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Compounds with the Marcasite Type Crystal Structure. X.

^{57}Fe Mössbauer Studies of Some Ternary Pnictides

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Room temperature ^{57}Fe Mössbauer data for 49 samples of the phases $Cr_tFe_{1-t}As_2$, $Cr_tFe_{1-t}Sb_2$, $Fe_{1-t}Co_tAs_2$, $Fe_{1-t}Co_tSb_2$, $Fe_{1-t}Ni_tAs_2$, and $Fe_{1-t}Ni_tSb_2$ are reported and discussed in relation to other (mostly structural) properties. Test of the current model for conversion between the classes A and B of the marcasite type structure in terms of these data, gives strong indications of inadequacies in the model. Associated problems concerning the arsenopyrite type structure are examined and the assumption of metal-metal bonding is rejected as the stabilizing element for its occurrence.

Compounds with the FeS_2-*m* (*m* = marcasite) type crystal structure have been subjected to regular investigations throughout most of this century. However, an inevitable lesson learned from the preceding studies is that in order to gain understanding into the chemical bonding in these compounds, there is an almost unlimited demand for decisive experimental facts. Of the compounds in question, $FeSb_2$ has received particular attention because of the anomalies observed in the temperature dependences of magnetic,[1-3] electrical,[3,4] and ^{57}Fe Mössbauer [5,6] parameters. A tentative explanation [6] of these anomalies invokes the thermal population of an empty conduction band as a function of temperature. As an alternative to the thermal influence on electronic band structure, one may examine the variations imposed by compositional parameters (*viz.* through substitutional solid solution). Thus the present paper concerns the compositional dependences of the ^{57}Fe Mössbauer parameters for the phases $Cr_tFe_{1-t}As_2$, $Cr_tFe_{1-t}Sb_2$, $Fe_{1-t}Co_tAs_2$, $Fe_{1-t}Co_tSb_2$, $Fe_{1-t}Ni_tAs_2$, and $Fe_{1-t}Ni_tSb_2$.

EXPERIMENTAL

The pure elements used as starting materials for the syntheses were flakes of 99.999 % Cr (Koch-Light Laboratories), 99.99+ % Fe, 99.999 % Co, 99.995 % Ni (Johnson, Matthey & Co.; turnings from rods), 99.9999 % As, and 99.9995 % Sb (Koch-Light Laboratories). In accordance with earlier findings,[7,8] equilibrium is attained rather slowly (particularly for the diantimonides) when synthesis of the ternary phases by direct combination of the elements is attempted. However, equilibrium is facilitated by the intermediate preparation of the binary compounds.[9-11]

$Fe_{1-t}Co_tAs_2$ and $Fe_{1-t}Ni_tAs_2$ are readily made from the binary end members at 800 °C by a sequence of annealings (with intermediate crushings) over a period of 3 to 6 months. $Cr_tFe_{1-t}Sb_2$ samples are made similarly at 600 °C using total heating periods of 8 to 10 months. Homogeneous Fe-rich samples of $Fe_{1-t}Co_tSb_2$ ($0 < t \lesssim 0.5$) and $Fe_{1-t}Ni_tSb_2$ ($0 < t \lesssim 0.3$) were obtained after 10 to 14 months (intermediate crushings) at 600 °C. However, more Co- and Ni-rich samples of the same phases contained *inter alia* variable amounts of $CoSb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ (*cf.*, *e.g.*, Ref. 8), respectively, which proved to reflect the equilibrium situation at 600 °C. On increasing the annealing temperature to 630 – 700 °C depending on composition, homogeneous samples and hence equilibrium could be attained after 6 to 8 months.

Samples of $Cr_tFe_{1-t}As_2$ could not be prepared in an analogous manner since the binary compound $CrAs_2$ is unattainable by the sealed silica capsule technique. (A variety of thermal (400 – 1000 °C) and compositional ($CrAs_2$-$CrAs_6$) conditions, including chemical transport reactions, were tried, but all endeavours failed. This result is consistent with earlier findings.[9] However, $CrAs_2$ with $NbAs_2$ rather than FeS_2-*m* type structure has recently been synthesized [12] under high pressure – high temperature conditions.) Alternatively, CrAs and FeAs were initially prepared (as described in Refs. 13, 14) and

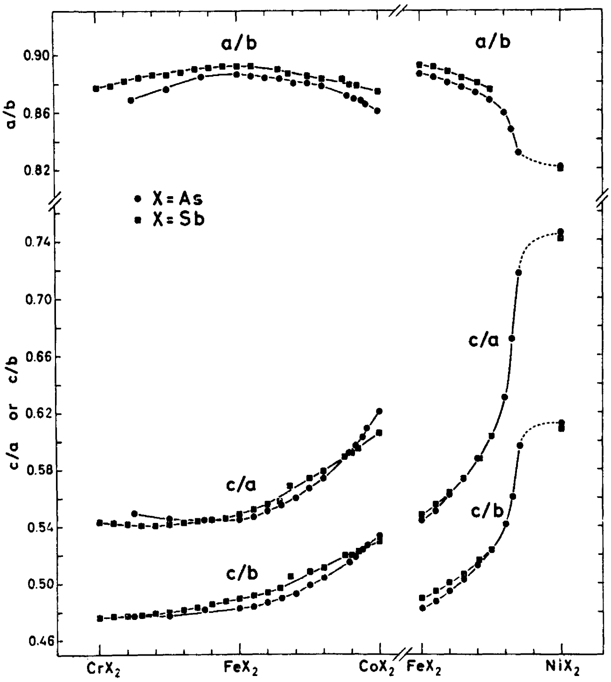

Fig. 1. Dependence of axial ratios on composition for the solid solution series CrX_2-FeX_2, FeX_2-CoX_2, and FeX_2-NiX_2. In this and the following diagrams, estimated error limits do not exceed the size of the symbols.

used to make $Cr_tFe_{1-t}As$ by three successive one-week annealings at 850 °C. Samples of $Cr_tFe_{1-t}As_2$ were subsequently obtained by adding the appropriate amounts of As, using heat treatments at 600 – 800 °C and quenching from 600 °C.

The homogeneity of all samples were ascertained from powder X-ray (Guinier) diagrams. The experimental details concerning the room temperature ^{57}Fe Mössbauer measurements and data reduction are reported earlier.[15]

RESULTS AND DISCUSSION

(i) *Solid solubility and unit cell proportions.* The phase analytical data for the five ternary phases $Cr_tFe_{1-t}Sb_2$, $Fe_{1-t}Co_tAs_2$, $Fe_{1-t}Co_tSb_2$, $Fe_{1-t}Ni_tAs_2$, and $Fe_{1-t}Ni_tSb_2$ confirm essentially those reported earlier.[7,8] Thus, continuous ranges ($0.00 \leq t \leq 1.00$) of random, substitutional solid solutions have been observed for $Cr_tFe_{1-t}Sb_2$, $Fe_{1-t}Co_tAs_2$, and $Fe_{1-t}Co_tSb_2$. The limited solid solubility ranges of the Fe-rich $Fe_{1-t}Ni_tAs_2$ and $Fe_{1-t}Ni_tSb_2$ phases are found to cover the intervals $0.00 \leq t \leq 0.75$ and $0.00 \leq t \leq 0.50$, respectively, the Ni-rich phases being uninteresting in this connection.

Considering the $Cr_tFe_{1-t}As_2$ phase, only the single composition with $t = 0.5$ has hitherto been recorded[16] in the literature. For the present purpose, compositions up to $t = 0.75$ were made (although not even this sample gave a good enough ^{57}Fe Mössbauer spectrum to be included in the final results reported here; see section ii). However, due to the special situation prevailing for the binary end member "$CrAs_2$",* supplementary information on the properties of $Cr_tFe_{1-t}As_2$ is of considerable interest, such data being reported in a forthcoming paper.[17]

The variations in axial ratios a/b, c/a, and c/b with composition for the phases in question are shown in Fig. 1. Since the binary end members belong to different classes[18,19] A ("$CrAs_2$", $CrSb_2$, $FeAs_2$, and $FeSb_2$), A/B ($CoAs_2$ and $CoSb_2$), and B ($NiAs_2$ and $NiSb_2$) of the FeS_2-*m* type structure, the continuous variations in unit cell proportions (Fig. 1) reflect corresponding continuous transitions between the classes. The

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* In the following text, quotation marks are used to emphasize the special situation for $CrAs_2$ (*cf.* Experimental).

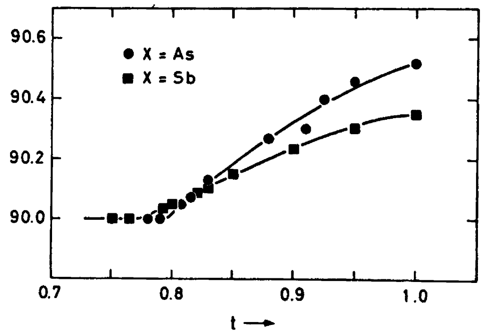

Fig. 2. Monoclinic angle (β') of pseudo-marcasite cell *versus* compositional parameter (t) for $Fe_{1-t}Co_tX_2$.

data for samples with the FeAsS (arsenopyrite; binary prototype $CoSb_2$) type structure refer to the pseudo-marcasite variant rather than the true unit cell (*cf.* Ref. 18).

The transitions from the FeS_2-*m* to the $CoSb_2$ type structure are of some special interest in this connection. Fig. 2 shows the angle β' of the pseudo-marcasite cell as a function of the compositional parameter t for $Fe_{1-t}Co_tAs_2$ and $Fe_{1-t}Co_tSb_2$. For both phases the transition is found at $t \approx 0.8$, the conversion appearing to occur at a slightly smaller t value in the antimonide than in the arsenide phase. However, an accurate determination of the conversion point is inaccessible through the determination of β' alone since the first sign of the reduced symmetry is indistinguishable from slight line broadenings of appropriate reflections on the Guinier diagrams.

Great care has been taken in the evaluation of the data for $Fe_{1-t}Ni_tAs_2$ and $Fe_{1-t}Ni_tSb_2$. (From considerations on average d^j configurations, $Fe_{0.5}Ni_{0.5}As_2$ and $Fe_{0.5}Ni_{0.5}Sb_2$ might have been expected to take the $CoSb_2$ type structure.[20]) However, no sign of any splitting nor broadening of reflections indicative of distortion from the FeS_2-*m* type structure could be detected within the ranges of solid solubility. These findings fully confirm the earlier results,[7,8] but appear on the other hand, to be difficult to correlate with the itinerant energy band considerations presented by Goodenough [20] without introducing additional assumptions, or alternatively, removing (some of) his extraneous assumption(s) concerning the $CoSb_2$ type structure.

(ii) *^{57}Fe Mössbauer spectra.* The ^{57}Fe Mössbauer spectra for the phases in question have been collected over a period of about three years. In all, some 350 spectra (including calibration runs) have been recorded, each run lasting from a few (≥ 6) hours to a few (≤ 3) days. For increasing t in a general formula $Fe_{1-t}T_tX_2$ (where T = Cr, Co, or Ni and X = As or Sb), the Mössbauer absorption became gradually reduced (due to the lowered Fe content) until ultimately comparable with the inherent statistical fluctuations. This limitation prevented unambiguous data reduction for samples with large t. However, the results presented below refer exclusively to spectra of acceptable quality obtained for, in all, 49 samples of the phases in question. In order to check the reproducibility and/or minimize random errors, each sample was run (with independent mountings and calibrations) two to five times.

The large number of spectra collected prevent presentation of the primary data.

(iii) *Chemical shifts.* The ^{57}Fe Mössbauer chemical shifts (relative to sodium nitroprusside) obtained for the $Fe_{1-t}T_tX_2$ phases are shown as functions of composition in Fig. 3, interpretations of which being called for.

The Mössbauer chemical shift (δ) is a relative measure of the total s electron density at the nucleus. (Increasing δ corresponds to decreasing total s electron density.) Since all electrons to some extent are influenced by chemical bonding, δ will reflect certain features of the bonding situation. As opposed to the apparently clear-cut direct contribution to δ from electrons of s symmetry, it is a common apprehension that electrons of p and d symmetry contribute indirectly through their shielding effects. Hence, increased p and/or d orbital participation in bonding should lead to decreased shielding of the nuclear charge and consequently, to increased s electron density.

The increase in δ for increasing t in the formula $Cr_tFe_{1-t}X_2$, suggests that Cr contributes more (*viz.* has a greater donor ability for electrons) to the $T-X$ bonds than Fe, in agreement with the fact that on going from Cr to Fe the "atomic 3*d* orbitals" experience an increased effective nuclear charge. The results of the inferred effective d electron transfer from Cr, through the $T-X$ bonds to Fe, may be interpreted as making the average $Cr-X$ bonds

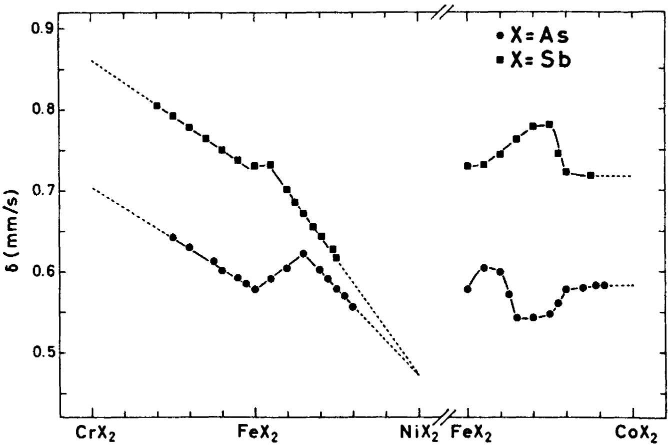

Fig. 3. Variation in ^{57}Fe Mössbauer chemical shift parameter (δ) with composition for the series CrX_2-FeX_2, FeX_2-NiX_2, and FeX_2-CoX_2.

stronger (*viz.* a decreased effective size of Cr) on the expense of the Fe$-X$ bonds (*viz.* an increased effective size of Fe). This interpretation concurs with the increasing average Fe$-X$ bond lengths that must be established for increasing t. (In the case of Cr$_t$Fe$_{1-t}$Sb$_2$, the assumption of increasing average $T-X$ bond lengths with increasing t is supported by the structural data for CrSb$_2$ and FeSb$_2$, *cf.* Ref. 11. For the Cr$_t$Fe$_{1-t}$As$_2$ phase, only circumstantial evidence from the corresponding variation of unit cell dimensions is at hand.[17]) At equilibrium, the distribution of $T-X$ bonding electrons in Cr$_t$Fe$_{1-t}X_2$ may be imagined such that the effective sizes of Cr and Fe are equal. This is consistent with the apparent equivalence of Cr and Fe in these phases as inferred from the sharp reflections on the X-ray diagrams.

In general, the attribution of such a mechanism to random solid solutions seems more likely than the common, simple picture based on distribution of individually sized atoms. Moreover, a model in terms of adjusted, averaged sized atoms offers the possibility of connecting solid solution properties to features of electronic band structure (*viz.* mutual compatibility in electronic band structure for solute and solvent,[21] including in elaborated form also the Hume-Rothery 15 % criterion,[22] *etc.*).

The dependence of δ on t for the two Fe$_{1-t}$Ni$_t X_2$ phases shows (Fig. 3) a somewhat different behaviour for $X=$As and $X=$Sb, and the identical chemical shifts obtained on extrapolating to NiX_2 is almost certainly accidental. It should also be noted that the extrapolations in these cases pass through regions with no solid solubility (see section i). As in the analogous Cr$_t$Fe$_{1-t}X_2$ case, the "atomic 3*d* orbitals" should experience an increased effective nuclear charge on going from Fe to Ni, and hence, an effective *d* electron transfer from Fe through the $T-X$ bonds to Ni might be expected. For increasing Ni content, each Fe must effectively contribute more *d* electrons in this process, and a steadily decreasing δ with increasing t in Fe$_{1-t}$Ni$_t X_2$ should result. This is apparently nearly the case for $X=$Sb but, for $X=$As the increase in δ for $0 \leq t \lesssim 0.3$ indicates that rivalling effects from *s* electrons are of importance and eventually, are balanced by the *d* electron effects at $t \approx 0.3$. However, the overall trend for Fe$_{1-t}$Ni$_t X_2$ shows a definite decrease in δ for increasing t, suggesting that *d* electron effects are most important. Moreover, an effective *d* electron transfer from Fe to Ni should make the effective size of Fe in Fe$_{1-t}$Ni$_t X_2$ smaller than in FeX_2. This is in conformity with structural data for FeSb$_2$ and NiSb$_2$ (*cf.* Ref. 11 and references therein) which indicate that the average $T-X$ bond length decreases with increasing Ni content. (The rivalling *s* electron effects should lead to an increased rather than decreased effective size of Fe with increasing t in Fe$_{1-t}$Ni$_t X_2$.)

Among the present phases, Fe$_{1-t}$Co$_t X_2$ reveals the most peculiar δ *versus* t relationships.

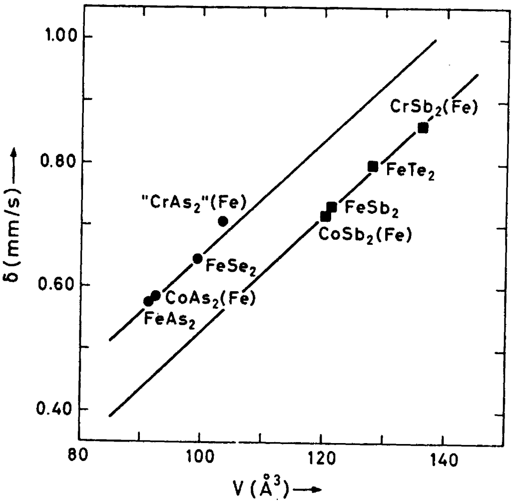

Fig. 4. ^{57}Fe Mössbauer chemical shift parameter (δ) *versus* cell volume (V) for some binary and quasi-binary compounds with FeS_2-*m* like structures.

However, on approaching CoX_2, the curves appear to suggest approximately constant values for δ. This finding is of particular interest in relation to the question concerning $T-T$ bonding [8,10,19,20,23-25] in compounds with the $CoSb_2$ type structure (see sections v and vi).

Connections between chemical shifts and unit cell dimensions for some phases with the FeS_2-*m* and FeS_2-*p* (*p* = pyrite) type structures have been pointed out earlier.[5,26] To test this on compounds with FeS_2-*m* like structures, available ^{57}Fe chemical shift data for some binary and extrapolated for some quasi-binary compounds are plotted in Fig. 4 against cell volumes. As indicated on the diagram, the compounds group on two parallel lines determined by the principal quantum number of X (As and Se *versus* Sb and Te). Of the ternary phases (omitted from the diagram for clarity), both $Cr_tFe_{1-t}As_2$ and $Cr_tFe_{1-t}Sb_2$ follow the trend outlined in Fig. 4. Attempted interpretation of correlations of this type is given in Refs. 5, 26. In common with other conclusions drawn from a limited amount of experimental evidence, this simple interpretation may no longer be valid when more data for phases with FeS_2-*m* like structures are included.

Even though the extrapolated δ values for $CoAs_2$ and $CoSb_2$ fit the scheme (Fig. 4), those for $Fe_{1-t}Co_tX_2$ show discrepancies. For the $Fe_{1-t}Ni_tX_2$ phases, these discrepancies are even more marked. This finding naturally provokes a discussion of to what extent the chemical shift data reflect the structural alterations accompanying the transitions from class A, through A/B, to B.

(iv) *Test of current model for class A to B conversion.* The cause of the existence of two distinct classes of binary compounds with the FeS_2-*m* type structure has been a controversial subject, the most recent model being advanced by Goodenough.[20] His treatment aims at explaining *inter alia* the class A to B conversion in terms of a combined molecular orbital – band theoretical description. Since the Mössbauer chemical shifts reflect certain features of the bonding situation, this model should be tested against these data.

According to Goodenough, the origin of class A is due to enhanced $T-X$ bonding in this class relative to class B (and the FeS_2-*p* type). In his itinerant model, T atoms with $j > 4$ in the d^j configurations, give rise to $T-X$ anti-bonding d electrons, implying that the gradual conversion to class B is caused by the corresponding reduction of their participation in $T-X$ bonding. This is accomplished by reduced covalent mixing of one d orbital per T with the X atomic orbitals, which consequently should increase the shielding of the s electrons from the nuclear charge. A gradual decrease in s electron density should therefore be observed over the class A to B conversion interval. This is exactly the opposite situation to that traced out by the general trend in the data for $Fe_{1-t}Ni_tX_2$. Hence, Goodenough's model must be considered as inadequate with respect to the class A to B conversion. Additional, independent support for this conclusion appears to be provided by the decreasing (definitely not increasing) tendency in the average $T-X$ bond length with increasing t for $Fe_{1-t}Ni_tX_2$, which fits rather badly in with the weakening in $T-X$ bonding prescribed by the model.

Although Goodenough's model has many attractive features and represents a definite improvement on the earlier models (*cf.* Ref. 20 and references therein), the physical origin of the different classes of compounds with the FeS_2-*m* type structure is still an open question.

(v) *Quadrupole splittings.* The ^{57}Fe Mössbauer

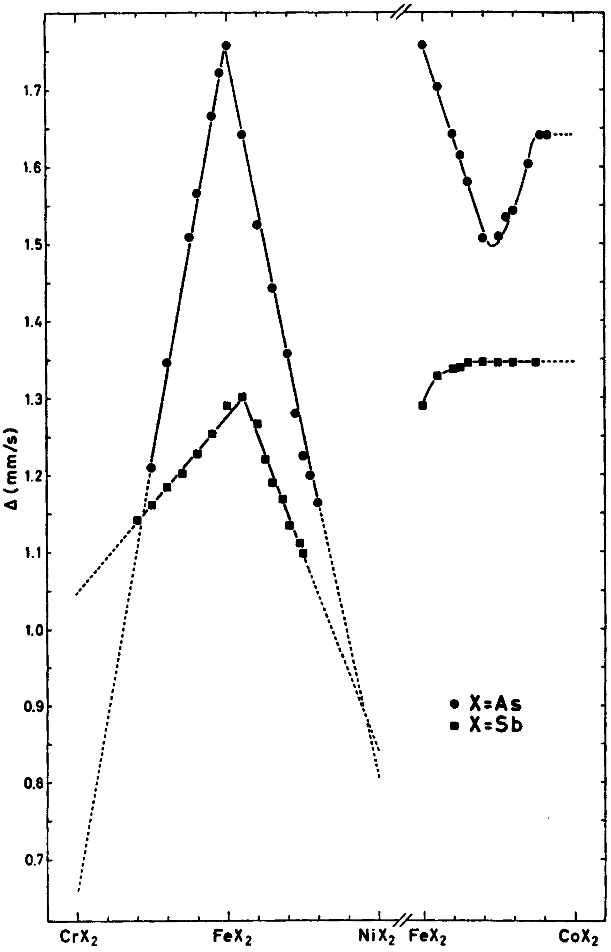

Fig. 5. Variation in ^{57}Fe Mössbauer quadrupole splitting parameter (Δ) with composition for the series CrX_2-FeX_2, FeX_2-NiX_2, and FeX_2-CoX_2.

quadrupole splitting parameter (Δ) is shown *versus* composition in Fig. 5. The total electronic asymmetry as observed by the nucleus is directly reflected in Δ. For the $Fe_{1-t}Ni_tX_2$ phases, decreasing Δ with increasing t could therefore qualitatively be attributed to the continuous structural alterations consequent on passing from class A to B. This could also apply to the first linear part of the curve for $Fe_{1-t}Co_tAs_2$. However, this interpretation is not generally applicable as most clearly demonstrated on Fig. 5 for $Cr_tFe_{1-t}X_2$. On inspection of Fig. 1, it is seen that the latter phases are members of class A. Nevertheless, the changes in Δ with t are compatible for $Cr_tFe_{1-t}X_2$ and $Fe_{1-t}Ni_tX_2$.

In order to gain a better understanding of these findings it appears necessary to dig more deeply into other properties of $Cr_tFe_{1-t}X_2$. The special situation prevailing for "$CrAs_2$" has already been noted, and moreover, also $CrSb_2$ is somewhat special among the binary compounds with the FeS_2-*m* type structure, being *inter alia* the only compound which exhibits cooperative magnetism.[2] Even though $CrSb_2$ definitely belongs to class A, it appears to differ significantly also in other respects from the remaining members of this class. For the well-determined structures of both classes A and B, there are two short and four longer $T-X$ bond distances, while $CrSb_2$ shows the opposite (four and two) tendency. Obviously, the change in the grouping of the $T-X$ bond distances for $Cr_tFe_{1-t}Sb_2$ must be reflected in Δ. In addition, the increasing magnitude of the average $T-X$ bond distances for increasing t must also have an effect on Δ. Further speculations concerning the interpretation of the quadrupole splittings for these phases must await the results of currently conducted studies on $Cr_tFe_{1-t}X_2$ by supplementary techniques.

The dependence of Δ on t for $Fe_{1-t}Co_tX_2$ shows (as was the case for δ) apparently constant values in the vicinity of CoX_2. The earlier assumption of $T-T$ bonding as the cause [8,10,19,23–25] of the structural distortion from the FeS_2-*m* to the $CoSb_2$ type structure should, if real, indeed be reflected in Δ and δ. Since such a correlation is not observed, this assumption must accordingly be considered as questionable.

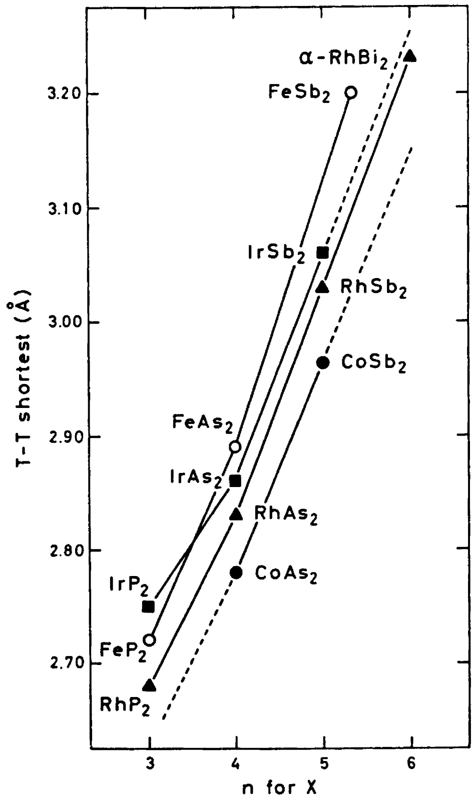

Fig. 6. Shortest $T-T$ distances *versus* principal quantum number (n) for X in TX_2 compounds with $CoSb_2$ type (●,▲,■) and three class A members of the FeS_2-*m* type (○) structures.

(vi) *On problems concerning the $CoSb_2$ type structure.* In order to approach the crucial problems concerning the $CoSb_2$ type structure, it is necessary to reexamine data accumulated for compounds of this type.

Fig. 6 shows the dependence of the shortest $T-T$ distance in the binary compounds with the $CoSb_2$ type structure (*cf.* Ref. 10) on the principal quantum number (n) for X. The series FeP_2-$FeAs_2$-$FeSb_2$, where the shortest $T-T$ distance equals the length of c in their FeS_2-*m* type structure, is included for the purpose of comparison. Although a variation in $T-T$ (as in $X-X$) bond length from compound to compound is expected, the dependence brought out in Fig. 6 shows marked and consistent trends. Even more striking is the fact that the curves for compounds with the $CoSb_2$ type structure show parallel behaviours to that for the comparison series FeP_2-$FeAs_2$-$FeSb_2$. This observation indicates that essentially the same effects are responsible for variations in shortest $T-T$ distances in compounds with the $CoSb_2$ as well as the class A, FeS_2-*m* type structure.

By qualitative bond strength arguments of the type presented in Ref. 27, the opposite trend to that shown on Fig. 6, *viz.* decreasing $T-T$ bond lengths with increasing n for X, is to be anticipated. (The P–P and T–P bonds should expectedly be stronger than (say) Bi–Bi and T–Bi bonds, and consequently, lead to weaker (longer) $T-T$ bonds for compounds of P compared to those of Bi.)

The ratios c/a and c/b (Fig. 1) for $CoAs_2$ and $CoSb_2$ fit nicely on to the curves traced out for phases with the FeS_2-*m* type structure. The c' axis of the pseudo-marcasite variant of the $CoSb_2$ type cell may be interpreted (*cf.*, *e.g.*, Ref. 18) as the average of a short and a long $T-T$ distance within the approximately linear T chains. The main structural distortion of CoX_2 compared with $Fe_{0.5}Ni_{0.5}X_2$ concerns just these alternating short and long $T-T$ distances, notably without producing a resultant shortening in the former case. Indeed, the formation of pairs with internal $T-T$ bonding in the $CoSb_2$ type structure should expectedly be accompanied by a marked shortening of c'.

In order to substantiate this inference, further attention should be focused on the T chains along $c(c')$ in $Fe_{1-t}Co_tX_2$. The mere fact that these phases gradually transform from FeS_2-*m* to $CoSb_2$ type structure with increasing *t* is in itself (at least to some extent) incompatible with the assumption of bonded $T-T$ pairs as the stabilizing element in the latter. Depending on *T* there are three kinds of $T-T$ "contacts" (*viz.* Co – Co, Co – Fe, and Fe – Fe nearest neighbours). If only Co – Co "contacts" are bonding, how should the others be interpreted? The further assumption of Co – Fe and Fe – Fe bonds is contradicted by a number of evidences and their rejection contradicts even the basic assumption of $T-T$ bonding as the stabilizing element of the $CoSb_2$ type structure. In order to remedy these *de facto*, inherent contradictions, a statistical approach was proposed,[8] showing that a certain amount of the Co atoms in CoX_2 may be tolerated replaced by Fe without destroying the basic stability of the $CoSb_2$ type structure. However, even if this statistical approach to the $T-T$ bond is accepted, the problem still lies in the interpretation of the Co – Fe and Fe – Fe "contacts". By assuming a statistical distribution of these "contacts", relatively large defects (*viz.* nonbonding "contacts") would occur, which appears incompatible with an essentially localized model implied by isolated Co – Co pairs. It seems on the contrary, more reasonable that the stabilizing effect for the $CoSb_2$ type atomic arrangement is transmitted through *all* participating *T* atoms. A basically itinerant model has no difficulties in explaining randomly distributed Co – Co, Co – Fe, and Fe – Fe "contacts". The alteration in starting point does not invalidate the statistical considerations advocated in Ref. 8, which, in reality, did not include specific assumptions about the bonding characteristic of Co *versus* Fe.

The shortest Fe – Fe distance in the structure of FeAsS (arsenopyrite)[28] is 2.89 Å, and can be compared with 2.72 Å and 2.88 Å for FeP_2 and $FeAs_2$, respectively. Hence, the claim of one Fe – Fe bond per Fe in FeAsS, appears to suggest the existence of two Fe – Fe bonds per Fe in FeP_2 and $FeAs_2$. This would in turn demand a delocalization of electrons in infinitely bonded *T* chains along *c* for the latter compounds. Since the $T-T$ bonding assumption for compounds with class A, FeS_2-*m* type structure has been rejected (*cf.* Ref. 18; the points being elaborated further in a forthcoming paper), an identical conclusion appears to be appropriate also for FeAsS.

The preceding considerations have hopefully demonstrated that there are no clear-cut structural evidences in favour of $T-T$ bonding in compounds with the $CoSb_2$ type structure. The rejection of $T-T$ bonding naturally provokes an alternative interpretation of the generally semiconducting and diamagnetic behaviours within this class of compounds, an aspect which has been taken up by Goodenough.[20] Unfortunately, his treatment merely represents a translation of the earlier assumed [19,23] splitting of non-bonding *d* orbitals (*viz.* resulting in $T-T$ bonding and anti-bonding orbitals), into splitting (still unsubstantiated) of a narrow $T-X$ anti-bonding *d* band (*viz.* resulting in a $T-X$ bonding and an anti-bonding band). The cause of the splitting and hence, the distortion from the FeS_2-*m* to the $CoSb_2$ type structure, therefore, still remains to be found.

Emancipation from the assumption of $T-T$ bonding in compounds with the $CoSb_2$ type structure, entitles a clarifying comment on recently published [30] ^{121}Sb Mössbauer data. Originally, the chemical shift data for the compounds $CoSb_2$, $RhSb_2$, and $IrSb_2$ were not examined in detail because of the constraints supposedly imposed on their properties due to $T-T$ bonding. When ^{121}Sb Mössbauer chemical shifts are plotted for the three series $FeSb_2$-$CoSb_2$-$NiSb_2$, $RuSb_2$-$RhSb_2$-$PdSb_2$, and $OsSb_2$-$IrSb_2$-$PtSb_2$, curves of mutually similar appearance are obtained. It is notable that the three curves show marked peaks for compounds with the $CoSb_2$ type structure. These peaks can be made to disappear when chemical shifts are plotted against the (perhaps more natural parameter) Sb – Sb bond length. Within the limits of accuracy of the Sb – Sb bond lengths,[11,31–34] the thus resulting plot shows a linear relationship of decreasing chemical shift with increasing Sb – Sb bond length.

(vii) *Concluding remarks.* In the preceding paper,[11] class-wise correlations between positional parameters for well-determined structures of the FeS_2-*m* type were noted. Similar correlations between the ^{57}Fe Mössbauer parameters (δ, Δ) may also be expected. Thus, dependences somewhat similar to those found in Ref. 11 (*cf.* also Ref. 29) are shown on Fig. 7. It is to be noted that the points for the quasi-

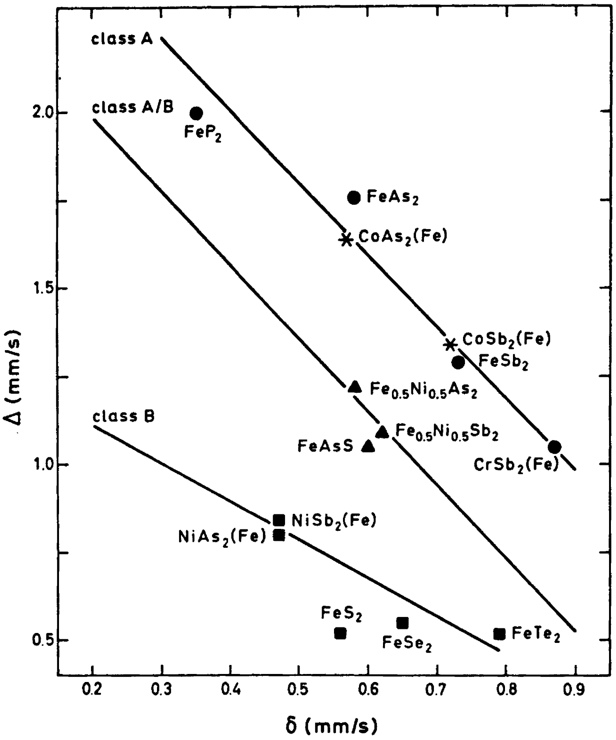

Fig. 7. ^{57}Fe Mössbauer parameters (δ and Δ) for some phases with FeS$_2$-*m* like structures.

binary compounds CoAs$_2$(Fe) and CoSb$_2$(Fe) occupy unexpected positions (marked with asterisks) on the diagram, suggesting that they belong to class A with respect to Mössbauer parameters.

The main purpose of this paper has been to present ^{57}Fe Mössbauer data for the phases $Cr_tFe_{1-t}X_2$, $Fe_{1-t}Co_tX_2$, and $Fe_{1-t}Ni_tX_2$. In attempts to interprete these data, results of supplementary experimental techniques have been consulted and/or called for. Moreover, since fruitful discussion in this field must draw heavily on theoretical model considerations, consultations of existing models were inescapable. At the present stage of development it was considered worthwhile to consult the model(s) presented by Goodenough,[20] earlier models being uninteresting since he has claimed that they all contain defects. As inferred *inter alia* on comparison with the Mössbauer data, not even Goodenough's treatment is free from inherent shortcomings. In order to improve on Goodenough's model(s), a critical reexamination of the basic bonding assumptions is necessary. This will be the subject of a forthcoming paper.

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