

Neutron Diffraction Experiments on CsCrI_3 at 300, 77, and 1.2 K

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CsCrI_3 has been investigated by neutron powder diffraction at room temperature and 77 and 1.2 K. It undergoes a phase transition at 150 K due to the cooperative Jahn-Teller effect. The high-temperature form, $\alpha\text{-CsCrI}_3$ (hexagonal, space group $P6_3/mmc$, $a = 8.127(1) \text{ \AA}$, $c = 6.944(1) \text{ \AA}$, $Z = 2$), adopts the BaNiO_3 structure with a local Jahn-Teller distortion. The low-temperature form, $\beta\text{-CsCrI}_3$ (orthorhombic, space group $Pbcn$, $a = 8.102(1) \text{ \AA}$, $b = 13.792(1) \text{ \AA}$, $c = 6.900(1) \text{ \AA}$, $Z = 4$), has a structure not yet been reported for a Jahn-Teller distorted BaNiO_3 structure. It is shown that the low-temperature form can be derived from the BaNiO_3 structure by means of a canting of triangles, formed by the three common I^- ions of two adjacent CrI_6^{4-} octahedra. The magnetic structure of $\beta\text{-CsCrI}_3$ at 1.2 K is found to consist of an antiparallel sequence of ferromagnetic (0 0 1) planes with a magnetic moment in the $|1 0 0|$ direction of $3.16 \mu_B$.

Introduction

The investigations on the compound described here are part of our current research on compounds in the series $A\text{I-BI}_2$, where A represents an alkali metal, In, or Tl and B a first-row transition metal, Zn, Cd, or Hg. Only two structure types occur for the investigated compounds $AB\text{I}_3$: the BaNiO_3 structure (1, 16) and the NH_4CdCl_3 structure (2, 16).

Two compounds $A\text{CrI}_3$ have been found: RbCrI_3 (H. W. Zandbergen, to be published) and CsCrI_3 (3), both having distorted BaNiO_3 structures.

Cr^{2+} and Cu^{2+} compounds are expected to distort due to a cooperative Jahn-Teller effect (4). Several distortions from the BaNiO_3 structure have been reported. For CsCuCl_3 (5) this effect leads to a destruction of the threefold axis (space group $P6_122$) whereby the elongation of the octahedra is realized mainly by a shift of the Cl^- ions in

the (0 0 1) plane. RbCrCl_3 (6, 7) has two phase transitions. The low-temperature form, $\gamma\text{-RbCrCl}_3$ ($C2_1$), has a monoclinically distorted BaNiO_3 structure with a doubled c -axis. $\beta\text{-RbCrCl}_3$, which is also monoclinic ($C2_1/m$), has a partly averaged $\gamma\text{-RbCrCl}_3$ structure. Because of this averaging the c -axis is no longer doubled. RbCrI_3 also has two phase transitions with structures equal to those of RbCrCl_3 . In the $\beta\text{-RbCrCl}_3$ and $\gamma\text{-RbCrCl}_3$ structures the elongation of the octahedra is realized mainly by a shift of the Cl^- ions in the z -direction.

Experimental

Single crystals of CsCrI_3 were grown by the Bridgman method. The sample used for neutron diffraction was prepared by melting a stoichiometric mixture of the binary compounds and—after powdering—annealing for 2 weeks in an evacuated glass tube at

450°C. CrI₂ was prepared from the elements in an almost horizontal evacuated glass tube with one side, containing Cr, at 950°C and the other side, containing fluid I₂, at 200°C. CrI₂ was purified by sublimation. DTA measurements show a first-order phase transition taking place at 150 K. Measurements on a single-crystal diffractometer reveal the structure to change at this temperature from hexagonal ($T > 150$ K) to orthorhombic. At about 100 K the crystal symmetry of the orthorhombic unit cell of β -CsCrI₃ was determined from zero and upper-level Weissenberg photographs. It was not possible to transform a single crystal from the α - to the β -phase without twinning. Because the a/b ratio is not equal to $3^{1/2}$ it was still possible to determine the systematically absent reflections. It was found that $k = 2n + 1$ was absent for $0\ k\ l$, $l = 2n + 1$ for $h\ 0\ l$, and $h + k = 2n + 1$ for $h\ k\ 0$. These results are consistent with the space group $Pbcn$. At room temperature, 77 K, and 1.2 K neutron powder diffraction diagrams (see Fig. 1) were recorded at the H.F.R. at Petten using $\lambda = 2.5718(2)$ Å with 30' collimation in the angular range $4^\circ < 2\theta < 139^\circ$. The sample holder consisted of a vanadium tube, closed by copper plugs fitted with rubber O-rings. The same sample was used for all three measurements. The diagram recorded at 77 K contained, in contrast with those recorded at room temperature and 1.2 K, some small extra reflections. This contamination is caused by leaking of oxygen and moisture into the sample holder, as the diagram of 77 K was recorded about 3 months after the other two. Because no information is available about oxyiodides and hydrates of CsCrI₃ the contamination could not be identified. In the refinement the 2θ regions containing these reflections were omitted.

For the refinements Rietveld's profile program (8) was used. No absorption correction was applied. The coherent scattering lengths (9) used are $b_{Cs} = 0.55$, $b_{Cr} = 0.352$,

and $b_I = 0.53$ all in units of 10^{-12} cm. The magnetic form factor was taken from Watson and Freeman (10).

Results and Refinements at Different Temperatures

Room Temperature

The refinement was started with the positions of the BaNiO₃ structure. Full matrix refinement in space group $P6_3/mmc$ of positional parameters and an overall isotropic thermal parameter leads to convergence at

$$R_{\text{total}} = \frac{\sum_i |I_i(\text{obs}) - I_i(\text{calc})|}{\sum_i I_i(\text{obs})} = 0.44$$

and

$$R_{\text{profile}} = \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum_i y_i(\text{obs})} = 0.098,$$

where I_i is the intensity of the i th reflection and y_i is the intensity of the i th measured point.

Because several measurements on similar Jahn-Teller active compounds (11-13) suggest an elongation of the octahedra above the phase transition also, a model was introduced describing an averaged β -CsCrI₃ structure. In this model the I⁻ ion is divided into three parts: one part above, one part on, and one part under the (0 0 1) mirror plane. The space group remains to be $P6_3/mmc$. The division is shown in Fig. 2. Taking into account the thermal motion of the I⁻ ions and the change in the direction of the elongation of the CrI₆⁴⁻ octahedra, all of these results in a banana-shaped distribution of the I⁻ ions (see Fig. 2).

Refinement of this model leads to $R_{\text{total}} = 0.041$ and $R_{\text{profile}} = 0.095$. Refinement of all parameters including individual isotropic thermal parameters with this model con-

verges at $R_{\text{total}} = 0.038$ and $R_{\text{profile}} = 0.092$. The results of this refinement are given in Table I. The observed and calculated profiles are depicted in Fig. 1a. Some distances and bond angles of both models are listed in Tables II and III.

77 K

The space group of β -CsCrI₃, $Pbcn$, determined from Weissenberg photographs, restricts the possibilities of elongation of the octahedra in the unit cell, thus simplifying the postulation of a model for the refinement. The deviation from the α -CsCrI₃ structure is not very large as can be seen from Fig. 1. Therefore the refinement was started with a model in which one of the octahedron axes is 10% longer than the other two. Full matrix refinement of posi-

TABLE I
UNIT-CELL DIMENSIONS, POSITIONAL AND THERMAL PARAMETERS OF α -CsCrI₃ AT ROOM TEMPERATURE AND OF β -CsCrI₃ AT 77 AND 1.2 K

| | x/a | y/b | z/c | b^a | |
|---|---------------|---------------|----------|--------|----------------|
| α -CsCrI ₃ , space group $P6_3/mmc$, room temperature $a = 8.127(1) \text{ \AA}$, $c = 6.944(1) \text{ \AA}$ | | | | | |
| Cs | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.75 | 4.1(3) | 2 ^b |
| Cr | 0 | 0 | 0 | 2.4(2) | 2 |
| I(1) | 0.170(2) | 0.339(4) | 0.226(4) | | 4 |
| I(2) | 0.153(3) | 0.305(7) | 0.25 | 2.7(4) | 2 |
| β -CsCrI ₃ , space group $Pbcn$, 77 K $a = 8.107(1) \text{ \AA}$, $b = 13.793(2) \text{ \AA}$, $c = 6.914(1) \text{ \AA}$ | | | | | |
| Cs | 0 | 0.333(2) | 0.25 | 1.3(5) | |
| Cr | 0 | 0 | 0 | 0.0(3) | |
| I(1) | 0.249(3) | 0.084(1) | 0.213(1) | 0.8(3) | |
| I(2) | 0 | 0.160(1) | 0.25 | 1.6(7) | |
| β -CsCrI ₃ , space group $Pbcn$, 1.2 K $a = 8.102(1) \text{ \AA}$, $b = 13.792(2) \text{ \AA}$, $c = 6.900(1) \text{ \AA}$ | | | | | |
| Cs | 0 | 0.336(1) | 0.25 | 1.1(4) | |
| Cr | 0 | 0 | 0 | 0.2(2) | |
| I(1) | 0.247(1) | 0.085(1) | 0.217(1) | 0.1(2) | |
| I(2) | 0 | 0.158(1) | 0.25 | 0.3(4) | |
| Magnetic moment: $\mu_x = 3.16(3) \mu_B$ | | | | | |

^a $b = 8\pi^2 U_s^2$ (15).

^b Occupation.

TABLE II
SOME DISTANCES (\AA) AND ANGLES ($^\circ$) FOR α -CsCrI₃ WITH A SPHERICAL DISTRIBUTION OF THE I IONS

| | | | |
|------|-------------|---------|----------|
| Cs-I | 4.210(2) 6x | Cr-I-Cr | 73.84(9) |
| Cs-I | 4.064(4) 6x | I-Cr-I | 87.65(7) |
| Cr-I | 2.890(3) 6x | I-Cr-I | 92.35(7) |
| I-I | distances: | | |
| | 4.00-4.17 | | |

tional and isotropic thermal parameters converges at $R_{\text{total}} = 0.065$ and $R_{\text{profile}} = 0.132$. The relatively large R values as compared to the R values of the other refinements are caused by the contamination of the sample. The results of the refinement are listed in Table I and Fig. 1b shows the calculated and observed profiles.

1.2 K

Because of the existence of a strong 0 0 1 reflection in the diagram recorded at 1.2 K, it is evident that β -CsCrI₃ must consist of ferromagnetic (0 0 1) planes which are coupled antiferromagnetically in the z -direction. Refinement of all parameters including the magnetic moment parameters in the three orthorhombic directions shows the moment to be parallel to the a -axis. The

TABLE III
SOME DISTANCES (\AA) AND BOND ANGLES ($^\circ$) FOR α -CsCrI₃ WITH A BANANA-SHAPED DISTRIBUTION OF THE I⁻ IONS BASED ON STATISTICALLY AVERAGED β -CsCrI₃ STRUCTURE^a

| | | | |
|---------|------------|--------------|----------|
| Cs-I(1) | 4.07(2) 4x | Cr-I(1)-Cr | 71.8(6) |
| Cs-I(1) | 4.03(3) 2x | Cr-I(2)-Cr | 77.9(14) |
| Cs-I(1) | 4.31(3) 2x | I(1)-Cr-I(1) | 84.7(9) |
| Cs-I(2) | 4.07(3) 2x | I(1)-Cr-I(1) | 95.3(9) |
| Cs-I(2) | 4.30(3) 2x | I(1)-Cr-I(2) | 85.0(9) |
| Cr-I(1) | 2.76(2) 2x | I(1)-Cr-I(2) | 95.0(9) |
| Cr-I(1) | 3.05(3) 2x | I(1)-Cr-I(2) | 88.9(8) |
| Cr-I(2) | 2.85(3) 2x | I(1)-Cr-I(2) | 91.1(8) |

^a The distances and angles are listed in the same sequence as those for β -CsCrI₃ in Table IV.

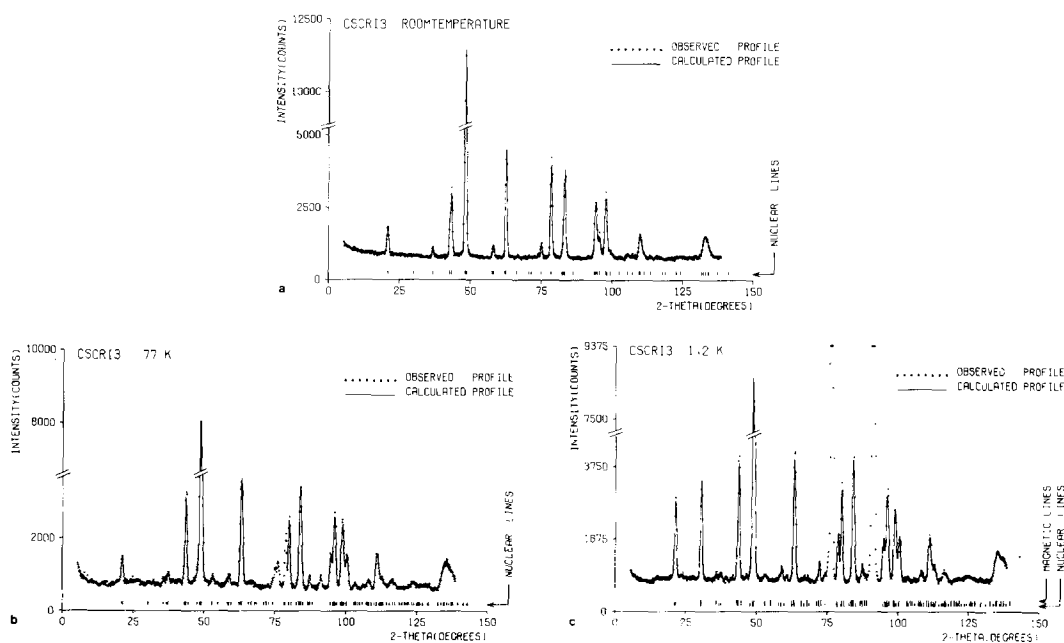


FIG. 1. Calculated and observed profiles for CsCrI_3 at room temperature (a), 77 K (b), and 1.2 K (c). The large extra reflections in the diagram of 1.2 K are due to the cryostat.

magnetic moment parameters of the other two directions converge to values less than twice the standard deviation ($\mu_y = 0.36(45)$, $\mu_z = -0.33(20) \mu_B$). Full matrix refinement of positional and isotropic thermal parameters and a magnetic moment parameter in the a -direction only to convergence at $R_{\text{total}} = 0.052$,

$$R_{\text{magnetic}} = \sum_i |I_{im}(\text{obs}) - I_{im}(\text{calc})| / \sum_i I_{im}(\text{obs}) = 0.058,$$

$$R_{\text{nuclear}} = \sum_i |I_{in}(\text{obs}) - I_{in}(\text{calc})| / \sum_i I_{in}(\text{obs}) = 0.051,$$

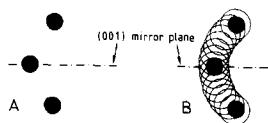


FIG. 2. (A) The distribution of the I^- ion in $\alpha\text{-CsCrI}_3$ due to a local Jahn-Teller distortion. (B) The bananashaped distribution of the I^- ions resulting from thermal motion and a change in the direction of elongation of the CrI_6^{4-} octahedra.

and $R_{\text{profile}} = 0.097$. The results of the refinement are given in Table I and Fig. 1c and some distances and bond angles are listed in Table IV.

Discussion

Jahn and Teller (14) showed that nonlinear molecules with a degenerate electronic ground state are unstable with respect

TABLE IV

SOME DISTANCES (\AA) AND ANGLES ($^\circ$) IN $\beta\text{-CsCrI}_3$ AT 1.2 K

| | | | |
|---------|------------|--------------|---------|
| Cs-I(1) | 4.01(2) 4x | Cr-I(1)-Cr | 73.0(2) |
| Cs-I(1) | 3.98(1) 2x | Cr-I(2)-Cr | 76.8(4) |
| Cs-I(1) | 4.36(1) 2x | I(1)-Cr-I(1) | 88.0(3) |
| Cs-I(2) | 4.05(1) 2x | I(1)-Cr-I(1) | 92.0(3) |
| Cs-I(2) | 4.24(1) 2x | I(1)-Cr-I(2) | 90.3(3) |
| Cr-I(1) | 2.76(1) 2x | I(1)-Cr-I(2) | 89.7(3) |
| Cr-I(1) | 3.04(1) 2x | I(1)-Cr-I(2) | 95.6(3) |
| Cr-I(2) | 2.78(1) 2x | I(1)-Cr-I(2) | 84.4(3) |

I-I distances: 3.91(2)–4.31(1)

to some distortion, e.g., small displacements of the ligands surrounding the Jahn–Teller active atom. These small displacements of the I⁻ ions change the crystal field acting on the electrons of the Cr²⁺ ion. In the crystal these displacements are coupled by elastic forces giving rise to an effective interaction between the Cr²⁺ ions. The cooperative operation leads to a spontaneous distortion of the entire lattice. For CsCrI₃ the distortion leads to an orthorhombic unit cell ($T < 150$ K) and for RbCrI₃ to a monoclinic unit cell.

Both structures are still very much related to the BaNiO₃ structure. They consist of chains of face-sharing CrI₆⁴⁻ octahedra along the c -axis as BaNiO₃. Due to distortions of the octahedra the 6₃ axis of the BaNiO₃ structure does not occur in the low-temperature forms of CsCrI₃ and RbCrI₃. The displacements of the atoms in β -CsCrI₃ and β -RbCrI₃ from the positions in the BaNiO₃ structure can be described qualitatively by a canting of the triangles, formed by three common I⁻ ions of two adjacent Cr²⁺ ions in a chain. In the BaNiO₃ structure this triangle of I⁻ ions is situated on the (0 0 1) mirror plane. The distortion in β -CsCrI₃ is obtained by a canting along the $|1\ 0\ 0|$ direction of the hexagonal unit cell of BaNiO₃. The distortion in β -RbCrI₃ is realized by a canting along the $|1\ 1\ 0|$ direction of the hexagonal unit cell of BaNiO₃. These two cantings are shown in Fig. 3 and the result of this canting for β -CsCrI₃ in Fig. 4. The distortion in β -CsCrI₃ is very easily realized by

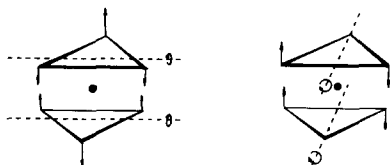


FIG. 3. Canting of the two iodine triangles of a CrI₆⁴⁻ octahedron along $|1\ 1\ 0|$ for β -RbCrI₃ (left) and along $|1\ 0\ 0|$ for β -CsCrI₃ (right). The Cr²⁺ ion is represented by a solid circle.

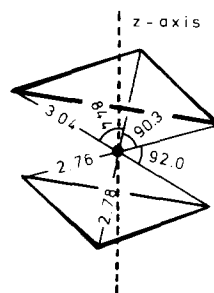


FIG. 4. The distortion found for the CrI₆⁴⁻ octahedra in β -CsCrI₃ at 1.2 K.

a shift of I⁻ layers in the $+z$ - or $-z$ -direction as is depicted in Fig. 5. With this shift of I⁻ planes the octahedra are deformed as indicated above. Because whole planes are shifted the structure loses its C centering.

Because for the high-temperature form, α -CsCrI₃, elongated octahedra were also expected, a statistically averaged β -CsCrI₃ model was introduced. Although the R -values are not much lowered by the introduction of elongated octahedra, the shifts of the I⁻ ions are significant. As is shown in Table III these shifts result in Cr–I distances comparable to those in β -CsCrI₃ (Table IV). The positional parameters agree reasonably well with the positions of the I⁻ ions in β -CsCrI₃ converted to a hexagonal unit cell:

$$\begin{aligned} \text{I(1)} \quad x/a &= 0.167(1), \\ & y/b = 0.334(1), \quad z/c = 0.217(1), \\ \text{I(2)} \quad x/a &= 0.156(1), \\ & y/b = 0.313(1), \quad z/c = 0.25. \end{aligned}$$

X-Ray single-crystal diffraction measurements on α -CsCrI₃ at room temperature yielded similar and more accurate results.

These results shall be published elsewhere.

It can be concluded that there is strong evidence for the existence of elongated octahedra above the phase transition.

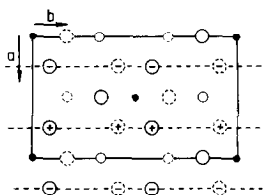


FIG. 5. The structure of α - CsCrI_3 in an orthorhombic setting. The solid circles represent Cr^{2+} ions at $z = 0$ and $z = \frac{1}{2}$, the large open circles I^- ions, and the small open circles Cs^+ ions. Ions at heights $\frac{1}{4}$ and $\frac{3}{4}$ are distinguished as full and broken circles. The β - CsCrI_3 structure can be derived from this figure by shifting the planes (indicated by the broken lines) with the I^- ions marked + into the $+z$ -direction and those with I^- ions marked - into the $-z$ -direction.

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