Structural and Magnetic Properties of $V_{1-t}Ti_tAs$

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The pseudo-binary $V_{1-t}Ti_tAs$ phase was investigated by X-ray diffraction, differential scanning calorimetry and magnetic susceptibility measurements. For slowly cooled samples, examined at room temperature, the MnP type structure prevails from $t = 0.00$ to 0.23 ± 0.03 and from $t = 0.37 \pm 0.03$ to 0.495 ± 0.005, the NiAs type from $t = 0.495 \pm 0.005$ to 0.77 ± 0.02 and the TiP type from $t = 0.97 \pm 0.02$ to 1.00. Non-equilibrium conditions (probably originating from a tendency to ordering of the V and Ti atoms within the metal sublattice) rule the interval $0.23 \pm 0.03 < t < 0.37 \pm 0.03$, whereas the interval $0.77 \pm 0.02 < t < 0.97 \pm 0.02$ represents a two phase region. A first order MnP to NiAs type transition was observed for $0.40 < t < 0.50$. $V_{1-t}Ti_tAs$ belongs to the gross category of Pauli paramagnetic materials.

The MnP $\rightleftarrows$ NiAs type phase transition has frequently been observed as function of composition,[1,2] temperature,[3,4] pressure [5] and magnetic field.[6] The present authors have recently reported[2] on the properties of the $Cr_{1-t}Ti_tAs$ phase where the temperature (T_D) for the second order MnP $\rightleftarrows$ NiAs type transition was found to vary almost linearly with the compositional parameter t. The situation for $V_{1-t}Ti_tAs$[7] appears to be similar, but the information concerning the latter phase is a little scanty. The purpose of the present communication is to remedy this situation by reporting on the VAs–TiAs system between 100 and 1300 K.

Experimental

TiAs was synthesized from 99.97% Ti (sponge; Johnson, Matthey & Co.) and 99.9999% As (lumps; Koch-Light Laboratories) as described in Ref. 2. VAs was made by heating weighed quantities of the elements (V, 99.5%, powder; A. D. Mackay) in evacuated, sealed silica tubes. After heat treatment at 900 °C for 5 d, the samples were cooled to room temperature, carefully ground and subjected to two further similar heat treatments (with intermediate crushings). The ternary $V_{1-t}Ti_tAs$ samples were prepared by mixing appropriate proportions of VAs and TiAs and subjecting the mixtures to annealings at 1000 to 1100 °C for 2 to 4 periods of 7 d with intermediate grindings. After the final heating cycle the samples were slowly cooled to room temperature over 1 d. Selected samples from the composition range $0.20 \le t \le 0.40$ were quenched in ice water from different temperatures between 850 and 1100 °C. The homogeneity and structural state of the samples were evaluated from room temperature powder X-ray diffraction data (Guinier technique, CuKα_1-radiation, Si as internal standard). High and low temperature powder X-ray diffraction data were obtained in an Enraf-Nonius Guinier Simon camera at temperatures between 100 and 1300 K. Unit cell dimensions were obtained through least squares refinements of the positions of approximately 20 well-defined Bragg reflections. Unknown powder X-ray diffraction patterns were attempted computer indexed by the TREOR programme.[8] Powder X-ray diffraction intensity data were derived from the Guinier photographs by means of a Nicolet filmscanning system L 18. The thus obtained integrated intensities were least squares processed by the SHELX programme[9] to extract values for the po-

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sitional parameters of the metal and non-metal atoms.

Differential scanning calorimetry (DSC) measurements were performed between 100 and 900 K using a Mettler TA 3000 system. Magnetic susceptibility data were recorded with a conventional Faraday magnet (maximum field ~8 kOe; 25–35 mg samples) between 80 and 1000 K.

Results and discussion

The binary end phases of $V_{1-t}Ti_tAs$ take the MnP ($t = 0.00$[10]) and TiP ($t = 1.00$[11]) type structures. In this way $V_{1-t}Ti_tAs$ resembles $Cr_{1-t}Ti_tAs$.[2] The phase relationships for $V_{1-t}Ti_tAs$ (at room temperature; for slowly cooled samples) marked at the bottom of Fig. 1 reveal similarities as well as distinctions when compared with the $Cr_{1-t}Ti_tAs$ case.
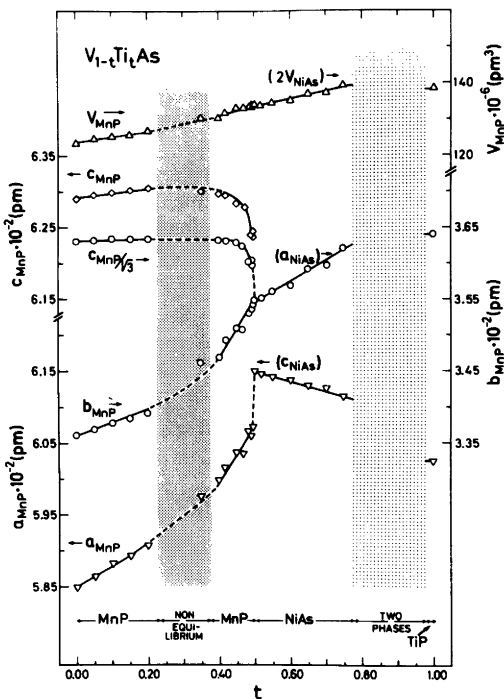

Fig. 1. Unit cell dimensions of $V_{1-t}Ti_tAs$ at 293 K. Data for MnP and NiAs type phases refer to *Pnma* setting: $a_{MnP} = c_{NiAs}$; $b_{MnP} = a_{NiAs}$; $c_{MnP} = 2a_{NiAs} + b_{NiAs}$. Data for TiP type phase show $c_{TiP}/2$ and $V_{TiP}/2$. *Calculated* error limits do not exceed size of symbols. Structural state is indicated at the bottom of the illustration.

The domain of the MnP type structure appears to be divided in two separated homogeneity ranges ($0.00 \leq t \leq 0.23 \pm 0.03$ and $0.37 \pm 0.03 \leq t \leq 0.495 \pm 0.003$) by a region ($0.23 \pm 0.03 \leq t \leq 0.37 \pm 0.05$) which seems to be ruled by conditions which give rise to non-equilibrium samples (*vide infra*). Sobczak *et al.*[7] did not apparently encounter any preparative difficulties within the existence range of the MnP type phase (but they report no X-ray data for $0.20 < t < 0.40$). As a more subtle distinction it may be mentioned that Sobczak *et al.* position the phase border at $t = 0.52$ whereas $t = 0.50$ is found to belong to the domain of the neighbouring NiAs type phase in this study. The non-equilibrium region in $V_{1-t}Ti_tAs$ has no parallel in $Cr_{1-t}Ti_tAs$. The shift of the MnP to NiAs type phase border from $t \approx 0.40$ in $Cr_{1-t}Ti_tAs$[2] to $t = 0.495 \pm 0.005$ in $V_{1-t}Ti_tAs$ is correlated with the fact that VAs retains the MnP type structure up to at least ~1400 K whereas CrAs undergoes the MnP $\rightleftarrows$ NiAs type transition at 1173 ± 20 K.[3]

The NiAs type structure rules in the interval $0.495 \pm 0.005 < t \leq 0.77 \pm 0.02$ and a miscibility gap ($0.77 \pm 0.02 < t < 0.97 \pm 0.02$) separates the NiAs and TiP type phase regions. Sobczak *et al.*[7] did not observe the two phase field and they extended the homogeneity range of the NiAs type phase to $t = 1.00$ (*viz.* TiAs). The present authors have searched, without success (see also Refs. 2,12), for the reported[7] (high temperature) NiAs type modification of TiAs. On the other hand, the TiP type structure is unequivocally confirmed for TiAs and this phase extends slightly into the ternary region ($0.97 \pm 0.02 \leq t \leq 1.00$). Hence, there is complete divergence between Ref. 7 and the present study for $0.77 \pm 0.02 < t \leq 1.00$. The extension of the homogeneity range for the TiP type phase is, within the experimental error, equal in $V_{1-t}Ti_tAs$, $Cr_{1-t}Ti_tAs$[2] and $Mn_{1-t}Ti_tAs$,[12] whereas the two phase field between the NiAs and TiP type phases is much wider for the former than for the two others.

With regard to the variation in the unit cell dimensions (referred to *Pnma* setting for the MnP and NiAs type regions) with the compositional parameter t, there are also similarities and differences between $V_{1-t}Ti_tAs$ (Fig. 1) and $Cr_{1-t}Ti_tAs$.[2] The shapes of a_{MnP}, b_{MnP} and V_{MnP} *versus* t in the MnP type phase (all increasing with increasing t) are very similar for $V_{1-t}Ti_tAs$ and $Cr_{1-t}Ti_tAs$, whereas c_{MnP} (or $c_{MnP}/\sqrt{3}$) which relative to b_{MnP}

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starts at a higher value for VAs than for CrAs must be adjusted more for $V_{1-t}Ti_tAs$ than for $Cr_{1-t}Ti_tAs$ to accomplish the MnP to NiAs type conversion. The striking distinction between $V_{1-t}Ti_tAs$ and $Cr_{1-t}Ti_tAs$ in the MnP type region is that the c_{NiAs} ($= a_{MnP}$) axis obtains a singularity maximum at the MnP to NiAs type transition composition. The compositional variations of the unit cell dimensions illustrated in Fig. 1 are judged to be consistent with the sparse structural data published by Sobczak et al.[7]

An interesting inference to be drawn from Fig. 1 is that the non-equilibrium region within the domain of the MnP type phase cannot be rooted in a reluctance of the unit cell dimensions to take values in the intermediate intervals. On the contrary, the voids would be smoothly covered by the broken curve portions in Fig. 1.

The powder X-ray diffraction photographs of the samples from the non-equilibrium region were complex and generally contained a mixture of fairly sharp and rather diffuse reflections. Repeated annealings, prolonged annealing periods, slow cooling and rapid quenching did not improve the situation for most of the samples with $0.20 < t < 0.40$ as judged from X-ray diffraction diagrams. The diagrams could normally be explained as two phase mixtures of phases with compositions corresponding to $t \approx 0.20$ and 0.40. However, some of the samples gave X-ray diffraction diagrams where all reflections were quite sharp. Most of the reflections could in these cases be indexed according to one single MnP type unit cell. The above-mentioned two phase situation could thus be ruled out, and the additional reflections do not appear to originate from other known phases of the V–As and Ti–As systems. Hence, one is left with the possibility that the additional reflections are due to superstructures with ordered long range distributions of V and Ti. Computer indexing of the unknown diffraction patterns by the TREOR programme managed to account for all reflections in terms of monoclinic unit cells. We do not give weight either to the symmetry or the dimensions thus obtained, but take these findings as an additional vague indication of the superstructure hypothesis. The occurrence of the mixture of sharp and diffuse reflections in the X-ray diffraction diagrams for other samples from the non-equilibrium region may also reflect non-uniform distributions of V and Ti over otherwise essentially MnP type metal sublattices. Similar findings have been made for $Mn_{1-t}Ni_tAs$ ($\sim0.25 < t < \sim0.65$), but for the latter case the short and/or long range order obstacles could relatively easily be overcome by trial and error adjustments of the heat treatment procedure.[13] Although the situation for the non-equilibrium region of $V_{1-t}Ti_tAs$ is more tangled, we hope to solve the challenging problems by systematic variation and testing of the preparative conditions.

The axial ratio c_{MnP}/b_{MnP} is often (cf., e.g., Ref. 3) used as a measure for the degree of MnP type distortion relative to the NiAs type structure (where $c_{MnP}/b_{MnP} \equiv \sqrt{3} = 1.732...$). On going from $t = 0.00$ to 0.20 c_{MnP}/b_{MnP} is slightly reduced from 1.872 to 1.860 (at room temperature; 1.852 to 1.838 at 1000 K), whereas there is an appreciable reduction from $c_{MnP}/b_{MnP} = 1.816$ at $t = 0.40$ to $c_{MnP}/b_{MnP} = 1.763$ at $t = 0.495$ (which appears to be single phase with MnP type struc-

Table 1. Unit cell dimensions and positional parameters for $V_{1-t}Ti_tAs$ with $t = 0.00$ (quoted from Ref. 10), 0.10, 0.20, 0.43, 0.47 and 0.52 as derived by least squares refinements of powder X-ray diffraction data collected at room temperature. Space group Pnma; T = V, Ti in 4c and P in 4c. (25–30 reflections; conventional R value 0.06–0.08.) Calculated standard deviations in parenthesis.

t	a_{MnP}(pm)	b_{MnP}(pm)	c_{MnP}(pm)	x_T	z_T	X_{As}	z_{As}
0.00	585.0(1)	336.2(1)	629.2(1)	0.0054(10)	0.1890(4)	0.1969(6)	0.05734(3)
0.10	588.3(2)	338.0(1)	630.0(1)	0.0044(31)	0.1895(25)	0.1948(18)	0.5753(21)
0.20	590.2(2)	340.0(1)	630.5(2)	0.0046(23)	0.1912(22)	0.1983(15)	0.5761(19)
0.43	601.8(2)	349.6(1)	629.6(1)	0.0038(28)	0.1991(28)	0.2172(15)	0.5807(18)
0.47	604.9(1)	352.5(1)	627.8(1)	0.0022(36)	0.2014(33)	0.2192(25)	0.5792(29)
0.52[a]	614.5(1)	355.2(1)	[615.2 (1)]	0	1/4	1/4	7/12

[a] NiAs type structure; $a_{MnP} = c_{NiAs}$; $b_{MnP} = a_{NiAs}$; $c_{MnP} = \sqrt{3} \cdot a_{NiAs}$

ture). $V_{0.500}Ti_{0.500}As$ takes the NiAs type structure at room temperature, but the X-ray diffraction (Guinier) technique is not sufficiently sensitive to exclude the presence of minute amounts of a second phase in the samples with $t = 0.495$ and 0.500. In view of the definitive first order character of the MnP to NiAs type transition for $V_{1-t}Ti_tAs$ with $0.40 < t < 0.50$ as a function of temperature (*vide infra*) a narrow two phase region is expected between the MnP and NiAs type regions (*viz.* the MnP to NiAs type transition is also of first order with respect to composition).

In order to test the connection between the exterior proportions of the MnP type unit cell (*e.g.* as expressed by c_{MnP}/b_{MnP}, *vide supra*) and the interior atomic arrangement, least squares refinements on the basis of powder X-ray diffraction data for $V_{1-t}Ti_tAs$ with $t = 0.10$, 0.20, 0.43, 0.47 and 0.52 (as reference) were carried out. The resulting unit cell dimensions and positional parameters are given in Table 1, together with the corresponding data for VAs quoted from Ref. 10. Within two calculated standard deviations the po-

sitional parameters remain unchanged when the Ti substitution increases from $t = 0.00$ to 0.20, and their values are in the typical range for the fully transformed MnP type structure.[3] This is consistent with the fact that the MnP to NiAs type transition in $V_{1-t}Ti_tAs$ with $0.00 \leq t \leq 0.20$ occurs above ~1300 K (if it takes place at all). The indicator [2,3,14] parameters z_T and x_{As} for the degree of MnP type distortion are closer to the corresponding orthohexagonal converted NiAs type values (*cf.* the data for $t = 0.52$ in Table 1) for $t = 0.43$ and 0.47 than for $0.00 \leq t \leq 0.20$, but their values are still appreciably different from $z_T = x_{As} = 1/4$ required by the NiAs type symmetry. This suggests that the MnP to NiAs type transition temperature for $V_{0.57}Ti_{0.43}As$ and $V_{0.53}Ti_{0.47}As$ is well above room temperature.[2,3]

T_D for the MnP to NiAs type transition in the composition range $0.40 < t < 0.52$ as evaluated from high and low ($t = 0.50$) temperature X-ray diffraction (Guinier Simon) photographs is shown in Fig. 2. T_D decreases almost linearly with t over this concentration span, passes through 293 K at $t = 0.496$ (*viz.* virtually perfect coincidence with the MnP type phase limit determined from the room temperature X-ray diffraction data) and goes to zero at $t \approx 0.53$. It is interesting to note that the value of t for (extrapolated) $T_D = 0$ K is almost identical for $V_{1-t}Ti_tAs$ and $Cr_{1-t}Ti_tAs$,[2] whereas T_D goes to zero at $t \approx 0.24$ for $Mn_{1-t}Ti_tAs$[12] (where, however, the extrapolation stretch is considerably longer).

As illustrated by the thermal expansion data for $t = 0.43$ and 0.485 (Fig. 3), the MnP to NiAs type transition in $V_{1-t}Ti_tAs$ is of first order up to $t \approx 0.490$, whereas the transition for $t = 0.500$ appears to be of second order. For (say) $V_{0.57}Ti_{0.43}As$ the expansion curves for $c_{MnP}/\sqrt{3}$ and b_{MnP} are seen to approach each other in the usual way upon increasing temperature, but at ~650 K (where $c_{MnP}/b_{MnP} = 1.762$) $c_{MnP}/\sqrt{3}$ flattens out and ultimately the first order transition takes place at $T_D = 820 \pm 10$ K. First order MnP to NiAs type transitions are known for MnAs as well as its transition metal substituted derivatives (*cf.*, *e.g.*, Refs. 5, 6, 12, 13), but in these cases the crystallographic transformation is also accompanied by a change of the magnetic state (cooperative to paramagnetic). A magnetic component for the MnP to NiAs type transition in $V_{1-t}Ti_tAs$ (and $Co_{1-t}Ni_tAs$[15]) can be ruled out (*vide infra*). Comparison of interatomic distances
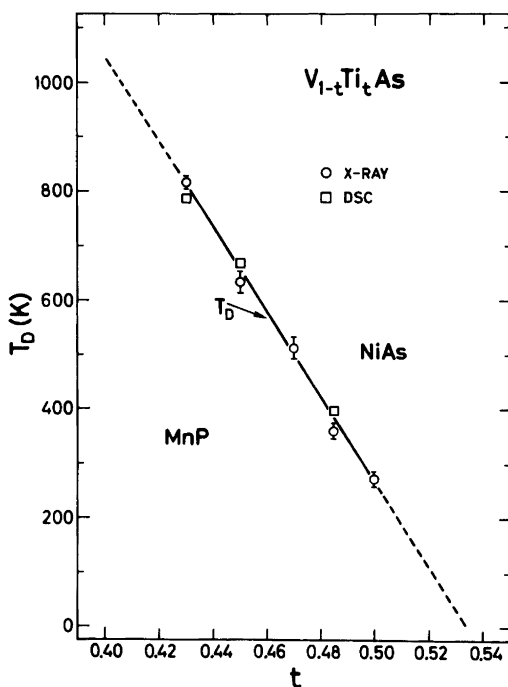

Fig. 2. Variation of T_D with t for $V_{1-t}Ti_tAs$ under increasing temperature conditions. Legends to symbols are given on the illustration.
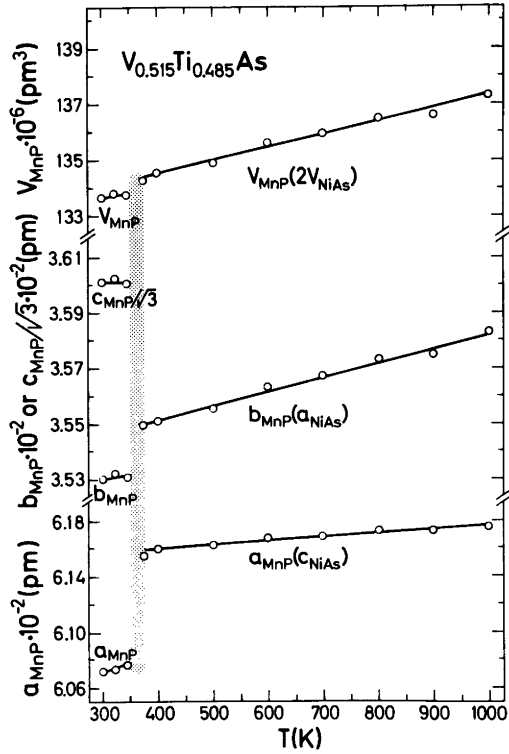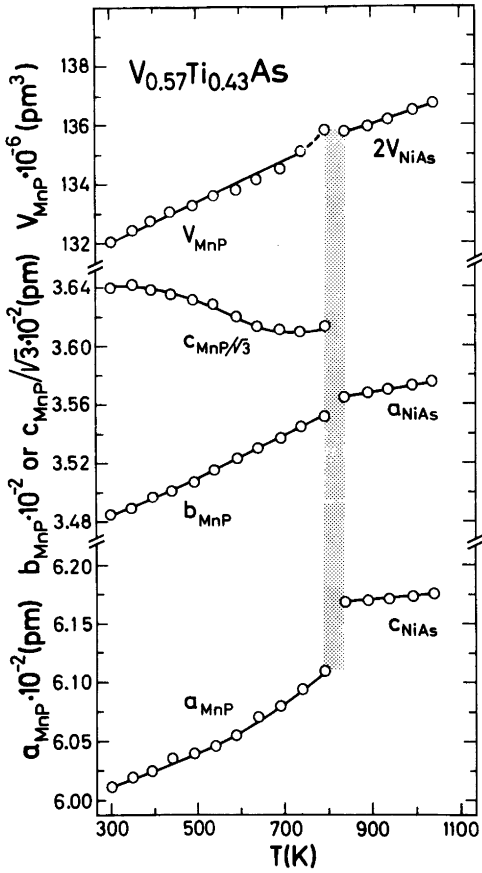
Fig. 3. Temperature dependence of unit cell dimensions for (a) $V_{0.57}Ti_{0.43}As$ and (b) $V_{0.515}Ti_{0.485}As$ between 300 and 1100 K and (c) $V_{0.500}Ti_{0.500}As$ between 90 and 300 K. Calculated error limits do not exceed twice the size of symbol. Hysteresis region of the MnP to NiAs type transition is hatched.

for MnP and NiAs type states above and below T_D for $V_{1-t}Ti_tAs$ and phases where the transition is of second order, gives no clue as to the discontinuous nature of the conversion in $V_{1-t}Ti_tAs$. A possible explanation for the unique standings of $V_{1-t}Ti_tAs$ and $Co_{1-t}Ni_tAs$ could be that no proper MnP to NiAs type transitions occur in these phases, but rather a decomposition of the MnP type phase, followed by recrystallization into the NiAs type structure. The origin of this peculiar behaviour could be a slight difference in composition between the MnP and NiAs type phases,
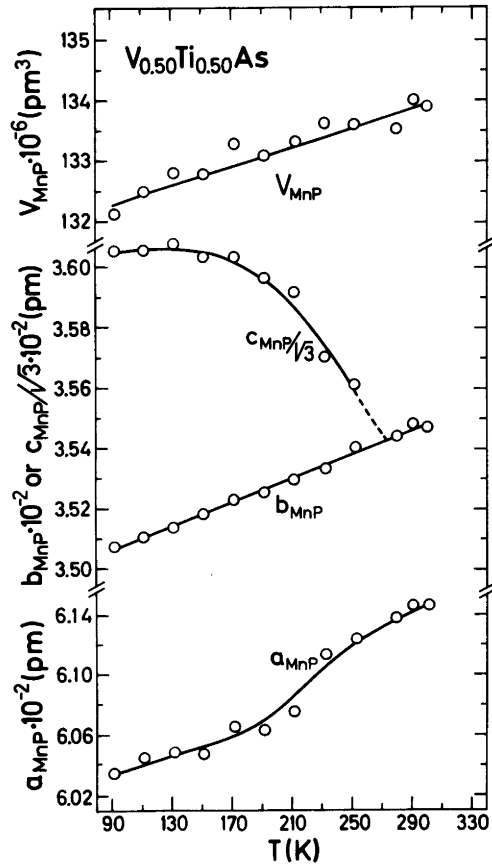
viz. one of them (probably the NiAs type phase) ought to take a metal to non-metal atomic ratio different from 1:1. This would in turn imply that there is a second phase present in the samples with $0.40 < t < 0.50$ (probably) above or below T_D, but due to a low fraction this could remain undetected by the powder X-ray diffraction technique. The second order MnP $\rightleftarrows$ NiAs type transition observed for $V_{0.500}Ti_{0.500}As$ (not detected by DSC) would thus simply imply that the two states have the same composition for $t = 0.500$.

The present magnetic susceptibility *versus* temperature curves for $V_{1-t}Ti_tAs$ comply with those published by Sobczak *et al.*[7] with regard to shape and susceptibility level ($1 < \chi_g \cdot 10^6 < 3$ e.m.u./g, for all samples measured and only very slight temperature variations). Thus, none of the samples gave $\chi^{-1}(T)$ curves which satisfy Curie-Weiss law over an extended temperature interval (and there is no distinction between the MnP and NiAs type states in this respect). The shape of the $\chi(T)$ curves place $V_{1-t}Ti_tAs$ in the gross category of Pauli paramagnetic materials for all compositions and temperatures studied. This conclusion is at complete variance with the antiferromagnetic properties for $V_{1-t}Ti_tAs$ with $0.37 \lesssim t \lesssim 0.52$ reported by Sobczak *et al.*[7] However, we believe that even the sparse documentation published by Sobczak *et al.* [virtually temperature independent $\chi(T)$ for $t = 0.52$ and "Néel temperatures" between 1400 K for $t = 0.37$ and 470 K for $t = 0.52$] support the classification of $V_{1-t}Ti_tAs$ as a Pauli paramagnetic material.

References

1. Kallel, A., Boller, H. and Bertaut, E. F. *J. Phys. Chem. Solids 35* (1974) 1139.
2. Fjellvåg, H. and Kjekshus, A. *J. Solid State Chem. 59* (1985) 9.
3. Selte, K. and Kjekshus, A. *Acta Chem. Scand. 27* (1973) 3195.
4. Franzen, H. F., Haas, C. and Jellinek, F. *Phys. Rev. B 10* (1974) 1248.
5. Menyuk, N., Kafalas, J. A., Dwight, K. and Goodenough, J. B. *Phys. Rev. 177* (1969) 972.
6. Selte, K., Kjekshus, A., Andresen, A. F. and Zięba, A. *J. Phys. Chem. Solids 38* (1977) 719.
7. Sobczak, R., Boller, H. and Bittner, H. *Monatsh. Chem. 99* (1968) 2227.
8. Werner, P. E. *Z. Kristallogr. 120* (1964) 375.
9. Sheldrick, G. SHELX – Programme for Crystal Structure Determination (1976).
10. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. 26* (1972) 4057.
11. Lukaszewicz, K. and Trzebiatowski, W. *Bull. Acad. Polon. Sci. Classe III 2* (1954) 277.
12. Zięba, A., Fjellvåg, H. and Kjekshus, A. *J. Phys. Chem. Solids 46* (1985) 275.
13. Fjellvåg, H., Kjekshus, A., Andresen, A. F. and Zięba, A. *J. Magn. Magn. Mat.* To be published.
14. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. 27* (1973) 3607.
15. Fjellvåg, H., Selte, K. and Stave, F. E. *Acta Chem. Scand. A 38* (1984) 687.