

Magnetic Structures and Properties of $\text{CrP}_{1-x}\text{As}_x$

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

^aKjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway, ^bInstitutt for Atomenergi, Kjeller, Norway, and ^cDelegation AF, Eidgenössisches Institut für Reaktorforschung, Würenlingen, Switzerland

X-Ray and neutron diffraction and magnetic susceptibility measurements show that CrP and CrAs exhibit a complete range of solid solubility, with P and As randomly arranged in an MnP type structure. Like CrAs, the As-rich samples undergo a transition from MnP to NiAs type structure at high temperatures. A double, *c* axis helimagnetic ordering is observed for $0.93 \lesssim x \leq 1$ in $\text{CrP}_{1-x}\text{As}_x$.

In our systematic investigations of structural and magnetic properties of phases with the MnP type structure, one of the most unexpected results has been the absence of cooperative magnetic behaviour for CrP above 17 K.¹ This finding places CrP in a special position in comparison with CrAs,^{2–4} MnP,^{5,6} MnAs,^{7,8} FeP,⁹ and FeAs,¹⁰ which take helimagnetic, ferromagnetic or canted magnetic structures below room temperature. In order to explore this problem further, the examination of CrP was extended down to 1.2 K and pursued into the domain of the ternary $\text{CrP}_{1-x}\text{As}_x$ phase.

EXPERIMENTAL

The binary compounds CrP and CrAs were prepared by heating stoichiometric quantities of the elements (99.0 % Cr (powder crystals), 99.999 % P, and 99.9999 % As (Koch-Light Laboratories)) in evacuated, sealed silica tubes as described in Refs. 1 and 3. Ternary $\text{CrP}_{1-x}\text{As}_x$ samples of desired compositions were prepared from appropriate proportions of CrP and CrAs, by means of a series of annealings at 950–1100 °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 and magnetic susceptibility measurements are included in Ref. 10. The

neutron diffraction data for CrP at 4.2 and 1.2 K were obtained in Würenlingen using a He bath cryostat and neutrons of wave length 2.319 Å.

RESULTS AND DISCUSSION

As demonstrated by the continuous variations in the orthorhombic unit cell dimensions of $\text{CrP}_{1-x}\text{As}_x$ with the composition parameter

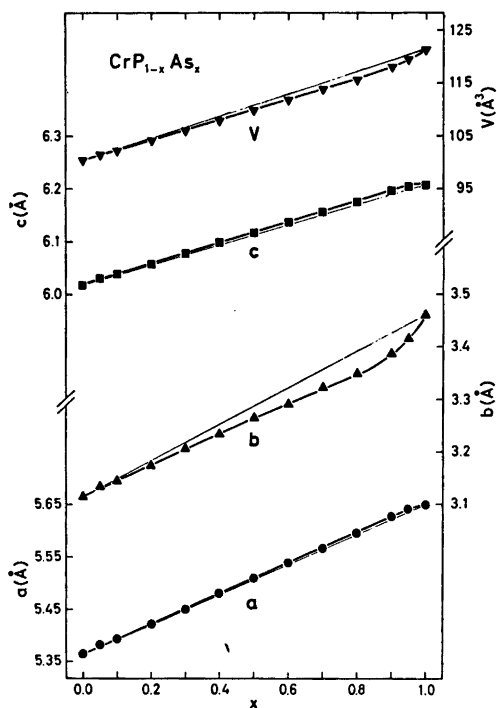


Fig. 1. Unit cell dimensions (at room temperature) of ternary solid solution series CrP–CrAs as functions of composition.

Table 1. Unit cell dimensions and positional parameters with standard deviations for some $\text{CrP}_{1-x}\text{As}_x$ samples; space group $Pnma$, positions 4(c). (Overall profile reliability factors ranging between 0.029 and 0.041.)

x	0			0.90			0.95		
	T(K)	1.2	4.2	293	5	80	293	5	80
$a(\text{\AA})$	5.346(6)	5.347(6)	5.367(7)	5.597(1)	5.609(1)	5.628(1)	5.581(4)	5.596(4)	5.640(2)
$b(\text{\AA})$	3.107(4)	3.108(4)	3.122(4)	3.350(1)	3.360(1)	3.398(1)	3.360(2)	3.367(2)	3.415(1)
$c(\text{\AA})$	5.999(6)	6.001(6)	6.017(8)	6.178(1)	6.187(1)	6.200(1)	6.188(3)	6.174(3)	6.206(2)
x_T	0.0078(5)	0.0080(5)	0.0068(12)	0.0086(12)	0.0105(14)	0.0101(13)	} as for CrAs		
z_T	0.1940(4)	0.1938(4)	0.1930(5)	0.1996(11)	0.1979(10)	0.2006(11)			
x_X	0.1853(3)	0.1852(3)	0.1852(3)	0.1966(6)	0.1971(6)	0.1999(7)			
z_X	0.5648(3)	0.5645(4)	0.5656(3)	0.5737(9)	0.5739(9)	0.5744(7)			

x (Fig. 1), CrP and CrAs exhibit complete, mutual solid solubility. Except for the binary end members^{1,3} of the series, a possible extension of the homogeneity range of $\text{CrP}_{1-x}\text{As}_x$ to metal/non-metal (atomic) ratios different from 1.00 has not been investigated. The X-ray data show that $\text{CrP}_{1-x}\text{As}_x$ ($0 \leq x \leq 1$) takes the MnP type structure with random distribution of the two kinds of non-metal atoms at room temperature.

As evinced by line broadening of reflections on the Guinier photographs, the successive annealings improved considerably the crystalline perfection of the samples. Since the reflections with $k \neq 0$ generally were observed to be more diffuse than those with $k = 0$, the incomplete randomization should occur mainly in the b direction of the crystallites. This problem proved to be rather acute for the large scale, neutron diffraction samples.

The structural data as deduced from neutron diffraction experiments (Table 1) show only minor variations in the unit cell dimensions of CrP and $\text{CrP}_{0.10}\text{As}_{0.90}$ below room temperature, whereas $\text{CrP}_{0.05}\text{As}_{0.95}$, which experiences helimagnetic ordering below 246–260 K, reveals appreciable changes in the unit cell dimensions associated with its superimposed first and second (or higher) order phase transformation (*cf.* Refs. 2–4, 11–13). The positional parameters derived for CrP at 4.2 and 1.2 K are only insignificantly different from those reported for 17 K in Ref. 1. Taking into account that CrAs and $\text{CrP}_{0.05}\text{As}_{0.95}$ undergo cooperative magnetic ordering whereas $\text{CrP}_{0.10}\text{As}_{0.90}$ does not, the present values for the positional parameters of the ternary samples are consistent with those reported³ for CrAs.

The fact that CrAs (as opposed to CrP) undergoes a second (or higher) order crystallographic

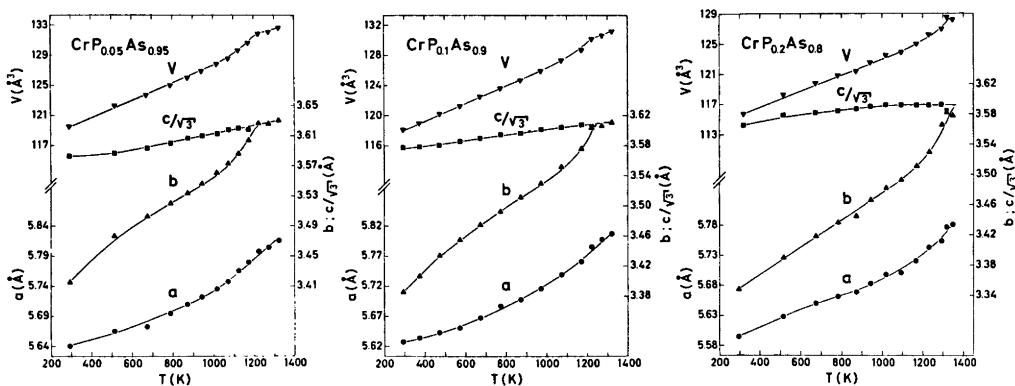


Fig. 2. Unit cell dimensions of three $\text{CrP}_{1-x}\text{As}_x$ samples as functions of temperature. Average relative expansion coefficients $\alpha_a = [(a_T - a_{T'})/a_{300}(T - T')]$, α_b , α_c multiplied by 10^6 K are 24, 54, 9; 27, 59, 9; and 22, 61, 15 for $\text{CrP}_{0.20}\text{As}_{0.80}$, $\text{CrP}_{0.10}\text{As}_{0.90}$, and $\text{CrP}_{0.05}\text{As}_{0.95}$, respectively.

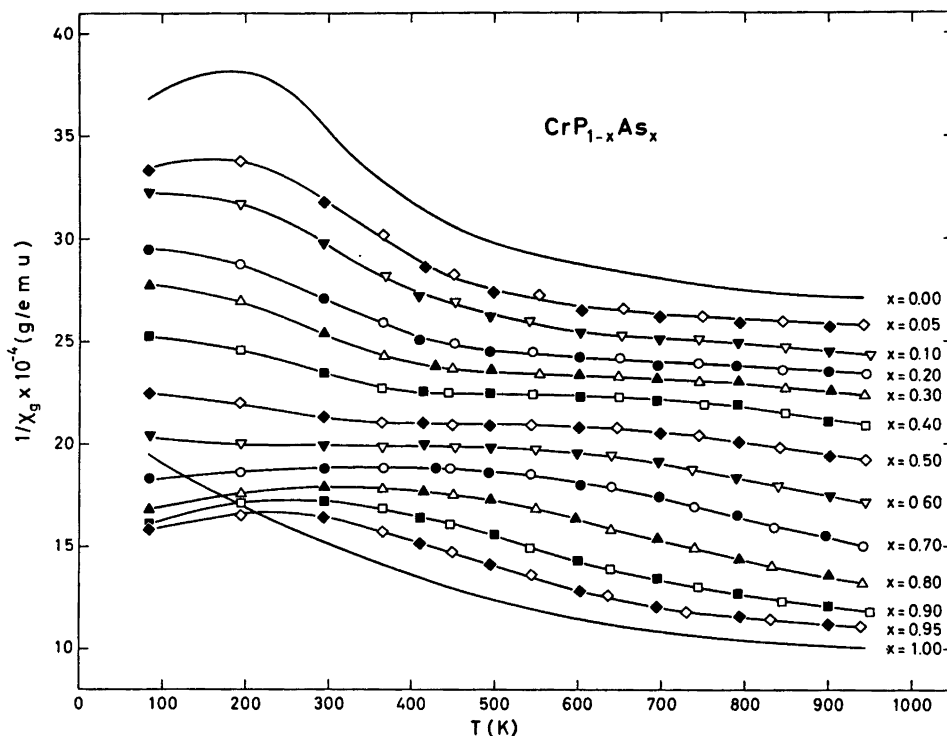


Fig. 3. Reciprocal magnetic susceptibility versus temperature for various $\text{CrP}_{1-x}\text{As}_x$ samples.

transformation to the NiAs type structure at 1173 ± 20 K,¹¹ has prompted a high temperature X-ray study of the As-rich $\text{CrP}_{1-x}\text{As}_x$ samples. As evident from Fig. 2, corresponding transitions to that in CrAs were observed at 1230 ± 50 , 1270 ± 50 , and 1350 ± 50 K for $x = 0.95$, 0.90 , and 0.80 , respectively. The latter temperature represents, in practice, the upper limit for our high temperature X-ray diffraction camera. Although the trend in the above temperatures suggests that the transformation continues at even higher temperatures in samples with $x < 0.80$, the approaching onset of melting or decomposition leads to little confidence in such an extrapolation.

Fig. 3 shows the gradual changes in the temperature dependence of the reciprocal magnetic susceptibility with the composition parameter x . Field strength dependent susceptibilities were not observed, and as seen from Fig. 3, none of the individual thermomagnetic curves fulfils the Curie-Weiss Law over any range of temperature.

The 4.2 and 1.2 K neutron diffraction dia-
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grams of CrP give no indication of any long range magnetic ordering, thus confirming the conclusion of Ref. 1.

The double, c axis type helimagnetic ordering of CrAs^{2-4} extends to a composition $x \approx 0.93$ of the $\text{CrP}_{1-x}\text{As}_x$ phase. At 80 K negligible changes

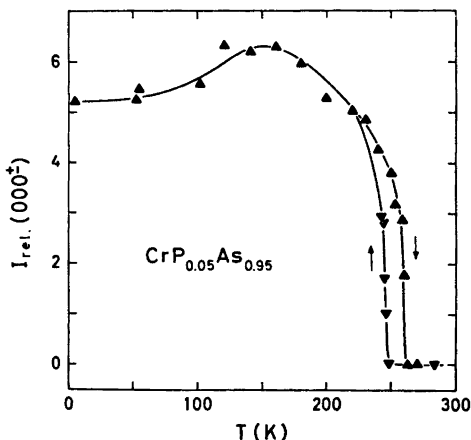


Fig. 4. Relative integrated intensity of 000^{\pm} versus temperature for $\text{CrP}_{0.05}\text{As}_{0.95}$.

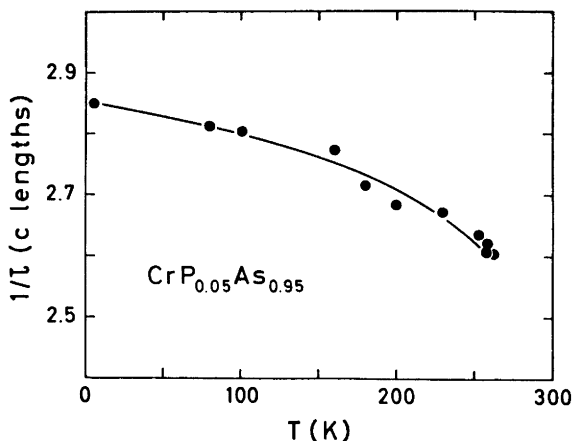


Fig. 5. Spiral periodicity as function of temperature for $\text{CrP}_{0.05}\text{As}_{0.95}$.

were experienced in all parameters specifying the spirals on going from CrAs to $\text{CrP}_{0.05}\text{As}_{0.95}$ ($\tau/2\pi c^* = 0.355(2)$, $\mu_T = 1.7(1) \mu_B$, $\phi = -132(3)^\circ$, and β fixed at 90°). As evident from Fig. 4, the onset of the cooperative magnetic phenomenon in $\text{CrP}_{0.05}\text{As}_{0.95}$ is accompanied by a marked hysteresis, resembling also in this respect CrAs. The 5 % content of P leads to a slight lowering of the Néel temperature (from 261–272 K for CrAs to 246–260 K). Both the spiral periodicity (Fig. 5) and the phase angle between the independent spirals are somewhat temperature dependent in $\text{CrP}_{0.05}\text{As}_{0.95}$. (The latter inference provides the only consistent explanation of the peculiar shape of the curve in Fig. 4 below 150K, since $\text{CrP}_{0.05}\text{As}_{0.95}$ has no ferromagnetic component.)

The results for $\text{Cr}_{1-x}\text{V}_x\text{As}$ ¹² and $\text{CrP}_{1-x}\text{As}_x$ are consistent in that the helimagnetic ordering in both phases is destroyed at some 5 % substitution of Cr or As with another metal or non-metal. A brief discussion of possible reasons for the breakdown of the helimagnetic mode in such phases is given in Ref. 12.

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