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A Probable Magnetic Behaviour for Cr_2F_5

Toshio TAKEHARA
Department of Physics, Shimane University

synopsis. The ordered arrangement of Cr^{3+} and Cr^{2+} ions, proposed by Steinfink and Burns, was confirmed by Osmond with application of the qualitative Goodenogh-Kanamori rules for superexchange interactions. This compounds should be antiferromagnetic, with equal numbers of ferromagneticallycoupled cations of both types in (011) planes and opposed spin directions in alternate planes. The magnetic behaviour of this antiferromagnetic crystal is discussed by the four sublatttice model.

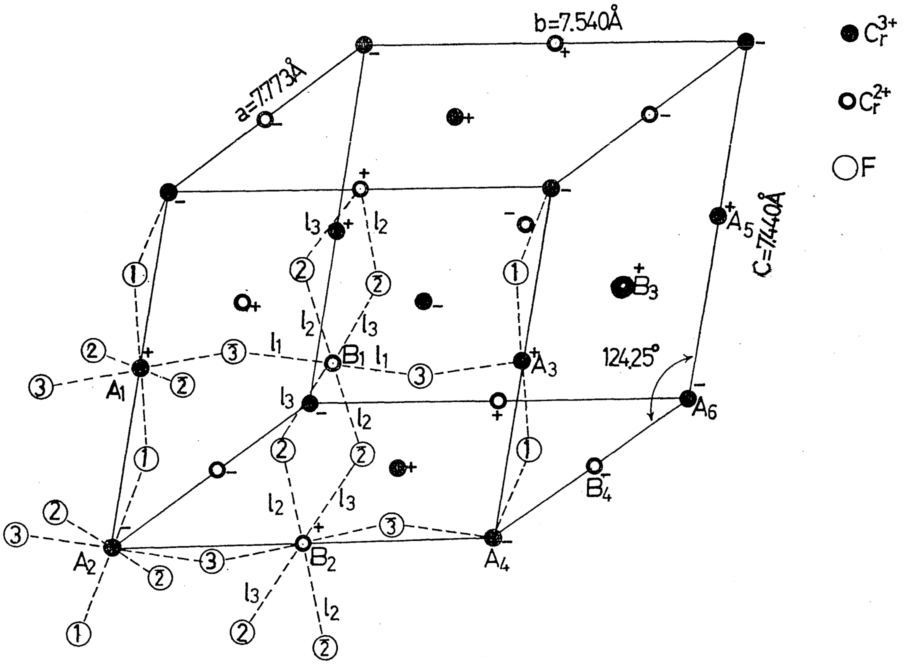

Fig. 1. The monoclinic unit cell of Cr_2F_5. Linked fluorine octahedra around two Cr^{3+} (A) and Cr^{2+} (B) cations in the (100) plane. + and − sign show the probable spin arrangement.

§1. Introduction

By means of a detailed x-ray study of single crystals in the composition range $CrF_{2.40}$-$CrF_{2.45}$ first discovered by Strum1), the monoclinic crystal structure of an ideal stoichiometric compound Cr_2F_5 has been established by Steinfink and Burns2). The monoclinic unit cell of Cr_2F_5 are shown in Fig. 1. It may be seen that there are two species of equally populated chromium cations and their sites are shown in the figure as full circles (A ions) and bold circles (B ions). The linked octahedra of fluorine anions around the four cations A_1, A_2, B_1, B_2 in the (100) plane ot the cell are also shown. There are three species of anions. They are F(1) in this plane (open circles), F(2) close to the (010) planes of cations, and F(3) close to the (100) and (001) planes of cations. Of the last two species of anions, those behind the (100) face are shown with bar on the number 2 and 3. The fluorine octahedra around the A ions were found to be very closely regular, with an average Cr-F bond length of 1.89 Å. The B ions have two F neighbours at a distance $l_1=1.95$Å and two in the same plane at a distance $l_2=2.01$Å, while two others are at a distance $l_3=2.57$Å in directions inclined to the normal to the plane of the other four anions. From somewhat similar situations of distorted octahedra of fluorines around Cr^{2+} ions in CrF_2 and almost identical regular octahedra around Cr^{3+} ions in CrF_3, Steinfink and Burns reasonably assumed that the A and B ions in Cr_2F_5 will be Cr^{3+} and Cr^{2+}, respectively.

As shown in the next section, Osmond[3)] proposed that the ordered arrangement of magnetic ions Cr^{3+} and Cr^{2+} in monoclinic Cr_2F_5 should be antiferromagnetic. It is of interest to study the probable magnetic behaviourof this ideal compound Cr_2F_5.

§ 2. Possible Magnetic Interactions and Magnetic Structure

Osmond[3)] proposed the magnetic structure in the following. As dictated by ligand field theory by Dunitz and Orgel[4)], in the distorted fluorine octahedron around each Cr_2^+(B) ion the long bond lengths l_3 are associated with the half-filled d_{z^2} orbital wave function of the cation and the shorter, almost equal, bond lengths l_2 and l_1 are associated with its empty $d_{x^2-y^2}$ orbital (Cr^{2+} is a $3d^4$ ion); in the nearly regular octahedra around the Cr^{3+} (A) ions each bond length is associated with an empty e_g orbital.

From Fig. 1 we find in the (100) plane probable exchange interactions with large obtuse angles between pairs of A ions along the *c* axes and between A and B ions along the *b* directions, all using empty e_g orbitals of the cations, hence all negative. These might give the spin arragement A_1, B_2, $A_3(+)$; A_2, B_1, $A_4(-)$. This neglects any B_1-B_2 interactions, which muct be the same as those between B_3 and B_4 in the (010) plane of the unit cell illustrated in part in Fig. 2.

Here the broken lines represent probable directions of p orbital axes of F (2) (just behind the plane of the cations) giving best overlap with the empty e_g orbitals of A_3 and B_4 and the half-filled d_{z^2} orbital of B_3. Then there should be a negative superexchange A_3-B_4 interaction, which from the geometry must be considerably stronger than a positive superexchange B_3-B_4 interaction. There should be another similar positive B_3-B_4 interaction using the other F (2) anion in Fig. 2, but also a negative direct interaction between these cations using possible overlap of half-filled t_{2g} orbitals within the F(2) BF(2) by Goodenough.[5)] Then there is a tendency for A_4 and B_4 to have parallel spins, both having negative interactions with A_3, and a similar tendency for parallel spins can be shown to exist for all pairs of A and B ions along the a directions. There is also a weak positive superexchange interaction between each such A$-$B pair, as may be seen from Fig. 2 for A_3-B_3. On the whole, therefore, the A$-$B interactions along *b*

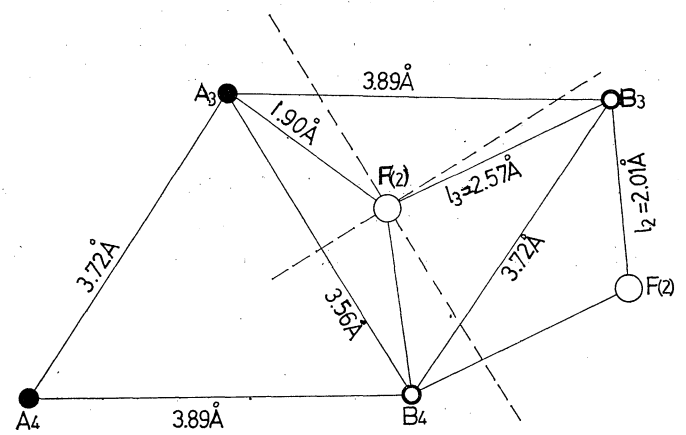

Fig. 2. Linkages between Cr^{3+} and Cr^{2+} cations in part of the (010) plane face of the unit cell of Cr_2F_5.

directions and tendencies along a directions, combined with the A—A interactions along *c* directions seem likely to annul the weak positive B—B interactions.

In short, the previous consideration leads to the probable magnetic structure at low temperature consists of antiferromagnetically coupled cations along both [010] and [001] directions, but ferromagnetically coupled cations along the [100] direction. Thus, in Fig. 1, if the spin of A_1 is (+) so also are those of B_2, A_3, B_3,A_5 while those of A_2, B_1, A_4, B_4, A_6 are (−). Thus one finds an antiferromagnetic substance consisting of (011) planes of ferromagnetically coupled cations with equal numbers of Cr^{2+} ans Cr^{3+} ions in each plane, the spin direction being opposite to that in the next plane on either side. This spin arrangement is indicated in Fig. 1.

§ 3. Weiss Field Theory Applied to Antiferromagnetic Cr_2F_5 Crystal

The spin arrangement in low temperature are composed of four sublattices, i. e., each sublattice consists of (+) or (−) spin only for A and B ions. An ion of a sublattice is arranged alternately. An ion of a given sublattice is surrounded by nearest neighbours on the *a*, *b*, *c* axes, so that the Weiss field acting on this ion depends upon the magnetization of all other sublattices. Accordingly

$$H_{wi} = \sum_{j=1}^{4} W_{ij} M_j \qquad (1)$$

The Weiss field coefficients W_{ij} are a measure of the exchange interaction between the spins of an ion from the *i*th sublattice with that of an ion from the *j*th sublattice. In the case we are concerned these W_{ij} values between different sublattices are negative along *b* and *c* axes, and positive along *a* axis. Since action is equal to reaction, $W_{ij} = W_{ji}$.

In the applied field *H*, the magnitude of the magnetization are given by the standard theory of the Weiss field approximation, and

$$M_i \,/\, M_{io} = B_S\,(a) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S}\, a - \frac{1}{2S} \coth \frac{a}{2S} \qquad (2)$$

For the srystal with N independent spins per cm^3, the maximum magnetization of *i*th sublattice is $M_{io} = \frac{1}{4} N g_i \mu_B$, where g_i is the Landé factor of ions in the *i*th sublattice, and μ_B the Bohr magneton. B_S is the Brillouin function and a is given by

$$a = g_i \mu_B S (H + H_{wi}) / kT \tag{3}$$

Each sublattice magnetization M_i is a decreasing function of temperatures and vanishes at the critical point, or the Néel point, T_N. Néel point can be found by expanding the Brillouin functions in (2) for small argument. For the *i*th sublattice this results in the equation :

$$T_N M_i - C_i \sum_{j=1}^{4} W_{ij} M_j = 0, \tag{4}$$

where $C_i = N g_{i_2} \mu^2{}_B S (S+1) / 12k$ and T has been replaced by the Néel temperature T_N, since the equation applies to the point only. These four linear homogeneous equation in the magnetization M_j of the sublattice cannot all be independent and they only give a solution differing from zero for the sublattice magnetizations if the determinant of the coefficients of M_i is zero. This gives an equation of the fourth degree in T_N with four roots. This does not mean that every sublattice has its own Curie temperature ; for the one sublattice magnetization exists solely by virtue of the others. It means only that there are four different M_S versus T curves for the resultant sublattice magnetization with four Curie points. These four roots of the determinant equation will be negative or imaginary, so that in these cases there will be no spontaneous magnetization.

In our case $i=1, 2, 3, 4$ stands for the sublattices A(+), A(−), B(+), B(−), respectively. Then $W_{11} = W_{22} = W_{33} = W_{44} = W_{23} = W_{14} = 0$ and $W_{13} = W_{24}$. Then we find for the Néel temperature

$$T_N = \left[\frac{1}{2} \left(C_1^2 W_{12}^2 + 2C_1 C_3 W_{13}^2 \right) + \sqrt{C_1^4 W_{12}^4 + 4C_1^3 C_3 W_{12}^2 W_{13}^2} \right]^{\frac{1}{2}} \tag{5}$$

where there is more than one real positive root for T_N only the state with the highest Néel temperature will occur ; the others have a higher free energy and are unstable.

§ 4. Paramagnetism above Néel Point

The paramagnetic susceptibility above the Néel point can again be found by expanding the Brillouin functions for a small argument, so that in the presence of an applied field H we may write for each i :

$$T M_i - C_i \sum_{j=1}^{4} W_{ij} M_j = C_i H. \tag{6}$$

From this we can find $M = \sum_{j=1}^{4} M_j$. The $1/\chi$ *versus* T curve is not a straight line. For $T \gg T_N$ the curve has an asymptote which canbe found from (6) by first neglecting the Weiss field terms, so that $M_i = C_i H/T$, and then filling these values in the Weiss field terms. For the asymptote we then find

$$\lim_{T \to \infty} 1/\chi = \frac{1}{C} (T - T_a) \tag{7}$$

where $$C = \sum_{i=1}^{4} C_i$$

and T_a is the asymptotic Curie temperature, which is given by

$$T_a = \sum_{i=1}^{4} \sum_{j=1}^{4} C_i \, W_{ij} C_j / C \tag{8}$$

In our case

$$T_a = \frac{C_1 C_3}{C_1 + C_3} (W_{12} + W_{13}) \tag{9}$$

For antiferromagnetic interactions ($W_{ij}<0$), T_a is negative. Formula (7) holds for antiferromagnetism not only asymptotically but also strictly above the Néel point, as follows from (6). Thus for $T>T_N$ the $1/\chi$ *versus* T curve is straight. At $T=T_N$ χ is not infinite.

For ferrimagnetism, $1/\chi$ becomes zero at Curie point; above the Curie point the $1/\chi$ *versus* T curve is therefore concave towards the T axis.

For the crystal like Cr_2F_5 the magnetic structure is considered as combined antiferromagnetic and ferrimagnetic, the $1/\chi$ *versus* T curve falls linearly with descending temperatures towards the negative temperature and is bent downwards and approach the point near the origin.

§ 5. Final Comments

In recent years a certain kinds of paramagnetics have been found, which are composed of two species of ions of the same atom and paramagnetic resonance studies in low temperature revealed such a situstion. $CuSO_4 . 5H_2O$, $K_2CuCl_4 . 2H_2O$ and $Mn(HCOO)_2 . 2H_2O$ etc. are studied by resonance experiment. But the susceptibility and specific measurement data in very low temperature are very few. Cr_2F_5 will belong the same category. Experimental data are desired.

As to the specific heat anomaly associated with Curie point, the elementary theoretical treatment, such as Weiss mean-field approximation, will not be able to provide a detailed explanation of critical behaviour near *Tc*, rigorous statistical treatment in this kind of problems will be treated later.

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