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The Magnetic Structure of Fe_2As

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The magnetic structure of Fe_2As has been determined by neutron diffraction. The compound Fe_2As is antiferromagnetic with the Néel point at about 80°C. Its magnetic structure is different from Mn_2As. The coupling between layers of iron atoms Fe(II) located at $(0, 1/2, z)$ and $(1/2, 0, \bar{z})$ is antiparallel, but the coupling between a layer of iron atoms Fe(I) located at $(0, 0, 0)$, $(1/2, 1/2, 0)$ and adjacent Fe(II) layers is parallel. The magnetic unit cell has the c-axis twice as large as that of the chemical unit cell. The magnetic moments are 1.28 and 2.05 Bohr magnetons for Fe(I) and Fe(II) atoms, respectively. The moments lie perpendicular to the c-axis.

§ 1. Introduction

The magnetic structures of various compounds with the Cu_2Sb type crystal structure have been reported by several authors. In this crystal structure, cations are divided into two types on the position of the crystal structure. Cations of type I are tetrahedrally coordinated by anions and cations of type II are octahedrally coordinated. Cations of a given type occupy a basal plane and along the c-axis the types of planes vary in the sequence; -I-II-II-I-II-II-I-. Each compound has a different magnetic order. For example, Mn_2As

is antiferromagnetic and its magnetic order is composed of ferromagnetic layers that are coupled antiparallel to one another.1) For Mn_2Sb of ferrimagnetism, coupling between type II layers is parallel.2) Furthermore, antiparallel coupling within a basal plane is realized in Cr_2As.3) Goodenough suggests the possibility of more complicated magnetic orders in some compounds from qualitative consideration about cation-cation and cation-anion-cation interactions.

The compound Fe_2As also has the Cu_2Sb crystal structure. According to M. Elander *et al.*,4) the lattice constant a is 3.627 Å and c is 5.98 Å. The iron atoms of type I are located at positions with coordinates (0, 0, 0), (1/2, 1/2, 0) and those of type II located at $(0, 1/2, z_1)$, $(1/2, 0, \bar{z}_1)$. While the arsenic coordinates are $(0, 1/2, z_2)$ and $(1/2, 0, \bar{z}_2)$. The values of the parameters are $z_1 = 0.33$ and $z_2 = -0.265$.

This paper reports on the temperature dependence of the magnetic susceptibility of Fe_2As and its magnetic structure decided by neutron diffraction.

§ 2. Preparations of Specimens

The compound Fe_2As has a very narrow homogeneous range with the melting point of 919°C.4) The mixture of electrolytic iron (99.98%) and distilled arsenic (99.999%) with a desired ratio, in a fused alumina crucible, was sealed in an evacuated silica tube and was heated by an electric furnace quite slowly from room temperature up to 600°C spending one day. As the vapor pressure of arsenic exceeds atmospheric pressure at 600°C, the sample was kept at this temperature for another day in order to avoid the explosion of the sample tube. The following two days were spent for heating the sample up to 1100°C. After the reaction was completed, the sample was cooled slowly down to room temperature. To get single crystals from an ingot, the Bridgman method was employed. An ingot was crushed and put in a fused alumina crucible and then sealed in an evacuated silica tube. After keeping the sample at 1100°C for several hours, it was lowered at the speed of 1 cm per hour which corresponds to the cooling rate of 50°C per hour. The single crystal obtained by this method was about 1 cm in diameter and 1.5 cm in height. Debye-Scherrer and Laue photographs showed that the structure of the obtained sample was the Cu_2Sb type with $a = 3.63$ Å and $c = 5.98$ Å in agreement with the values reported by M. Elander *et al.*.4)

§ 3. Magnetic Susceptibility Measurement

The temperature dependence of magnetic susceptibility was measured on powder sample from liquid nitrogen temperature to 900°K by magnetic torsion balance. Figure 1 shows the susceptibility per gram versus temperature. As can be seen from the figure, the compound Fe_2As is antiferromagnetic with the Néel temperature at 80°±1°C which agrees with the neutron diffraction result in the next section. The magnetic susceptibility above the Néel temperature obeys the Curie-Weiss law as follows:

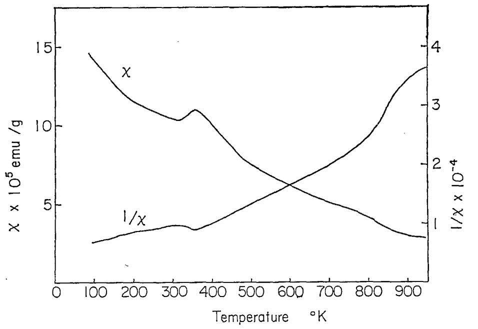

Fig. 1. Susceptibility and reciprocal susceptibility v.s. temperature of Fe_2As.

$$\chi = \frac{5.40}{T-90} \text{ emu/mol} .$$

Deviation from the Curie-Weiss law above 500°C is attributed to the impurity such as magnetite of which Curie temperature is 570°C. Although Fe_2As is antiferromagnetic, its asymptotic Curie temperature is positive, 90°K. The effective Bohr magneton per an iron atom is estimated to be 4.66 μ_B on the average of the two sublattices. This value is much larger than that of neutron diffraction result. Below the Néel temperature, the magnetic susceptibility increases after slight decrease with decreasing temperature. These might be due to paramagnetic impurity.

§ 4. Neutron Diffraction Results

a) Results from powder sample

The initial neutron diffractions were performed on powder sample at liquid nitrogen, at room temperature and at about 100°C. Figure 2 shows the powder pattern obtained at room temperature, where indexing is based on the chemical unit cell. As can be seen from the figure, several peaks with half integer values of the index l were observed. At 100°C above the Néel temperature,

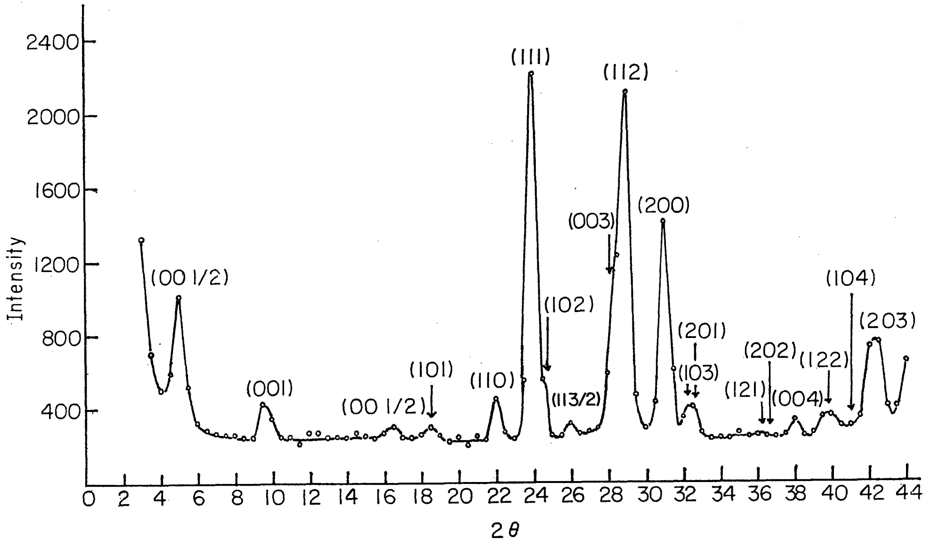

Fig. 2. Neutron diffraction pattern at room temperature for the powder sample of Fe_2As.

these extra peaks were not observed, while the other normal peaks were invariant within the uncertainty of experiment. It is clear therefore that the extra peaks are due to magnetic scattering and the magnetic unit cell has twice the *c*-axis of the chemical unit cell. Furthermore, the normal peaks are due to nuclear scattering only, corresponding with antiferromagnetism of this material as inferred from the susceptibility measurement. The detailed arrangement and the values of the magnetic moments will be given in the next paragraph describing results from single crystals. The observed values of the intensities of all reflections will be also compared with the calculated values based on the proposed magnetic structure. In the measurement at nitrogen temperature appearances of all reflections were similar to those at room temperature and there was no change which suggested some transformation of the magnetic structure.

b) *Results from single crystals*

Room temperature measurements

Single crystal measurements at room temperature were performed on three specimens of pillar shape. The one has its long axis parallel to the *c*-axis and the others parallel to the direction [110]. The reflections (h00) were measured with the former specimen. Any magnetic super reflection was not observed as expected from the result obtained with the powder sample. Then it is undoubtful that the *a*-axis of the magnetic unit cell is the same as that of the chemical unit cell. The one of the two specimens with their long axes parallel to the direction [110] is roughly 2×10 mm in area and 1 mm in thickness. The other is 2×10 mm in area and 0.5 mm in thickness. The *c*-plane of each specimen coincides with the large area of the pillar. The (hh0) and (00 *l*) reflections were observed with these specimens. Figure 3 shows the diffraction pattern obtained with the thin crystal. Magnetic super reflections appear in the (00 *l*) reflections with half integer values of the index *l*. The relative values of the intensities of reflections were almost the same in both specimens, except for the intense reflections of (003) and (220). The values of these reflections were smaller in the thick specimen than in the thin one. Such a difference seems to have been caused by the effect of the secondary extinction which prevails for intense reflection and for thick crystal. The extinction effect will be negligible for the other weak reflections.

Magnetic structure analysis

Yuzuri *et al.*5) have made an investigation on the magnetic property of Mn_2As and proposed two kinds of antiferromagnetic structure from the standpoint of the molecular field theory. Figure 4 shows the magnetic structures proposed by them, where circles correspond to cations of type I and squares correspond to cations of type II. Anions are omitted. Signs + and − denote directions of magnetic moments which are antiparallel to each other. A. E. Austin *et al.*1) have found by neutron diffraction that Mn_2As has the magnetic structure of Fig. 4(a) with the direction of the magnetic moment perpendicular to the *c*-

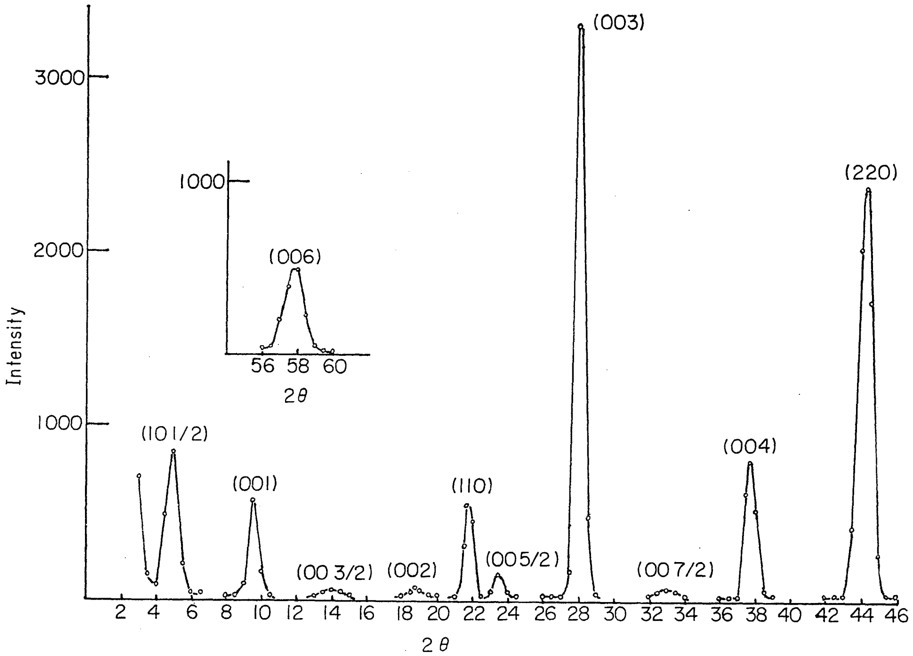

Fig. 3. Neutron diffraction pattern at room temperature for the single crystal of Fe_2As.

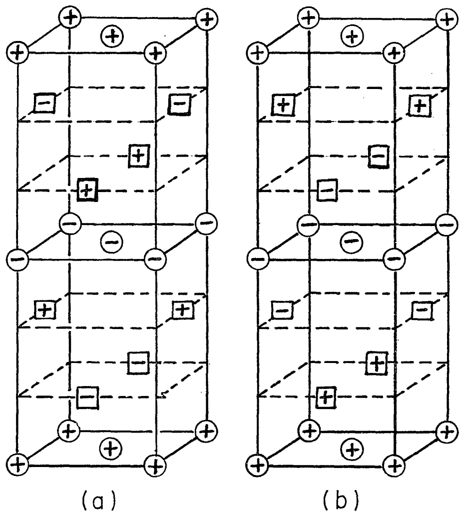

Fig. 4. (a) Magnetic structure of Mn_2As. Layers of Mn(I) atoms (circles) are aligned antiparallel to layers of Mn(II) atoms (squares).
(b) Magnetic structure of Fe_2As. Layers of Fe(I) atoms are aligned parallel to layers of Fe(II) atoms. The moments are perpendicular to the *c*-axis.

axis. An antiferromagnetic structure of Fe_2As seems to be different from Mn_2As. If Fe_2As has the same magnetic structure as Mn_2As, the intensity of $(00\,^3/_2)$ reflection should be stronger than that of $(00\,^5/_2)$. That is not the case as can be seen from the diffraction pattern of the single crystal.

We have assumed that Fe_2As has the magnetic structure of Fig. 4(b) with the direction of the magnetic moment perpendicular to the *c*-axis. Table I shows the comparison between the observed intensities of reflections and those calculated on the basis of this structure. The observed values were obtained from the diffraction pattern

Table I. Observed and calculated, integrated intensities at room temperature for the single crystal.

hkl	Observed intensities	Calculated intensities	
001	63	57.6	
002	4.6	4.5	
003	375	450	
004	95	102	
005	0	0	
006	92	104	
110	54	50	
220	356	434	
		Fe(I)=0.95 μ_B Fe(II)=1.52 μ_B	Fe(I)=1.32 μ_B Fe(II)=0.75 μ_B
$00\,^1/_2$	105	110	107
$00\,^3/_2$	3.6	3.5	3.5
$00\,^5/_2$	11	10.7	13.8
$00\,^7/_2$	4	4.7	4.4

shown in Fig. 3. The intensity agreement of the nuclear reflections appears satisfactory with the exception of the (003) and (220) intensities for which the observed values are lower than the calculated values. Both reflections seem to be subject to the secondary extinction effect even in the thin crystal. The third column below the nuclear data lists the calculated intensities of the magnetic reflection obtained using an iron moment at I-site of 0.95 μ_B and an iron moment at II-site of 1.52 μ_B and the fourth column lists those obtained using an iron moment at I-site of 1.32 μ_B and an iron moment at II-site of 0.75 μ_B. The magnetic form factor of an iron calculated by R. E. Watson and A. J. Freeman6) was used. Both of the two sets of the calculated values give a satisfactory agreement with the observed values, so that there is an ambiguity in the determination of the magnetic moment of an iron at each site.

This is owing to the following reasons: (1) there are only two independent forms in the magnetic structure factor of the ($00l$) reflections, because of the z_1 parameter of 0.33, (2) the intensity of reflection is proportional to the square of the structure factor. Then this ambiguity must be eliminated from the measurement for another type of magnetic reflection.

For this purpose, the intensity analysis of the powder diffraction pattern shown in Fig. 2 has been performed. Table II shows the comparison between the observed intensities and the calculated ones. In the intensity calculation of magnetic reflection, an iron moment at I-site of 0.95 μ_B and an iron moment at II-site of 1.52 μ_B were used. The intensity agreement appears quite satisfactory all over the reflections. The magnetic structure factor of the ($10\,{}^1/_2$) reflection includes only an iron moment at II-site, so that the calculated intensity obtained using an iron moment at II-site of 0.75 μ_B will be lower about a quater than the one listed in Table II, showing a pronounced disagreement with the observed value.

It is therefor concluded that at room temperature Fe_2As has the magnetic structure shown in Fig. 4(b) with the direction of the magnetic moment perpendicular to the c-axis and an iron moment at I-site is 0.95 μ_B and an iron moment at II-site is 1.52 μ_B.

Table II. Calculated and observed, integrated intensities at room temperature for the powder sample.

hkl	Calculated intensities	Observed intensities
$00\,{}^1/_2$	480	430
001	114	126
$10\,{}^1/_2$	36	37
101	30	21
002	4.5	0
110	89	90
111, 102	1019	1000
$11\,{}^3/_2$	37	32
003, 112	1470	1480
200	750	740
103, 201	120	116
113	5.5	0
121, 202	21	14
004	52	52
122	141	126
104	56	42
203	576	546

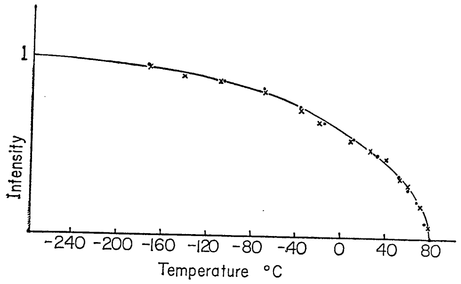

Fig. 5. Variations of the ($00\,{}^3/_2$) and ($00\,{}^5/_2$) reflections with temperature. Sign × corresponds to the ($00\,{}^3/_2$) reflection and sign ● to the ($00\,{}^5/_2$).

Temperature dependence of magnetic reflections

The determination of the saturation value of an iron moment at each site has been made by measurements of the changes in the intensities of ($00\,{}^3/_2$) and ($00\,{}^5/_2$) reflections from 90°C to liquid nitrogen temperature. Figure 5 shows the result obtained for both reflections, where small extraporations are made to 0°K and the intensities at 0°K are normalized to 1. Both reflections disappeared at 80°C in good agreement with the result from the susceptibility measurement.

Any distinct difference was not found between the temperature dependences of the two reflections. This indicates that the two magnetic sublattices have the similar temperature dependence of the spontaneous magnetization, since these two reflections have their own structure factors which depend differently on the magnetic moment of the individual sublattice. The saturation values of iron moments at I-site and II-site were determined to be 1.28 μ_B and 2.05 μ_B, respectively.

§ 5. Summary

The neutron diffraction measurements made on powder sample and single crystals of Fe_2As confirmed the magnetic structure and the magnetic moment for the individual sublattice. In the magnetic structure of Fe_2As there is ferromagnetic coupling between a Fe(I) layer and the adjacent two Fe(II) layers. This property is quite different from that of the compounds which contain Mn atoms as cation.

Chromium-modified Mn_{2-x} Cr_x Sb,[7] for example, can exist in three magnetic structures, ferrimagnetic, antiferromagnetic, helical, depending upon temperature and chromium content. In all of these structures, however, the coupling between a Mn(I) layer and the adjacent two Mn(II) layers is antiparallel. Then, the coupling between those layers seems to depend on the kind of cation contained in the compound.

The low temperature measurements were made to nitrogen temperature and no transformation from the magnetic structure at room temperature was found. The saturation values of iron moments at I-site and at II-site are 1.28 μ_B and 2.05 μ_B, respectively.

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