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Submitted on 1 Jan 1982

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MAGNETIC MOMENT DISTRIBUTION IN THE IONIC FERROMAGNET Rb$_2$CrCl$_4$


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Résumé. — La densité d’aimantation de Rb$_2$CrCl$_4$ a été étudiée sur un monocristal par neutrons polarisés. Les résultats semblent indiquer qu’un ordre orbital induit par l’effet Jahn-Teller donne une configuration qui approche $(xz)^1 (yz)^1 (xy)^1 (z^2)^0$ sur le site de Cr$^{2+}$. Cet ordre orbital est compatible avec le ferromagnétisme du composé.

Abstract. — The magnetisation density of Rb$_2$CrCl$_4$ has been studied on a single crystal by means of polarised neutron diffraction. The derived results are consistent with a Jahn-Teller induced orbital ordering to give a configuration approximating to $(xz)^1 (yz)^1 (xy)^1 (z^2)^0$ at each Cr$^{2+}$ site. This orbital ordering is compatible with the ferromagnetic nature of this compound.

1. Introduction. — Rb$_2$CrCl$_4$, one of the extremely few optically transparent ferromagnets [1], belongs to the family of perovskite-type layer structures. In early experiments the crystal structure was assumed to be of the K$_2$NiF$_4$-type, space group I4/mmm [2,3] (Figure 1). Crystal structure refinements in I4/mmm by x-ray [2] and neutron [3] powder methods were compatible with compressed CrCl$_6$-octahedra, which can be understood as the consequence of the Jahn-Teller effect, which lifts the orbital degeneracy of the octahedral 5$E_g$ ground state of

![Fig. 1: The K$_2$NiF$_4$-structure](image-url)
Following arguments originally given by Khomskii and Kugel \cite{4} for the 3d\(^9\) configuration in K\(_2\)CuF\(_4\) and later generalized to include the 3d\(^4\) configuration \cite{5,6} a compression of the Cr\(_\text{Cl}_6\)-coordination cannot be reconciled with the observed ferromagnetic sign of the nearest neighbour exchange constant.

More detailed structure analyses of Rb\(_2\)CrCl\(_4\) by single crystal neutron diffraction lead to a structure which is a small deviation from the K\(_2\)NiF\(_4\)-structure, namely a superstructure of space group Cmca \cite{7,8}. In this structure there is an antiferrodistortive ordering of elongated Cr\(_\text{Cl}_6\)-octahedra so that the long axes of adjacent octahedra are at right angles. The structure is the same as that of K\(_2\)CuF\(_4\) proposed by Ito and Akimitsu \cite{9} but differs from the earlier proposal of Haegele and Babel \cite{10} in the sense of the packing of alternate layers. An elongation of the Cr\(_\text{Cl}_6\) octahedra should give orbital ordering on each Cr\(^{2+}\) site such that d\((z^2)\) is half-filled and d\((x^2-y^2)\) empty. By the arguments of refs. 5 and 6 this would result in parallel alignment of the spins in the basal plane, as shown in Figure 2.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{Figure_2.png}
\caption{Spin-spin coupling between d\(^4\) cations in the basal plane of Rb\(_2\)CrCl\(_4\) (\(\leftrightarrow\), displacements of Cl\(^-\)ions)}
\end{figure}

The strong correlations between magnetic interactions and cooperative orbital order have also been detected in the mixed crystal system Rb\(_2\)Cr\(_1-x\)Mn\(_x\)Cl\(_4\), for which ferromagnetic coupling coexists with the Jahn-Teller induced superstructure in the concentration range 0\(<x<0.41\) \cite{11,12}. In order to confirm the model of orbital ordering shown in Fig. 2 and to obtain information on covalency and detailed exchange mechanism the magnetic moment distribution of Rb\(_2\)CrCl\(_4\) has been investigated by polarised neutron diffraction.

2. Experimental procedure and data processing. - The experiment has been performed at the D-3 polarised-neutron diffractometer at the Institut Laue-Langevin, Grenoble. The incident neutron wavelength was 0.9002\(\AA\) and an Er-filter was used to suppress \(\chi/2\) contamination. The crystal of size 2.8x2.8x5 mm was wrapped in Al-foil to avoid decomposition and mounted with its [110] direction (referred to the superstructure cell) parallel to the magnetic field direction. It was cooled to 4.47(5)K in a liquid helium cryostat and a magnetic field of 4.6 Tesla was applied.

The data set to be measured can be divided into two classes of reflections. Those with Miller indices that are all odd or all even refer to the K\(_2\)NiF\(_4\)-pseudocell. These main structure reflections combine intensity from the two possible nuclear-domains such that a hkl-reflection of domain 1 is simultaneously reflecting with a reflection of domain 2 indexed as khl in terms of domain 1. The expanded equation
of the flipping ratio for the two-domain situation may be written:
\[
R = \frac{x (F_N \ hkl + F_M \ hkl)^2 + (1-x)(F_N \ k\ h\ l + F_M \ k\ h\ l)^2}{x (F_N \ hkl - F_M \ hkl)^2 + (1-x)(F_N \ k\ h\ l - F_M \ k\ h\ l)^2}
\]
where \(x\) represents the respective volume proportion of the two domains and \(F_N\) and \(F_M\) are the nuclear and magnetic structure factors of the main structure reflections. The measured flipping ratio is independent of the volume ratio if
\[
F_N \ hkl = F_N \ k\ h\ l \quad \text{and} \quad F_M \ hkl = F_M \ k\ h\ l.
\]
This is indeed valid in Cmca if the \(Cl^-\) ions move out of their I4/mmm position, midway between the \(Cr^{2+}\) ions along the Cr-C1-Cr direction. This is found to be the case [7,8], and the domain situation can be handled as a single domain problem for these main reflections. Thus a total of 201 independent main structure reflections was measured up to \(\theta/A \leq 0.82\AA^{-1}\).

The second group of reflections are superstructure ones, of type eoe, oeo and oee (e=even, o=odd) referring to domain 1 and domain 2, respectively. As the actual volume ratio of domain 1 to domain 2 was roughly 2:1 superstructure reflections of domain 1 were included in the data set. Due to their very weak intensity we could only measure in the available time flipping ratios of a selection of 57 of those, whose relatively 'high' nuclear intensity was known from unpolarised neutron work [12] on D-15 at the Institut Laue-Langevin. This experiment, which was carried out on a Mn-doped (\(~1%\) \(Rb_2CrCl_4\) crystal at \(15K\), also yielded the nuclear structure factors \(F_N\) which were used to evaluate the magnetic structure factors \(F_M\) from the polarised neutron data by \(F_M = \rho \cdot F_N\).

3. Results.- As the present data set for superstructure reflections is incomplete and the strongest main structure reflections measured are suspected of being affected by extinction, it would be rather questionable to obtain the magnetic moment distribution directly by making Fourier syntheses from the measured Fourier coefficients of the periodic magnetisation, \(F_M\). In order to obtain a quantitative analysis of the spin density distribution another approach to the data treatment was made using the modified RAPMAB-program of J. Schweizer and F. Tasset [13]. In this program the magnetisation density of \(Rb_2CrCl_4\) is considered to be centered independently on the \(Cr^{2+}\)-ions and magnetic structure factors \(F_{M\ \text{calc}}\) may be calculated using a 3d free ion \(Cr^{2+}\) form factor [14].

In fitting the calculated magnetic structure factors \(F_{M\ \text{calc}}\) to the observed ones \(F_{Mobs}\) one has to take into account six unknown parameters. These are the localised magnetic moment, the orbital contribution and four occupation parameters for the 3d-orbitals. Provided that the spin density is distributed spherically around the \(Cr^{2+}\) ions one would expect the value 0.20 for the occupation of each of the five d-states, whose degeneracy has been completely removed by the point symmetry (\(C_{2h}\)) of the \(Cr^{2+}\)-site in space group Cmca. Any asphericity of the spin density distribution will lead to a magnetic contribution to the superstructure reflections, and should result in deviations of the refined occupation parameters from the values 0.20. The data set refined by the method of least squares in order to determine the 6 parameters included the 57 measured superstructure reflections, which are all very sensitive to the asphericity of the magnetic moment distribution, and a selected 104 of the main structure reflections,
with intensities comparable to the superstructure ones so as to mini-
mimize the effect of extinction.
The results of the refinement are displayed in Table 1. The refined value of $3.1 \mu_B$ for the localised magnetic moment of Cr$^{2+}$, which is less than the $3.8 \mu_B$ found by magnetisation measurements for Rb$_2$CrCl$_4$ [12,15], may be mainly due to the absence of data for the FMs of the main structure reflections in the low sin $\Theta/\lambda$ range $\leq 0.2$ Å$^{-1}$. The spin proportion of 0.96 shows that the orbital moment for Cr$^{2+}$ is almost quenched as expected. The main interest concerns the distribution of magnetic electrons between the five d-orbitals. The $d_{x^2-y^2}$ orbital is found to be empty, whereas the magnetic electrons are nearly equally distributed among the remaining d-orbitals. This result

Table 1  Refined magnetic parameters for Rb$_2$CrCl$_4$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>localised magnetic moment:</td>
<td>$3.1(1) \mu_B$</td>
</tr>
<tr>
<td>spin proportion:</td>
<td>$0.96(2)$</td>
</tr>
<tr>
<td>occupation parameters for the 3-d orbitals</td>
<td></td>
</tr>
<tr>
<td>$d_{z^2}$</td>
<td>$0.23(1)$</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>$-0.03(1)$</td>
</tr>
<tr>
<td>$dxz$</td>
<td>$0.28(1)$</td>
</tr>
<tr>
<td>$dyz$</td>
<td>$0.25(1)$</td>
</tr>
<tr>
<td>$dxy$</td>
<td>$0.27$</td>
</tr>
</tbody>
</table>

Fig. 3: Results of a fit of calculated magnetic structure factors $F_{\text{Mcalc}}$ (crosses) to experimentally derived structure factors $F_{\text{Mobs}}$ (squares) for Rb$_2$CrCl$_4$ as described in the text.
confirms the proposed orbital ordering model of Fig. 2 involving an antiferrodistortive arrangement of elongated \(CrCl_6\) octahedra with empty \(d_{x^2-y^2}\) and half-filled \(d_{z^2}\) orbitals. Fig. 3 illustrates the good agreement between the calculated and observed magnetic structure factors \(\text{FM}_{\text{calc}}\) and \(\text{FM}_{\text{obs}}\). The points distributed around the \(0\mu_B\)-line in the lower \(\sin \theta / \lambda \) range apply to superstructure reflections which would be exactly \(0\mu_B\) for a spherical spin density distribution around the \(Cr^{2+}\) ions. Further measurements are in progress because a lot of strong main structure reflections have been omitted in the lower \(\sin \theta / \lambda \) range because of extinction. These will be remeasured at various short wavelengths at D5 at the Institut Laue-Langevin to refine an extinction model and the corrected \(\text{FM}_{\text{obs}}\)'s will be included in the refinement procedure described above. Furthermore since the effects of covalency are only to be observed at low angles, the remeasured reflections in the range \(\sin \theta / \lambda \leq 0.2 \, \text{\AA}^{-1}\) will provide data in order to refine a model of covalency in \(\text{Rb}_2\text{CrCl}_4\).

Acknowledgments.- The work has partly been supported by the BMFT (Bundesministerium für Forschung und Technologie), the UK Science and Engineering Research Council and AERE Harwell.

References: