

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

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The pseudo-binary CrAs—CoAs and FeAs—CoAs systems have been investigated by X-ray and neutron diffraction and magnetic susceptibility measurements. Both systems are characterized by complete solid solubility, and the structures of the ternary, random solid solution phases are of the MnP type at and below room temperature. Like CrAs and CoAs, all  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  samples and Co-rich  $\text{Fe}_{1-t}\text{Co}_t\text{As}$  samples undergo a transition from MnP to NiAs type structure at high temperatures. The double, *c* axis helimagnetic orderings in CrAs and FeAs extend slightly into the ternary regions ( $t \approx 0.07$  in  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  and  $t \approx 0.03$  in  $\text{Fe}_{1-t}\text{Co}_t\text{As}$ ).

The MnP type atomic arrangement has proved to give rise to various interesting cooperative magnetic structures (*viz.* ferromagnetic,<sup>1</sup> anti-ferromagnetic,<sup>2</sup> and helimagnetic<sup>1-3</sup> modes or varieties<sup>2-10</sup> thereof, depending on composition, temperature, pressure and magnetic field). In order to explore the factors which influence the occurrence of the various modes, attention has recently been focussed on ternary MnP type phases. With the present contribution on  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  and  $\text{Fe}_{1-t}\text{Co}_t\text{As}$ , together with forthcoming papers on  $\text{V}_{1-t}\text{Co}_t\text{As}$  and  $\text{Cr}_{1-t}\text{Fe}_t\text{As}$ , all possible combinations  $T\text{As}-T'\text{As}$ <sup>2,7,11-14</sup> of binary compounds with MnP type structure have been examined.

### EXPERIMENTAL

Batches of CrAs, FeAs, and CoAs were prepared from the elements [99.5 % Cr (Koch-Light Laboratories; crushed powder from commercial, electrolytic grade material), 99.99 % Fe and 99.99+ % Co (Johnson, Matthey & Co.; turnings from rods), and 99.9999 % As (Koch-Light Laboratories)] as described in Refs. 15–17. Ternary samples of desired

compositions were prepared from appropriate proportions of the binary compounds by 3–4 heat treatments of one week's duration at 850 °C, interrupted by intermediate crushings. The samples were finally cooled to room temperature over a period of three days.

Experimental details concerning X-ray and neutron diffraction (including data reduction) and magnetic susceptibility measurements have been reported earlier.<sup>16</sup>

### RESULTS AND DISCUSSION

(i) *Chemical crystal structures.* Fig. 1 shows the room temperature unit cell dimensions of  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  and  $\text{Fe}_{1-t}\text{Co}_t\text{As}$  as functions of the composition parameter *t*. The continuous variations in all unit cell dimensions with *t* demonstrate the complete solid solubility in the CrAs—CoAs and FeAs—CoAs systems. The possibility that the homogeneity ranges of  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  and  $\text{Fe}_{1-t}\text{Co}_t\text{As}$  extend to metal/non-metal (atomic) ratios different from 1.00 has not been examined for  $t \neq 0$  and 1.<sup>15-17</sup>

X-Ray and neutron diffraction data confirm an MnP type atomic arrangement at and below room temperature for  $0 \leq t \leq 1$  in both phases. Moreover, the data show that the substituted atoms are distributed randomly over the metal sub-lattices. The sample  $\text{Cr}_{0.95}\text{Co}_{0.05}\text{As}$ , which exhibits helimagnetic ordering below 130–160 K, reveals appreciable changes in the dimensions of its MnP type unit cell (Table 1) connected with the superimposed first and second (or higher) order phase transformation. This peculiarity, which is typical of CrAs and its slightly substituted ternary derivatives (*cf.* Refs. 7, 12, 15, 18–20), is not observed for  $\text{Cr}_{0.90}\text{Co}_{0.10}\text{As}$  and  $\text{Fe}_{0.95}\text{Co}_{0.05}\text{As}$ . The least

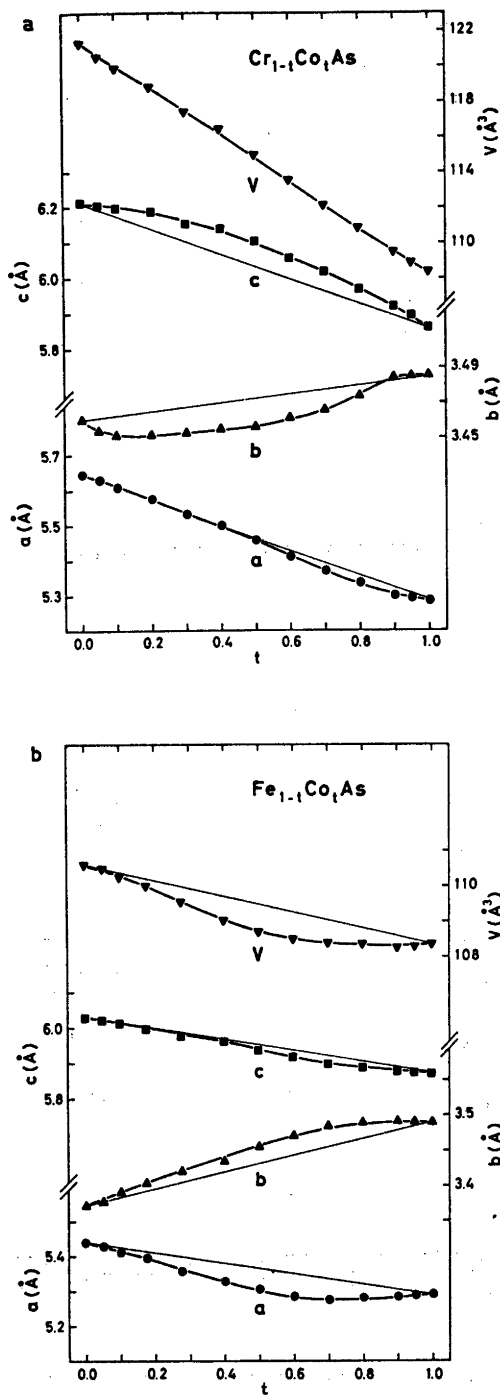


Fig. 1. Orthorhombic unit cell dimensions of ternary, solid solution series (a) CrAs-CoAs and (b) FeAs-CoAs as functions of composition.

Table I. Unit cell dimensions and positional parameters with standard deviations for Cr<sub>0.95</sub>Co<sub>0.05</sub>As, Cr<sub>0.90</sub>Co<sub>0.10</sub>As, and Fe<sub>0.95</sub>Co<sub>0.05</sub>As; space group *Pnma*, positions 4(c). (Overall profile reliability factors ranging between 0.029 and 0.047.)

Sample	Cr <sub>0.95</sub> Co <sub>0.05</sub> As		Cr <sub>0.90</sub> Co <sub>0.10</sub> As		Fe <sub>0.95</sub> Co <sub>0.05</sub> As	
	4.2	80	293	4.2	80	293
$a$ (Å)	5.565(1)	5.562(1)	5.633(1)	5.594(1)	5.604(1)	5.421(1)
$b$ (Å)	3.555(1)	3.556(1)	3.454(1)	3.384(1)	3.443(1)	3.328(1)
$c$ (Å)	6.114(1)	6.110(1)	6.211(1)	6.187(1)	6.187(1)	6.002(1)
$x_T$	0.0089(15)	0.0079(11)	0.0047(12)	0.0114(15)	0.0077(13)	0.0030(5)
$z_T$	0.2015(11)	0.2004(8)	0.2008(9)	0.2000(13)	0.2011(10)	0.1994(3)
$x_X$	0.2043(5)	0.2036(4)	0.2011(5)	0.1992(7)	0.2004(5)	0.2014(5)
$z_X$	0.5794(15)	0.5847(10)	0.5773(6)	0.5742(8)	0.5771(6)	0.5769(5)

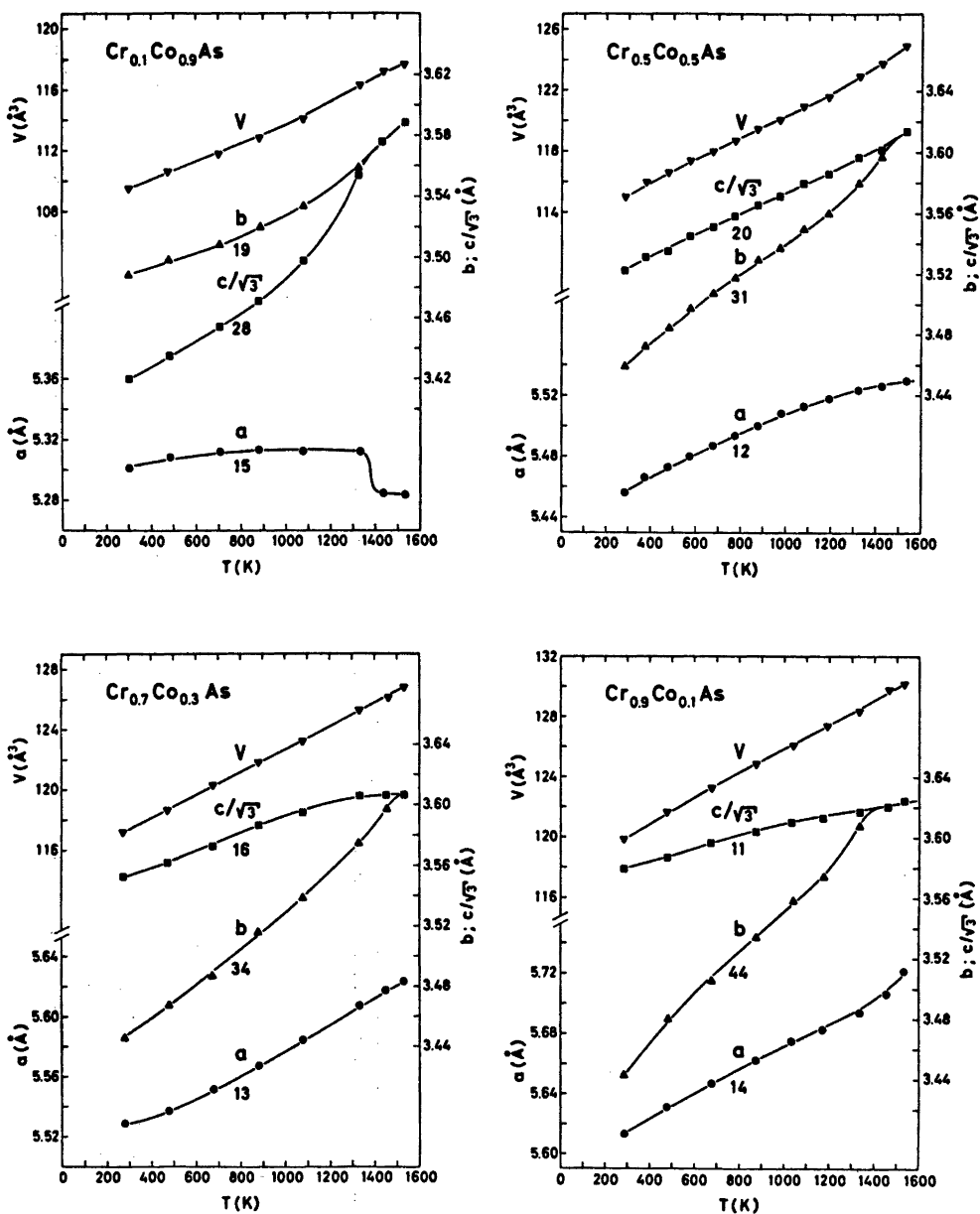


Fig. 2. Unit cell dimensions of representative Cr<sub>1-x</sub>Co<sub>x</sub>As samples versus temperature. Average relative expansion coefficients  $\alpha_a = (a_T - a_{300})/a_{300}(T - 300)$ ,  $\alpha_b$ , and  $\alpha_c$  multiplied by  $10^4$  K are positioned below the appropriate curves (300–1200 K).

squares, profile refined positional parameters (Table 1) derived for Fe<sub>0.95</sub>Co<sub>0.05</sub>As at various temperatures fit nicely in with the data for FeAs,<sup>18</sup> those for Cr<sub>0.95</sub>Co<sub>0.05</sub>As vary in the same way as for CrAs,<sup>15,18</sup> whereas those for

Cr<sub>0.90</sub>Co<sub>0.10</sub>As stay virtually constant at values matching CrAs at room temperature.

CrAs and CoAs exhibit second (or higher) order crystallographic transformations to the NiAs type structure at temperatures of  $1173 \pm 20$  and

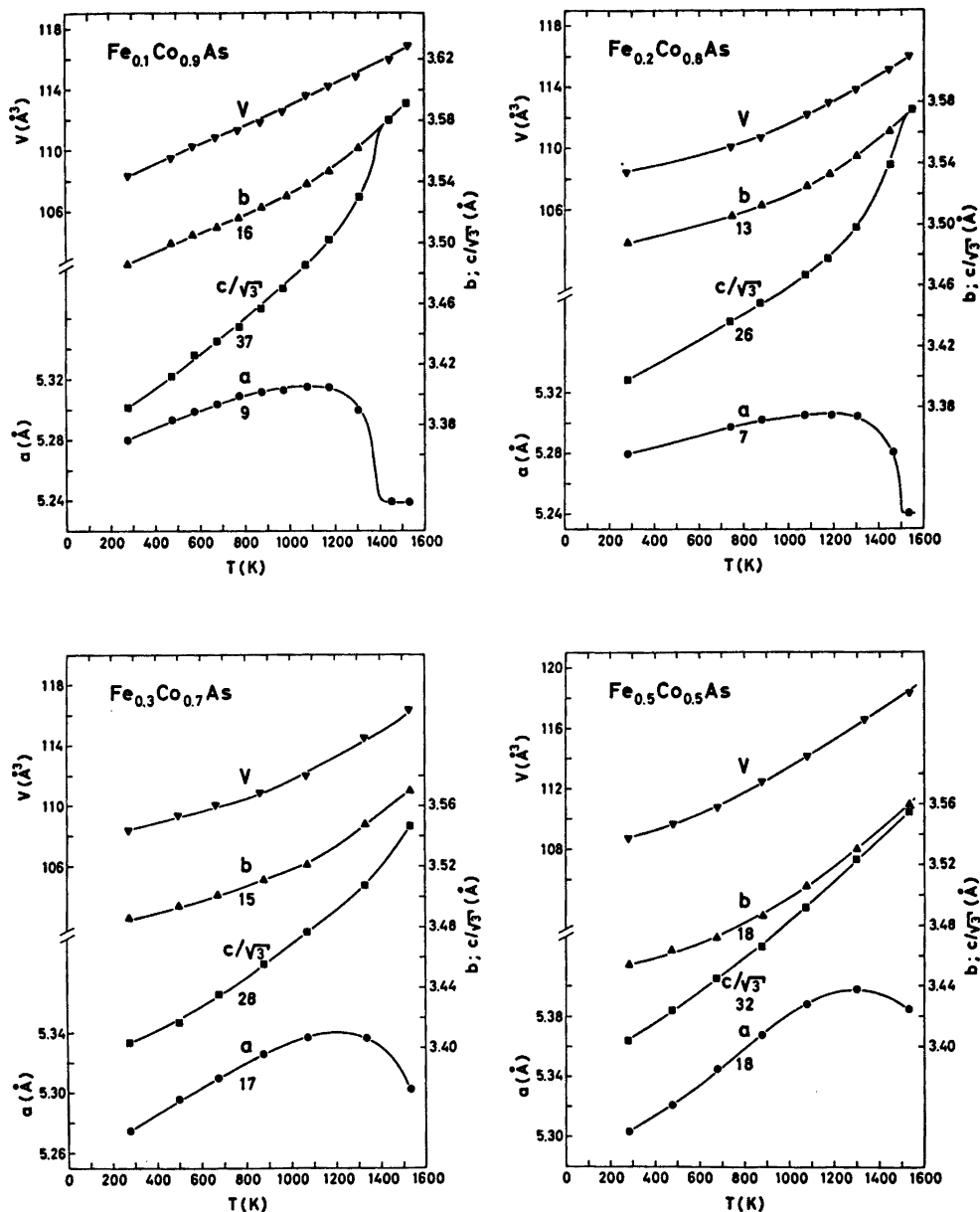


Fig. 3. Unit cell dimensions of Fe<sub>1-t</sub>Co<sub>t</sub>As samples versus temperature. Average relative expansion coefficients  $\alpha_a$ ,  $\alpha_b$ , and  $\alpha_c$  ( $\times 10^6$  K) are given on the diagrams (300–1100 K).

1248 ± 20 K, respectively, whereas no such transformation occurs in FeAs below its melting point of 1343 ± 20 K.<sup>16,21</sup> This distinction is projected into the ternary samples, where Cr<sub>1-t</sub>Co<sub>t</sub>As, as seen from Fig. 2, undergoes transformation at temperatures close to those

for CrAs and CoAs. For Fe<sub>1-t</sub>Co<sub>t</sub>As transformations are only found for 0.8 ≤ t ≤ 1 (cf. Fig. 3).

(ii) *Magnetic susceptibility.* Figs. 4 and 5 show that the temperature dependences of the reciprocal magnetic susceptibility of Cr<sub>1-t</sub>Co<sub>t</sub>As

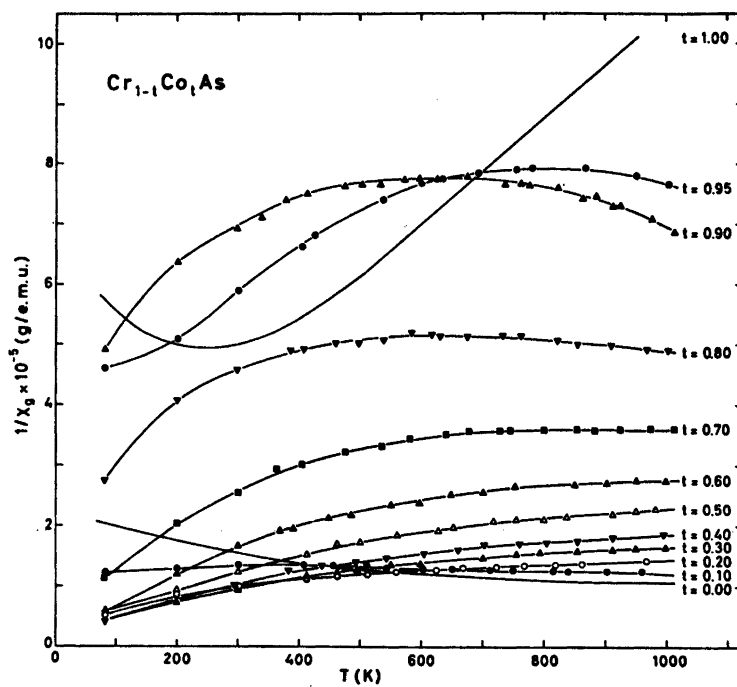


Fig. 4. Reciprocal magnetic susceptibility versus temperature for  $\text{Cr}_{1-t}\text{Co}_t\text{As}$  samples.

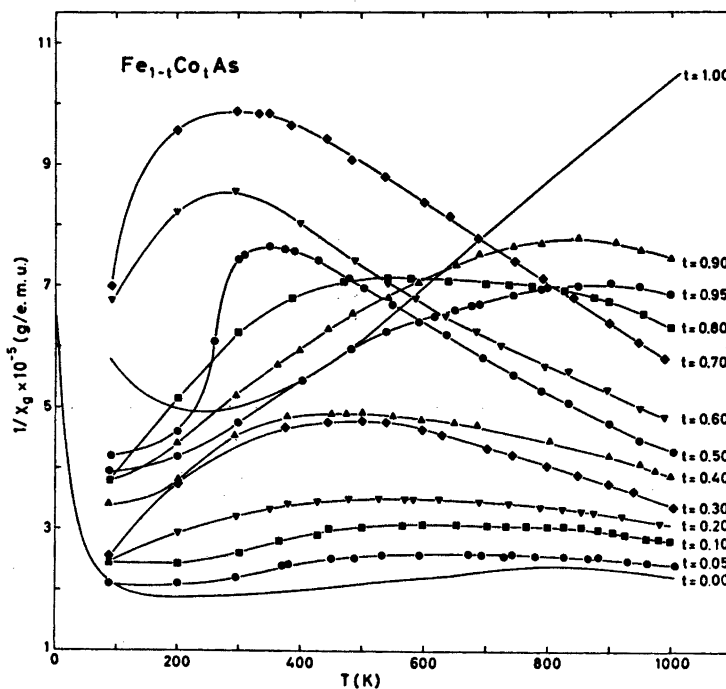


Fig. 5. Thermomagnetic data for  $\text{Fe}_{1-t}\text{Co}_t\text{As}$ .

and Fe<sub>1-t</sub>Co<sub>t</sub>As undergo progressive changes with the composition parameter *t*. No field strength dependent susceptibilities were observed. The thermomagnetic curves for the binary compounds agree with corresponding data reported in Refs. 12, 16, and 17. Apart from FeAs (~300 ~ 650 K) and CoAs (> 490 K) none of the Cr<sub>1-t</sub>Co<sub>t</sub>As and Fe<sub>1-t</sub>Co<sub>t</sub>As samples satisfies the Curie-Weiss Law.

(iii) *Magnetic structures.* Helimagnetism has previously been observed for CrAs<sup>7,15,18</sup> and FeAs,<sup>14</sup> whereas CoAs<sup>17</sup> exhibits no cooperative phenomenon above 4.2 K. The helimagnetic ordering in CrAs and FeAs is of the double, *c*-axis type, and it extends in both the investigated systems only slightly into the ternary composition ranges (*t* ≈ 0.07 for Cr<sub>1-t</sub>Co<sub>t</sub>As and (say) *t* ≈ 0.03 for Fe<sub>1-t</sub>Co<sub>t</sub>As).

Only small changes were experienced in the variable spiral parameters (*β* fixed at 90°) on going from CrAs (80 K:  $\mu_T = 1.70 \pm 0.05 \mu_B$ ,  $\tau/2\pi c^* = 0.353(1)$ ,  $\phi = -133 \pm 1^\circ$ )<sup>15</sup> to Cr<sub>0.95</sub>Co<sub>0.05</sub>As (4.2 K:  $\mu_T = 1.65 \pm 0.05 \mu_B$ ,  $\tau/2\pi c^* = 0.346(1)$ ,  $\phi = -124 \pm 1^\circ$ ; 80 K:  $\mu_T = 1.65 \pm 0.05 \mu_B$ ,  $\tau/2\pi c^* = 0.360(1)$ ,  $\phi = -128 \pm 1^\circ$ ; 145 K:  $\tau/2\pi c^* = 0.373(1)$ ). However, already a 5% substitution of CrAs by CoAs leads to a substantial lowering of the Néel temperature (from 261–272 K for CrAs to 130–160 K). Significant indication of reflections characteristic of the helimagnetic arrangement was not found for Cr<sub>0.90</sub>Co<sub>0.10</sub>As.

The cooperative magnetism in Cr<sub>0.95</sub>Co<sub>0.05</sub>As is associated with a marked hysteresis which involves two distinct MnP type phases. As shown in Fig. 6 the hysteresis is brought out in both nuclear and magnetic reflections of the neutron diffraction diagrams. Similar hystereses are observed for CrAs<sup>7,15,18</sup> and CrAs-rich samples of V<sub>1-t</sub>Cr<sub>t</sub>As,<sup>12</sup> Cr<sub>1-t</sub>Mn<sub>t</sub>As,<sup>7</sup> Cr<sub>1-t</sub>Fe<sub>t</sub>As,<sup>20</sup> and CrP<sub>1-x</sub>As<sub>x</sub>.<sup>19</sup> The helimagnetic structures of these phases have also another feature in common in that both the phase angle ( $\phi$ ) between the spirals and the spiral turn angle ( $\alpha$ ) vary little with temperature.

The helimagnetic arrangement in pure FeAs<sup>16</sup> extends slightly into the ternary range of Fe<sub>1-t</sub>Co<sub>t</sub>As. The neutron diffraction diagrams of Fe<sub>0.95</sub>Co<sub>0.05</sub>As gave only insignificant indications of magnetic reflections, and the magnetic phase boundary was tentatively positioned at *t* = 0.03.

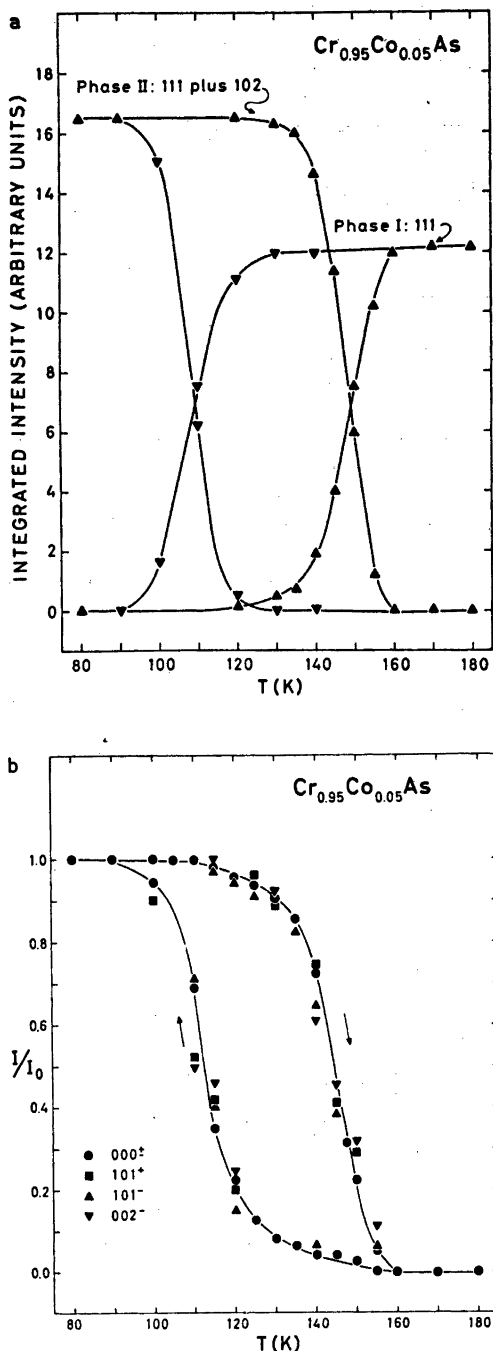


Fig. 6. Integrated intensities versus temperature of (a) 111 of paramagnetic, high temperature state (phase I) and 111 plus 102 for helimagnetic, low temperature (phase II) state and (b) 000<sup>±</sup>, 101<sup>±</sup>, 101<sup>-</sup>, and 002<sup>-</sup> of Cr<sub>0.95</sub>Co<sub>0.05</sub>As.

The data for the cooperative magnetic states of  $T_{1-t}T'_tAs$  and  $TP_{1-x}As_x$  phases which have been collected hitherto, have revealed the contours of a pattern.<sup>2,7,12-14,19,22</sup> Among the mono-phosphides and -arsenides of the 3d series which take the MnP type structure, cooperative magnetic states are found for Cr, Mn, and Fe, but are lacking for V and Co. Appreciable composition regions for cooperative modes in ternary phases are only observed when Mn is one constituent. The cooperative modes in CrAs, FeP, and FeAs are destroyed at some 5–10 % substitution with a metal different from Mn or another non-metal.<sup>12,19,22</sup> Possible reasons for the breakdown of the helimagnetic modes in these phases are briefly discussed in Refs. 12 and 22. These considerations, which were based on the findings for  $V_{1-t}Cr_tAs$  and  $FeP_{1-x}As_x$ , are necessarily somewhat speculative, since the parameters specifying the helimagnetic states ( $\mu_T$ ,  $\alpha$ ,  $\phi$  and  $T_N$ ) show an almost discontinuous drop at the magnetic phase boundary. Including also the present knowledge concerning  $Cr_{1-t}Co_tAs$  and  $Fe_{1-t}Co_tAs$  the most likely explanation of the limited extensions of the helimagnetic regions in  $Cr_{1-t}T_tAs$ ,  $CrP_{1-x}As_x$ ,  $Fe_{1-t}T_tAs$ , and  $FeP_{1-x}As_x$  appears to be that the magnetic exchange parameters decrease rapidly with small variations in  $t$  or  $x$ , thus inducing corresponding decreases in  $T_N$  for such phases.

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