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Structural and Magnetic Properties of VP and VAs

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The VP and VAs phases have been investigated by X-ray and neutron (for VAs only) diffraction, density, magnetic susceptibility, and diffuse reflectance measurements. Both VP and VAs adopt the stoichiometric 1 : 1 composition without any appreciable ranges of homogeneity. The crystal structure of VP is of the NiAs type, while that of VAs (as determined at room temperature from three-dimensional single crystal X-ray data) is essentially of the MnP type. The crystal structure of VAs remains virtually unchanged between room and liquid helium temperatures, and there is no evidence of magnetic ordering. The paramagnetic susceptibilities of VP and VAs are generally small and their temperature dependencies do not follow the Curie-Weiss Law.

In continuation of our examination of compounds with the MnP type structure,[1–6] we present some structural and magnetic data for VP and VAs. According to the literature [7–9] VP breaks the pattern formed by the mono-phosphides and mono-arsenides of chromium, manganese, iron, and cobalt in adopting the NiAs rather than the MnP type structure. It seems, on the other hand, well established that VAs [10,11] crystallizes with the MnP type structure, although rather approximate structural data are available. Hence, VAs is a suitable candidate for structure redetermination on the present research programme. It seems of particular interest to obtain more precise structural data on VAs since extreme values of axial ratios within the MnP class are associated with this compound. The interesting cooperative magnetic phenomena which recently have been discovered among compounds with MnP type structure [2,6,12–19] and the trends in these data, suggested that it also could be rewarding to subject VAs to a low temperature neutron diffraction study.

EXPERIMENTAL

Materials. The pure elements used in this study were 99.5 % V (A. D. Mackay), 99.999 % red P, and 99.999 % As (Koch-Light Laboratories).

Preparations. Polycrystalline samples of VP and VAs were prepared by heating weighed quantities of the components in sealed, evacuated silica tubes. Several samples with different initial compositions were made of each phase, on both sides of the stoichio-

metric 1 : 1 ratio. During the syntheses the temperature was slowly increased to 850°C, the samples were kept at this temperature for 8 days, and then cooled to room temperature over 3 days. The samples were afterwards crushed and reannealed several times at 850°C, using 8 days intervals, until X-ray powder photographs showed no further detectable changes in composition equilibria. For the VP phase this method gave homogeneous samples after 3 such treatments, whereas the homogenization of the VAs samples required some 10 repetitions. However, the presence of traces of iodine in the capsules speeds up the homogenization process in the VAs samples considerably, only 1 – 2 reannealings being necessary. A considerable number of VAs single crystals could be found in the capsules after the latter treatment.

X-Ray diffraction. All samples were crushed, and X-ray powder photographs were taken in a Guinier type camera of 80 mm diameter with monochromatized Cu$K\alpha_1$-radiation ($\lambda = 1.54050$ Å) using KCl ($a = 6.2919$ Å[20]) as internal standard.

Single crystal X-ray photographs of VAs were taken in an integrating Weissenberg camera of 57.3 mm diameter with Nb-filtered Mo$K\alpha$-radiation using the multiple-film technique. Three-dimensional data of, in all, 382 independent reflections (93 with zero intensity) were collected from the layers 0*kl* to 4*kl*. The intensity measurements were carried out microphotometrically except for the weakest reflections which were estimated visually. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption (the crystal shape being approximately spherical with $\mu R = 2.5$) and secondary extinction. (No correction for dispersion was carried out.)

The computational work on the X-ray data, including least squares refinements of the unit cell dimensions, corrections, data reductions, scaling, and full matrix least squares refinements of the structure factors, was performed on a CDC 3300 computer using in most cases the programmes of Dahl *et al.*[21] The atomic scattering factors were taken from Hanson *et al.*[22] The unobserved reflections were omitted from the least squares refinements, and were not included in the calculations of the average and weighted reliability factors:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$
$$R^* = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}}$$

where w denotes the weight factor. Anisotropic and isotropic thermal vibrations of the atoms were considered, using the expressions:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$
$$\exp[-B\sin^2\theta/\lambda^2]$$

(The observed and calculated structure factor data are available from the authors upon request.)

Neutron diffraction. Powder neutron diffraction data for VAs were collected at 293 and 4.2 K using cylindrical vanadium sample holders. Neutrons of wavelength 1.863 ± 0.001 Å were obtained from the JEEP II reactor. The nuclear scattering lengths ($b_V = -0.05 \times 10^{-12}$ cm and $b_{As} = 0.64 \times 10^{-12}$ cm) were taken from the table published by The Neutron Diffraction Commission.[23] The least squares profile refinement programme written by Rietveld [24] was applied in the final fitting of the variable parameters to the observed intensity data. The following parameters were refined: the scale factor, the counter zero point, three profile parameters, the unit cell dimensions, the positional parameters and isotropic temperature factors for the As atoms.

The magnetic susceptibilities of stoichiometric VP and VAs samples were measured between 80 and 1000 K by the Faraday method (maximum field ~ 8 kØ) using ~ 80 mg samples.

Diffuse reflectance measurements were made in the range 2400 to 20 000 Å using a Cary 14 dual-beam spectrophotometer fitted with a diffuse reflectance accessory. $MgCO_3$ was used as a standard, and the integrating sphere was coated with MgO.

Density measurements were carried out pycnometrically at 25.00°C with kerosene as displacement liquid. To remove gases adsorbed by the sample (weighing ~ 2 g), the pycnometer was filled with kerosene under vacuum.

RESULTS

(i) *Homogeneity range, composition, and unit cell dimensions.* The compositions of the VP and VAs phases, which have no appreciable ranges of homogeneity, were determined by applying the disappearing phase principle to Guinier photographs of samples with different nominal compositions. The results showed the compounds to be stoichiometric according to the formulae $VP_{1.00\pm0.04}$ and $VAs_{1.00\pm0.02}$, the uncertainties in the determinations being indicated by the error limits. The stoichiometric 1 : 1 compositions were also confirmed by comparing the pycnometrically measured densities (4.92 g cm^{-3} for VP and 6.69 g cm^{-3} for VAs) with those calculated from the unit cell dimensions and a cell content of 2 VP ($Z_c = 1.97$) and 4 VAs ($Z_c = 3.96$) groups, respectively.

The room temperature unit cell dimensions $a = 3.180(4)$ Å, $c = 6.224(3)$ Å for VP and $a = 5.8500(8)$ Å, $b = 6.2923(10)$ Å, $c = 3.3618(4)$ Å (setting according to space group $Pna2_1$) for VAs, as determined from Guinier photographs, were found to be constant within experimental error for the different samples of each compound. Furthermore, the values for VAs agree well with the corresponding values $a = 5.844(5)$ Å, $b = 6.287(7)$ Å, $c = 3.369(7)$ Å derived from the neutron diffraction data. The values for VP are in good agreement with those found by Schönberg [7] and Lundström,[9] whereas the data for VAs differ somewhat from those reported by Bachmayer and Nowotny.[10]

(ii) *Refinement of the structures.* The crystallographic description of the atomic arrangement in the ideal NiAs type structure is as follows, in terms of the space group $P6_3/mmc$: 2 Ni in (*a*) 0,0,0; 0,0,1/2 and 2 As in (*c*) 1/3,2/3,1/4; 2/3,1/3,3/4. The hexagonal symmetry and the systematic extinctions evident from the diffraction data for VP, are consistent with $P6_3/mmc$. Comparison of observed and calculated X-ray intensities, moreover, confirms that the structure of VP is of the ideal NiAs type. Thus, these results unambiguously verify Schönberg's [7] structure determination.

In addition to the evidence presented by Bachmayer and Nowotny [10] the overall correctness of the assigned MnP type structure to VAs was readily ascertained on comparison with our findings [1,2,4] for CrAs, FeAs, and CoAs. Analogous refinement models to those tried for FeP,[5] FeAs,[1] and CoAs [4] were considered, including the possibility of anisotropic as well as isotropic temperature factors. Least squares refinements of the structure factor data were continued until no shifts were obtained in all the variables for each model. Using the Hamilton [25] test it was found that the model specified by the following parameters ($R = 0.095$ and $R^* = 0.119$): $x = 0.0054(10)$, $y = 0.1890(4)$, $z = 1/4$ (fixed), $\beta_{11} = 0.0032(20)$, $\beta_{22} = 0.0017(3)$, $\beta_{33} = 0.0083(13)$ for V and $x = 0.1969(6)$, $y = 0.5734(3)$, $z = 0.2673(17)$, $\beta_{11} = 0.0057(14)$, $\beta_{22} = 0.0020(3)$, $\beta_{33} = 0.0070(8)$ for As (in 4(*a*) according to space group $Pna2_1$), is superior to all models based on $z_{As} = 1/4$ at a significance level < 0.005. Concerning the question of anisotropic *versus* isotropic thermal motion for both kinds of atom for models involving space group $Pna2_1$, the latter possibility can be rejected only at a significance level of 0.05. The restriction $\beta_{12} = \beta_{13} = \beta_{23} = 0$ fixes the principle axes of the vibration ellipsoids to coincide with the crystallographic axes. The final conclusion reached by application of the Hamilton test concurs

with that derived from the values of the parameters for the various models and their associated standard deviations, *viz.* that space group $Pna2_1$ gives the most correct description of the crystal structure of VAs. The parameter z_{As} differs from the special value 1/4 required by the more symmetric space group *Pnam* by approximately ten standard deviations for all models where it has been allowed to vary.

The single crystal (X-ray) results may be compared with those obtained from powder samples by means of the neutron diffraction technique. The rather few reflections accessible by the latter method and the small scattering length of V impose a number of constraints in the models subject to refinement. Firstly, both z-parameters are fixed at 1/4 in accordance with the requirements of space group *Pnam*. Secondly, isotropic temperature factors are assumed for both kinds of atom. Since attempted refinements of the room temperature data with variable positional parameters for V gave no convergence in the calculations of these, x_V and y_V were finally fixed at the values obtained from the single crystal X-ray data (*vide supra*) and B_V at 0.3 Å^2. With these constraints, the profile refinements rapidly converged to $x_{As}=0.1954(7)$, $y_{As}=0.5735(9)$, and $B_{As}=0.3(1)$ Å^2 (with $R=0.069$) for the remaining variable parameters, the values for x_{As} and y_{As} being in excellent agreement with those found by X-ray diffraction (*vide supra*).

The results of the powder neutron diffraction measurements at liquid helium temperature show that the crystal structure remains the same as at room temperature. The profile refinement technique (subject to the above constraints, except for a change of B_V to 0.0 Å^2) gave the following values for the accessible crystallographic parameters at 4.2 K: $a=5.837(3)$ Å, $b=6.277(4)$ Å, $c=3.345(4)$ Å, $x_{As}=0.1947(6)$, $y_{As}=0.5732(8)$, and $B_{As}=0.06(5)$ Å^2 with $R=0.072$. The values of x_{As} and y_{As} derived from these data agree, within standard deviations, with those given above.

(iii) *Interatomic distances.* The present values for the unit cell dimensions and positional parameters lead to 2.407(2) Å for the bonding V–P distances and 2.448(6), 2.488(6), 2.503(6), 2.568(6), 2.582(6), and 2.666(4) Å (average 2.543 Å) for the corresponding V–As distances. The values of the shortest V–V separations (3.112(2) and 3.180(5) Å in VP and 2.913(3) and 3.024(8) Å in VAs) are smaller than the critical value of 3.21 Å for the V–V distance proposed by Goodenough.[26] On this basis bonding interactions between the metal atoms would appear to be significant. A discussion of the chemical bonding in these and closely related compounds will be presented in a forthcoming paper.

(iv) *Magnetic properties.* The reciprocal magnetic susceptibility *versus* temperature curves for VP and VAs are shown in Fig. 1. Excellent reproducibility has been found between a number of different samples of each compound. Field strength dependent susceptibilities were not observed, and the experimental points represent mean values at different field strengths without corrections for induced diamagnetism.

The reciprocal magnetic susceptibility of VP (Fig. 1) cannot usefully be expressed as a simple linear function of temperature over an appreciable range of this variable, implying that the Curie-Weiss Law is not satisfied. Furthermore, the slope of the $\chi^{-1}(T)$ curve of VP at (say) 300 K corresponds to a spin

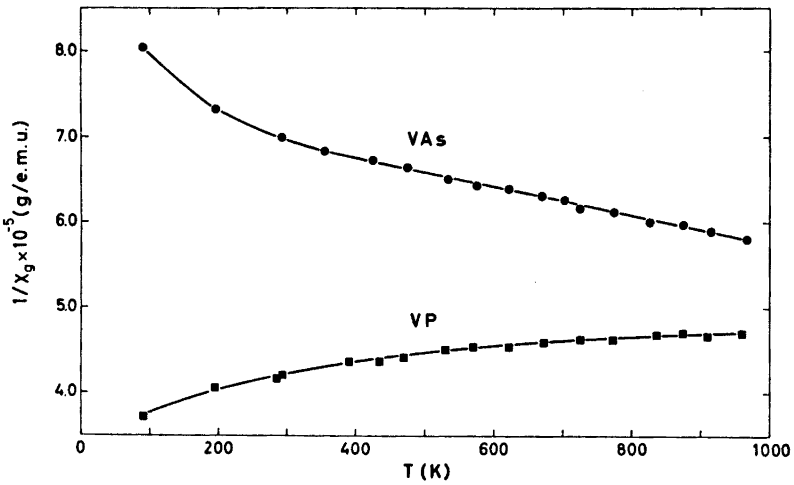

Fig. 1. Inverse magnetic susceptibility as a function of temperature for VP and VAs.

quantum number $2S = 1.9 \pm 0.1$ (according to the "spin only" approximation), which appears to be anomalously large in relation to the overall magnitude of the susceptibility. Hence, it may be safely concluded that the $\chi^{-1}(T)$ curve of VP is not consistent with a normal type of paramagnetism arising from the presence of localized unpaired electrons on the V atoms.

For VAs the monotonic decrease of the $\chi^{-1}(T)$ curve which confirms the findings of Sobczak *et al.*,[11] is clearly anomalous in relation to the Curie-Weiss Law. The shape of the thermomagnetic curve of VAs shows, on the other hand, a pronounced similarity with that of CrAs[2] above ~ 300 K. In view of the fact that the latter compound adopts a helimagnetic structure below 261 – 272 K, a low temperature neutron diffraction study was made in order to gain further insight into its magnetic properties. The neutron diffraction pattern at 4.2 K showed no purely magnetic reflections, and any contributions of magnetic origin to the nuclear reflections must be small. In spite of a thorough search at small angles, using narrow collimation, it proved impossible to find any indication of a $000^{\pm}$ satellite, which would have been characteristic of a spiral structure similar to those found in MnP,[12,13] CrAs,[2,16,18] FeP,[19] and FeAs.[6] A small magnetic contribution to the nuclear peaks is difficult to detect, but we estimate that any possible ordered moment in VAs must be less than $0.2\mu_B$. In view of the absence of cooperative magnetism in VAs and the trends which have been found [6] in the helimagnetic properties of MnP, CrAs, FeP, and FeAs, the ternary phases $V_{1-t}Cr_tAs$, $Cr_{1-t}Fe_tAs$, and $Mn_{1-t}Fe_tAs$ are being investigated.

(v) *Diffuse reflectance.* The diffuse reflectance spectra of VP and VAs show a uniform decrease from 2400 to 20 000 Å without any indications of absorption edges or other anomalies. Both compounds belong accordingly to the metallic class of conductors.

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