

Co-operative Jahn–Teller Ordering in the Crystal Structure of Rb_2CrCl_4 : a Two-dimensional Easy-plane Ionic Ferromagnet

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Summary Single crystal neutron diffraction at 77 and 5.5 K shows that the Cl atoms in the basal plane in Rb_2CrCl_4 are moved 0.16 Å from the midpoint of the line joining adjacent Cr atoms giving tetragonally elongated CrCl_6 with principal axes alternately along [011] and $[0\bar{1}1]$ of the $D_{2h}^{18}(\text{Cmca})$ unit cell; this is the microscopic origin of the ferromagnetic exchange.

THE compounds A_2CrCl_4 (A = K, Rb, Cs, or monoalkylammonium) have an exceptional interest for the theory of co-operative magnetism.¹ They are among the very few ionic transition metal compounds which order as ferromagnets (T_c ca. 50–60 K) and even in that small group they are unique in having well resolved spin-forbidden ligand field bands in the visible, whose intensity correlates directly with spin fluctuations in the ground state. They are also

interesting from a structural point of view. Cr^{II} compounds have $3d^4$ electron configuration and are thus expected to show strong static Jahn–Teller distortion. However, early powder X-ray² and powder neutron diffraction³ experiments suggested that Rb_2CrCl_4 and Cs_2CrCl_4 had the K_2NiF_4 structure, in which the co-ordination around the $3d$ ion is almost octahedral, with only a small tetragonal flattening along the crystalline four-fold axis. Tetragonal flattening in a Jahn–Teller ion would be highly unusual and, moreover, would not explain why the near-neighbour exchange is ferromagnetic.⁴ We now report preliminary results of single crystal neutron diffraction experiments on Rb_2CrCl_4 which reveal a small antiferro-distortive displacement of the Cl atoms in the basal plane such that the CrCl_6 octahedra are tetragonally elongated.

The neutron diffraction experiments were made on the Mark VI two-circle diffractometer at A.E.R.E., Harwell

using a neutron wavelength of 1.093 Å. The sample, cut from a Czochralski-grown boule,⁵ was mounted in a Cryogenics Associates CT14 cryostat. Data from 447 (77 K) and 487 (5.5 K) reflections were averaged over equivalents to give 99 (77 K) and 124 (5.5 K) inequivalents. Data were analysed by the method of least-squares, including correction for extinction. In the related $3d^9$ compound K_2CuF_4 it was originally suggested⁶ that the presence of a Jahn-Teller distortion lowered the space-group from D_{4h}^{17} (that of K_2NiF_4) to D_{2d}^{10} . In the case of Rb_2CrCl_4 , a search for reflections allowed in D_{2d}^{10} proved negative¹ but later it was shown⁷ that the unit-cell of K_2CuF_4 may not necessarily be doubled along the K_2NiF_4 c -axis. We find weak reflections in the single crystal neutron diffraction of Rb_2CrCl_4 which confirm that its cell is not doubled along this axis and that it has the D_{2h}^{18} space group. The sample consisted of two crystallographic domains with different populations, both of which contribute to the major reflections but only one to each superlattice reflection.¶ The relative domain population w was included as a variable in the least-squares fitting procedure, and converged to the values shown in the Table.

TABLE. Structural parameters of Rb_2CrCl_4 from single crystal neutron diffraction (D_{2h}^{18}).

	Temperature/K	
	77	5.5
a_0 (Å) ^a	15.67 (4)	15.67 (4)
$b_0 \sim c_0$ (Å)	7.184 (18)	7.194 (18)
x_{Cl} (8d)	0.1504 (15)	0.1507 (16)
x_{Rb} (8d)	0.3550 (18)	0.3566 (21)
B_{Cr}^b	0.38 (15)	0.45 (9)
B_{Rb}^b	0.46 (9)	0.37 (6)
B_{Cl} (axial) ^b	1.45 (9)	0.59 (5)
B_{Cl} (equatorial) ^b	0.48 (3)	0.37 (4)
$y_{Cl} = z_{Cl}$ (8f)	0.2658 (1)	0.2653 (1)
w^c	0.413 (4)	0.416 (4)
Ferromagnetic moment (μ_B)	—	3.0 (4)
Weighted R^d	0.0548	0.0570

^a a_0 in D_{2h}^{18} corresponds to c_0 in D_{4h}^{17} . ^b Debye-Waller factors defined as $\exp[B_i(\sin^2\theta/\lambda^2)]$ in the structure factor (Å^{-2}). ^c Defined in the text. ^d Weighted R (minimized) is

$$\sum_i \left\{ \frac{[I_{obs}^i - I_{calc}^i/\sigma_i]^2}{\sum_i [I_{obs}^i/\sigma_i]^2} \right\}^{\frac{1}{2}}$$

where σ is the error on the observation.

To explain the magnetic properties of Rb_2CrCl_4 it is important to know how close the Cr–Cl–Cr angle in the basal plane is to 180°. In D_{2h}^{18} the Cl atoms are not constrained to the Cr–Cr axis but we find that the off-axis displacement is <0.0001 of the D_{2h}^{18} cell, *i.e.*, <0.0008 Å. However, the major displacement of the equatorial Cl atoms is along the Cr–Cr axis and amounts to *ca.* 3% of the Cr–Cr separation, *i.e.*, 0.16 Å. As a result of this displacement each Cr atom is subjected to a ligand field of effective point symmetry D_{2h} , although approximating quite closely to D_{4h} . For example at 77 K the Cr–Cl bond lengths are 2.379(1) and 2.700(1) Å within the basal plane and 2.357(24) Å perpendicular to it. Thus the principal axes of the elongated octahedra are in the basal plane and directed alternately along $[011]$ and $[0\bar{1}1]$ of the

D_{2h}^{18} cell, as shown in the Figure. Note that in K_2CuF_4 the difference between the 'short' and 'long' bonds is greater (1.92 and 2.22 Å).⁶

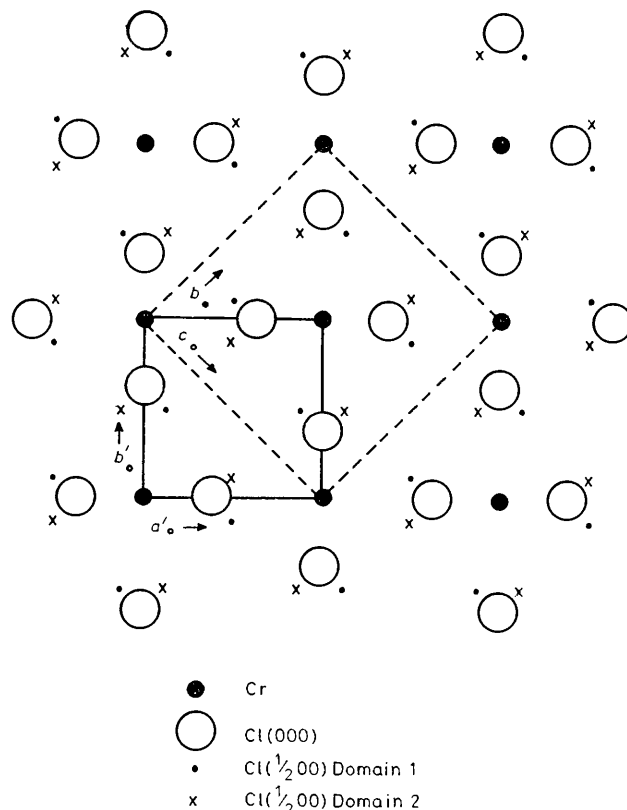


FIGURE. Displacement (exaggerated) of Cl atoms in the layers of Rb_2CrCl_4 . Dotted lines define b_0 and c_0 of the D_{2h}^{18} unit cell, the full lines are a'_0 , b'_0 of related D_{4h}^{17} (K_2NiF_4).

The co-operative Jahn-Teller distortion of the $CrCl_6$ units in Rb_2CrCl_4 clarifies many of its unusual physical properties. For example, two Cr sites with principal axes at right angles had already been postulated from the angular variation of ^{53}Cr n.m.r. frequency.⁸ The existence⁹ of a small anisotropy gap in the magnon spectrum at the Brillouin zone centre is also explained. Most important, though, is the relation of the distortion to the ferromagnetic exchange. Single-ion anisotropy from the Jahn-Teller distortion constrains the single $e_g(O_h)$ electron of each Cr^{2+} to the z^2 orbital. This type of co-operative Jahn-Teller ordering has not previously been found in Cr^{II} compounds though a very similar atomic arrangement exists in the (001) plane of MnF_3 , where it is also associated with ferromagnetic exchange.¹⁰ Although there are apparent analogies between the structural and magnetic properties of Rb_2CrCl_4 and K_2CuF_4 , there are exchange pathways in the d^4 compound which are not available to the d^9 compound. In K_2CuF_4 the ferromagnetic exchange arises from the orthogonality of $x^2 - y^2$ orbitals on the nearest

¶ The two domains arise by interchanging b and c in the pseudo-tetragonal unit cell.

neighbouring Cu; in Rb_2CrCl_4 , on the other hand, orthogonality of z^2 to the xz, yz, xy set on the neighbouring Cr should contribute substantially. In either case the Jahn-Teller ordering is fundamental to the ferromagnetism. The distortion in Rb_2CrCl_4 is still present at room temperature and we are continuing our structural work at high temperatures to see if it undergoes a phase transition to the K_2NiF_4 structure.

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