On the Crystallographic Phase Transformation in $Mn_{0.9}Fe_{0.1}As$

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Some phases which have the orthorhombic MnP type crystal structure at room temperature transform continuously to the hexagonal NiAs type at higher temperatures.[1] The former type may be regarded as a distorted variant of the latter, the distortion of the atomic arrangement being completed when the positional parameters z_T (T: metal) and x_X (X: non-metal) both have reached a value of ~ 0.20, as compared with 1/4 in the orthohexagonal NiAs cell, with setting according to *Pnma*. The positional parameters x_T and z_X take value of ~ 0 and $\sim 7/12$, respectively, in both structure types.

The purpose of the present communication is to report the *simultaneous* variations in positional parameters and unit cell dimensions over a complete transformation interval between the MnP and NiAs type structures. Previous studies have either concerned the temperature dependence of the unit cell dimensions or the positional parameters. An idea of the behaviour of the structural variables during transformation can be obtained by comparing the data for the unit cell proportions of $MnAs_{0.9}P_{0.1}$ by Ido [2] with the positional parameters z_T and x_X of $MnAs_{0.92}P_{0.08}$ by Hall *et al.*[3]

Several factors are of importance in the selection of suitable candidates for such a study. When the sample is in a polycrystalline state, the neutron diffraction technique is best fitted for the purpose in view of the convenient profile refinement procedure,[4] which evaluates all structural variables simultaneously. $Mn_{0.9}Fe_{0.1}As$ was chosen due to its relatively low transformation temperature. This phase has previously been subjected to a detailed neutron diffraction study of its cooperative magnetic properties at low temperatures ($T_N = 206 \pm 1$ K).[5] There is, however, one complicating factor associated with our choice in that the crystallographic transformation in $Mn_{0.9}Fe_{0.1}As$ is accompanied by a change of Mn from a "high spin" state in the region where the NiAs type structure prevails, to a "low spin" state in the MnP type region.[5] (A similar behaviour is found for other Mn-rich $Mn_{1-t}T_tAs$ phases.) This change in electronic state of the Mn atoms results in a distinct volume change of the MnP type unit cell during the transformation, as opposed to the situation in, *e.g.*, CrAs and CoAs.[1]

The variation above room temperature of the relative intensity (background subtracted) of the characteristic reflection 101 of the MnP type cell of $Mn_{0.9}Fe_{0.1}As$ is shown in the upper part of Fig. 1. According to these data, the transformation ($MnP \rightleftharpoons NiAs$) temperature is determined as 673 ± 20 K, which is considerably higher than that (553 ± 50 K) obtained [1] more qualitatively by X-ray diffraction.

The profile refinement technique was found to be quite suitable up to 560 K. Above this temperature the deviations from the orthohexagonal NiAs symmetry have become too small for a simultaneous refinement of so many coupled parameters.

The refined structural parameters of $Mn_{0.9}Fe_{0.1}As$ are presented in Fig. 1 as $(a/b)_{MnP}$, $(c/a)_{MnP}$, $(c/b)_{MnP}$, x_T, $(1/4 - z_T)$, $(1/4 - x_X)$, and $(7/12 - z_X)$ *versus* temperature. In the range $558 - 673$ K the most probable temperature variations of the parameters are indicated by broken lines. As is clearly evident from the diagram all these variables show a continuous variation through the region of transformation, thus confirming that the transition is of second or higher order. The virtually parallel behaviour of z_T and x_X presents additional confirmation of the geometrical model outlined in Ref. 1. The transformation interval is seen to extend over some 500 K which is appreciably larger than in $MnAs_{0.9}P_{0.1}$ (~ 200 K [2,3]). When expressing the data in terms of a reduced temperature variable, $T/T_{trans.}$, it is also found that the transformation characteristics are no universal function. The latter inference is furthermore supported by the more qualitative data for CrAs and CoAs.[1]

Unfortunately, the relatively sparse neutron diffraction data at each temperature do not permit an evaluation of anisotropic temperature factors. The latter type of data would be of considerable interest in relation to the question of whether the "soft modes" formalism can describe the kinetics of this transformation.

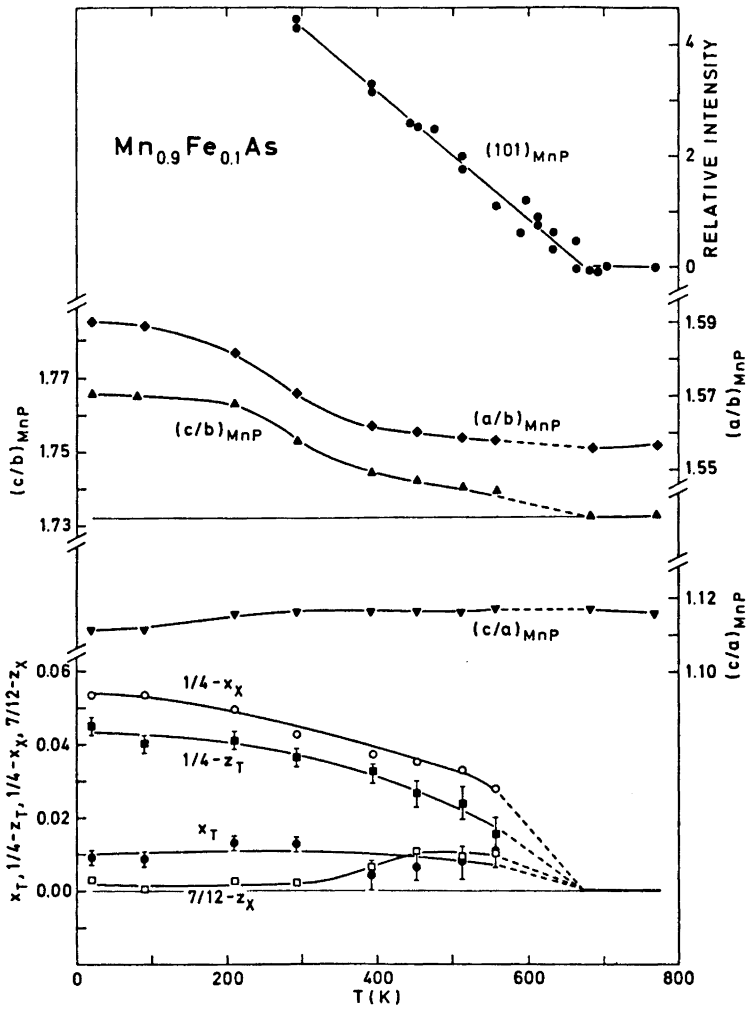

Fig. 1. Relative intensity of $(101)_{MnP}$, $(a/b)_{MnP}$, $(c/a)_{MnP}$, $(c/b)_{MnP}$, x_T, $(1/4-z_T)$, $(1/4-x_X)$, and $(7/12-z_X)$ for $Mn_{0.9}Fe_{0.1}As$ as functions of temperature. Error bar gives estimated standard deviation when this exceeds size of symbol.

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