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Structural Properties of $VP_{1-x}As_x$; $0.00 \leqq x \leqq 1.00$

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The VP—VAs system has been studied by powder diffraction and magnetic susceptibility measurements. Three regions of solid solubility, separated by two phase regions, are found for $VP_{1-x}As_x$ as function of composition (x). An NiAs type phase prevails for $0.00 \leqq x \leqq 0.07 \pm 0.02$, a hexagonal phase of unknown crystal structure for $0.17 \pm 0.02 \leqq x \leqq 0.63 \pm 0.02$ and an MnP type phase for $0.83 \pm 0.02 \leqq x \leqq 1.00$. No phase transition is observed between 10 and 1 300 K. The various $VP_{1-x}As_x$ phases exhibit *Pauli* paramagnetism.

(Keywords: NiAs *type structure;* MnP *type structure; Hexagonal solid solution phase; Pauli paramagnetism)*

Strukturelle Eigenschaften von $VP_{1-x}As_x$; $0.00 \leqq x \leqq 1.00$

Das System VP—VAs wurde mittels Pulverbeugungsmethoden und magnetischer Suszeptibilitätsmessungen untersucht. Drei durch Zweiphasengebiete getrennte homogene Bereiche wurden für $VP_{1-x}As_x$ in Abhängigkeit von der Zusammensetzung (x) beobachtet. Eine Phase mit NiAs-Struktur existiert im Bereich $0.00 \leqq x \leqq 0.07 \pm 0.02$, eine hexagonale Phase unbekannter Struktur im Bereich $0.17 \pm 0.02 \leqq x \leqq 0.63 \pm 0.02$ und eine Phase mit MnP-Struktur im Bereich $0.83 \pm 0.02 \leqq x \leqq 1.00$. Zwischen 10 und 1 300 K konnten keine Phasenumwandlungen entdeckt werden. Die verschiedenen $VP_{1-x}As_x$-Phasen zeigen alle *Pauli*-Paramagnetismus.

Introduction

Most of the binary TX phases ($T = 3\,d$ element, $X =$ P, As) crystallize with one or both of the related NiAs and MnP type structures [1]. Second order phase transitions between these structure types have frequently been observed as function of composition and temperature [2–5]. Furthermore

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[*] Dedicated to Professor Dr. *Kurt L. Komarek* on his 60th birthday June 23, 1986.

the *TX* phases show a common ability to build solid solution phases; $T_{1-t}T'_tX$ or $TX_{1-x}X'_x$. The transition temperature (T_D) for the continuous MnP ⇄ NiAs type transition for several such ternary solid solution phases has been found to vary smoothly with *t* or *x* [3, 4, 6]. Among the possible candidates, which not yet have been studied, for such a behaviour is $VP_{1-x}As_x$, where the binary end members VP [7] and VAs [7] take the NiAs and MnP type structure, respectively. On the other hand, VP is atypical among the NiAs type phases in having eight rather than two close metal (V) atom neighbours around a given metal atom [1, 7]. Hence, a study of the ternary solid solution $VP_{1-x}As_x$ phase may also shed some light on the structural pecularities of VP itself. In this study the structural and magnetic properties of $VP_{1-x}As_x$ have been studied by means of powder X-ray and neutron diffraction, DSC and magnetic susceptibility measurements.

Experimental

VP and VAs were synthesized by heating stoichiometric amounts of the elements (V, powder, 99.5%, A. D. Mackay; P, lumps, 99.999%, Koch-Light Laboratories; As, lumps, 99.9999%, Koch-Light Laboratories) in evacuated, sealed silica tubes. The temperature was slowly increased (4 × 50 K/d) to 1 300 K, and after 5 d the samples were cooled to room temperature, carefully crushed and subjected to another annealing at 1 250 K for 10 d, before finally cooling to room temperature over 1 d. In some cases, a third similar annealing cycle was required in order to obtain homogeneous samples. Ternary $VP_{1-x}As_x$ samples were synthesized similarly from VP and VAs, and were generally subjected to three heat treatments at 1 300 K for 7 d with intermediate grindings at room temperature. The homogeneity and structural state of the reaction products were checked by room temperature, powder X-ray diffraction (*Guinier* technique, CuKα_1 radiation, Si as internal standard).

Low and high temperature powder X-ray diffraction data were collected with a *Guinier Simon* camera (Enraf-Nonius, CuKα_1 radiation) between ~ 100 and 1 300 K. DSC measurements were carried out between ~ 100 and 900 K using a Mettler TA 3000 system. Magnetic susceptivility measurements were carried out with a conventional *Faraday* balance (maximum field ~ 8 kOe) between 80 and 1 000 K. Powder neutron diffraction data were collected with the OPUS III diffractometer accommodated at the JEEP II reactor, Kjeller, using neutrons of wavelength 187.7 pm. Profile refinements were performed according to the *Hewat* [8] version of the *Rietveld* [9] programme, scattering lengths $b_V = -0.4$, $b_P = 5.1$ and $b_{As} = 6.4$ fm were taken from Ref. [10]. Intensities of *Bragg* reflections on *Guinier* photographs were evaluated using a Nicolet L 18 filmscanning system and the SCANPI [11] computer programmes.

Results and Discussion

Solid Solution Ranges

For different *x* of $VP_{1-x}As_x$ within $0.00 \leqq x \leqq 1.00$ there occur three different structure types. This is demonstrated in Fig. 1 which shows a section through the ternary phase diagram at room temperature for slowly cooled samples. The three different solid solution regimes are separated by two phase regions. The NiAs type phase of VP extends slightly into the ternary composition interval, covering $0.00 \leqq x \leqq 0.07 \pm 0.02$. For compositions close to VAs a solid solution phase with the MnP type structure is found for $0.83 \pm 0.02 \leqq x \leqq 1.00$. For intermediate compositions of $VP_{1-x}As_x$, in the interval $0.17 \pm 0.02 \leqq x \leqq 0.63 \pm 0.02$, a third solid solution phase, of hexagonal symmetry, prevails. The existence of the intermediate phase (which neither takes the NiAs or MnP type structure nor bears any obvious relation to these) is surprising since, to our knowledge, no other ternary system comprising the said structure types shows such a behaviour.

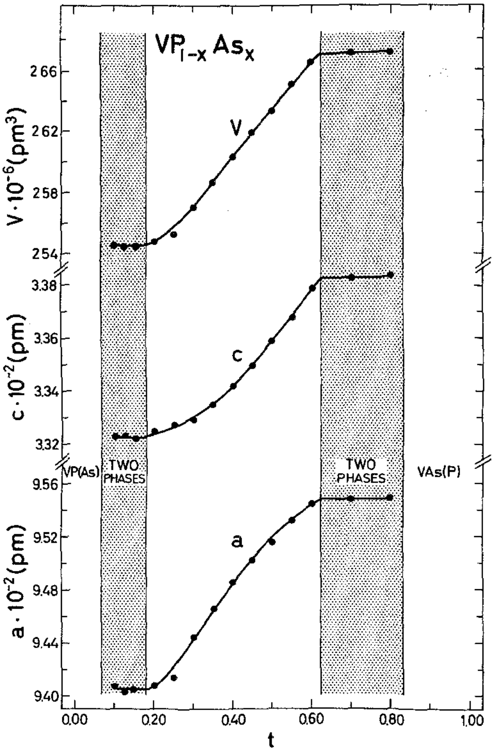

Fig. 1. Phases and homogeneity ranges in the VP—VAs system (slowly cooled samples, 295 K). Unit cell dimensions as function of composition (x) for the intermediate ternary solid solution phase of $VP_{1-x}As_x$. *Calculated* error limits do not exceed the size of symbols

Atomic Arrangement for $0.00 \leqq x \leqq 0.07 \pm 0.02$

The solid solution phase in the range $0.00 \leqq x \leqq 0.07 \pm 0.02$ takes the NiAs type crystal structure. Substitution of As for P leads, as expected, to increased unit cell dimensions, viz. from $a = 317.7 \pm 0.1$ and $c = 622.2 \pm 0.1$ pm for VP to $a = 317.9 \pm 0.1$ and $c = 622.6 \pm 0.1$ pm for $VP_{0.93}As_{0.07}$.

The NiAs type crystal structure of VP is ascertained for all temperatures between 10 and 1 300 K according to powder X-ray and neutron diffraction measurements. Several binary and ternary arsenides (but notably not phosphides) which have the NiAs type structure at high temperatures undergo a second order phase transition to the MnP type structure at a certain temperature, e.g. CrAs [2], MnAs [6], CoAs [2], and ternary derivatives thereof [3–5]. Among the *T*P phases, VP is the only example taking the NiAs type structure; for *T* = Cr, Mn, Fe and Co the MnP type structure is found [1]. The fact that no transition is found for VP must probably be understood in terms of its unusually high axial radio $c/a = 1.958$ which leads to a characteristic feature of eight, roughly equally close, V neighbours around each V atom. The variation in the unit cell dimensions of VP between 300 and 1 300 K is shown in Fig. 2. Whereas

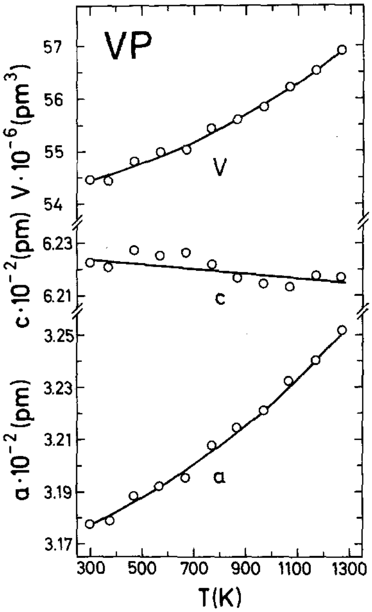

Fig. 2. Variation of unit cell dimensions for VP (NiAs type, space group $P6_3/mmc$) between 300 and 1 300 K. *Calculated* error limits do not exceed the size of symbol

the a axis undergoes normal thermal expansion between 300 and 1 300 K $[\alpha_a = (1/a_{293}) \cdot (\Delta a/\Delta T) = 2.3 \cdot 10^{-5} K^{-1}]$, c is seen to contract slightly with increasing temperature $[\alpha_c = -1.3 \cdot 10^{-6} K^{-1}]$. This feature is not commonly observed for other binary or ternary NiAs type phases, and it is accordingly tempting to connect this behaviour with the rather unique metal to metal coordination in VP. A similar behaviour is observed for $VP_{0.95}As_{0.05}$.

Atomic Arrangement for $0.83 \pm 0.02 \leqq x \leqq 1.00$

$VP_{1-x}As_x$ with $0.83 \pm 0.02 \leqq x \leqq 1.00$ crystallizes with the MnP type structure [1, 7] (an orthorhombically distorted variant of the NiAs type). The unit cell dimensions (*Pnma* setting of the unit cell) decrease almost linearly with decreasing x (viz. increasing VP content) from $a = 585.0 \pm 0.1$, $b = 336.2 \pm 0.1$ and $c = 629.2 \pm 0.1$ pm for VAs to $a = 578.5 \pm 0.1$, $b = 333.5 \pm 0.1$ and $c = 626.3 \pm 0.1$ pm for $VP_{0.15}As_{0.85}$. The structural

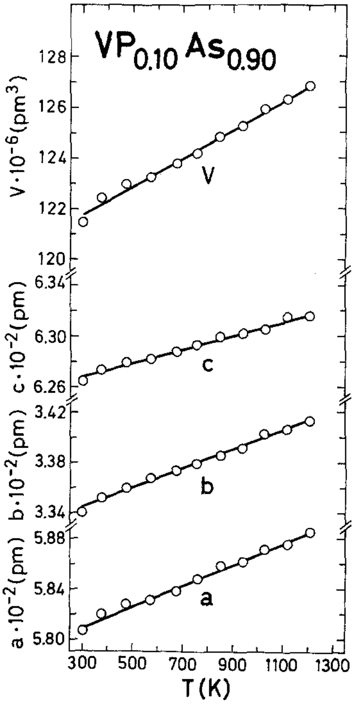

Fig. 3. Variation of unit cell dimensions for $VP_{0.10}As_{0.90}$ (MnP type, space group *Pnma*) between 300 and 1 300 K. *Calculated* error limits do not exceed the size of symbols

arrangement for the VAs rich phase was confirmed by powder X-ray diffraction data. No significant shifts in the (four unconstrained) positional parameters were observed on going from VAs [7] to $VP_{0.15}AS_{0.85}$. The axial ratio c/b (which equals $\sqrt{3} = 1.7320\ldots$ for the undistorted NiAs type atomic arrangement) increases slightly with increasing substitution (from 1.872 for $x = 1.00$ to 1.878 for $x = 0.85$). This finding corresponds with the behaviour of other similar $TP_{1-x}As_x$ (T = Cr, Mn, Fe, Co) MnP type solid solution phases [12–14] where the deviation in c/b from $\sqrt{3}$ increases with decreasing x. VAs itself does not undergo the MnP $\rightleftarrows$ NiAs type transition at elevated temperatures [2], and this feature is retained for $VP_{0.10}As_{0.90}$ (see Fig. 3, which shows no indication of any transition). This concurs also with the fact that the positional parameters for VAs [7] and $VP_{0.15}As_{0.85}$ take values which are typical for the fully distorted MnP type state [3, 5].

Crystal Structure for $0.17 \pm 0.02 \leqq x \leqq 0.63 \pm 0.02$

The solid solution phase in the intermediate composition interval $0.17 \pm 0.02 \leqq x \leqq 0.63 \pm 0.02$ takes neither the NiAs nor the MnP type structure. The diffraction patterns can satisfactorily be indexed according to a hexagonal unit cell [also confirmed through trial and error indexing by the TREOR [15] programme with a figure of merit [16] M(20) = 21]. However, even other indexings came out fairly probable, and single crystal data are accordingly required for an unambiguous determination of the unit cell. The variations of the thus derived unit cell dimensions throughout the solid solution range are shown in Fig. 1, and the unit cell volume shows an approximately linear dependence on x. Using the unit cell volumes per formula unit for VP and VAs at room temperature as measures, a cell content of $Z = 9$ for the intermediate $VP_{1-x}As_x$ phase is obtained. The pycnometrically measured densities for samples with different x (25 °C, kerosene as displacing liquid) gave $Z = 8.80$—8.85. Since there is no indication for a second phase in the diffraction diagrams, it is concluded that the metal to non-metal ratio of the intermediate phase is 1 : 1.

From the observed hkl reflections in the powder X-ray and neutron diffraction diagrams it was not possible to disclose any systematic extinctions, and hence several space groups are possible. On the basis of the unit cell dimensions for the intermediate phase one arrives at the approximate relationships $a = 3\,a_{\mathrm{NiAs}}$ and $c = 1/2\,c_{\mathrm{NiAs}}$, which in turn complies with $Z = 9$. However, due to the short c axis the packing sequence and hence also the co-ordination in the intermediate phase must be markedly different from that of the NiAs and MnP type structures. It is entertaining to think of possible structural similarities with types like WC

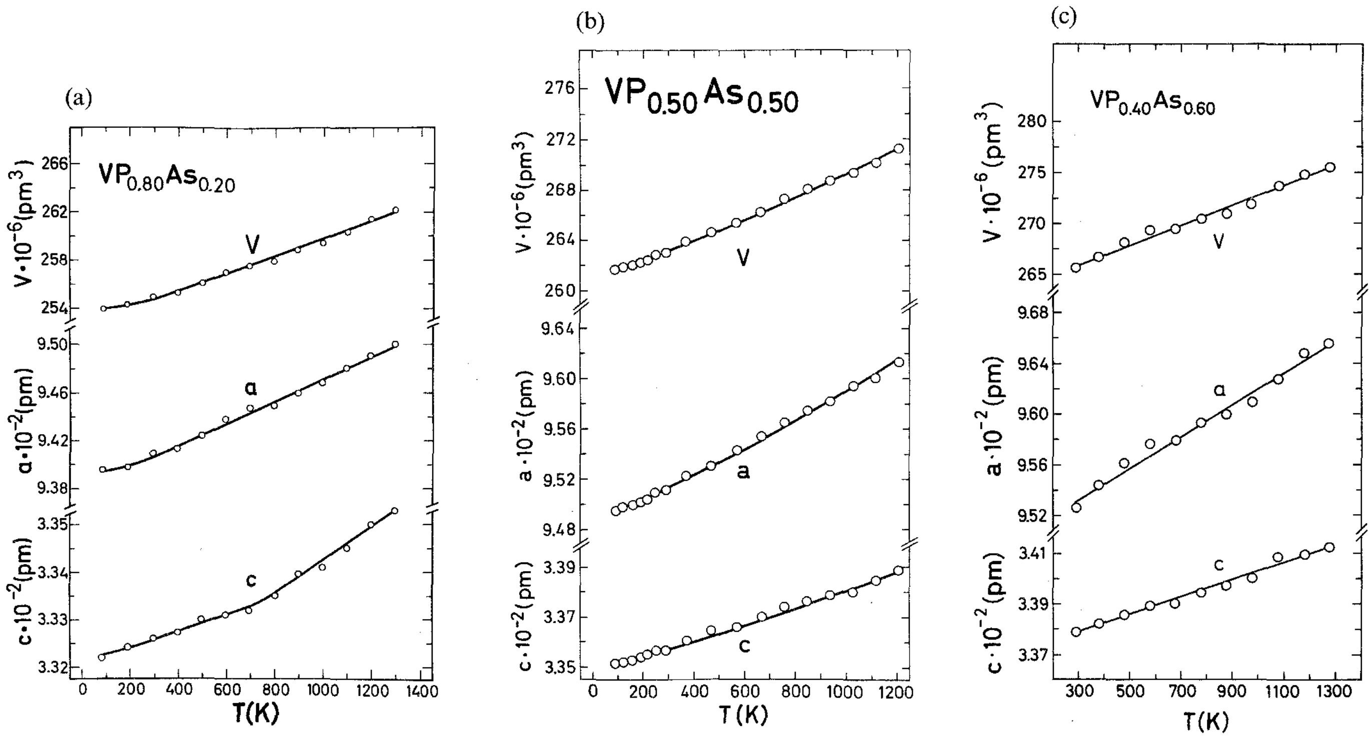

Fig. 4. Variation of unit cell dimensions with temperature for (a) $VP_{0.80}AS_{0.20}$ between 90 and 1 300 K, (b) $VP_{0.50}AS_{0.50}$ between 90 and 1 300 K and (c) $VP_{0.40}AS_{0.60}$ between 300 and 1 300 K. *Calculated* error limits do not exceed the size of symbols

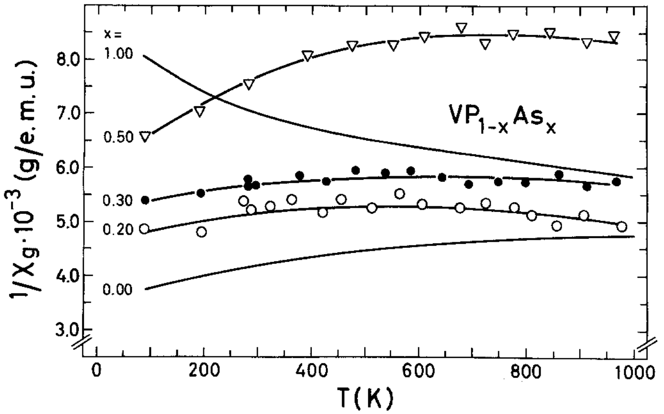

Fig. 5. Inverse magnetic susceptibility versus temperature for samples of $VP_{1-x}As_x$ with $x = 0.00$, 0.20, 0.30, 0.50, and 1.00

[1] (enlarged cell), $V_{12}P_7$ [17] (modified to account for the difference in composition) etc., but for a decisive crystal structure determination single crystal data is required.

Representative examples of the temperature dependence (between 90 and 1300 K) of the unit cell dimensions for the intermediate phase are given in Fig. 4. In this temperature interval no phase transition manifests itself in the diffraction patterns. For $VP_{0.80}As_{0.20}$ (Fig. 4a) a marked change in the expansion coefficient of *c* is observed at ~ 750 K. However, this was not found for $x = 0.30$, 0.50 and 0.60 (see Fig. 4b, c) and the reason for this pecularity for $x = 0.20$ is not understood. The average volume expansion coefficients $\alpha_V (= 2.8—3.7 \cdot 10^{-5} K^{-1})$ for this phase are somewhat smaller than those of the binary end phases (4.3 and $4.1 \cdot 100^{-5} K^{-1}$ for VP and VAs, respectively).

Magnetic Properties

The magnetic susceptibility of various samples of $VP_{1-x}As_x$ were recorded between 80 and 1000 K, and the $\chi_g^{-1}(T)$ curves are presented in Fig. 5. The curves include representatives of the three structure types in the VP—VAs system, but no notable distinctions are manifested on this basis. However, they all signalize low, slightly temperature dependent paramagnetism (no corrections for diamagnetic core contributions are carried out). The phases can accordingly be considered as belonging to the group of *Pauli* paramagnetic materials, and the observed susceptibility for VP concurs with band structure calculations [18]. The short V—V distances, at least in VP and VAs correlate with the itinerant behaviour.

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