

# $^{57}\text{Fe}$ Mössbauer Studies of $\text{Fe}_{1-t}\text{T}_t\text{As}$ Phases with MnP Type Structure

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Room temperature  $^{57}\text{Fe}$  Mössbauer data for the ternary  $\text{Fe}_{1-t}\text{T}_t\text{As}$  phases ( $T = \text{V}, \text{Cr}, \text{Mn}, \text{or Co}$ ) are reported and discussed in relation to their MnP type structure.

A comprehensive research programme on binary and ternary phases with the MnP type structure has been carried out to gain insight into their chemical bonding situation and to elucidate the factors governing the MnP *versus* NiAs type relationships. In the present work, solid solutions of the type  $\text{Fe}_{1-t}\text{T}_t\text{As}$  ( $T = \text{V}, \text{Cr}, \text{Mn}, \text{or Co}$ ) have been investigated by Mössbauer spectroscopy at room temperature in order to study the variation of the  $^{57}\text{Fe}$  Mössbauer parameters with composition.

## EXPERIMENTAL

The samples were prepared as described in Refs. 1–5, their homogeneity being ascertained from powder X-ray (Guinier) photographs. Details concerning the  $^{57}\text{Fe}$  Mössbauer experiments (at room temperature) and data reduction are given in Ref. 6. Chemical shift values are reported relative to  $\text{Na}_2[\text{Fe}(\text{CN})_6\text{NO}] \cdot 2\text{H}_2\text{O}$  which was run before and after each sample and also used for velocity calibration.

## RESULTS AND DISCUSSION

The  $^{57}\text{Fe}$  Mössbauer chemical shift ( $\delta$ ) and quadrupole splitting ( $\Delta$ ) parameters for the  $\text{Fe}_{1-t}\text{T}_t\text{As}$  phases are shown in Fig. 1, the present values for FeAs being in reasonable agreement with those given in Refs. 7 and 8. The interval of  $t$  values studied varies: for

$T = \text{Mn}$  the two-phase field of the MnAs–FeAs system constitutes the limitation ( $0 \leq t \leq 0.35$ ),<sup>8</sup> whereas the inherent statistical fluctuations (due to the lowered Fe-content) prevented unambiguous data reduction for large  $t$  in the other systems.

The overall decreasing tendency in  $\delta$  on going from the left to the right of FeAs on Fig. 1 may be given an analogous interpretation to that proposed for the  $\text{CrX}_3$ – $\text{FeX}_3$ – $\text{NiX}_3$  ( $X = \text{As}$  or  $\text{Sb}$ ) series in Ref. 9. This implies that there should occur an effective transfer of  $d$  electron density (through the  $T$ –As bonds) from  $T = \text{V}, \text{Cr}, \text{or Mn}$  to Fe and from Fe to  $T = \text{Co}$ . The interpretation allows the metal atoms, randomly distributed over the metal sublattices, to be of adjustable size, and concurs with the decreasing average metal–non-metal bond lengths that must be established (*viz.* as inferred from structural data in Refs. 1–5, 10–12) in the series VAs–FeAs, CrAs–FeAs, MnAs–FeAs, and FeAs–CoAs. In addition to the more indirect effective transfer of electrons through the metal–non-metal bonds, the MnP type structure (as opposed to the  $\text{FeS}_2$ -*m* type discussed in Ref. 9) permits adjustments of the  $d$ -electron distribution through the direct metal–metal exchange routes in the atomic arrangement.

The parameter  $\Delta$  reflects the degree of asymmetry of the overall electron density around the observer nuclei. A detailed account of  $\Delta$  requires a comprehensive knowledge of the electronic states, and the very qualitative band structure information on phases with the MnP type structure will necessarily give the following discussion a rather speculative character.

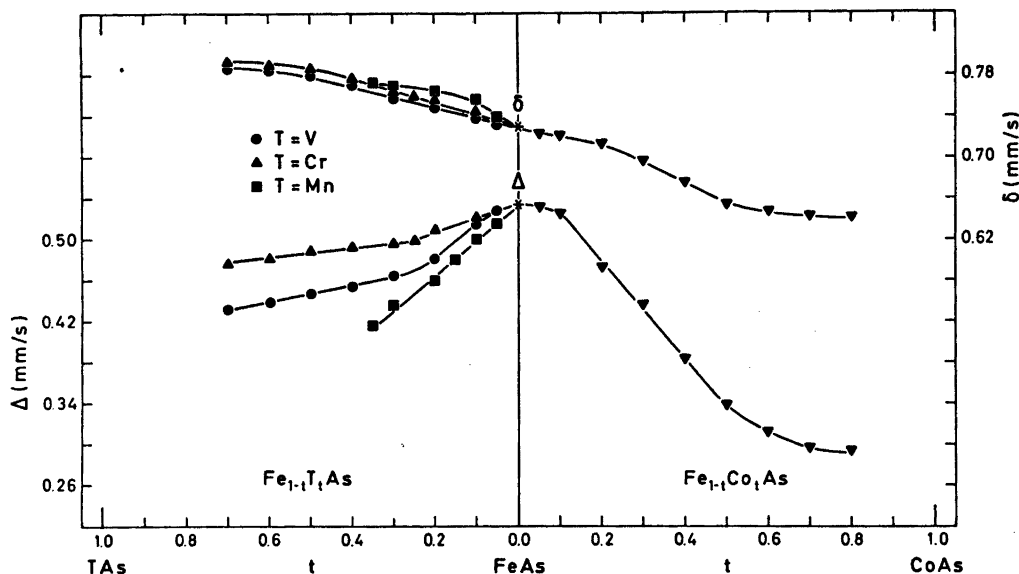


Fig. 1. Variation in <sup>57</sup>Fe Mössbauer chemical shift ( $\delta$ ) and quadrupole splitting ( $\Delta$ ) parameters with composition for  $\text{Fe}_{1-t}\text{T}_t\text{As}$  at room temperature. Estimated error limits do not exceed size of symbols.

In fact, even more crucial parameters for the interpretation, such as number of unpaired electrons in the paramagnetic state ( $2S$ ; "spin only" approximation) and the intra-atomic exchange splitting energy ( $E_{\text{ex}}$ ), are lacking for the phases in question.

The influence on  $\Delta$  by delocalized electrons must be comparatively small since these spend less time near the observer nuclei than localized. For the MnP type phases in particular, it should also be recalled that binary as well as ternary representatives show remarkable constancy in the unit cell proportions and positional parameters.<sup>13</sup> Moreover, due to the similarity in atomic arrangement, any difference in the effective atomic charges (which may be crucial in relation to  $\delta$ ) gives rise to only second order effects in the overall electronic asymmetry. Since contributions from localized bonding electrons in MnP type phases are likely to be insignificant, the variation in  $\Delta$  must arise from corresponding distinctions in the metal-metal interactions and/or the non-bonding electrons on the metal atoms.

General band theoretical considerations as well as experience from special cases, suggest that bands representing metal-non-metal in-

teractions are broad for both binary and ternary phases. On turning from binary to ternary MnP type phases, the band structure parameters that describe the bonding characteristics, may undergo changes which are compatible with the assumption of "averaged" metal atoms, as outlined in Ref. 9. Corresponding considerations lead to the suggestion that non-bonding states are to be represented by narrow bands, this common picture being somewhat modified for the MnP type phases for which the metal-metal interactions lead to broadening of the bands designated as "non-bonding" (cf. the discussion on MnAs in Ref. 14). In situations where the term "non-bonding" is fully applicable, no distinction between well defined compounds and solid solution phases is needed. Even in cases where the "non-bonding" states are not strictly non-bonding (e.g. resulting from perturbations due to metal-metal interactions as in MnP type phases), band descriptions for the binary end members cannot be mixed into an average "non-bonding" band picture for a given ternary composition. On the contrary, the "non-bonding" states of the  $\text{Fe}_{1-t}\text{T}_t\text{As}$  phases may be assumed to maintain much of their original

identity as FeAs and  $T$ As states in the ternary composition region.

The use of ionic formulae provides a convenient tool in the evaluation of valence states even in cases where a covalent description should be more adequate (*cf.*, *e.g.*, Ref. 15). Thus, for phases with the MnP type structure, a valence state of three appears reasonable for the metal component (three electrons per metal atom engaged in metal–non-metal bonding). One therefore arrives at 2, 3, 4, 5, and 6 “non-bonding”  $d$  electrons for V, Cr, Mn, Fe, and Co in their monoarsenides. (This assumption concurs with that of Menyuk *et al.*<sup>14</sup> for MnAs.) Essentially the same number of “non-bonding” electrons must be associated with the individual metal atoms throughout the solid solution series. This constitutes a constraint on the mixing of bands in the ternary regions.

One factor which greatly influences the “non-bonding  $d^5$  manifold” for Fe in  $Fe_{1-t}T_tAs$  is the parameter  $E_{ex}$ , which is reflected in the number of unpaired electrons. (Data referring to cooperative states are used below.) Following the schematic one-electron band description given for MnAs by Menyuk *et al.*<sup>14</sup>, the situation in VAs and CoAs is assumed to be governed by  $E_{ex} \approx 0$ , whereas  $E_{ex} \neq 0$  for CrAs, MnAs, and FeAs. Thus, the substitution of V or Co for Fe in FeAs may simulate a decrease in  $E_{ex}$  of FeAs, leading to a gradually more symmetrical (*viz.* with respect to  $\alpha$  and  $\beta$  spin splitting, *cf.* Fig. 13 in Ref. 14) population of the Fe “ $d^5$  manifold”. The substitution of Cr or Mn for Fe in FeAs is, on the other hand, expected to increase  $E_{ex}$  of FeAs. Starting from the hypothetical FeAs band diagram, an increase in  $E_{ex}$  will lift the energies of the  $\beta$  spin states, thus promoting a more complete filling of the  $\alpha$  spin states, and consequently a more symmetrical distribution of the “non-bonding” electrons of Fe. The decreasing tendency of  $\Delta$  with  $t$  for all four  $Fe_{1-t}T_tAs$  phases is accordingly explicable on the basis of this type of band model consideration. The individuality of the curves reflects distinctions in the population and symmetry of the “ $d^5$  manifold”.

The present discussion for the <sup>57</sup>Fe Mössbauer parameters of  $Fe_{1-t}T_tAs$  is, in principle, also applicable to the corresponding data for  $Fe_{1-t}T'_tP$  ( $T' = W, Mn, \text{ or } Co$ ) given in Ref. 7.

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