂ and Fe₆Ni₈Sb₁₂ exhibit c/a, c/b values of 0.605, 0.525 and 0.603, 0.528, respectively, at room temperature and decreases only slightly with increasing temperature (these compounds are, for clarity, not included in Fig. 8). The same applies to the CoSb₃ type compounds (class A/B) well below Tᵣ (see v) for all members and also from just above Tᵣ for CoAs₂, CoSb₂, and RhSb₂.

The approximate temperature independence of axial ratios for class A/B, FeS₂-m or CoSb₃ type compounds (neglecting in this connection the CoSb₃→FeS₂-m type transition regions) is consistent with the increasing and decreasing axial ratios with temperature for the classes A and B, respectively, and also with the idea of class A/B as a “mixture” of the classes A and B (see vii). A common decrease in axial ratios is, however, observed in the CoSb₃→FeS₂-m type transition regions for CoAs₂, CoSb₂, and RhSb₂. (This finding is not a consequence of our neglect to correct c'/a' and c'/b' for β' = 90° which amounts to a rather minor effect in these cases.) Generalizing from the relative magnitude of the observed decreases for CoAs₂ and CoSb₂, the changes in axial ratios during the CoSb₃→FeS₂-m type transitions should be successively smaller (for fixed T atoms) along the sequence: phosphides, arsenides, antimonides, bismuthides. Although the α→β transition for RhBi₃ complicates the situation, it is worth noting that the above observation is consistent with the absence of an anomaly in c (see iii and ic) and/or a beginning decrease in axial ratios for this compound. Similarly, this finding may also shed new light on the scatter in the room temperature axial ratios for the CoSb₃ type compounds: [0.604

\( (\alpha\text{-RhBi₃}) \leq c'/a' \leq 0.680 (\text{IrP₄}) \), \( 0.528 (\alpha\text{-RhBi₃}) \leq c'/b' \leq 0.563 (\text{IrP₄}) \), which may be considerably reduced on referring to their (real or hypothetical) FeS₂-m type modifications.

(viii). Further aspects. Previous discussions concerning the relationship between the CoSb₃ and FeS₂-m type structures have focused attention on that effect of the distortion which produces alternately shorter and longer T–T distances along c'. This “pair formation” and the formal d⁻ manifold attributed to T for the CoSb₃ type compounds have led a number of workers in the field (cf. Refs. 4, 7, 27, and references therein) to suggest that localized, normal T–T σ-bonds are the stabilizing element of the CoSb₃ type structure. The rejection of this hypothesis is discussed in Refs. 2, 20 and a few relevant remarks will be made here.

With the attention still focused on the T atoms, it is recognized that six of the twelve \( X–T–X \) angles for CoSb₃ type compounds show some resemblance to the octahedral angles for class A, FeS₂-m type compounds, whereas the other six correspond with those in class B.

![Fig. 9. Arrangement of classes A and B FeS₂-m type fragments in the CoSb₃ type structure.](image)

However, a simpler and closer similarity between the CoSb$_2$ and the two FeS$_2$-m type classes emerges when attention is shifted to the two crystallographically non-equivalent $X_1$ and $X_2$ atoms in the CoSb$_2$ type structure. The immediate coordination (3T and 1X$_{11}$) of $X_1$ resembles that for the X atoms in class A, whereas the neighbours (3T and 1X$_{11}$) of $X_2$ are arranged as in class B. This aspect is illustrated in Fig. 9, where a distinct pattern of four-membered A and B clusters is evident.

In this pictorial way, the CoSb$_2$ type structure occurs as a natural consequence of mixing equal amounts of structural elements from the FeS$_2$-m type classes A and B. This interpretation lends support to the use of the notation A/B also for the CoSb$_2$ type and reduces in a way the cause of the existence of this structure type to the effects responsible for the distinction between the FeS$_2$-m type classes A and B. Referring to our discussion in Ref. 22 (where we conclude that there is indeed no experimental evidence in favour of a regular type of $T-T$ bonding in class A, FeS$_2$-m type compounds) this observation makes it even more unlikely that the CoSb$_2$ type should be stabilized by normal, localized $T-T$ σ-bonds. This conclusion is also supported by the observed thermal contraction of $c$ for CoAs$_2$, CoSb$_2$, and RhSb$_2$ (Fig. 4) during their CoSb$_2$$\rightarrow$FeS$_2$-m type transitions. If $T-T$ bonds had been present in their CoSb$_2$ type modifications, the opposite result with an increased $c$ would have been expected through relaxation of these bonds.

Without specifying the bonding situation in the FeS$_2$-m and CoSb$_2$ type structures, it seems that the variation in bonding character of the $X-T$ ($T-X$) bonds (cf. Ref. 22; the points being elaborated further in a forthcoming paper) is responsible for the occurrence of their different variants A, B, and A/B. The distinct A and B pattern in the CoSb$_2$ type class A/B (Fig. 9) shows that the effects in question occur in a regular, ordered manner, as opposed to the disordered distribution of bonding characteristics in the FeS$_2$-m type class A/B. On this basis, it is only natural that CoSb$_2$ type compounds transform gradually to the class A/B, FeS$_2$-m type structure at higher temperatures by increasing disorder of bonding characteristics.

REFERENCES


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