

Magnetic Structures and Properties of $V_{1-t}Cr_tAs$

KARI SELTE,^a HJALTE HJERSING,^a ARNE KJEKSHUS^a and ARNE F. ANDRESEN^b

^aKjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway and ^bInstitutt for Atomenergi, Kjeller, Norway

The pseudo-binary VAs-CrAs system has been investigated by X-ray and neutron diffraction and magnetic susceptibility measurements. VAs and CrAs are completely soluble in each other, and the structure of the ternary, random solid solution phase is of the MnP type at and below room temperature. Like CrAs, the Cr-rich samples undergo a transition from MnP to NiAs type structure at high temperatures. The double, helimagnetic *c* axis type ordering in CrAs extends only to $V_{0.06}Cr_{0.96}As$.

The purpose of the protracted research programme¹⁻¹⁵ of which the work described in this paper forms a part, is to elucidate the structural and magnetic properties of compounds with the NiAs and MnP type structures and, especially, the factors which govern the similarities and distinctions between the two classes. The present paper concerns $V_{1-t}Cr_tAs$, the properties of VAs and CrAs being relatively well documented through earlier work.^{2,7,16,17} The quasi-binary system VAs—CrAs has previously been studied, among others, by Sobczak *et al.*¹⁸ who, unfortunately, present only a brief account of their data. In view of the current knowledge of the magnetic properties¹³ of compounds with the MnP type structure, the unusually high Néel temperatures reported by Sobczak *et al.* call for reexamination.

EXPERIMENTAL

Samples of VAs and CrAs were prepared by heating weighed quantities of the elements [99.5% V (A.D. Mackay), 99.0% Cr (powder crystals; Koch-Light Laboratories), and 99.9999% As (Koch-Light Laboratories)] in evacuated, sealed silica tubes, as described in Refs. 2 and 7. Ternary $V_{1-t}Cr_tAs$ samples of desired compositions were prepared from ap-

propriate proportions of VAs and CrAs, by 3–4 heat treatments of one week's duration at 950 °C, interrupted by intermediate crushings. The samples were finally cooled to room temperature over a period of two days.

Experimental details concerning X-ray and neutron diffraction (including data reduction) and magnetic susceptibility measurements have been reported earlier.⁶

RESULTS

(i) Composition and chemical crystal structure.

Fig. 1 shows the room temperature unit cell dimensions of $V_{1-t}Cr_tAs$ as functions of the composition parameter *t*. The contin-

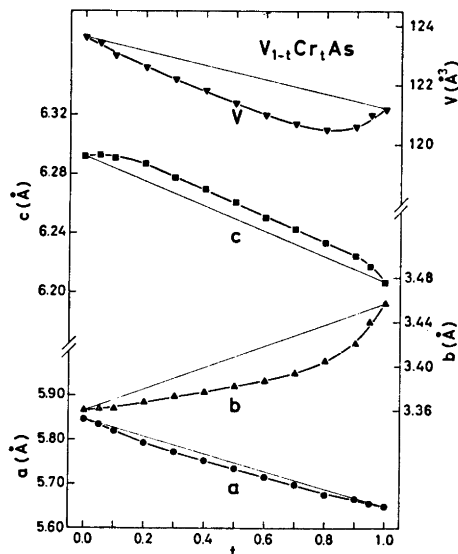


Fig. 1. Orthorhombic unit cell dimensions of ternary solid solution series VAs-CrAs as functions of composition.

Table 1. Unit cell dimensions and positional parameters with standard deviations for some $V_{1-t}Cr_tAs$ samples; space group $Pnma$, positions 4(c). (Overall profile reliability factors ranging between 0.027 and 0.056.)

t	T (K)	a (Å)	b (Å)	c (Å)	x_T	z_T	x_X	z_X
0.50	80	5.707(1)	3.368(1)	6.237(1)	0.0069(22)	0.1960(20)	0.1975(4)	0.5737(6)
	293	5.724(1)	3.382(1)	6.250(1)	0.0086(20)	0.1970(18)	0.1986(4)	0.5728(6)
0.75	4.2	5.661(1)	3.373(1)	6.215(1)	0.0066(14)	0.1966(12)	0.1980(6)	0.5733(5)
	80	5.663(1)	3.374(1)	6.215(2)	0.0060(11)	0.1982(9)	0.1982(4)	0.5739(5)
	293	5.678(1)	3.396(1)	6.225(1)	0.0057(12)	0.1987(10)	0.1990(4)	0.5746(5)
0.90	4.2	5.645(1)	3.375(1)	6.209(1)	0.0061(11)	0.1964(9)	0.1983(6)	0.5735(5)
	80	5.641(1)	3.376(1)	6.204(1)	0.0066(9)	0.1981(7)	0.1981(5)	0.5740(4)
	293	5.652(1)	3.411(1)	6.208(1)	0.0062(9)	0.2012(7)	0.1990(5)	0.5745(4)
0.93	4.2	5.638(1)	3.376(1)	6.205(1)	0.0073(10)	0.1989(8)	0.1981(6)	0.5733(5)
	80	5.646(1)	3.384(1)	6.213(1)	0.0079(9)	0.1997(8)	0.1976(5)	0.5742(5)
	293	5.656(1)	3.426(1)	6.216(1)	0.0056(8)	0.2012(7)	0.1988(5)	0.5744(4)
0.95	80	5.590(2)	3.564(2)	6.124(3)	0.0085(21)	0.2029(17)	0.2036(14)	0.5808(23)
	293	5.645(2)	3.447(1)	6.205(2)	0.0095(15)	0.2053(13)	0.1985(10)	0.5776(8)

uous variations in all unit cell dimensions with t demonstrate that VAs and CrAs are completely soluble in each other. According to earlier findings^{2,7} VAs and CrAs are well defined, stoichiometric compounds. The possibility of an extension of the homogeneity range of $V_{1-t}Cr_tAs$ to metal/non-metal (atomic) ratios different from 1.00 has not been systematically studied for the ternary samples. It should be noted, however, that apart from the vanadium-rich samples ($0 \leq t \leq 0.2$), disengagement of small amounts of arsenic was observed in the capsules after the heat treatments. Weighing of the disengaged As shows that the implied non-metal deficiency corresponds to less than 1% of the original As content. No attempts have been made to pursue this problem further, and the apparent non-stoichiometric nature of these samples may well originate from imperfections in the preparative procedure.

The X-ray data confirm an MnP type structural arrangement for $0 \leq t \leq 1$ at room temperature. The absence of additional superstructure reflections shows that the substituted atoms are randomly distributed over the metal sub-lattice. As seen from Fig. 1 the variations in unit cell dimensions with compositions do not follow Vegard's Law.

Samples with $t=0.50, 0.75, 0.90, 0.93,$ and 0.95 were prepared primarily for the purpose of studying the magnetic structures, but data collected in this connection were conveniently utilized to evaluate the variable positional parameters of the MnP type structure. The final values for the least squares, profile refined parameters at and below room temperature are listed in Table 1. Due to the generally small differences in positional parameters between VAs and CrAs and the relatively high, calculated values for the standard deviations given in Table 1, it is difficult to unveil the expected continuous changes in these variables with composition. Like CrAs,^{2,16,17} $V_{0.95}Cr_{0.05}As$ undergoes a first order transition at 240 K (onset on cooling; accompanied by hysteresis) between two MnP type phases (associated with the magnetic transition; see section iii). This is reflected in the unit cell dimensions, but not in the positional parameters in Table 1.

Since CrAs also is known to undergo a second (or higher) order transformation to the NiAs type structure at a temperature of 1173 ± 20 K,¹⁰ three representative samples with compositions $t=0.80, 0.90,$ and 0.95 were studied in the interval 293–1350 K. The temperature dependences of the unit cell dimensions (Fig. 2) demonstrate corresponding

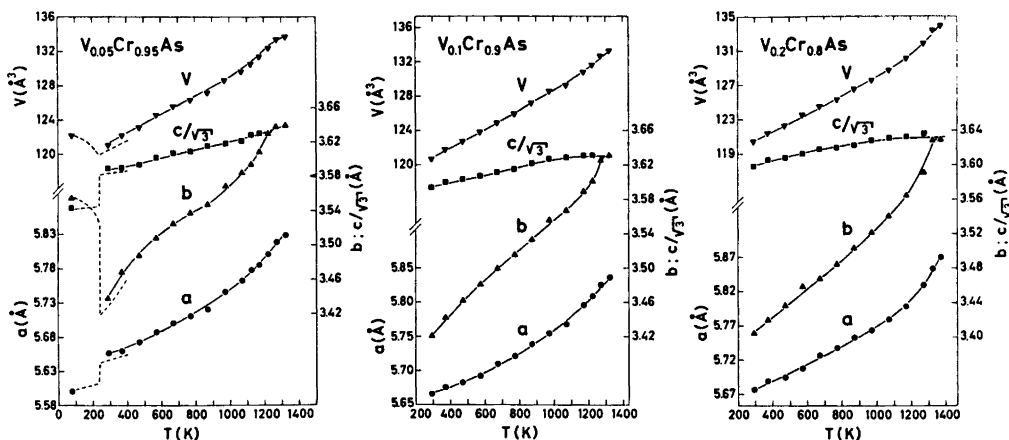


Fig. 2. Unit cell dimensions of three $V_{1-t}Cr_tAs$ samples *versus* temperature. Average relative expansion coefficients $\alpha_a = [(a_T - a_{T'})/a_{300}(T - T')]$, α_b , α_c multiplied by 10^6 K are 25, 52, 12; 28, 52, 13; and 28, 47, 14 for $V_{0.2}Cr_{0.8}As$, $V_{0.1}Cr_{0.9}As$, and $V_{0.05}Cr_{0.95}As$, respectively.

transitions at 1250 ± 50 , 1300 ± 50 , and 1350 ± 50 K for $V_{0.05}Cr_{0.95}As$, $V_{0.10}Cr_{0.90}As$, and $V_{0.20}Cr_{0.80}As$, respectively.

(ii) *Magnetic susceptibility.* The gradual change in the temperature dependence of the reciprocal magnetic susceptibility with composition parameter t of $V_{1-t}Cr_tAs$ is shown in Fig. 3. No field strength dependent susceptibilities were observed. In this respect the thermo-

magnetic curve for CrAs differs from that reported in Ref. 2, the difference being probably caused by slight impurities in the samples used in the earlier investigation. None of the samples within the entire composition range of the VAs-CrAs system satisfies the Curie-Weiss Law.

(iii) *Magnetic structure.* CrAs has previously^{2,16,17} been found to exhibit helimagnetism, whereas no cooperative magnetic phenomenon

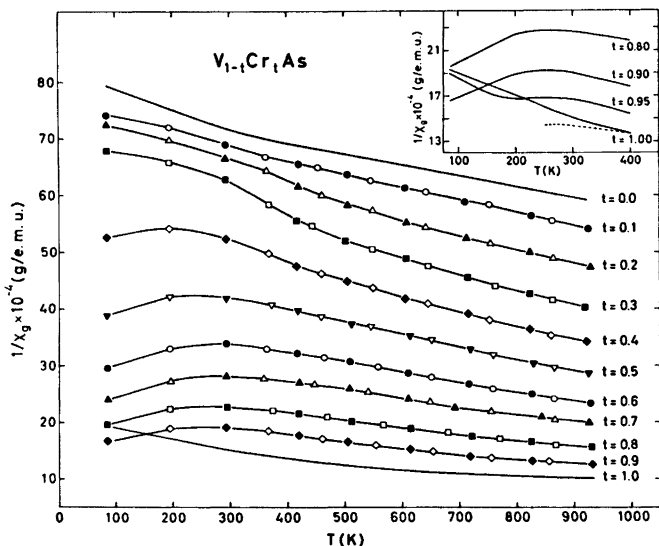


Fig. 3. Reciprocal magnetic susceptibility *versus* temperature for various $V_{1-t}Cr_tAs$ samples. Inset shows low temperature portions of $\chi_g^{-1}(T)$ curves for $0.80 \leq t \leq 1.00$; broken curve quoted from Ref. 2.

has been detected ⁷ for VAs down to 4.2 K. The double, helimagnetic *c* axis type ordering extends to a composition $t=0.95$ of the $V_{1-t}Cr_tAs$ phase. The samples with $0.50 \leq t \leq 0.93$ gave no indication of reflections characteristic of the helimagnetic arrangement. Only small changes were experienced in all parameters specifying the spirals on going from CrAs to $V_{0.05}Cr_{0.95}As$, the values (at 80 K) being for CrAs $T_N=261$ K (onset on cooling; followed by hysteresis), $\mu_T=1.70 \pm 0.05 \mu_B$, $\tau=0.353 \times 2\pi c^*$, $\phi=-133 \pm 1^\circ$, and for $V_{0.05}Cr_{0.95}As$ $T_N=240$ K (onset on cooling; followed by hysteresis), $\mu_T=1.70 \pm 0.05 \mu_B$, $\tau=0.360 \times 2\pi c^*$, $\phi=-115 \pm 1^\circ$. As demonstrated in Figs. 4 and 5 the onset of the cooperative magnetic phenomenon in $V_{0.05}Cr_{0.95}As$ is accompanied by a marked hysteresis, resembling also in this respect CrAs. The pronounced similarity in temperature dependence of the integrated intensity of 000^\pm and 101^- suggests that the phase angle between the spirals in $V_{0.05}Cr_{0.95}As$ varies relatively little with temperature. Similarly, only minor variations are observed in the temperature dependence of the spiral turn angle ($\tau=0.38 \times 2\pi c^*$ at 232 K).

Fig. 5 demonstrates that the magnetic ordering in $V_{0.05}Cr_{0.95}As$ is accompanied by a first order structural transformation. At first

sight the transition in this substance seems to be somewhat peculiar, in that the reflection characteristic of the high temperature, paramagnetic phase does not completely vanish at low temperatures. However, there appears to be a very simple explanation of this observation, involving the imposition of the magnetic phase boundary at $t=0.95$. The slight variation in composition which necessarily must be present in all samples of non-stoichiometric phases, would, on the assumption of the phase borderline being located at the composition of the investigated sample, account for the coexistence of (say) 10 % of the paramagnetic phase in admixture with the bulk of the sample in the low temperature, helimagnetic state.

The termination of the helimagnetic region of the $V_{1-t}Cr_tAs$ phase already at $t=0.95$ is somewhat unexpected and provokes some discussion. The only omen of this result is perhaps brought out in Fig. 3, where a similarity in the low temperature portions of the $\chi^{-1}(T)$ curves for $t=0.95$ and 1.00 is noted. Several possibilities are open for speculations.

On crossing the magnetic phase boundary at $t=0.95$ the cooperative ordering could change from helimagnetism to ferromagnetism. However, if such an interpretation applies, the

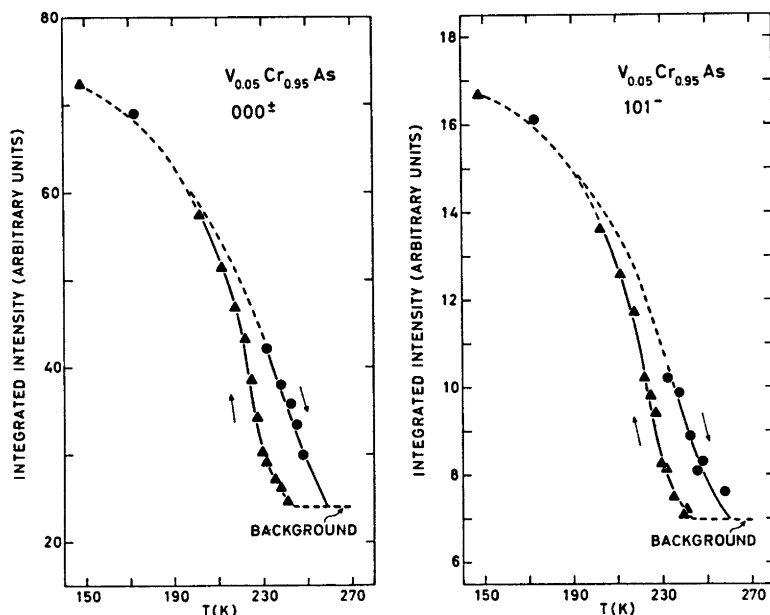


Fig. 4. Temperature dependencies of integrated intensities of 000^\pm and 101^- for $V_{0.05}Cr_{0.95}As$.

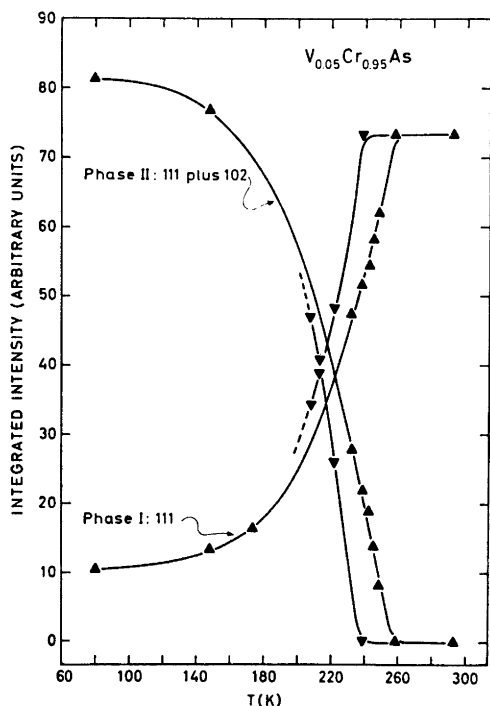


Fig. 5. Integrated intensities versus temperature of 111 for paramagnetic, high temperature phase (I) and 111 plus 102 for helimagnetic, low temperature phase (II) for $V_{0.05}Cr_{0.95}As$.

number of unpaired electrons would have to drop from 1.70 ± 0.05 in the helimagnetic mode to less than 0.5, which represents the detection limit for various models with different orientations of the assumed ferromagnetic moments. Considerations along this line are presented in Refs. 12, 13, 15, and 19, but it should be emphasized that the spiral parameters for $V_{0.05}Cr_{0.95}As$ (like those for $CrAs_{1-x}Sb_x$; $\sim 0.14 \leq x \leq \sim 0.50$ ¹⁹) do not satisfy Kallel *et al.*'s¹⁹ model for cooperative magnetism in phases with the MnP type structure. As pointed out by these authors the shortcomings may be mendable by increasing the number of exchange interactions.

It is feasible although not probable that the Néel temperature of the $V_{1-x}Cr_xAs$ phase exhibits an almost discontinuous drop at $x = 0.95$. In terms of the molecular field approximation this would require a correspondingly rapid decrease in the magnetic exchange parameters or their linear combinations.

Another variable which more likely could show a rapid change with composition, is the magnitude of the magnetic moment. An explanation along this line would be consistent with our present experience which shows that small substitutions of another metal in binary phases with MnP type structure seem to have a radical influence on their electronic band structures.

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