

## Magnetic Structures and Properties of $\text{Cr}_{1-t}\text{Fe}_t\text{As}$

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The pseudo-binary CrAs–FeAs system has been investigated by X-ray and neutron diffraction and magnetic susceptibility measurements.  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  is characterized by complete solid solubility, the structure of the ternary, random solid solution phase being of the MnP type. Cr-rich samples undergo a transition from MnP to NiAs type structure at high temperatures. The paramagnetic susceptibilities do not follow the Curie-Weiss Law. A double, *c* axis helimagnetic ordering is observed at low temperatures for  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  samples with  $0 \leq t < 0.05$  and  $\sim 0.82 < t \leq 1.00$ ; for  $0.10 \leq t \leq 0.80$  the samples exhibit weak ferromagnetism.

CrAs<sup>1–3</sup> and FeAs<sup>4</sup> must be regarded as magnetically isostructural compounds, despite the fact that some of the parameters specifying their double, *c* axis spiral structures differ appreciably. Hence, the present study was started in order to establish the variations in the spiral parameters as function of the compositional parameter *t* for  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$ . However, even before this report was written, we have obtained data for similar quasi-binary systems (exemplified by the findings for  $\text{FeP}_{1-x}\text{As}_x$  where a similar situation prevails for the binary end members<sup>4–6</sup>), which led us to question our original working hypothesis. A brief account of the magnetic and structural properties of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  has previously been published by Kazama and Watanabe.<sup>7</sup>

### EXPERIMENTAL

Samples of CrAs and FeAs were made from the elements [99.0 % Cr (powder crystals; Koch-Light Laboratories), 99.99 % Fe (turnings from rods; Johnson, Matthey & Co.), and 99.9999 % As (Koch-Light Laboratories)] according to the specifications in Refs. 2 and 4. Ternary  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  samples

were prepared by heating appropriate mixtures of CrAs and FeAs in evacuated and sealed quartz tubes at 850 °C for four periods of 8 days, interrupted by quenchings and intermediate crushings. Finally, the samples were cooled to room temperature over 3 days.

Details of the experimental methods (X-ray and neutron diffraction, magnetic susceptibility, and magnetization measurements) have been presented in previous communications.<sup>2,4</sup> [The nuclear scattering lengths  $b_{\text{Cr}} = 0.353$ ,  $b_{\text{Fe}} = 0.951$ , and  $b_{\text{As}} = 0.64$  (in  $10^{-12}$  cm) were taken from the 1976-compilation of The Neutron Diffraction Commission.]

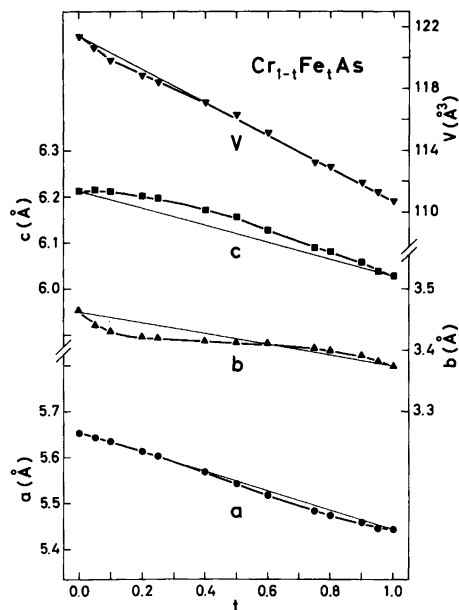


Fig. 1. Room temperature unit cell dimensions of ternary solid solution series CrAs–FeAs as functions of composition.

Table 1. Unit cell dimensions and positional parameters with standard deviations for some  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  samples as derived by least squares profile refinements of neutron diffraction data. (Space group  $Pnma$ ; positions 4(c); overall profile reliability factors ranging between 0.03 and 0.08.)

$t$	T (K)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$x_T$	$z_T$	$x_X$	$z_X$
0.05	10	5.6300(7)	3.3820(3)	6.2077(7)	0.0073(28)	0.1985(21)	0.1969(17)	0.5730(15)
	293	5.6403(5)	3.4350(2)	6.2095(4)	0.0075(20)	0.2007(16)	0.1995(12)	0.5753(11)
0.25	10	5.5929(6)	3.3840(2)	6.1814(5)	0.0048(9)	0.1974(7)	0.1997(7)	0.5752(7)
	293	5.5995(6)	3.4148(2)	6.1916(6)	0.0045(8)	0.2005(7)	0.2002(5)	0.5765(6)
0.50	10	5.5287(7)	3.3899(3)	6.1320(7)	0.0048(15)	0.1992(13)	0.1951(15)	0.5764(16)
	293	5.5386(9)	3.4115(5)	6.1418(7)	0.0048(18)	0.1995(13)	0.1972(15)	0.5769(16)
0.75	10	5.4772(16)	3.3786(6)	6.0852(12)	0.0061(10)	0.1980(8)	0.1964(13)	0.5748(13)
	293	5.4848(14)	3.4045(5)	6.0873(12)	0.0051(14)	0.1974(8)	0.1969(11)	0.5769(14)
0.90	10	5.4545(5)	3.3508(2)	6.0421(5)	0.0035(14)	0.1968(9)	0.1967(14)	0.5768(16)
	293	5.4700(5)	3.3932(3)	6.0578(5)	0.0060(19)	0.1998(13)	0.1999(19)	0.5760(18)
0.95	10	5.4569(5)	3.3455(2)	6.0386(5)	0.0052(16)	0.1966(9)	0.1990(15)	0.5764(17)
	293	5.4435(8)	3.3797(3)	6.0439(7)	-0.0001(19)	0.1916(11)	0.2001(19)	0.5841(20)

## RESULTS AND DISCUSSION

(i) *Chemical crystal structure.* The continuous variations in the orthorhombic unit cell dimensions of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  with the compositional parameter  $t$  (Fig. 1) show that CrAs and FeAs exhibit complete, mutual solid solubility. A possible extension of the homogeneity range of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  to metal/non-metal (atomic) ratios different from 1.00 has not been examined for  $t \neq 0$  and 1. The X-ray and neutron diffraction data confirm that  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  ( $0 \leq t \leq 1$ ) takes the MnP type structure with random distribution of the two kinds of metal atoms at and below room temperature. Like CrAs the Cr-rich  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  samples undergo a transition from MnP to NiAs type structure at temperatures of  $1173 \pm 20$ ,<sup>8</sup>  $1123 \pm 50$ ,  $1273 \pm 50$ , and  $1373 \pm 50$  K for  $t = 0, 0.05, 0.15$ , and  $0.30$ , respectively.

The unit cell dimensions and positional parameters (derived from neutron diffraction data by least squares profile refinements) at and below room temperature for samples with  $t = 0.05, 0.25, 0.50, 0.75, 0.90$ , and  $0.95$  are listed in Table 1, values for  $t = 0$  and 1 being given in Refs. 2 and 4. Within the accuracy of the study, continuous changes in all variables with the composition are observed. This finding concurs with our observations on several isostructural, ternary phases.<sup>6,9-15</sup> The magnetic orderings in  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  take place below room temperature (see iii) and their occurrence has

accordingly no influence on the room temperature unit cell dimensions. The marked cusps at  $t = 0.5$  in the curves for  $a$  and  $c$ , reported by Kazama and Watanabe,<sup>7</sup> are not verified in this study.

(ii) *Magnetic susceptibility.* The thermomagnetic curves for some fifteen samples covering the entire homogeneity range of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  were registered between 4.2 and 1000 K. There is a systematic trend in the level and shape of the  $\chi^{-1}(T)$  curves with the compositional parameter  $t$ , and, for the purpose of clarity, Fig. 2 includes only the results for about half of the samples which were measured. In the range  $0.10 \leq t \leq 0.80$  a ferromagnetic behaviour of the samples was observed at low temperatures. As evident from Fig. 2, the Curie temperature goes through a maximum value in the vicinity of  $t = 0.5$ , where also a maximum in magnetization (at 4.2 K) is observed. As an example of this behaviour, the complete thermomagnetic curve for  $\text{Cr}_{0.50}\text{Fe}_{0.50}\text{As}$  is presented in Fig. 3.

The present findings for  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  are essentially in good agreement with the data published by Kazama and Watanabe.<sup>7</sup> Within the limiting accuracies of the two studies there is a perfect match in the Curie temperatures. The paramagnetic moments ( $\mu_p = \sqrt{8C_{\text{mol}}}$ ) as derived from the slopes of the  $\chi^{-1}(T)$  curves at 300 K, show little variation over the interval  $0.20 \leq t \leq 0.80$  (changing from  $2.4 \pm 0.2 \mu_B$  for  $t = 0.20$  to  $2.1 \pm 0.2 \mu_B$  for  $t = 0.80$ ), concurring roughly with the results of Kazama and

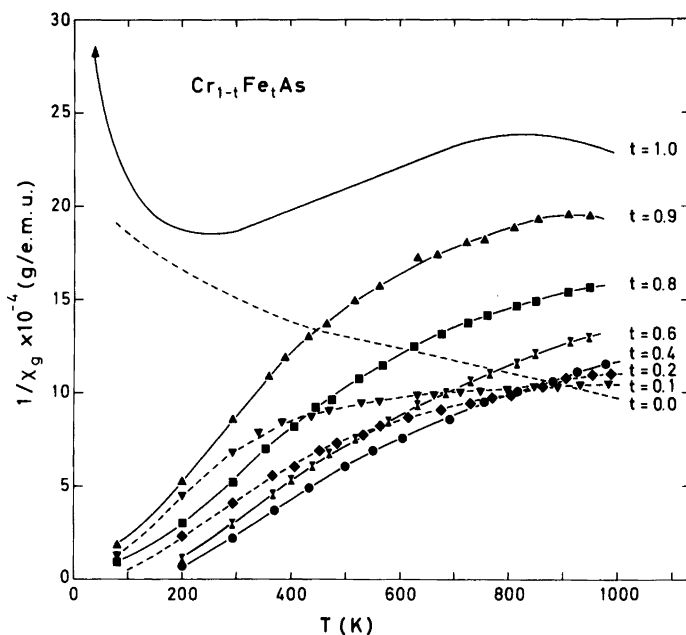


Fig. 2. Inverse magnetic susceptibility versus temperature for some  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  samples. Results for CrAs and FeAs are quoted from Refs. 11 and 4.

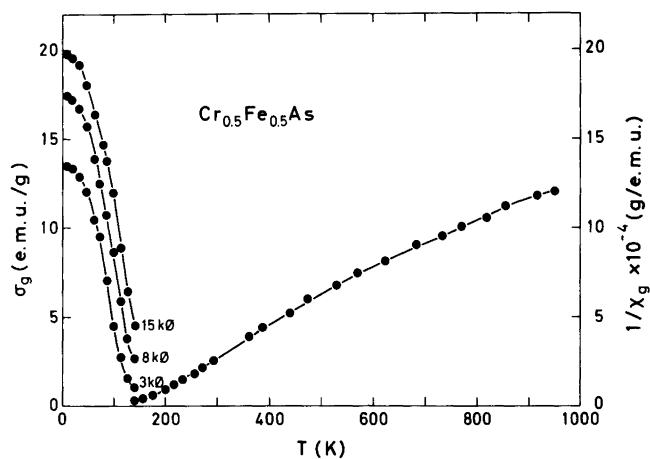


Fig. 3. Thermomagnetic data for  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$ .

Watanabe. However, as noted for the unit cell dimensions, the present data show no cusp in  $\mu_p$  at  $t=0.5$ . It should nevertheless be emphasized that the evaluation of the magnetic moments from the present data are rather dubious, since, actually,

none of our  $\chi^{-1}(T)$  curves (*cf.*, Figs. 2 and 3) follow the Curie-Weiss Law.

(iii) *Magnetic structures.* Both  $\text{CrAs}^2$  and  $\text{FeAs}^4$  take a helimagnetic arrangement of the double,  $c$  axis type below  $261-272$  and  $77 \pm 1$  K, respectively

Table 2. Helimagnetic parameters and Néel temperatures for  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$ . (Angle between magnetic moment and propagation vector fixed at  $90^\circ$ .)

$t$	T (K)	$\tau/2\pi c^*$	$\mu_H(\mu_B)$	$\phi$ ( $^\circ$ )	$T_N$ (K)
1.00	12	$0.375 \pm 0.005$	$0.5 \pm 0.1$	$140 \pm 10$	$77 \pm 1$
0.95	10	$0.452 \pm 0.005$	$0.7 \pm 0.1$	$141 \pm 10$	$56 \pm 2$
0.90	10	$0.456 \pm 0.005$	$0.6 \pm 0.1$	$137 \pm 10$	$37 \pm 3$
0.00	80	$0.353 \pm 0.003$	$1.70 \pm 0.05$	$-133 \pm 1$	$261 - 272$

(Table 2). The neutron diffraction diagram of  $\text{Cr}_{0.95}\text{Fe}_{0.05}\text{As}$  at 10 K shows neither purely anti-ferromagnetic nor helimagnetic reflections. The sample does not undergo the characteristic first order phase transition (see Table 1) from the paramagnetic to the cooperative magnetic state as found for CrAs<sup>2</sup> and CrAs-rich samples of  $\text{V}_{1-t}\text{Cr}_t\text{As}$ ,<sup>11</sup>  $\text{Cr}_{1-t}\text{Mn}_t\text{As}$ ,<sup>1</sup>  $\text{Cr}_{1-t}\text{Co}_t\text{As}$ ,<sup>13</sup> and  $\text{CrP}_{1-x}\text{As}_x$ .<sup>12</sup> The helimagnetic ordering in CrAs extends only slightly ( $t < 0.05$ ) into the ternary range of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$ .

The helimagnetic ordering in FeAs, however, extends to  $t \sim 0.82$ . No pronounced changes are observed in the parameters specifying the spiral structure [*i.e.*, the magnetic moment ( $\mu_H$ ), the propagation vector ( $\tau$ ) and the phase angle between independent spirals ( $\phi$ )] on going from FeAs to  $\text{Cr}_{0.10}\text{Fe}_{0.90}\text{As}$  (Table 2). It may, however, be interesting to note the increase in  $\tau$  from  $0.375 \times 2\pi c^*$  in FeAs to  $0.456 \times 2\pi c^*$  in  $\text{Cr}_{0.10}\text{Fe}_{0.90}\text{As}$ , the latter being the largest propagation vector observed for helimagnetic MnP type phases.

The substitution of FeAs by CrAs leads to an appreciable lowering of the Néel temperature ( $T_N$ ) from  $77 \pm 1$  K for FeAs to  $56 \pm 2$  K for  $t=0.95$  and  $37 \pm 3$  K for  $t=0.90$  (average values determined from the temperature dependences of the intensities of  $101^-$  and  $000^\pm$ , *cf.* Fig. 4). The uncertainties in  $T_N$  also reflect the problem of estimating the background level in the neutron diffraction diagrams. The almost linear dependence between  $T_N$  and  $t$  suggest a magnetic phase boundary at  $t \sim 0.82$  (where  $T_N$  extrapolates to 0 K). We have not found it worthwhile to investigate samples with  $\sim 0.82 < t < 0.90$ .

The slightly different shapes of the intensity curves (integrated intensity *versus* temperature) for the satellite reflections  $000^\pm$  and  $101^-$  (Fig. 4) indicate minor variations in  $\phi$  with the temperature. The propagation vector increases slightly with increasing temperature. Due to the few magnetic reflections and their low intensities the magnetic parameters

for  $\text{Cr}_{0.05}\text{Fe}_{0.95}\text{As}$  and  $\text{Cr}_{0.10}\text{Fe}_{0.90}\text{As}$  are encumbered with relatively large uncertainties (*cf.*, FeAs<sup>4</sup>). The helimagnetic ordering of FeAs extends further into the ternary region of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  than has been observed for  $\text{Mn}_{1-t}\text{Fe}_t\text{As}$ ,<sup>9</sup>  $\text{Fe}_{1-t}\text{Co}_t\text{As}$ ,<sup>13</sup> and  $\text{FeP}_{1-x}\text{As}_x$ .<sup>6</sup>

The rather weak ferromagnetism of  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$  ( $0.10 \leq t \leq 0.80$ ) observed by magnetic susceptibility and magnetization measurements, is difficult to explore by the powder neutron diffraction technique. A ferromagnetic model based upon a magnetic moment along  $b$  (*viz.*, in analogy with the ferromagnetic mode observed for MnP<sup>16</sup>) gave only a minor improvement in the nuclear and profile  $R$  factors and a rather unsatisfactory value for the magnetic

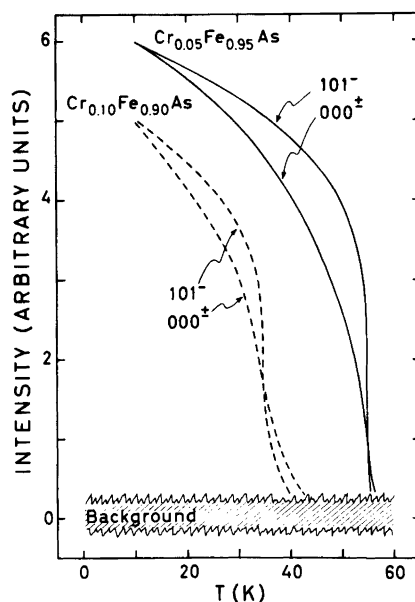


Fig. 4. Relative intensities of  $000^\pm$  and  $101^-$  as functions of temperature for  $\text{Cr}_{0.05}\text{Fe}_{0.95}\text{As}$  (solid lines) and  $\text{Cr}_{0.10}\text{Fe}_{0.90}\text{As}$  (broken lines).

R factor for the sample  $\text{Cr}_{0.50}\text{Fe}_{0.50}\text{As}$ . The best fit was, however, obtained with a magnetic moment of  $0.5 \mu_{\text{B}}$  at 10 K, which is in accordance with the value from magnetization measurements.<sup>7</sup> The corresponding refinements for  $\text{Cr}_{0.75}\text{Fe}_{0.25}\text{As}$  and  $\text{Cr}_{0.25}\text{Fe}_{0.75}\text{As}$  were not successful, due to a still smaller ferromagnetic moment in these samples. Thus, there is an appreciable reduction in the magnetic moment of  $\text{Cr}_{1-x}\text{Fe}_x\text{As}$  on going from the paramagnetic to the ferromagnetic state.

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