On the Structural and Magnetic Properties of $V_{1-t}Fe_tAs$

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The pseudo-binary VAs-FeAs system has been investigated by X-ray diffraction, magnetic susceptibility, and magnetization measurements. VAs and FeAs are completely soluble in each other, and the structure of the ternary, random solid solution phase is of the MnP type. The paramagnetic susceptibilities do not follow the Curie-Weiss Law over an appreciable range of temperature for any of the ternary samples.

The present contribution on the structural and magnetic properties of the $V_{1-t}Fe_tAs$ phase is a link in continued studies at this Institute on ternary phases with the MnP type structure. The properties of VAs and FeAs have been reported earlier.[1-4]

EXPERIMENTAL

Samples of VAs and FeAs were prepared by heating weighed quantities of the elements (99.5 % V (A. D. Mackay), 99.99 % Fe (Johnson, Matthey & Co; turnings from rods), and 99.9999 % As (Koch-Light Laboratories)) in evacuated, sealed quartz tubes, as described in Refs. 1 − 3. The desired $V_{1-t}Fe_tAs$ samples were prepared by mixing appropriate proportions of VAs and FeAs and subjecting the mixtures to a series of annealings at 850 °C, interrupted by intermediate crushings. The samples were finally cooled to room temperature over a period of 3 days.

The experimental details concerning X-ray diffraction, magnetic susceptibility, and magnetization measurements have been presented in Refs. 2 and 3.

RESULTS

The orthorhombic unit cell dimensions of $V_{1-t}Fe_tAs$ (as determined from room temperature X-ray powder diffraction (Guinier) diagrams) are presented in Fig. 1 as functions of t.
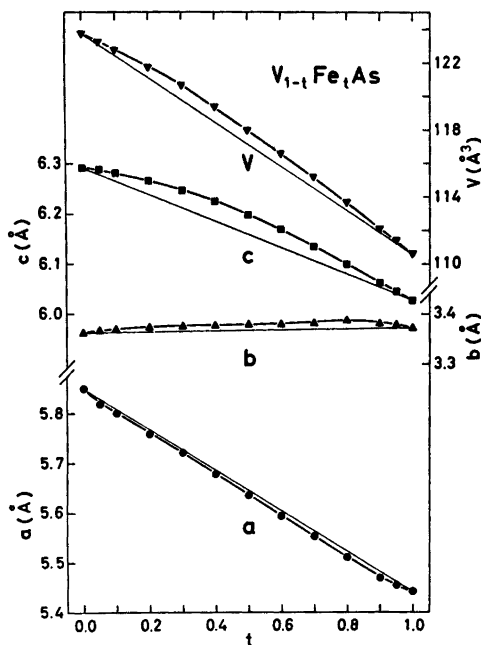
Fig. 1. Unit cell dimensions of the ternary solid solution series VAs-FeAs as functions of composition.

The continuous variations in all unit cell dimensions with composition, from $t = 0$ to $t = 1$, show that VAs and FeAs are completely soluble in each other. The curves for a and b follow closely Vegard's Law over the whole range of t-values. The well defined stoichiometric nature of both VAs and FeAs has been confirmed earlier.[1,3] The possibility of an extension of the homogeneity range of $V_{1-t}Fe_tAs$ to metal/non-metal (atomic) ratios different from 1.00 has not been examined for $t \neq 0$ and 1, and, thus, cannot be excluded.
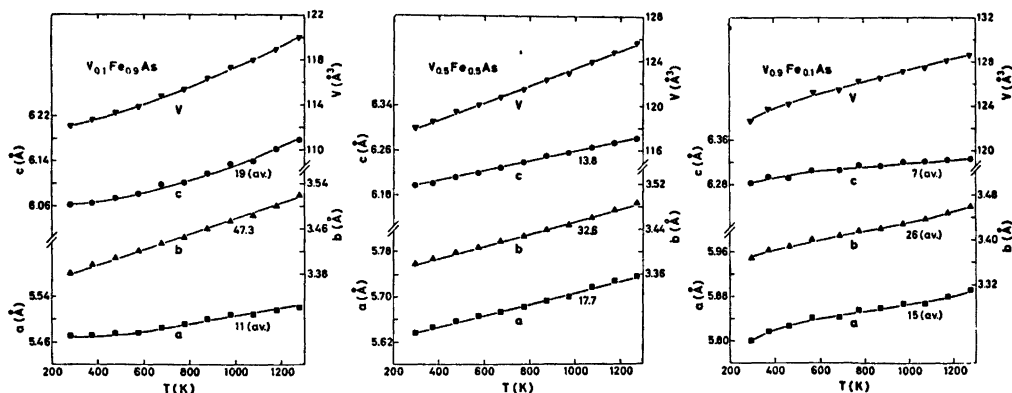
Fig. 2. Unit cell dimensions of three $V_{1-t}Fe_tAs$ samples as functions of temperature. The relative expansion coefficients $\alpha_a (= (a_T - a_{T'})/a_{300}(T - T'))$ α_b, α_c multiplied by 10^6 K are positioned below the appropriate curves. Corresponding triplets for VAs and FeAs are 12.2, 20.8, 7.7, and 11 (av.), 44 (av.), 22 (av.), respectively, *cf.* Ref. 5.

The MnP type structure, with random distribution of the two kinds of metal atoms, is easily confirmed for the $V_{1-t}Fe_tAs$ phase (0.00 $\leqq$ $t \leqq 1.00$) at room temperature. In order to examine whether the phase undergoes a crystallographic transformation to the NiAs type structure at higher temperatures, three representative samples with compositions $t = 0.10$, 0.50, and 0.90 were studied in the interval 293 – 1273 K. In conformity with earlier data for VAs [5] and FeAs [2] no such transformation was observed. The unit cell dimensions for the three samples as functions of temperature are shown in Fig. 2. The relative, linear expansion coefficients of the samples are included on the diagram. Also these parameters are seen to vary continuously with t.

The reciprocal magnetic susceptibility curves for different $V_{1-t}Fe_tAs$ samples are shown as functions of temperature in Fig. 3. No field strength dependent susceptibilities were observed. It is seen that the $\chi^{-1}(T)$ curve for $t = 0.00$ is unique. The characteristics for $0.1 \leqq t \leqq 0.9$ are very similar, and none of these curves is seen to obey the Curie-Weiss Law relationship over an appreciable temperature range. There is a gradual progression in the data as evidenced by the reduction in χ^{-1} with increasing t. This trend is interrupted in the vicinity of $t = 0.8$ where the overall value of χ^{-1} begins to increase, and the shape of $\chi^{-1}(T)$ undergoes gradually more and more rapid
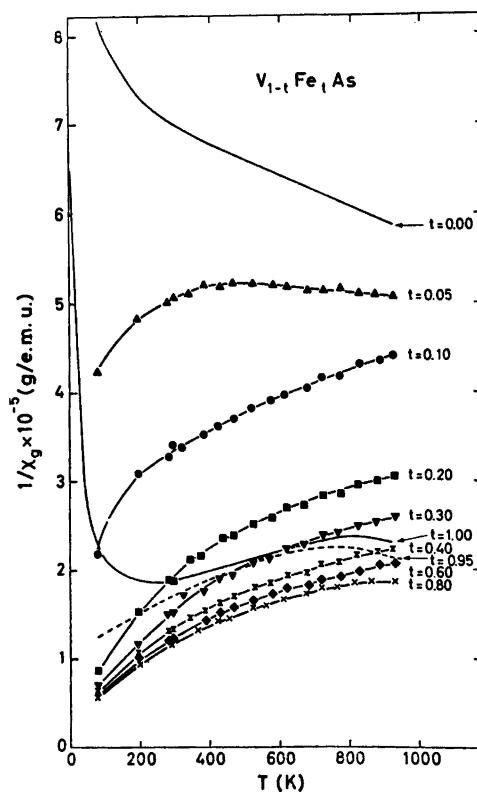

Fig. 3. Reciprocal magnetic susceptibility *versus* temperature for various $V_{1-t}Fe_tAs$ samples.

changes until $t = 1.00$. The latter variation is somewhat peculiar, and, if it had not been for the definite resemblance between curves for $t = 0.95$ and 1.00 (data points omitted in Fig. 3 for clarity), one would have been tempted to search for experimental errors.

The rapid change in characteristic near $t = 1.00$ suggests that small amounts of VAs have radical effects on the electronic band structure of FeAs. The fact that the $\chi^{-1}(T)$ curve for $t = 0.95$ continues to fall below $T = \sim 200$ K (as opposed to that for $t = 1.00$) indicates that the helimagnetic ordering in FeAs [2] may be destroyed already with a small substitution of V for Fe. (A corresponding observation has, more surprisingly, been made for $Mn_{0.05}Fe_{0.95}As$.[6]) In view of the very small ordered moment, corresponding to 0.5 unpaired electron per metal atom, in FeAs it has been considered worthless to prepare large scale samples of $V_{1-t}Fe_tAs$ for neutron diffraction experiments.

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