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Neutron Diffraction Study of Cr_2As

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Cr_2As is known as an antiferromagnet with the Néel temperature T_N of 393 K. Its magnetic structure is determined by neutron diffraction by using single crystals as well as powdered samples. The magnetic structure obtained has such a symmetry that any isotropic exchange interaction vanishes between Cr(I) and Cr(II) sublattices, while dipole-dipole like interactions remain finite between them. Values of $0.40 \pm 0.08\,\mu_B$ and $1.34 \pm 0.06\,\mu_B$ are obtained for the magnetic moments of Cr(I) and Cr(II) respectively. Contrary to a previous study, it is observed that the magnetizations of Cr(I) and Cr(II) sublattices vanish at the same temperature, T_N. This inconsistency is considered to come from the mis-indexing of lines which are actually due to Cr_2O_3 contamination in the previous work.

§ 1. Introduction

It is very interesting to study a series of intermetallic compounds that are composed of 3*d*-transition elements and arsenic or antimony with the crystal structure of Cu_2Sb type (Space group $D_{4h}^7 - P4/nmm$). In this structure, there are two kinds of cation sites, M(I) and M(II), which, in the usual crystallographic nomenclature, are called 2(a) and 2(c) sites, respectively.

One of the points of interest is that there are many kinds of magnetic structure in this group of compounds. For example, Mn_2Sb[1,2] is a ferrimagnet ($T_c = 550$ K) with antiparallel coupling of Mn(I) and Mn(II) moments. Cr-modified Mn_2Sb[3] is a well known example of exchange inversion, transforming from an antiferromagnet to a ferrimagnet as the temperature increases. Fe_2As,[4] Mn_2As,[5] and Cr_2As[6] are all antiferromagnets, whose Néel temperatures are 353 K, 573 K, and 393 K, respectively, while their magnetic structures differ from one another.

A neutron diffraction study of Cr_2As was carried out by Watanabe *et al.*[6] on powdered samples, and they proposed two probable magnetic structures. In these structures, the magnetic period of Cr(II) sublattice is twice the chemical period along the *c*-axis, while that of Cr(I) sublattice is equal to the chemical period. According to these authors, the magnetizations of Cr(I) and Cr(II) sublattices vanished at different temperatures, and they interpreted as this had occurred because there were no magnetic interaction between these sublattices. This conclusion, however, is doubtful because, according to our experience, an antiferromagnet usually has only one Néel temperature, even when it is composed of two independent antiferromagnetic systems.

In the present study, single crystal specimens were prepared in order to examine in detail the temperature dependence of the sublattice magnetization and to obtain a conclusive model for the magnetic structure. Lattice parameters of Cr_2As are $a = 3.60$Å and $c = 6.34$Å. The parameters u and v, representing the positions of Cr(II) and As atoms respectively, are $u = 0.325 \pm 0.003$ and $v = 0.725 \pm 0.003$.[6]

The procedure of the sample preparation is described in § 2, and the results of neutron diffraction experiments and an analysis of the data are given in § 3. The last section is devoted for a discussion of the magnetic interactions which are considered to be predominant in this compound.

§ 2. Sample Preparation

Watanabe *et al.* used powdered samples of $Cr_{2.2}As$ which were slighly richer in chromium than the stoichiometric composition in order to reduce the amount of contaminating ferromagnetic Cr_3As_2.

In the present study, it was examined how the magnetic properties and neutron diffraction data were affected by the composition and the heat treatment of the samples. Chromium (99.9%) and arsenic (99.9%) powders were mixed in the molar proportion of 2.0, 2.1, and 2.2, and sealed into evacuated quartz tubes. The specimens were heated up to 900°C at which they were kept for 48 hours. After the reaction was completed, they were cooled down to room temperature in 2 hours. In order to obtain homogeneous specimens, all the reaction products were crushed, mixed well, and subjected again to the same heat-treatment. Especially, a part of Cr$_{2.2}$As was melted at 1300°C and crushed to powder.

Single crystals of Cr$_{2.0}$As and Cr$_{2.2}$As were obtained from the corresponding powder samples with the Bridgeman method. The powder samples were put in aluminum crucibles, sealed in evacuated silica tubes, heated up to 1360°C and kept for an hour. They were cooled slowly with a cooling rate of 60°C/hr to 1000°C and quenched in water.

§ 3. Neutron Diffraction Data and Spin Structure Analysis

(*1*) *Neutron diffraction data on the powdered specimens*

Neutron diffraction study was carried out for the specimens of various composition and heat treatment on TOG neutron diffractometer at JAERI (Japan Atomic Energy Research Institute). The relative intensities of the reflections were found to be rather insensitive to the change in composition and heat-treatment except the reflection (100). Reflections (100), (10 1/2), (10 3/2), (00 5/2), and (00 7/2) were assigned as magnetic reflections from the temperature dependence of their intensities.

Concentration and heat-treatment dependence of (100) reflection is shown in Table I, with (10 3/2) reflection for comparison. It is apparent that a distinct difference in (100) intensity is present between the sintered and the melted samples. Two causes are considered for this difference. One is the change in the magnetic structure, and the other is mixing of another phase or impurity. The fomer is rather improbable, while the latter is reasonable in this case, since the relative intensities of the other reflections do not vary so much. The contaminating impurity is considered to be Cr$_2$O$_3$ as follows. Brockhouse[7] studied Cr$_2$O$_3$ with powder neutron diffraction, and observed two intense reflections, (110) and (210) in rhombohedral indexing. Inter-layer spacing is 3.63Å for (110) of Cr$_2$O$_3$, and 3.60Å for (100) of Cr$_2$As, so these reflections would not be able to be separated from each other in powder diffraction patterns, if they are coexistent. After Brookhouse, about two third of (110) reflection from Cr$_2$O$_3$ is of magnetic origin at 80 K, so the intensity of this reflection becomes one third above its Néel temperature, 310 K. This temperature dependence agrees closely with that of Cr$_2$As (100) reflection in the previous report.[6] (210) reflection of Cr$_2$O$_3$ was also observed in the previous data,[6] but it was supposed to be from vanadium foil. Now, it is naturally concluded that (100) reflection of Cr$_2$As was actually absent, but its deceiving presence came from contamination with Cr$_2$O$_3$ in the previous experiment.

Table I. Concentration and heat-treatment dependence of diffracted neutron intensity at 130 K. (I(002)+I(101)=100).

	Cr$_{2.2}$As		Cr$_{2.1}$As		Cr$_{2.0}$As	
	900°C	melted	900°C	melted	900°C	melted
I(100)	14 (*p*)	4.3> (*p*) 1.3 (*s*)	17±7 (*p*)	—	17±5 (*p*)	1.0> (*s*)
I(10 3/2)	31 (*p*)	30±5 (*p*) 30.2 (*s*)	29±7 (*p*)	—	28±7 (*p*)	30.8 (*s*)

p: powder sample *s*: single crystal

In Table I, intensity of (100) reflection is seen to be small for melted and subsequently powdered Cr$_2$As. This came from the procedure of sample preparation; before the molten ingot of Cr$_2$As was crushed, the dark green irregular substance, which was Cr$_2$O$_3$ floating on liquid of Cr$_2$As, had been taken off from the top of the ingot.

(*2*) *Spin structure analysis*

Neutron diffraction study was carried out for a Cr$_{2.0}$As single crystal which was 5 mm in diameter and 12 mm in length. KUR* neutron diffractometer was used with 1.00Å incident neutrons. Intensities of Bragg reflections are shown in the second column of Table II, and their temperature

Table II. Observed and calculated intensities in the neutron diffraction pattern of Cr$_{2.0}$As at 126 K.

h *k* *l*	Iobs.	Icalc.
0 0 2	1940	1930
1 0 1	1135	924
2 0 0	10000	10000
0 0 3/2	0	0
0 0 5/2	334	327
0 0 7/2	188	71
1 0 1/2	8	22
1 0 3/2	501	541
1 0 0	0	0

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* The Research Reactor Institute, Kyoto University.

dependence is shown in Fig. 1. No correction was made for absorption and extinction effects, as the true absorption was considered to be small from calculation, and the extinction effect was found to be very small for this specimen by comparing the observed nuclear intensities with the calculated ones.

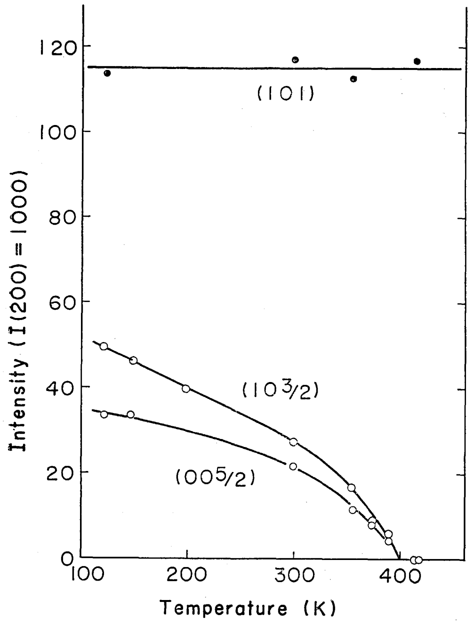

Fig. 1. Temperature dependence of the intensity of a few reflections.

Within the experimental accuracy (100) reflection was not observed, and no temperature dependence was detected on (101) reflection. Then, all of the magnetic reflections were indexed as ($h\ k\ l$) with l of half integers. It was concluded therefore, that the magnetic unit cell had twice the c-axis of the chemical cell.

The magnetic structure was analyzed by using Yamada's[8] group theoretical method. Cr_2As has the space group P4/nmm which contains the point group D_{2d} as a subgroup. The unit cell is constituted from five atoms of Cr(I) and four atoms of Cr(II) as shown in Fig. 2.

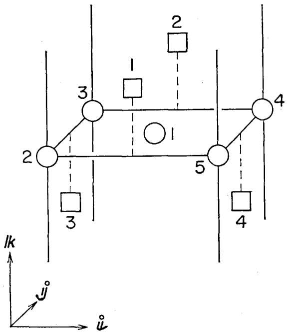

Fig. 2. Atom comfiguration in the symmetrical unit cell of Cu_2Sb structure. Only metal atoms are shown.

The coefficients $C_j^{(\alpha,n)}$ of symmetrized Bloch function[8,12] for $q=(0, 0, 0)$ and $(0, 0, 1/2)$ are given in Table III. There are unsuitable scalar bases which are $b^{(1)}$, e_1, e_2 for site I, and e_1, e_2 for site II in Table III. They are introduced from definition of the periodic unit in which five atoms of site I and four atoms of site II are treated as if they are independent at all.

Table III. The value of $C_j^{(\alpha,n)}$.

site	$\phi^{(\alpha)}$	atom-number j				
		1	2	3	4	5
I	$a^{(1)-1}$	1	1	1	1	1
	$a^{(1)-2}$	−4	1	1	1	1
	$b^{(1)}$	0	1	−1	1	−1
	e_1	0	1	1	−1	−1
	e_2	0	−1	−1	−1	1
II	$a^{(1)}$	1	1	1	1	
	$b^{(1)}$	1	1	−1	−1	
	e_1	1	−1	−1	1	
	e_2	1	−1	1	−1	

An orthogonal set of unit vectors $\boldsymbol{i}$, $\boldsymbol{j}$ and $\boldsymbol{k}$ is taken along the crystal axes. In the case of D_{2d}, the vector $\boldsymbol{i}$ and $\boldsymbol{j}$ constitute the basis of E, and the vector $\boldsymbol{k}$ constitutes the basis of $B^{(2)}$. Irreducible representations based on the vector basis are found by decomposing the direct product

$$\left.\begin{aligned} &A^{(1)}\times B^{(2)}=B^{(2)}\ , \\ &A^{(1)}E\times=E\ , \\ &B^{(2)}B\times^{(2)}=A^{(1)}\ , \\ &B^{(2)}\times E=E\ . \end{aligned}\right\} \qquad (1)$$

The vector basis functions are constructed as follows;

$$\left.\begin{aligned} &\boldsymbol{b}^{(2)-1}=a^{(1)-1}\ \boldsymbol{k}\ , \\ &\boldsymbol{b}^{(2)-2}=a^{(1)-2}\ \boldsymbol{k}\ , \\ &\begin{cases} \boldsymbol{e}_1^1 & =a^{(1)-1}\,\boldsymbol{i}\ , \\ \boldsymbol{e}_2^1 & =a^{(1)-1}\,\boldsymbol{j}\ , \end{cases} \\ &\begin{cases} \boldsymbol{e}_1^2 & =a^{(1)-2}\,\boldsymbol{i}\ , \\ \boldsymbol{e}_2^2 & =a^{(1)-2}\,\boldsymbol{j}\ , \end{cases} \\ &\begin{cases} \boldsymbol{e}_1^3 & =b^{(2)}\quad \boldsymbol{i}\ , \\ \boldsymbol{e}_2^3 & =b^{(2)}\quad \boldsymbol{j}\ , \end{cases} \\ &\boldsymbol{a}^{(1)}\quad =b^{(2)}\ \boldsymbol{k}\ . \end{aligned}\right\} \qquad (2)$$

By Yamada's postulate for simple magnetic materials, magnetic structure of Cr_2As can be constructed from the vector basis functions of an irreducible representation of the space group. It is observed in Table IV that representations $B^{(2)}$ and E (on the vector basis) is common to the two sites. Torque measurement shows that spins are in *c*-plane as shown in Fig. 3, so representation E is realized in Cr_2As.

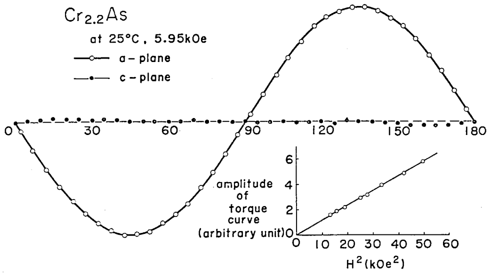

Fig. 3. Torque measurement.

Hereafter, analysis is developed by comparing the calculated intensity with the observed one. From the observation that the intensity of (0,0, 3/2) reflection is zero, we conclude that the spins of site I couple antiparallel in *c*-plane (e^2 mode), and that those of site II are in e^3 mode. Intensity of the (00 *l*) reflections with *l* of half-integer give the magnitude of Cr(II) spin. Intensity ratio of (1, 0, 1/2) to (1, 0, 3/2) gives relative magnitude of Cr(I) and Cr(II) spins, and the angle between their directions. Then we arrive at the final spin structure of Fig. 4. This is a collinear spin structure, and the magnitude of the magnetic moments are $0.40\pm0.08\,\mu_B$ for Cr(I) and $1.34\pm0.06\,\mu_B$ for Cr(II) at 130 K with the magnetic form factor of metallic chromium.[9] Assuming equipopulation of magnetic domains, the neutron diffraction experiment does not give spin direction in the *c*-plane. Field cooled torque measurements were tried with field cooling direction of [100] and [110] under the magnetic field of 7 kOe, but did not give any conclusive results about the spin direction in the *c*-plane. Agreement is good on the whole, except for (0, 0, 7/2) reflection, for which the calculated value is too small. The reason of this disagreement is not clear as the value of *u*-parameter is accurately known from the intensity of the nuclear reflection, and the geometrical structure factor of (0, 0, 7/2) is the same as (0, 0, 5/2). The remaining possibility is the difference between the shapes of the magnetic form factor for Cr(II) and metallic chromium.

As the result, the magnetic structure obtained is such a structure that the magnetic coupling is not described in the bilinear form. One may consider Yamada's group theoretical method to be incomplete in this case, as the bilinear form of the magnetic coupling energy is assumed in the method. But it is sure that there is no other magnetic structure in the region covered by Yamada's method, and the same magnetic structure was obtained in any other processes.

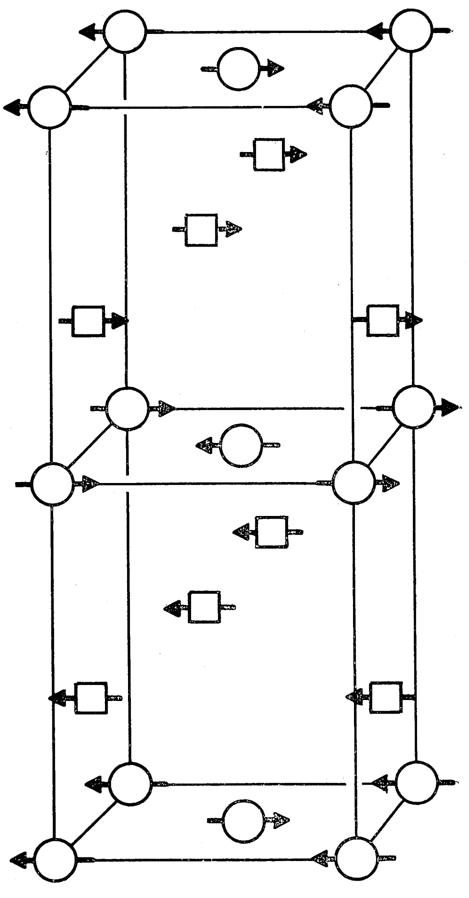

Fig. 4. Spin structure of Cr_2As.
Only metal atoms are shown.
Cr(I) $\mu_I=0.40+0.08\,\mu_B$
Cr(II) $\mu_{II}=1.34+0.06\,\mu_B$

§ 4. Discussion

As for the magnetic structure of Cr_2As, Goodenough[10] predicted that the magnetic moments of Cr(I) should couple antiparallel in the *c*-plane. This is based on the assumption that Cr_2As is considered to be an ionic substance with Cr^+(I), Cr^{++}(II) and As^{3-} (Fig. 5). It is further assumed that Cr(I)-Cr(I) bonding in the *c*-plane causes a sufficiently large tetragonal ($c/a>1$) component of the ligand fields at both Cr(I) and Cr(II) sites. Figures 6 and 7 are schematic one electron energy

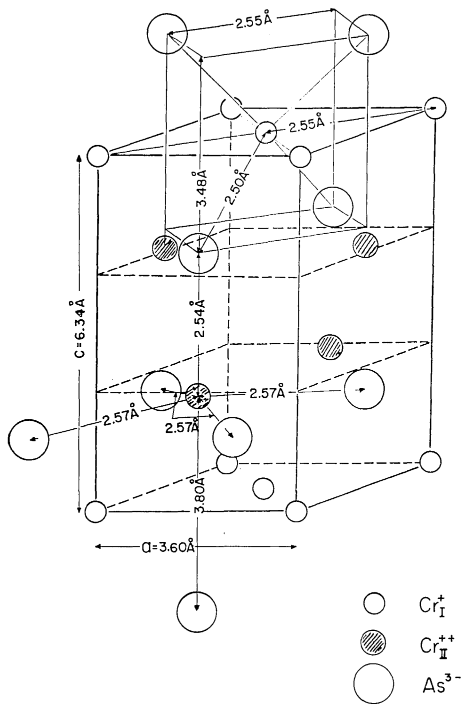

Fig. 5. Interatomic distances.

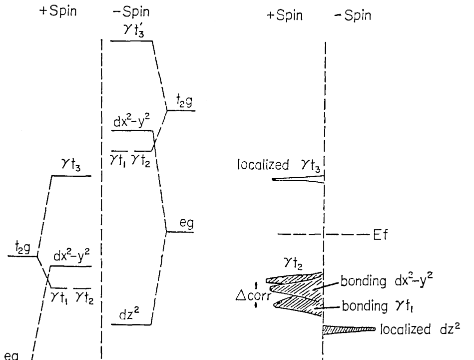

Fig. 6. Schematic one electron energy diagram for Cr(I) in Cr_2As. With formal valence Cr^+(I), anticipate five outer 3d electrons. Δ_{corr} is a splitting due to electron correlations among narrow band electrons. (a) shows splitting for localized levels. (b) shows narrow band formation of γt_1 and γt_2 electrons.

diagrams for Cr(I) and Cr(II), respectively.

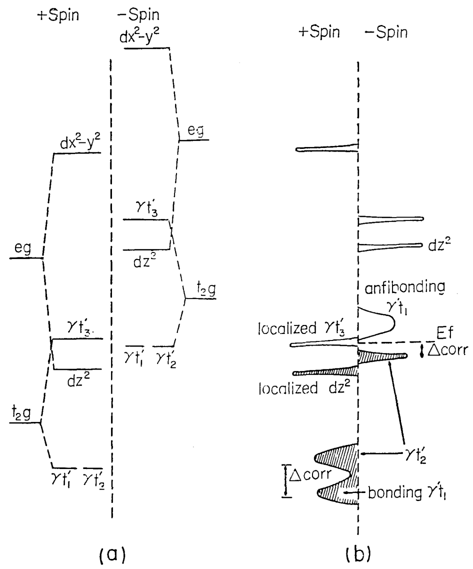

Fig. 7. Schematic one electron energy diagram for Cr(II) in Cr_2As. Δ_{corr} and δ_{corr} are splittings due to electron correlations among narrow band electrons. With $Cr_{(II)}^{++}$ formal valance, anticipate four outer 3d electrons. (a) shows splitting for localized levels. (b) shows narrow-band formation of $\gamma t_1'$ and $\gamma t_2'$ electrons.

At Cr(I) site, the $t_{2\gamma}$ orbitals of cubic symmetry become γt_1 and γt_2 orbitals directed along the Cr(I)-Cr(II) bonds, and localized γt_3 orbitals that are not directed along near neighbor bonds. Note that in Cr(I) both γt_t and γt_2 orbitals are half-filled, while in Cr(II) γt_1 is half-filled and γt_2 is filled, so that the interaction is antiferromagnetic or ferromagnetic according as Cr(II) γt_1 or γt_2 patricipate in the bonding.[10,11]

The magnetic moment of a Cr(I) atom is given by

$$\mu_{\mathrm{CrI}}=(\delta_{t_1}+\delta_{x^2-y^2})\mu_{\mathrm{B}} ,$$

where δ's mean fractional spin moment contributed from the corresponding orbitals. The exchange between $d_{x^2-y^2}$ electrons is antiferromagnetic through Anderson's mechanism.[11] This makes the Cr_I moments in a given c-plane order antiferromangetically.

In the case of Cr(II), a localized d_{z^2} electron contributes a fractional moment δ_{t_1}, so that

$$\mu_{\mathrm{CrII}}=(1+\delta_{t_1})\mu_{\mathrm{B}} .$$

The above prediction about the moments is compatible with the observation.

As stated above, there are two kinds of Cr(I)-Cr(II) interactions, antiferromagnetic and ferromagnetic, which are actually observed. At the same time these interactions serve to make the Cr(II) moments align ferromagnetically in a given c-plane. Also dipole-like interactions are favorable for this alignment. The Cr(II)-Cr(II) interaction along *c*-direction acts via half-filled d_{z^2} orbitals, and is antiferromagnetic.

It is not easy to know apriori the sign of Cr(II)-Cr(II) interaction between neighboring *c*-planes. The experimental result shows that it is ferromagnetic.

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