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The Cooperative Jahn–Teller Distorted Structure of $RbCuCl_3$

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As a function of temperature, $RbCuCl_3$ appears in three different structure types, all with a slight deviation from the $CsMgCl_3$, or hexagonal perovskite (2*L*) structure. Above 339 K it crystallizes with space group $P6_3/mmc$ (α-$RbCuCl_3$), probably isostructural to α-$CsCrCl_3$. Between 339 and 262 K it has space group *Pcan* (β-$RbCuCl_3$), isostructural to β-$CsCrI_3$ and below 262 K space group *C*2 (γ-$RbCuCl_3$), isostructural to γ-$RbCrCl_3$. The β and γ phase consist of chains of face-sharing $CuCl_6$ octahedra which are elongated along a principal axis (pseudo D_{4h} symmetry) as a consequence of the $E \otimes \epsilon$ Jahn–Teller effect.

Introduction

As a part of the work of our department on the cooperative Jahn–Teller effect in ternary halides containing Cr^{2+} or Cu^{2+}, we have already reported on the Jahn–Teller distorted crystal structures of $RbCrCl_3$ and $CsCrCl_3$ (*4, 5*). Because the crystal structure of $CsCuCl_3$ is also known, it would be valuable to have additional structural information from $RbCuCl_3$ to get a more complete picture of the cooperative Jahn–Teller effect in such hexagonal systems.

In obtaining single crystals of $RbCuCl_3$ we were confronted with the same difficulties as were found for β-$RbCrCl_3$ and γ-$CsCrCl_3$ (*5*). Thus, in the present case it was impossible to get single-domain crystals of $RbCuCl_3$ at room temperature. Therefore, the structure refinements have been performed by neutron powder diffraction.

It has been found that the crystal structure of $RbCuCl_3$ is a slightly distorted $CsMgCl_3$ structure (*1*) as a consequence of the cooperative Jahn–Teller effect. By means of differential thermal analysis (DTA), we have detected two structural phase transitions, indicating three different phases as a function of temperature.

Experimental

$RbCuCl_3$ has been prepared by melting stoichiometric amounts of the binary compounds in an evacuated quartz tube (450°C) and annealing for 2 weeks at 300°C. By means of DTA (Mettler TA1), two phase transitions with a clear latent heat at 339 ± 2 and 262 ± 2 K were found. We have labeled the different structure types as: α, β, and γ phase, indexed with decreasing temperature.

Neutron powder diffraction recordings were done at the HFR at Petten using a Cu monochromator ($\lambda = 2.587$ Å) and collimators of 30′. Diagrams were recorded at 293

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± 1, 4.2 ± 0.1, and 2.1 ± 0.1 K. For the refinements, the profile program of Rietveld (7) was used. An absorption correction was not applied. The coherent scattering lengths used are: $b(\mathrm{Rb}) = 0.72$, $b(\mathrm{Cu}) = 0.79$, and $b(\mathrm{Cl}) = 0.96$, all in units of 10^{-12} cm. The positional parameters of $CsMgCl_3$ (1) with small deviations and γ-$RbCrCl_3$ were taken as starting values for β, resp., γ-$RbCuCl_3$.

Full matrix refinement of the positional and isotropic thermal parameters of all ions leads to convergence at

$$R(\text{profile}) = \left[\sum_i w(I_0 - I_c)^2 \Big/ \sum_i w I_0^2\right]^{1/2} = 0.086$$

and

$$R = \sum_j |I'_0 - I'_c| \Big/ \sum_j I'_0 = 0.047$$

for β-$RbCuCl_3$ at 293 K, where I_0 and I_c are the observed resp. calculated intensity of the ith measured point and I'_0 and I'_c the observed resp. calculated intensity of the jth reflection, w is a statistic weight factor. Similar refinements of the recordings at 4.2 K, but now with equal isotropic thermal parameters for ions for the same type, resulted in $R(\text{profile}) = 0.119$ and $R = 0.096$.

Structure Determinations

It is shown by the neutron powder diffraction diagrams (Fig. 1) that β- and γ-$RbCuCl_3$ are slightly distorted from the hexagonal perovskite (2L) structure ($CsMgCl_3$) with space group $P6_3/mmc$. At three different temperatures we have determined the crystal structure by neutron powder diffraction. The crystal structure determination of α-$RbCuCl_3$ was done with X-ray powder diffraction and no other crystallographic data than the unit cell parameters were determined because of the resemblance with α-$CsCrCl_3$ (7).

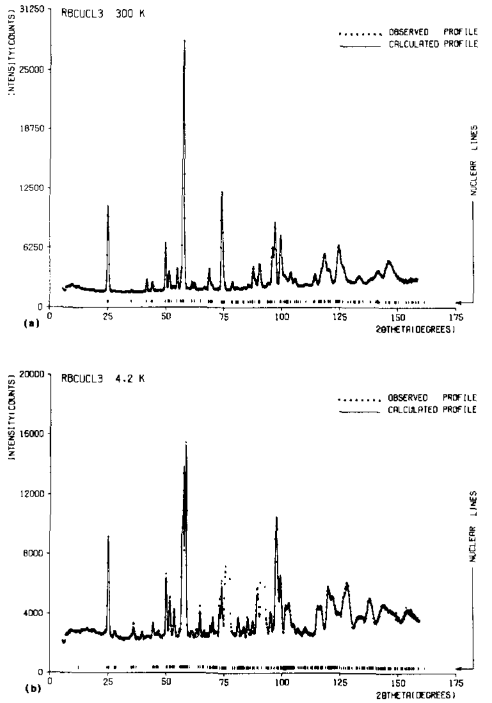

FIG. 1. Experimental and calculated profile intensities of β-$RbCuCl_3$ (a) and γ-$RbCuCl_3$ (b). The two observed reflections at $\theta = 75$ and 90° are from the cryostate.

α-$RbCuCl_3$. In the X-ray powder diffraction diagram (390 K), no indication of a distortion from a hexagonal space group could be found. Therefore it is very probably that α-$RbCuCl_3$ is isostructural to α-$CsCrCl_3$ (7), with space group $P6_3/mmc$ (D^4_{6h}). The hexagonal unit cell parameters are given in Table I.

β-$RbCuCl_3$. This phase is slightly orthorhombically distorted. The unit cell parameters are given in Table I. From systematic absences, $hk0$: $h + k = 2n + 1$, $0kl$: $l = 2n + 1$ and $h0l$: $l = 2n + 1$, the space group appeared to be $Pcan$ ($=Pbcn$) (D^{14}_{2h}). The positional and thermal parameters are given in Table II. The final calculated profile together with the experimental

TABLE I

UNIT CELL PARAMETERS OF $RbCuCl_3$ WITH STANDARD DEVIATIONS INDICATED INSIDE PARENTHESES

	α-$RbCuCl_3$ (~390 K) X-Ray diff.	β-$RbCuCl_3$ (293 K) Neutron diff.	γ-$RbCuCl_3$ (4.2 K) Neutron diff.
a, Å	6.978(2)	11.9286(7)	11.932(1)
b, Å		6.9705(4)	6.844(1)
c, Å	6.156(2)	6.1638(2)	12.244(1)
β			91.93(1)°
γ	120°		

data are given in Fig. 1a. This structure is isostructural to β-$CsCrI_3$ (3).

γ-$RbCuCl_3$. Oscillation photographs with X-rays show a doubling of the *c* axis with respect to the β-phase. From systematic absences *hkl*: $h + k = 2n + 1$ we expect γ-$RbCuCl_3$ to have the same space group as γ-$RbCrCl_3$ (*3*): *C*2. Although the resulting *R* indices are not as well converged as for β-$RbCuCl_3$, it gives the best fit with the experimental data (see Fig. 1b). The monoclinic unit cell parameters of the γ phase are given in Table I. The positional and thermal parameters are given in Table III. It should be remarked that the thermal parameters are calculated to be negative. This might be attributed to the extremely low temperature. Also, an absorption correction might improve these results.

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF β-$RbCuCl_3$[a] AT 295 K

		x	*y*	*z*	*b*
Rb	4*c*	0.3313(7)	0	$\frac{1}{4}$	2.6(2)
Cu	4*a*	0	0	0	1.1(1)
Cl(1)	8*d*	0.0831(7)	0.2427(6)	0.1972(4)	1.3(1)
Cl(2)	4*c*	0.1509(5)	0	$\frac{3}{4}$	2.6(2)

[a] Space group: *Pcan*, $Z = 4$.

Discussion

The parent structure, $CsMgCl_3$ (*1*), consists of chains of face-sharing $MgCl_6$ octahedra of which the symmetry is approximately O_h. Cu^{2+} in octahedral coordination exhibits an $E \otimes \epsilon$ Jahn–Teller effect, mostly manifested by an elongation of the octahedron leading to pseudo D_{4h} symmetry. Just like in the other examples ($CsCrCl_3$, $RbCrCl_3$, and $CsCuCl_3$) the local distortions of the octahedra have experimentally be found to be of pseudo D_{4h} symmetry. These local distortions can appear along one of the three principal axes of the octahedron (*x*, *y*, or *z*) (See (*4*) and Fig. 2c). The static configurations (β and γ) are defined by the way of "stacking" of these elongation possibilities (cooperative Jahn–Teller effect).

In the α phase the three possibilities are equally divided (orientational disorder (*8*)), contributing to an additional configurational entropy content of *Nk* ln 3 per mole (*2*), where *N* is the Avogadro number and *k* the Boltzmann constant. The average octahedron has pseudo O_h symmetry. In β-$RbCuCl_3$, only two directions of elongation are found: *x* and *y* (See Table IV and Fig. 2a). The sequence of elongation along the chain of face-sharing octahedra is *xyxyx yxy*, etc. As a consequence of the inter-

TABLE III

POSITIONAL AND THERMAL PARAMETERS OF γ-$RbCuCl_3$[a] AT 4.2 K

		x	*y*	*z*	*b*
Rb(*a*)	4*c*	0.342(3)	−0.029(7)	0.381(3)	−1.2(4)
Rb(*b*)	4*c*	0.324(3)	0.007(8)	0.868(3)	−1.2(4)
Cu(1*a*)	2*a*	0	0	0	−0.6(3)
Cu(1*b*)	2*b*	0	−0.051(5)	$\frac{1}{2}$	−0.6(3)
Cu(2)	4*c*	−0.001(4)	−0.016(7)	0.245(3)	−0.6(3)
Cl(1*a*)	4*c*	0.168(2)	−0.019(7)	0.158(2)	−0.4(1)
Cl(1*b*)	4*c*	0.157(2)	−0.060(8)	0.659(2)	−0.4(1)
Cl(2*a*)	4*c*	0.093(2)	0.158(7)	0.392(3)	−0.4(1)
Cl(2*b*)	4*c*	0.087(3)	0.254(8)	0.896(3)	−0.4(1)
Cl(3*a*)	4*c*	0.073(3)	−0.302(7)	0.394(3)	−0.4(1)
Cl(3*b*)	4*c*	0.068(2)	−0.241(7)	0.880(3)	−0.4(1)

[a] Space group: *C*2, $Z = 2$.

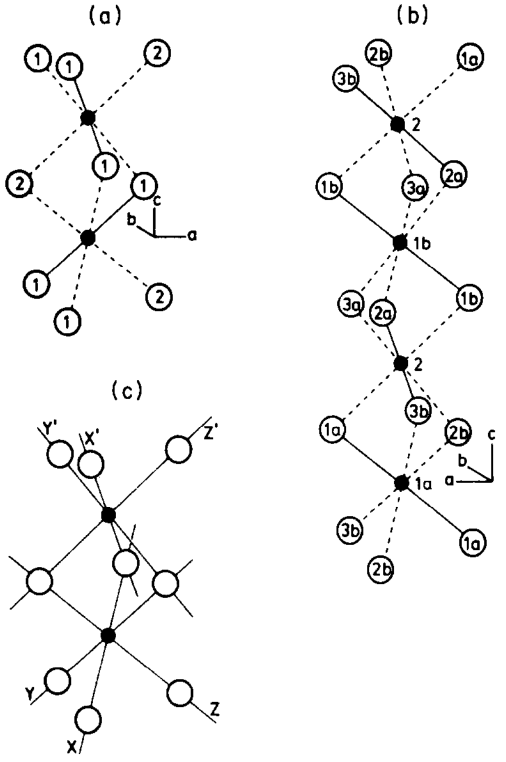

FIG. 2. (a) Relevant part of the unit cell of β-RbCuCl$_3$. (b) Relevant part of the unit cell of γ-RbCuCl$_3$. (c) Definition of the local octahedron axes x, y, and z.

TABLE IV

Cu-Cl DISTANCES IN β- AND γ-RbCuCl$_3$ (Å)

	β-RbCuCl$_3$		
Cu-Cl(1)	2.307(4)	(2x)	
Cu-Cl(1)	2.706(3)	(2x)	
Cu-Cl(2)	2.369(5)	(2x)	
Cu(1*a*)-Cl(1*a*)	2.74(3)	Cu(1*b*)-Cl(1*b*)	2.66(3)
Cu(1*a*)-Cl(2*b*)	2.41(4)	Cu(1*b*)-Cl(2*a*)	2.26(5)
Cu(1*a*)-Cl(3*b*)	2.37(5)	Cu(1*b*)-Cl(3*a*)	2.34(6)
Cu(2) -Cl(1*a*)	2.30(5)	Cu(2) -Cl(1*b*)	2.26(5)
Cu(2) -Cl(2*a*)	2.40(6)	Cu(2) -Cl(3*b*)	2.30(6)
Cu(2) -Cl(2*b*)	2.71(6)	Cu(2) -Cl(3*a*)	2.80(6)

TABLE V

MAGNITUDE OF DISTORTION ($q = 3^{1/2}(d_l - d_a)$) OF THE CuCl$_6$ OCTAHEDRA[a]

	γ phase	β phase
Cu(1*a*)	0.40(7)	0.42(2)
Cu(1*b*)	0.42(8)	
Cu(2)	0.51(10)	

[a] d_l: Longest Cu-Cl distance, d_a: average Cu-Cl distance of the considered octahedron.

chain stacking, the orthorhombic cell is not C-centered as in γ-RbCuCl$_3$, but primitive. The direction of elongation of the Cu ion at the center of gravity of the basal unit cell plane is not the same as that of the Cu ions on the corners of the unit cell (e.g., y instead of x elongation). The sequence of stacking ($xyxy$) is identical for every chain.

In the case of β-RbCrCl$_3$, the phase transition is ascribed to a coupling with the strain component e_{xz} (E_{1g} symmetry in D_{6h}) (*9*). On the same grounds, a coupling with the strain component $e_{xx} - e_{yy}$ might occur. This strain component also has the necessary symmetry (E_{2g} in D_{6h}) and can induce a local distortion of an octahedron with E_g symmetry in order to fulfill an $E \otimes \epsilon$ Jahn-Teller effect. This is probably what happens in the β-RbCuCl$_3$. Note therefore the contraction of the a axis with respect to the b axis ($a < b\ 3^{1/2}$), indicating an orthorhombical $e_{xx} - e_{yy}$ strain.

At temperatures below 262 K, also, elongated octahedra with approximately D_{4h} symmetry are existing. The elongation sequence on the contrary is different: $zxzyzx$, etc., which is identical to what has been found in γ-RbCrCl$_3$ (*4*) (See Table IV and Fig. 2b). Probably coupling of the E_g electronic levels of the Cu^{2+} with the strain component e_{xz} (E_{1g} symmetry in D_{6h}) is favored.

In Table V we have listed the magnitude of the Jahn-Teller distortions q as defined in (*4*); From these it appears that the magnitude of q does not change very much on going from β- to γ-RbCuCl$_3$.

The refinement of the diagram recorded at 2.1 K results in the same structure with no significant changes with respect to the one recorded at 4.2 K. Small indications are found for some magnetic contributions at 2.1 K, which are probably not present at 4.2 K.

Until now, four different structure types in the hexagonal perovskite (2*L*) structure have been found as a consequence of the cooperative Jahn–Teller effect. In the future we hope to investigate the relation between these structures and provide the description of these distortions.

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