Magnetic Behaviour of Mn$_{1-x}$Cr$_x$As (0.20 < t < 0.40)

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The low temperature magnetic properties of Mn$_{1-x}$Cr$_x$As for 0.20 < t < 0.40 have been re-examined by X-ray and neutron diffraction and differential scanning calorimetry. Double, helimagnetic arrangements with propagation vectors along the crystallographic $a$ and/or $c$ directions prevail in the co-operative magnetic state. As a unique feature for Mn$_{1-x}$Cr$_x$As among the MnP type phases, the H$_c$- and H$_a$-mode coexist (H$_a$ being the low temperature variant) in a narrow composition range around $t = 0.37$. Characteristic parameters for the two modes, such as the Neél temperature, the enthalpy change at the MnP-H to MnP-P type transition and the spiral propagation vector decrease monotonically towards $t = 0.37$ (viz. both from above and below $t = 0.37$).

A remarkable feature of the MnP type atomic arrangement is that it can accommodate a number of differently ordered magnetic structures, viz. a variety of ferro-(F), antiferro-(AF) and helimagnetic (H) modes depending on composition, temperature, pressure, external magnetic field, etc. However, the characteristic double H$_a$ and H$_c$ configurations (cf. Ref. 1) have apparently become almost a trademark for the MnP type family (at least for its magnetic frontage).

Table 1 gives an account of the binary compounds and ternary solid solution phases which take the MnP type chemical structure as well as the co-operative magnetic H$_a$- and/or H$_c$-mode. (A number of ternary, particularly phosphide, phases have recently been studied at this Institute, but since the results are yet unpublished they are not included in Table 1.) In view of the rather overwhelming amount of experimental data, the engagement on the theoretical aspects of these apparently interesting and unique findings is surprisingly scarce (cf. Refs. 18,21). The prototype itself, MnP, is by far the most thoroughly studied, and for this compound the contours of a theoretical framework have emerged (cf. Ref. 22 and references therein).

According to the number of representatives listed in Table 1 the H$_c$ variant is far more

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Table 1. Survey of MnP type phases which have been reported to adopt the (co-operative magnetic) H$_a$- and/or H$_c$-mode.

<table>
<thead>
<tr>
<th>Helimagnetic sub-class</th>
<th>Binary representative</th>
<th>Ternary (solid solution) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H$_a$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn$_{1-x}$T$_x$As</td>
<td>$T = V^2$, Cr$_{3.4}$, Fe$_1$, Co$_5$, Ni$_6$</td>
</tr>
<tr>
<td></td>
<td>MnAs$_{1-x}$X$_x$</td>
<td>$X = P^{7,8}$</td>
</tr>
<tr>
<td><strong>H$_c$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnP$_2$</td>
<td>Mn$_{1-x}$T$_x$P</td>
<td>$T = Fe^{10}$</td>
</tr>
<tr>
<td></td>
<td>Fe$_{1-x}$T$_x$P</td>
<td>$T = Mn^{10}$</td>
</tr>
<tr>
<td></td>
<td>FeP$_{1-x}$X$_x$</td>
<td>$X = As^{12}$</td>
</tr>
<tr>
<td>CrAs$_{13,14}$</td>
<td>Cr$_{1-x}$T$_x$As</td>
<td>$T = V^{15}$, Mn$_{3.4}$, Co$_6$, Ni$_6$</td>
</tr>
<tr>
<td></td>
<td>CrAs$_{1-x}$X$_x$</td>
<td>$X = P^{17}$, Sb$_{18}$</td>
</tr>
<tr>
<td>FeAs$_{19}$</td>
<td>Fe$_{1-x}$T$_x$As</td>
<td>$T = Cr^{20}$, Mn$<em>1$, Co$</em>{16}$</td>
</tr>
<tr>
<td></td>
<td>FeAs$_{1-x}$X$_x$</td>
<td>$X = P^{12}$</td>
</tr>
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</table>

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common than $H_a$, the latter variant being confined to Mn$_{1-r}$T$_r$As, MnAs$_{1-x}$X$_x$ and probably MnAs when subjected to pressure. Only three of the ternary phases can apparently accommodate both the $H_a$ and $H_c$ configurations (under the government of composition and temperature). For Mn$_{1-r}$Fe$_r$As$^3$ and MnAs$_{1-x}$P$_x$,$^{7,24}$ the $H_a$ and $H_c$-mode are separated by two-phase regions in the pseudo-binary phase diagrams. For Mn$_{1-r}$Cr$_r$As, however, the available experimental data$^{3,4,25}$ suggest that the $H_a$- and $H_c$-mode may coincide in the composition range 0.35$\leq r$$\leq$0.40.

The present study of Mn$_{1-r}$Cr$_r$As was undertaken in order to choose between the possibilities:

(i) magnetic transformation $H_a$ to $H_c$ (or vice versa) with temperature,

(ii) chemical and/or magnetic segregation into two phases.

In order to clarify this problem the composition range 0.20$\leq r$$\leq$0.40 and temperature interval 10$^\circ$T<~300 K were re-examined.

EXPERIMENTAL

The pure elements used as starting materials for the syntheses were 99.999% Cr-flakes (Koch-Light Laboratories Ltd.), 99.99% Mn-flakes (Johnson, Matthey & Co. Ltd.) and 99.9999% As-lumps (Koch-Light Laboratories Ltd.). According to earlier experience, equilibria in syntheses of ternary phases are most readily attained when preparations of the binary compounds are introduced as intermediate steps in the procedures.

The binary compounds MnAs and CrAs were prepared by heating stoichiometric quantities of the elements (ground powders of Cr- and Mn-flakes) in evacuated, sealed silica tubes. The temperature in the horizontally positioned furnaces was slowly increased ($2\times50$ °C/d) to 900 °C for MnAs and 1000 °C for CrAs. After cooling to room temperature over 1 d the samples were crushed and subjected to one further heat treatment at 900 °C for 1 week, followed by cooling to room temperature over 1 d.

Ternary Mn$_{1-r}$Cr$_r$As samples were made similarly from the binary compounds. After a first heat treatment at 950 °C for 1 week, the samples were crushed and reheated at 700 °C for 3 weeks, and finally slowly cooled to room temperature over 1 d.

Room temperature X-ray powder diffraction photographs were taken in a Guinier camera (CuK$_\alpha_1$ radiation, $\lambda$=1.540598 pm, Si$^{26}$ as internal standard, $a$=543.1065 pm). Unit cell dimensions were derived by applying the method of least squares (to the generally sharp, well-defined Guinier photographs).

Low temperature X-ray photographs were obtained between $\sim$120 and $\sim$300 K in an Enraf-Nonius (FR 553) Guinier-Simon camera (CuK$_\alpha_1$ radiation, quartz crystal monochromizer, Si or Ag as internal standards). The samples were contained in sealed, thin-walled quartz capillaries. The temperature was regulated via a Pt resistance thermometer and a digital programmer synchronized the temperature with the movement of the film cassette. The difference between the programmed and actual temperature at the sample position reflects the thermal gradient between the sensor and the sample. The actual sample temperature is considered to be well within 2 K from the registered temperature.

The powder neutron diffraction data were collected with the OPUS II two-axis spectrometer between 10 K and room temperature. Cylindrical sample holders of vanadium were used. The temperature was controlled and regulated within $\pm$0.5 K by a Thor (3010) controller (chromel/gold 0.07% Fe thermocouple) connected to a Displex cooling system. Neutrons of wavelength 187.7 pm were obtained from the Kjeller reactor JEEP II. The nuclear scattering lengths (in 10$^{-12}$ cm) $b_{\text{Cr}}$=0.353, $b_{\text{Mn}}$=−0.370 and $b_{\text{As}}$=0.64 were taken from Ref. 27. The magnetic formfactor for Mn$^{2+}$ was taken from Ref. 28. The Hewat$^{29}$ version of the profile refinement programme by Rietveld$^{30}$ was applied in the final fitting of the variable parameters.

The helimagnetic parameters were derived from the intensities of the appropriate reflections by the programme SPIRAL$^{31}$.

Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field $\sim$8 kOe using 10~−15 mg samples).

Low temperature differential scanning calorimetry (DSC) measurements were performed with a Mettler TA 3000 system consisting of a TG10 TA processor and a DSC30 cell. Samples of $\sim$100 mg were used, the heating rate was 10 K/min and the temperature range $\sim$100~−~500 K was covered. Data reduction and evaluation of thermodynamic parameters were performed with standard programmes for the system.
CRYSTAL STRUCTURE DATA

Although the principal aim of this study has been to elucidate the low temperature magnetic properties of Mn$_{1-t}$Cr$_t$As, various other experimental data have come to hand as by-products.

In complete accordance with Ref. 3, Mn$_{1-t}$Cr$_t$As with 0.20 ≤ $t$ ≤ 0.40 takes the MnP type atomic arrangement at, and below, room temperature. Since the Bragg reflections are generally sharp and no additional super-structure reflections were observed, the substituted atoms appear to be randomly distributed over the metal sub-lattice (as seen by the X-ray and neutron diffraction techniques). The unit cell dimensions and positional parameters (as derived from powder neutron diffraction data) given in Table 2, fall in quite well with the corresponding data in Ref. 3. The room temperature unit cell dimensions versus the compositional parameter $t$ for the additional small scale samples of Mn$_{1-t}$Cr$_t$As (Fig. 1) also matches the corresponding data in Ref. 3. (The few, negligible distinctions that nevertheless occur are easily attributed to sample quality and data handling in the present study or methodological differences between X-ray and neutron diffraction.)

When judging or using the data in Table 2 it should be remembered that the positional parameters for the metal atoms are burdened with relatively large uncertainties due to their small effective scattering lengths. An additional structure refinement complication stems from the marked overlapping of reflections which occurs when $c/b$ approximates $\sqrt{3}$ for certain compositions (most pronounced for $t=0.39$) and temperatures.

The conical perturbation of the H$_4$-mode reported for 0.25 ≤ $t$ ≤ 0.35 in Ref. 3, represents a

![Figure 1](attachment:figure1.png)

**Fig. 1.** Room temperature unit cell dimensions of Mn$_{1-t}$Cr$_t$As (0.35 ≤ $t$ ≤ 0.40). Error limits do not exceed twice the size of symbol. Circles and squares represent results derived from X-ray and neutron diffraction data, respectively. (1 Å = 10$^2$ pm.)

Fig. 2. Unit cell dimensions versus temperature for selected samples of Mn$_1$Cr$_x$As at temperatures below 300 K; (a) Mn$_{0.3}$Cr$_{0.4}$As, (b) Mn$_{0.7}$Cr$_{0.3}$As, (c) Mn$_{0.65}$Cr$_{0.35}$As, (d) Mn$_{0.65}$Cr$_{0.37}$As, and (e) Mn$_{0.615}$Cr$_{0.385}$As. Error limits do not exceed the size of symbols. Filled and open circles represent results derived from X-ray and neutron diffraction data, respectively. (1 Å = 10$^{-10}$ pm.) $T_{N2}$ refers to temperature of the MnP$_2$H$_{12}$ = MnP$_2$P$_2$ type transition. Shaded regions refer to two-phase regions between MnP$_2$H$_{12}$ and MnP$_2$P$_2$ type states (for Mn$_{0.9}$Cr$_{0.1}$As and Mn$_{0.7}$Cr$_{0.3}$As) or between MnP$_2$H$_{12}$ and MnP$_2$P$_{12}$ type states (for Mn$_{0.65}$Cr$_{0.35}$As and Mn$_{0.65}$Cr$_{0.37}$As).

The variations in the unit cell dimensions of Mn$_1$Cr$_x$As for $t$ = 0.20, 0.30, 0.35, 0.37 and 0.385 with temperature are shown in Fig. 2. One or more phase transformations are distinctly reflected in these curves. The hysteresis accompanied, first order transitions for $t$ = 0.20, 0.30,
0.35 and 0.37 [Fig. 2 (a)–(d)] where the hysteresis loop increases in the said order, represent the most prominent feature in this picture.

The thermal expansion curves for $t=0.35$, 0.37 and 0.385 also show sign of a second (or higher) order phase transition through a marked change in slope of $b$ versus temperature. As may be expected from the data in Fig. 2 the axial ratios $c/a$ and $c/b$ demonstrate peculiar and interesting temperature dependences and the results for $\text{Mn}_0.63\text{Cr}_{0.37}\text{As}$ (Fig. 3) can serve as an example. When $c/b$ obtains the value $\sqrt{3}$ at higher temperatures this is merely a manifestation of that the $\text{MnP}_{\pm 2}\text{NiAs}$ type transition has taken place (cf. Refs. 3,25,32). The fact that $\text{Mn}_{1-t}\text{Cr}_{t}\text{As}$ also takes $c/b=\sqrt{3}$ at lower temperature is accidental in the sense that the $\text{MnP}$ type atomic arrangement is retained. This again demonstrates that little significance should be attached to the axial ratio alone as a structure determining criterion.

**PHASE DIAGRAM DATA**

A section of the phase diagram for $\text{MnAs}–\text{CrAs}$ is presented in Fig. 4. The diagram is constructed on the basis of the structural data considered in the preceding section together with magnetic and thermo-analytical DSC data outlined in succeeding sections.

The widths of the hysteresis regions in Fig. 4 correspond to temperature intervals hatched on Fig. 2 (a)–(d). As seen on comparing Figs. 2(e) and 4, the sample with $t=0.385$ is considered to be a borderline case which just escapes the hysteresis accompanied, first order transition.

As indicated on the inset illustration in Fig. 4 all transitions are believed to be of magnetic origin. Apart from the question of conical spiral deformation, which is left open in this study, the phase diagram in Fig. 4 is merely a detailed version of the relevant section of the phase diagram given in Ref. 3, where also comments to the phase diagram of Kazama and Watanabe$^{25}$ are found. Fig. 4 is, on the other hand, distinctly different from the magnetic phase diagram proposed in Ref. 4. The distinction is probably less pronounced than at first sight, and may be mainly a consequence of the external field applied in the study of Wohlf et al.$^4$

For $t=0.20$ and 0.30 the transition occurs between the $\text{MnP},\text{H}_2$ and $\text{MnP},\text{P}$ type states at the temperature denoted $T_{N,1}$. This transition was earlier considered to be of the continuous second (or higher) order type in $\text{Mn}_{1-t}\text{Cr}_{t}\text{As}$ (in
Fig. 4. Magnetic phase diagram for Mn$_{1-t}$Cr$_t$As (0.20 $\leq$ $t$ $\leq$ 0.40). The bars represent the width of hysteresis as determined by X-ray diffraction.

A hysteresis accompanied transition is also observed for $t$=0.35, 0.355, 0.37 and 0.38. Although this transition manifests itself in the low temperature X-ray and DSC data similarly to the transition described for $t$=0.20 and 0.30, examination by neutron diffraction reveals that it is of the MnP$_2$H$_a$ to MnP$_2$H$_c$ type (see inset to Fig. 4). Despite the difference in magnetic nature of the latter transition (denoted $T_s$) it appears as a continuation of $T_{N,1}$ in Fig. 4. However, the details of the phase diagram are not well established in the region between $t$=0.30 and 0.35. In this composition range the three curves $T_{N,1}$, $T_{N,2}$ and $T_s$ probably meet in a triple point.

In addition, the samples $t$=0.35, 0.355, 0.37 and 0.38, undergo another, second (or higher) order, transition at the somewhat higher temperature $T_{N,2}$. According to neutron diffraction this transition is of the MnP$_2$H$_c$ $\Rightarrow$ MnP$_2$P type. Only this latter transition is observed in the samples $t$=0.385, 0.39 and 0.40. The MnP$_2$H$_c$ $\Rightarrow$ MnP$_2$P type transition is reflected in the inflection point of the thermal expansion curves for the $b$-axis [Fig. 2 (c)$-$ (e)]. This phenomenon is probably a

Fig. 5. Change in unit cell volume at the MnP$_2$H$_a$ to MnP$_2$P type transition (for $t$$\leq$0.30) or MnP$_2$H$_a$ to MnP$_2$H$_c$ type transition (for $t$$\leq$0.35). (1 Å=$10^8$ pm.) Broken curve see text.

Table 3. Characteristics of helimagnetic modes in MnP type phases (cf., e.g., Refs. 1, 37, 9).

<table>
<thead>
<tr>
<th>Property</th>
<th>Magnetic unit cell</th>
<th>Numbering of magnetic atoms</th>
<th>Spinal propagation rules</th>
<th>Extinction rules for helimagnetic reflections</th>
<th>Phase relations for spirals</th>
<th>Thermal dependence of $\phi_1$</th>
<th>Temperature dependence of $T/\Delta V$</th>
<th>Magnetic propagation index $m$ for $\phi_1$</th>
<th>Temperature dependence of $T/\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
<td>$H_\perp$-mode</td>
</tr>
</tbody>
</table>

Magnetostrictive effect, which appears to be a general feature for the MnP$_x$H$_{1-x}$ to MnP$_x$P$_y$ transition.

The discontinuous change in the unit cell volume ($\Delta V=V_\perp-V_\parallel$; $T_\parallel>T_\perp$) at the first order transition varies with the compositional parameter $t$ as shown by the solid curve in Fig. 5. $\Delta V$ is seen to increase by a factor $\sim 2$ between $t=0.30$ and 0.38. However, this substantial increase is closely connected with:

(i) The occurrence of the $H_\perp$-mode with its unusual thermal expansion properties for the unit cell volume (cf. Fig. 2),

(ii) The temperature span of the $H_\perp$-mode varies appreciably with $t$ (cf. Fig. 4).

When $\Delta V$ is corrected for the combined effect of these factors the broken curve in Fig. 5 is obtained, and the compositional dependence of the corrected $\Delta V$ has become almost negligible.

Another feature which seems worth noting is that $\Delta V$ at the first order, co-operative to paramagnetic transition is positive ($\Delta V=+2\times10^6$ pm$^3$) in Mn$_{0.75}$Cr$_{0.25}$As (0.20$\leq t \leq 0.30$) as opposed to its binary end members MnAs ($\Delta V=-3\times10^6$ pm$^3$) and CrAs ($\Delta V=-2.5\times10^6$ pm$^3$).

HELMAGNETIC STRUCTURES

Characteristic features of the helimagnetic structures in MnP type phases are summarized in Table 3. In this study experimental data have been collected for samples with $t=0.25, 0.37$ and 0.39. Mn$_{0.75}$Cr$_{0.25}$As was studied mainly to clarify whether the magnetic transition is accompanied with a hysteresis or not. On the other hand, the samples with $t=0.37$ and 0.39 are both in the composition range where coexistence of the $H_\perp$- and $H_\parallel$-modes is expected.

As evident from Table 3 the two helimagnetic modes have many features in common. However, the systematic absences for the satellite reflections in the neutron diffraction patterns facilitate an unambiguous determination of the mode present in each case.

The magnetic reflections could be indexed as required by an $H_\parallel$-mode for $t=0.25$ and 0.37 for $T<T_\perp$ and as an $H_\perp$-mode for $t=0.37$ for $T_\parallel<T<T_{N,2}$ and $t=0.39$ for $T<T_{N,2}$. (Numerical values for the temperatures are: $T_{N,1}=203-207$ K for $t=0.25$ and $T_\perp=150-175$ K for $t=0.37$; $T_{N,2}=223\pm 2$ K and 228\pm 2 K for $t=0.37$ and 0.39,

Table 4. Helimagnetic parameters for Mn$_{1-x}$Cr$_x$As. ($R_{\text{spiral}}$ ranging between 0.05 and 0.09; 6–7 magnetic satellite reflections.)

<table>
<thead>
<tr>
<th>$t$ (K)</th>
<th>0.37</th>
<th>0.39</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>140</td>
</tr>
<tr>
<td>$\tau_{\text{f/2}\mu}$*</td>
<td>0.062(4)</td>
<td>0.073(4)</td>
</tr>
<tr>
<td>$\tau_{e/2}\mu_e$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{Hf}}(\mu_0)$</td>
<td>1.84(10)</td>
<td>1.45(10)</td>
</tr>
<tr>
<td>$\phi_{1,2}\mu_1(\mu_0)$</td>
<td>39(10)</td>
<td>46(10)</td>
</tr>
<tr>
<td>$\phi_{1,2}\mu_2(\mu_0)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_s$ (K)</td>
<td>175(3)*</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{N,2}}$ (K)</td>
<td>223(3)</td>
<td></td>
</tr>
</tbody>
</table>

* Upon heating.

respectively.) The spiral parameters $\mu_{\text{Hf}}$ and $\phi_{1,2}$ (see Table 3) were deduced from the best fit as judged from the reliability factor $R_{\text{spiral}} = \Sigma |I_i(\text{obs}) - s \cdot I_i(\text{calc})| / \Sigma I_i(\text{obs})$.

The spiral parameter $\beta^1$ was fixed at 90° in all calculations. The possibility of magnetic contributions to the Bragg (nuclear) reflections could not be established with certainty. A ferromagnetic component along $a$ would be consistent with deductions in Refs. 3,4,25, and this assumption led in fact to somewhat lower reliability factors in some of the structural refinements (see the section on crystal structure data). Single crystal neutron diffraction and/or polarized neutron analysis could resolve this question.

The results given in Table 4 are generally in agreement with the data presented in Ref. 3. The numerical values for $\phi_{1,2}$ for the $H_\text{c}$-mode are indeed somewhat larger than the corresponding values in Refs. 3,13. However, the error limits are easily underestimated due to the fact that the satellite intensities are generally low and super-imposed on a fluctuating background.

The transition between the $H_a$- and $H_c$-mode in Mn$_{0.63}$Cr$_{0.37}$As is clearly demonstrated in Fig. 6 which shows how the integrated intensity of the well resolved 000$^\pm$ satellites for the two modes change with temperature. This magnetic phase transition is directly coupled to the first order structural phase transition described earlier. The width of the hysteresis region for the magnetic transition determined by neutron diffraction complies well with the temperature range determined from X-ray diffraction for the chemical

![Fig. 6. Relative intensities of 000$^\pm$ for the $H_a$- and $H_c$-mode versus temperature. Open and filled symbols refer to data obtained upon cooling and heating, respectively.](image-url)

transition (cf. preceding section). Repeated measurements showed that the equilibrium condition is reasonably well established in the examination of the MnP,H_a to MnP,H_c type transition. The sigmoidal shape of the hysteresis loop curves may to some extent be attributed to the inevitable minute concentration variations within the large scale neutron diffraction samples.

Fig. 7 shows the composition dependence of the propagation vectors (τ_a/2πc* or τ_c/2πc*) at 10 K. The value of τ_c/2πc* for t=0.37 refers to 150 K, but in this composition range (cf. Table 4) τ_c/2πc* varies only slightly with temperature. It is worthwhile to denote that both propagation vectors decrease towards t=0.37, and in this respect Fig. 7 shows some resemblance to Fig. 4. In addition to the change in propagation direction, there is also a discontinuous shift in the magnitude of the propagation vector at the MnP,H_a to MnP,H_c type transition (see Table 4, Fig. 7 and Ref. 3). The transition has a similar effect on φ_{1,2}, whereas the magnetic moment μ_H is maintained essentially unaltered through the transition. As emphasized above, φ_{1,2} is hampered with larger inaccuracy, but at least for the H_a-mode its composition dependence follows the same trend as for the propagation vector.

The present study has unequivocally showed that the H_a- and H_c-mode occur as low and high temperature variants, respectively, in a composition range around t=0.37. This is the first evidence for this type of co-operative magnetic coexistence for the MnP type phases, but similar phenomena are well known for other phases (cf., e.g., Refs. 33,34). The stability conditions for the H_a- and H_c-mode have been examined by the group theoretical Bertaut method. However, while the stability conditions for the H_c-mode could be derived on the basis of isotropic exchange interactions, the account for the H_a-mode required a far more sophisticated exchange mechanism. Hence, the relative stability of two modes is not established.

MAGNETIC SUSCEPTIBILITY

Thermomagnetic curves for Mn_{1-x}Cr_xAs samples with 0.10≤x≤0.60 are shown in Fig. 8. (They were recorded primarily as a means to characterize the present samples.)

Starting from the high temperature side, the linear sections reflect the NiAs,P type state with defined values of μ_P and θ (μ_P ranging between 3.9±0.3 and 4.5±0.2 μ_B, θ ranging between

$225 \pm 25$ and $250 \pm 10$ K, as compared with $\mu_p = 4.5 \pm 0.1 \mu_B$ and $\theta = 270 \pm 10$ K for MnAs. In the intermediate section of the $\chi^{-1}(T)$ curves the MnP,P type state prevails, where the curve shape is influenced by the gradual reduction from a “high” to a “low” spin state, which in turn is related to how far the MnP type conversion has progressed (cf. Ref. 36). The low temperature section of the curves corresponds to the co-operative magnetic state.

TRANFORMATION ENTHALPIES

In order to obtain an estimate of the energy quantities involved in the MnP,H$_8$ to MnP,P, MnP,H$_6$ to MnP,H$_c$ and MnP,H$_c$ \(\rightleftharpoons\) MnP,P type transformations, DSC data were collected for various Mn$_{1-t}$Cr$_t$As samples. The results are summarized in Table 5, which also gives the transformation temperatures (upon heating) obtained by the X-ray and neutron diffraction techniques as well as literature values for the transformation enthalpies and temperatures for MnAs and CrAs. The transformation temperatures found by the different methods are generally in good agreement (Table 5).

The transformation enthalpies show a consistent trend with the compositional parameter $t$ (Fig. 9). At first sight, it is somewhat remarkable that MnAs, which undergoes the NiAs,F to MnP,P type transition, fits the data for the MnP,H$_8$ to MnP,P type transition. However, the

<table>
<thead>
<tr>
<th>$t$</th>
<th>$T_{N,1}$ or $T_5$ (K)</th>
<th>ND</th>
<th>$\Delta H$(J/g)</th>
<th>$T_{N,2}$ (K)</th>
<th>$\Delta H$(J/g)</th>
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<tr>
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<td>172</td>
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<td>1.00$^b$</td>
<td>261</td>
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</tbody>
</table>

* For $t=0.00$, $T_c$ (NiAs,F to MnP,P) = 318.6 K (DSC), 315 K (X-ray), 317 K (ND) and $\Delta H = 15.6$ J/g (literature: 315 K, 21.0 J/g$^{37,39}$, 315.6 K, 25.2 J/g$^{37}$, 318 K$^{40}$). $^b$ For $t=1.00$, literature values for $T_N$ and $\Delta H$ are: 259.86 K, 5.84 J/g$^{38}$, 265 K, 4.09 J/g$^{31}$; 272 K$^{13}$, 280 K$^{42}$. $^c$ Quoted from Ref. 3.

essential point is that the transitions take place between co-operative- and paramagnetic states. On the other hand, attention should be paid to the fact that the literature (cf. Ref. 37) gives scattered values for $\Delta H$ for the NiAs,F to MnP,P type transition in MnAs.

Contrary to the findings for MnAs the present $\Delta H$ value for the MnP,H$_2$ to MnP,P type transition in CrAs concurs with that published by Blachnik et al.$^{38}$ In view of this somewhat conflicting situation for MnAs and CrAs it is not appropriate to suggest a general scaling of the present $\Delta H$ values.

The $\Delta H$ versus $t$ relationship shows a distinct minimum around $t=0.37$, i.e. just the composition region where both the H$_2$- and H$_c$-mode coexist depending on temperature. In the composition range where both modes are found, the individual $\Delta H$ values for the MnP,H$_2$ to MnP,H$_c$ and MnP,H$_c$ to MnP,P type transitions approach zero, and it is the sum of these contributions that constitutes the minimum.

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REFERENCES

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