

Non-Stoichiometry of Chromium Monoarsenide

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The structural properties of chromium monoarsenide has repeatedly and extensively been studied by powder X-ray and neutron diffraction, electrical, magnetic, calorimetric and other methods (cf. Refs. 1–7 and references therein). At high temperatures, $T > T_D = 1173 \pm 20$ K,^{3,7} CrAs adopts the hexagonal NiAs-type structure, whereas for $T < T_D$ the structure progressively becomes orthorhombically distorted with an MnP-type atomic arrangement. Below room temperature, at $T_N \approx 270$ K, a first-order, magnetic order–disorder transition accompanied by hysteresis and considerable jump in the unit cell volume takes place. However, a strange feature is that different studies have given rather different transition temperatures for CrAs, with T_N ranging between 240 and 280 K. Such discrepancies are not found for related phases, and the variations in T_N seem to be much larger than any probable experimental error. We have earlier briefly reported⁷ that CrAs indeed exhibits a small range of homogeneity and that this is probably the cause of the observed spread in T_N . The purpose of this communication is to document these findings.

Experimental

Samples of Cr_tAs with $0.90 \leq t \leq 1.10$ were prepared by heating weighed amounts of the elements (Cr, crushed flakes, 99.9999%, and As, lumps, 99.9999%, Koch-Light Laboratories) in sealed, evacuated silica-glass tubes as described for CrAs in Ref. 8 (in the final step, the samples were cooled from 700 °C to room temperature over a period of 1 d). Several series of samples

were prepared, and the compatibility of the results is generally very good. However, in order to eliminate effects of even slight differences in conditions pertaining during the synthesis, all data reported in this paper refer to samples prepared simultaneously, in the same furnace, and subjected to essentially identical treatment during the intermediate crushings and at other stages of the preparation procedure. The samples were characterized at room temperature by means of powder X-ray diffraction using a Guinier camera ($\text{CuK}\alpha_1$ radiation, $\lambda = 154.0598$ pm; Si as internal standard). Low-temperature powder X-ray photographs were obtained with an Enraf-Nonius (FR 553) Guinier Simon camera between 100 and 350 K. Differential scanning calorimetry (DSC) measurements were carried out between 100 and 900 K using a Mettler TA 3000 system.

Results and discussion

The crystal structure of stoichiometric and non-stoichiometric Cr_tAs is clearly of the MnP type. At room temperature, all samples were found to be in a paramagnetic state. The variation in the unit cell dimensions (*Pnma* setting of the unit cell) with *t* is shown in Fig. 1. Although the variations in *a*, *b*, *c* and *V* are all only very slight (and hence easily can be overlooked), trends of increasing *b* and *V* for more chromium-rich samples are evident. Thus, the conclusion that the variation reflects the existence of a homogeneity range seems inescapable. The extent of this homogeneity range can hardly be established accurately, neither from the variation in the unit cell dimensions (Fig. 1), nor by application of the dis-

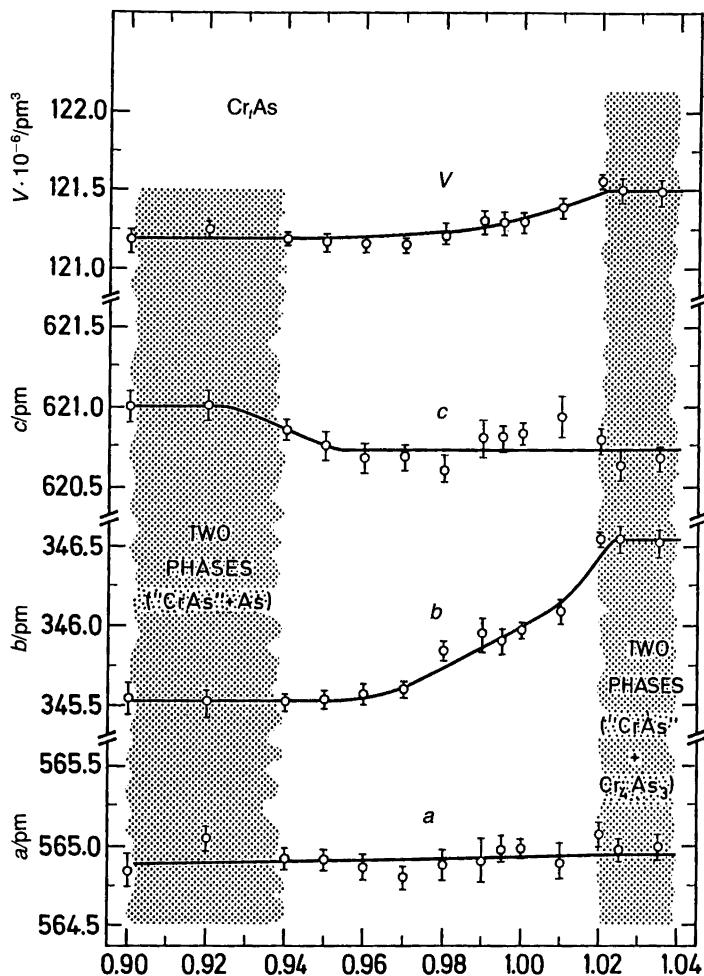


Fig. 1. Variation in unit cell dimensions for Cr_tAs (measured at room temperature) with composition, *t*.

appearing-phase principle to the primary diffraction data. By combining the results with those from DSC measurements (see below) it is concluded that the range is defined by $0.94 \pm 0.02 \leq t \leq 1.02 \pm 0.01$. The difference in unit cell volume between the most Cr-rich and -poor samples is estimated to be $\Delta V \approx 0.30 \cdot 10^6 \text{ pm}^3$ [If the volume increment of the "additional" Cr in Cr_tAs is stipulated to be $8 \cdot 10^6 \text{ pm}^3$ (cf. the size of "additional" Ni in Ni₃S₂, Ni₃Sn₂ and Ni₃Sn₄^{9,10}) the just mentioned ΔV value amounts to $\Delta t \approx 0.04$, which is about half the width of the indicated interval].

The variation in the Néel temperature ($T_{N,i}$ and $T_{N,d}$ for increasing and decreasing temperature

conditions, respectively) with composition was established on the basis of DSC measurements. As seen from the results in Fig. 2 there is a pronounced, approximately stepwise variation in $T_N(t)$. For $t < 0.94$ $T_{N,i} = 239 \pm 1 \text{ K}$ and $T_{N,d} = 225 \pm 1 \text{ K}$, for $0.94 \leq t < 0.98$ $T_{N,i} = 244 \pm 1 \text{ K}$ and $T_{N,d} = 230 \pm 1 \text{ K}$, whereas for $0.98 \leq t \leq 1.02$ $T_{N,i}$ varies continuously between $256 \pm 1 \text{ K}$ and $264 \pm 1 \text{ K}$, and $T_{N,d}$ between $244 \pm 1 \text{ K}$ and $255 \pm 1 \text{ K}$. Thus, the width of the hysteresis, ΔT_N , becomes smaller for larger Cr contents. These observations provide a nice explanation of the earlier reported discrepancies in T_N for chromium monoarsenide. The DSC data for some samples, e.g. $t = 0.98$, show, in addition to the

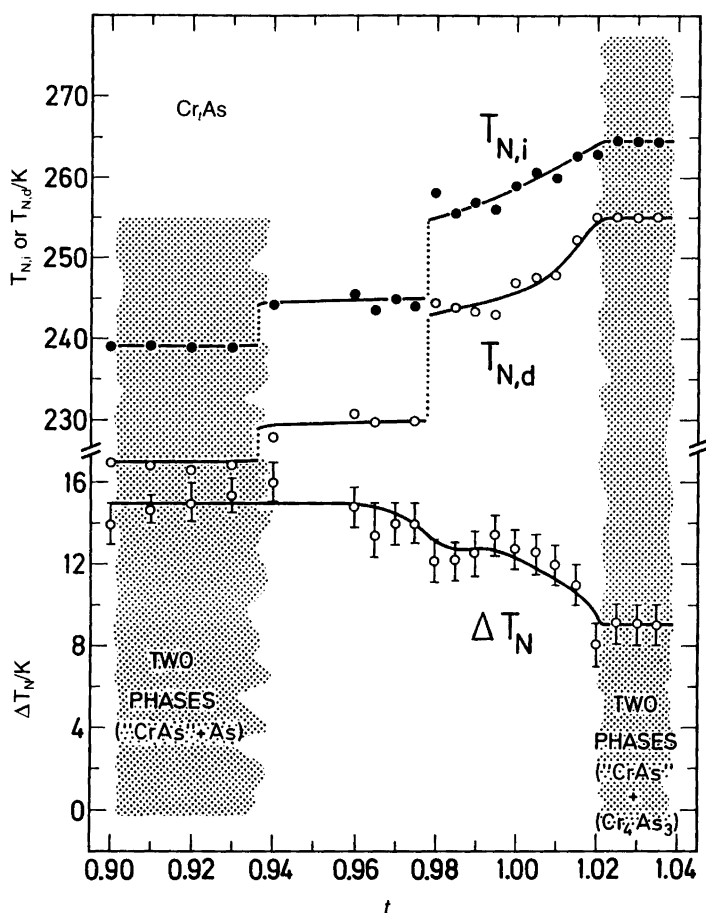


Fig. 2. Variation in Néel temperature for Cr_tAs ($T_{N,d}$ and $T_{N,i}$ for decreasing and increasing temperature conditions, respectively) and width of temperature hysteresis (ΔT_N) with composition, t .

peak at $T_{N,i}$ or $T_{N,d}$, a further tiny peak. This may be interpreted as if the sample really is in a two-phase state. According to the diffraction data, these two phases must be of the MnP type with almost identical unit cells. The marked and apparently stepwise variation in T_N , without having distinct counterparts in a , b or c , strongly suggests that different defect structures are operative in different composition intervals of Cr_tAs .

Similar homogeneity regions are not reported for other MnP-type pnictides. However, such a property is almost a trademark for phases which adopt the NiAs-type structure, although distinctly more rare among the pnictides than among the chalcogenides of the NiAs-type family. However, as the homogeneity range has little impact on the unit cell dimensions of chromium monoarsenide (cf. Fig. 1) it is quite plausible that

similar behaviour in related MnP- and NiAs-type phases simply has been overlooked. Only the very strong coupling between T_N and t made the homogeneity region detectable in Cr_tAs . The present data do not allow any definite deductions concerning the details of the defect arrangement. This problem will be further pursued by powder neutron diffraction experiments.

The discontinuous changes in the unit cell dimensions at the first-order para- to helimagnetic transition at T_N were evaluated from low-temperature powder X-ray diffraction photographs. The jumps in a , b , c and V at the transition are only slightly dependent on composition. The jumps in Δb and ΔV are somewhat reduced on going from $Cr_{0.960}As$ ($\Delta b = 12.8$ pm and $\Delta V = 2.83 \cdot 10^6$ pm³) to $Cr_{1.02}As$ ($\Delta b = 11.2$ pm and $\Delta V = 2.39 \cdot 10^6$ pm³). The smaller jumps in Δb and ΔV for Cr-

rich samples correlate with the reduction in hysteresis, ΔT_N . This correlation is similar to what is observed for the CrAs–MnAs solid solution phase.⁷

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