

The Magnetic Properties of $\text{CrAs}_{1-x}\text{Se}_x$

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The magnetic susceptibility of the $\text{CrAs}_{1-x}\text{Se}_x$ phase ($0 \leq x \leq 1$) has been investigated by the Faraday technique, and unit cell dimensions have been obtained from Guinier photographic data. The NiAs type structure prevails in the region $0.5 \leq x \leq 1$, where the paramagnetic moment decreases smoothly from $4.3 \pm 0.1 \mu_B$ for CrSe to $3.7 \pm 0.1 \mu_B$ for $\text{CrAs}_{0.5}\text{Se}_{0.5}$. At higher As content, the X-ray data indicate a smooth transition into the MnP type structure, and the paramagnetic moment increases to $3.9 \pm 0.2 \mu_B$.

As a part of a continuing investigation of the NiAs and related phases, a project has been undertaken to study the factors which cause certain transition metal compounds to adopt the MnP type structure rather than the more symmetrical NiAs type structure. Recent studies^{1,2} have shown that CrAs has interesting magnetic properties, and in order to elucidate this further, a study of the ternary phase $\text{CrAs}_{1-x}\text{Se}_x$ has been undertaken.

The binary ends of this phase obtain different crystallographic as well as magnetic structures. The CrSe phase has an undistorted NiAs type structure³⁻⁶ in the vicinity of the equiatomic composition, and Corliss *et al.*⁵ have reported an antiferromagnetic type of ordering, in which the spins on the Cr atoms form an "umbrella-like" array with three-fold symmetry. Above a Néel temperature of $\sim 300^\circ\text{K}$, the magnetic susceptibility of CrSe exhibits a Curie-Weiss relationship.^{4,7,8}

The CrAs phase, on the other hand, adopts the MnP type structure,² and below $T_N \sim 261$ to $\sim 272^\circ\text{K}$, this compound shows a helimagnetic ordering with spirals propagating in the c direction.^{1,2} The magnetic susceptibility curve of CrAs is anomalous above T_N , and this finding has been attributed to an increasing number of unpaired electrons with increasing temperature.²

EXPERIMENTAL

Samples of CrAs and CrSe were prepared from flakes of 99.999 % Cr (Koch-Light Laboratories, Ltd), 99.999 % As (Fluka AG), and 99.998 % Se (Bolidens Gruvaktiebolag, Sweden) by heating weighed quantities of the components in evacuated and sealed silica

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tubes. The tubes were heated at 750°C for 14 days, after which the samples were crushed and ground, reheated for 6 days at 770°C and quenched to room temperature. The CrSe sample was subjected to additional heating at 850°C for 1 week to insure homogeneity, and finally quenched to room temperature.

Samples of $\text{CrAs}_{1-x}\text{Se}_x$ were then prepared for $x = 0.2, 0.4, 0.5, 0.6,$ and 0.8 by mixing weighed quantities of the CrAs and CrSe powders. It was found that single phase solid solutions could not be formed by heating the mixtures in silica tubes due to reactions with the quartz at high temperatures. Therefore, the samples were placed in Al_2O_3 crucibles, which were sealed in evacuated silica tubes. In this manner, single phase homogeneous samples were obtained after heating for 2 weeks at 1100°C.

X-Ray powder photographs were taken of all samples with a Guinier type camera of 80 mm diameter, using monochromatized $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$). Potassium chloride ($a = 6.2919 \text{ \AA}$) was added as an internal standard. The unit cell dimensions were obtained by refining the data according to the least squares method. The calculated standard deviations are given in brackets after the corresponding parameter values.

Magnetic susceptibility measurements were made by the Faraday technique between room temperature and 1000°K and, in some cases, at dry ice and liquid nitrogen temperatures. Because of the high magnetic susceptibilities of the samples, a compromise had to be made between sample size and usable magnetic field strength. In order to make measurements at field strengths where the magnet could be calibrated accurately, the sample size was restricted to ~ 8 mg. With these small samples, weighing errors are large. These were minimized by averaging data for several samples, and by checking with measurements made on 20 to 40 mg samples at lower field strengths.

The magnetization of CrSe was measured between liquid nitrogen and room temperatures on a vibrating sample magnetometer (Princeton Applied Research Model FM-1), using 110 and 130 mg samples.

RESULTS AND DISCUSSION

(i) *Structure.* The X-ray photographs showed that complete homogeneity had been obtained for each sample, since no trace of a second phase was observed. The unit cell dimensions for the individual samples are listed in Table 1. A plot of the corresponding parameters *versus* composition (Fig. 1)

Table 1. Unit cell dimensions for the $\text{CrAs}_{1-x}\text{Se}_x$ phase.

Composition	Structure type	a (Å)	b (Å)	c (Å)
CrAs	MnP	5.6490 (6)	3.4609 (6)	6.2084 (7)
$\text{CrAs}_{0.8}\text{Se}_{0.2}$	MnP	5.7822 (10)	3.5453 (9)	6.2369 (10)
$\text{CrAs}_{0.6}\text{Se}_{0.4}$	MnP	5.8449 (11)	3.5711 (7)	6.2805 (10)
$\text{CrAs}_{0.5}\text{Se}_{0.5}$	NiAs	3.6430 (4)	—	5.8945 (6)
$\text{CrAs}_{0.4}\text{Se}_{0.6}$	NiAs	3.6530 (2)	—	5.9180 (2)
$\text{CrAs}_{0.2}\text{Se}_{0.8}$	NiAs	3.6618 (6)	—	5.9882 (9)
CrSe	NiAs	3.6991 (4)	—	6.0721 (8)

shows a smooth transition from the NiAs to the MnP type structure, demonstrating that CrAs and CrSe are completely miscible in all proportions. The setting of the unit cell for the MnP type region is in accordance with space group $Pnma$ ($c > a > b$). Thus, the c axis of the NiAs type region corresponds to the a axis of the MnP type region, whereas a and $a\sqrt{3}$ of the former correspond to b and c of the latter.

The unit cell dimensions of CrSe determined in this study agree reasonably well with those reported by Haraldsen and Mehmed³ and Chevreton⁶ for quenched samples, whereas they are somewhat higher than those found by Chevreton for slowly cooled samples. This is consistent with the homogeneity

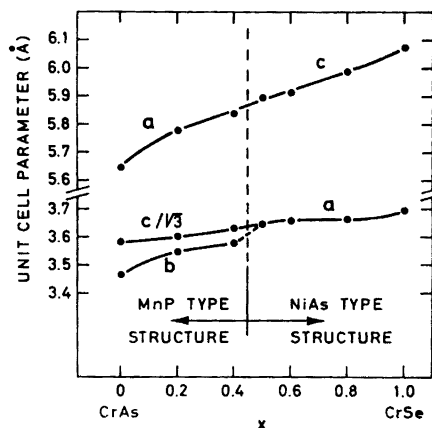


Fig. 1. Unit cell parameters of $\text{CrAs}_{1-x}\text{Se}_x$ as a function of composition.

range extending to higher Cr concentration at elevated temperatures. According to the present study, the phase limit lies at the stoichiometric composition above $\sim 800^\circ\text{C}$. The unit cell dimensions of CrAs are quoted from the previous study.²

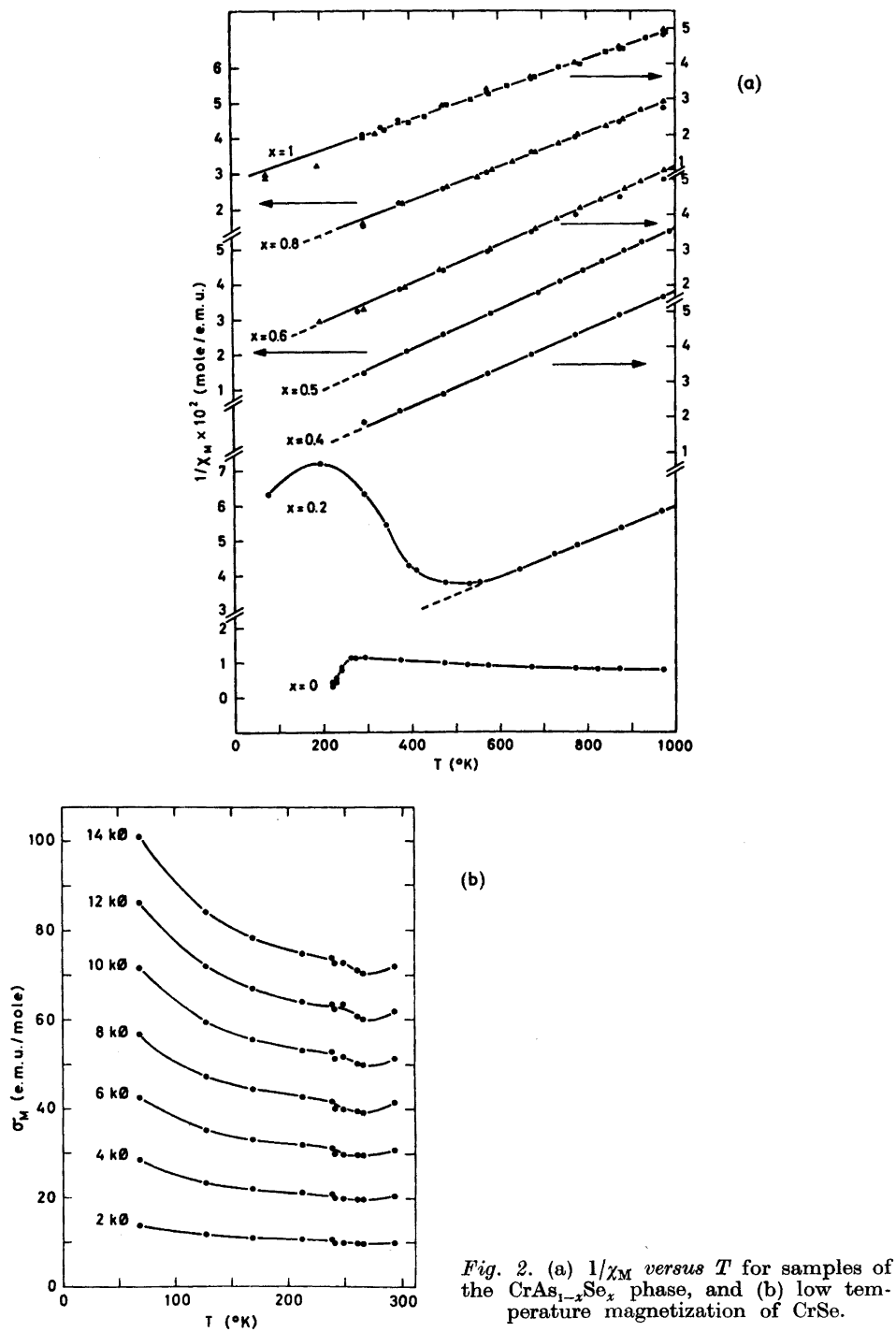
It is seen from Fig. 1 that the NiAs type structure is retained $0.5 \leq x \leq 1$, whereas the MnP type prevails for $0 \leq x \leq 0.4$.

(ii) *Magnetic properties.* All samples with $x > 0$ showed a Curie-Weiss relationship at high temperatures (Fig. 2a). The high temperature susceptibility and magnetization data below T_N for CrSe (Fig. 2b) show nothing to dispute

Table 2. Magnetic susceptibility data for the $\text{CrAs}_{1-x}\text{Se}_x$ phase.

Composition	$\mu_F (\mu_B)$	$2S_{Cr}$	$\theta (^\circ\text{K})$
$\text{CrAs}_{0.8}\text{Se}_{0.2}$	$3.9_5 \pm 0.2$	3.0_7	-164 ± 20
$\text{CrAs}_{0.6}\text{Se}_{0.4}$	$3.8_0 \pm 0.1$	2.9_2	-10 ± 10
$\text{CrAs}_{0.5}\text{Se}_{0.5}$	$3.7_2 \pm 0.1$	2.8_5	$+34 \pm 10$
$\text{CrAs}_{0.4}\text{Se}_{0.6}$	$3.7_7 \pm 0.1$	2.9_0	$+36 \pm 10$
$\text{CrAs}_{0.2}\text{Se}_{0.8}$	$4.0_5 \pm 0.1$	3.1_8	-64 ± 10
CrSe	$4.3_2 \pm 0.1$	3.4_3	-163 ± 10

the "umbrella-like" spin arrangement, suggested by Corliss *et al.*⁵ The slope of the inverse susceptibility curve at higher temperatures yields a paramagnetic moment of $4.3_2 \pm 0.1 \mu_B$ for CrSe, which corresponds to $2S_{Cr} = 3.4$ unpaired



electrons on the assumption of complete quenching of the orbital moment. Extrapolation of the data gives a θ -value of $-163 \pm 10^\circ\text{K}$. Similar data for the other samples are listed in Table 2. It was previously reported that the susceptibility for CrAs does not obey the Curie-Weiss relationship, and the values of μ_p and θ are thus unobtainable. The $\chi^{-1}(T)$ curve for CrAs from Ref. 2 is included in Fig. 2 for completeness.

The data from Fig. 2a do not indicate a clearly defined Néel temperature for CrSe, although it is observed that with decreasing temperature $\chi^{-1}(T)$ makes a negative deviation from the linear relationship before increasing. The samples with $x=0.8$ and 0.6 also show the same behaviour, and indicate an increase in T_N with increasing As content. In the sample with $x=0.5$, which also has the NiAs type structure, the negative deviation is within the experimental scatter of the data. However, the samples with $x=0.2$ clearly indicate a "normal" paramagnetic \rightarrow antiferromagnetic transition, with $T_N \approx 600^\circ\text{K}$.

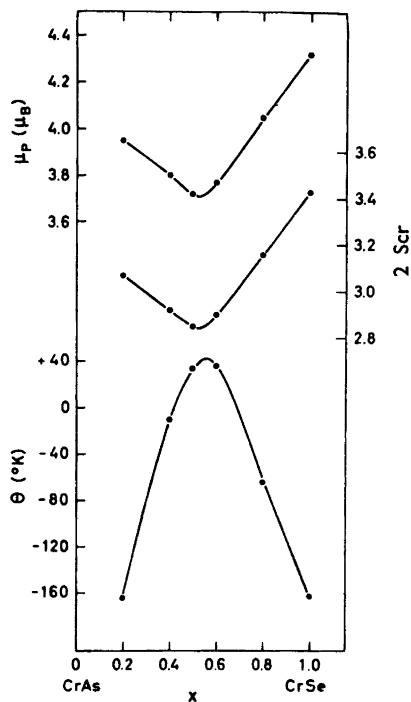


Fig. 3. μ_p , $2S_{Cr}$, and θ versus x in $\text{CrAs}_{1-x}\text{Se}_x$.

In Fig. 3, the paramagnetic moments, the number of unpaired electrons according to the spin-only approximation, and θ -values are plotted versus composition. These data show a decrease in the number of unpaired electrons and an increase in θ , with increasing As content as long as the NiAs type structure is retained. When $x \leq 0.4$, the distortion leading to the MnP type

structure is observed, the number of unpaired electrons increases anew, and θ decreases.

The number of unpaired electrons for the helimagnetic state of CrAs as determined by neutron diffraction² is 1.70 ± 0.05 . However, the number of unpaired electrons in the paramagnetic state is unknown at present.

(iii) *Discussion.* The data of Figs. 1 and 3 are not readily interpreted in terms of classical bonding schemes. It is seen that the number of unpaired electrons per Cr atom decreases more rapidly than the average number of electrons per formula unit, when As atoms are substituted for Se atoms in the region where the NiAs type structure is maintained. After the appearance of the MnP type structure, the number of unpaired electrons apparently increases, as the total number of electrons continues to decrease. This, together with the variation of θ with composition, suggests that the occupation of electron orbitals and the exchange interactions differ drastically between the NiAs and MnP type structures. Indeed the magnetic structures of CrAs² and CrSe⁵ are quite different. Goodenough and Kafalas¹⁰ have proposed a model based on band theory which explains the magnetic transformations in MnAs as a balance between the crystal field splitting energy and an exchange energy required for spin pairing within each band. A more logical choice of coordinate axes for the metal atoms permits an explanation of the magnetic structures of MnP and CrAs, as well as MnAs, and will be discussed in a forthcoming paper.

The decrease in the number of electrons as As atoms are substituted for Se atoms suggests that, at some point, the total number of electrons becomes insufficient to satisfy the requirements for virtually regular octahedral coordination. Thus the NiAs type structure distorts to the MnP type structure.

An alternative view may be taken, in which the appearance of the MnP type structure results from a more efficient packing of spherical atoms. Calculations have been made of the volume of a hypothetical NiAs type structure for $x = 0, 0.2, \text{ and } 0.4$. In these calculations, the MnP type a spacing was taken as the NiAs type c dimension (a conservative figure), and the NiAs type a dimension was obtained from both an extrapolation of the c/a curve for the observed NiAs phases ($x = 0.5, 0.6, 0.8, \text{ and } 1$) and from a hypothetical $a = \frac{1}{2}(c/\sqrt{3} + b)$ for the MnP type phases. In all cases, the observed MnP type structure is found to have the smallest volume.

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