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The Jahn–Teller Distorted Structure of Caesium Copper(II) Trichloride

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Abstract

α-$CsCuCl_3$, hexagonal, $P6_3/mmc$; at 430 K: $Z = 2$, $a = 7{\cdot}212\,(2)$, $c = 6{\cdot}141\,(1)$ Å, $V = 276{\cdot}57\,(16)$ Å^3; at 470 K: $a = 7{\cdot}229\,(2)$, $c = 6{\cdot}149\,(1)$ Å, $V = 278{\cdot}22\,(16)$ Å^3. Least-squares refinements of 1608 (1604 at 470 K) measured reflections resulted in R values of 2·1% (2·3%) for the high-temperature structure (α phase) having a slightly distorted $BaNiO_3$ structure. A model is introduced in which the Jahn–Teller effect is accounted for. The local Jahn–Teller distortion, that is elongation of the face-sharing octahedral coordination spheres in three possible ways, is disordered, resulting in a seemingly non-distorted octahedron with large anisotropic thermal motion of the Cl^- ions. The additional configurational entropy obtained by the disordering favours this structure, rather than a static cooperative Jahn–Teller distorted structure.

Introduction

A recent structure redetermination of $CsCrCl_3$ and $CsCrI_3$ (Crama & Zandbergen, 1981) shows that there is still an $E \otimes \varepsilon$ Jahn–Teller effect above the phase-transition temperature and the space group $P6_3mc$ is very probably not correct. Also, $CsCuCl_3$ (Kroese, Maaskant & Verschoor, 1974) has been reported to have a structure with space group $P6_3mc$ and slight deviations from the $BaNiO_3$ or $CsMgCl_3$ structure (McPherson, Kistenmacher & Stucky, 1970). In order to check the relation with $CsCrCl_3$ and $CsCrI_3$ we redetermined the crystal structure of $CsCuCl_3$ above its phase transition (α phase).

In $CsCrCl_3$ and $CsCrI_3$ it was seen that there are small displacements of the anions, mainly parallel to the c axis, as they are the low-temperature phases (Zandbergen & IJdo, 1980; Crama, Maaskant & Verschoor, 1978; Crama, Bakker, Verschoor & Maaskant, 1979). In $CsCuCl_3$ the displacements of the Cl^- ions in the β phase (below 423 K) are mainly perpendicular to the c axis (Schlueter, Jacobson & Rundle, 1966). Because of the possible relation of the β phase with a soft mode in the α phase (Hirotsu, 1975), it is interesting to investigate whether any features of the β phase are already present just above the phase transition. We therefore determined the crystal structure at two different temperatures (430 and 470 K).

The purpose of this is to separate the pseudo thermal motion caused by a disordered Jahn–Teller distortion (Crama & Zandbergen, 1981; Höck, Schröder & Thomas, 1978) from the other contributions to the pseudo thermal motion of the Cl^- ions. Our conclusion from the redeterminations on $CsCrCl_3$ and $CsCrI_3$ was that the anisotropic motion of the Cl^- ions in the former structure determinations (Guen, Marchand, Jouini & Verbaere, 1974; McPherson, Kistenmacher, Folkers & Stucky, 1972; Li & Stucky, 1973) is caused by the Jahn–Teller effect and, indeed, after accounting for this effect isotropic thermal motion of the anions remained. An identical situation, a disordered Jahn–Teller distorted structure, is to be expected for α-$CsCuCl_3$.

Experimental

Single crystals of $CsCuCl_3$ in the shape of hexagonal prisms were obtained from an HCl solution with equimolar quantities of $CuCl_2.4H_2O$ and CsCl. The crystal symmetry was determined from zero- and upper-level Weissenberg photographs. Systematically absent reflections ($hh\bar{2h}l$: $l = 2n + 1$) show the space group to be $P6_3/mmc$, $P\bar{6}2c$ or $P6_3mc$.

The crystals (0·10 × 0·12 × 0·25 and 0·20 × 0·20 × 0·40 mm) were mounted along the [001] direction on an Enraf–Nonius four-circle κ-geometry CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The lattice constants (Table 1) at various temperatures were determined using a least-squares refinement of the measured Bragg angles of 20 reflections. The calculated density at 430 (and 470 K) for $Z = 2$ and a molecular weight of 302·8 is 3·64 (3·61) Mg m^{-3}. Intensities were recorded by the ω-scan method for all reflections with θ between 4 and 30° using Mo $K\alpha$ radiation. The scan angle was $(1{\cdot}2 + 0{\cdot}8 \tan\theta)°$. In all, 1608 (1604) reflections were measured. Reflections with intensities less than twice

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Table 1. *Unit-cell parameters of* $CsCuCl_3$ *at different temperatures*

	400 K	430 K	470 K
a (Å)	7·235 (2)	7·212 (2)	7·229 (2)
b (Å)	18·242 (4)	6·141 (1)	6·149 (1)
V (Å^3)	827·29 (45)	276·57 (16)	278·22 (16)
Z	6	2	2

the standard deviation were considered not to be significant.

A correction for the absorption (carried out on an imaginary crystal form that corresponds to the measured transmission curves for the main reflections 002, 004 and 006) was made with a program developed by de Graaff (1973). Scattering factors and anomalous-dispersion terms for all ions were taken from *International Tables for X-ray Crystallography* (1974). After correction for Lorentz and polarization effects the intensities were reduced to F_o values. The function minimized during the least-squares refinement process was $w_F(F_o - F_c)^2$ using the weighting scheme $w_F = 1/\sigma_F^2$ (σ_F: standard deviation of F_o).*

In the refinements two models were used to try to describe the effect of the Jahn–Teller distortion; *viz* model *A*, derived theoretically and related to β-$CsCrI_3$: disorder over three Cl^- ion sites, space group $P6_3/mmc$; and model *B*, more related to β-$CsCrCl_3$: disorder over four Cl^- ion sites, space group $P6_3/mmc$. In addition, model *C*, which has already been used in the refinements of α-$CsCrCl_3$ by McPherson *et al.* (1972), was used: disorder over two Cl^- ion sites, space group $P6_3/mmc$. Finally, models *D* (ordered, space group $P6_3/mmc$) and *E* (ordered, space group $P6_3mc$) were refined for comparison of the results.

A description of the models follows. The basic structure ($CsMgCl_3$) consists of chains of face-sharing octahedra along the **c** direction. The Jahn–Teller effect of the Cu^{2+} ion causes a distortion of the regular $CuCl_6$ octahedra in such a way that an elongated octahedron with pseudo $4/mmm$ (D_{4h}) symmetry (one long and two short axes) is formed. Because of the sharing of the Cl^- ions between two adjacent (face-sharing) octahedra, the Cl^- ions are displaced by the Jahn–Teller effect of both octahedra involved. So, a Cl^- ion could be part of four different situations as shown in Fig. 1 wherein one of the three equivalent Cl^- ions between two Cu^{2+} ions along the **c** direction is depicted.

For crystallographic reasons and because no significant electron density at a position occupied by the Cl^- ion shown in Fig. 1(*d*) was found in a difference Fourier analysis, the configuration in which two long axes intersect on the same Cl^- ion is omitted. This leaves three possibilities of finding a Cl^- ion with equal probability ($\frac{1}{3}$), *i.e.* $x_2,\bar{x}_2,\frac{1}{4}$ and $x_1,\bar{x}_1,\frac{1}{4}\pm\delta$. When there is disorder as described by Höck *et al.* (1978), resulting in an additional entropy content, this leads to model *A* as described in Figs. 1(*e*) and 2(*a*). So far we are assuming that the Jahn–Teller effect induces only elongations, as is most probable (Crama & Zandbergen, 1981). Also, the possibility of a compression together with an elongation as was first found in β-$RbCrCl_3$ (Crama *et al.*, 1978) could be considered. If an elongated axis joins a compressed axis the Cl^- ion involved occupies the position $x_1,\bar{x}_1,\frac{1}{4}+\delta_1$, while the other two Cl^- ions occupy the position $x_2,\bar{x}_2,\frac{1}{4}-\delta_2$ ($\delta_2 < \delta_1$). If the elongated and the compressed octahedra are interchanged, the positions $x_1,\bar{x}_1,\frac{1}{4}-\delta_1$ and $x_2,\bar{x}_2,\frac{1}{4}+\delta_2$ are occupied. When there is configurational disorder this leads to model *B* as depicted in Fig. 2(*b*). In model *C* the Cl^- ions are only split in two parts with no physical meaning just to compare with the results of McPherson *et al.* (1972). Model *D* represents the $CsMgCl_3$ structure with one fixed Cl^- ion position at $x,\bar{x},\frac{1}{4}$ and model *E* represents the structure of $CsCrCl_3$ proposed by McPherson *et al.* (1972), which lacks a centre of inversion.

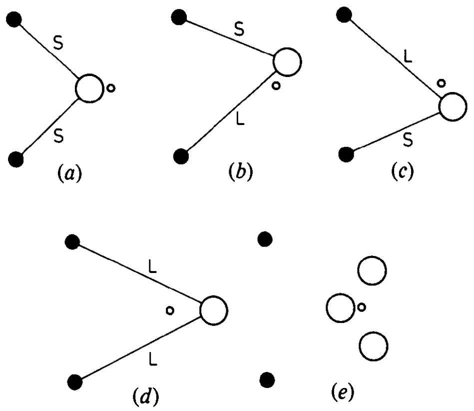

Fig. 1. Possible Cu–Cl–Cu configurations with long (L) and short (S) distances. One Cl^- ion (open circle) between two Cu^{2+} ions (black circles) along the face-sharing octahedra chains is shown. The small open circles represent the positions of the Cl^- ion when no Jahn–Teller effect is present.

The results of the full-matrix refinement of all parameters and extinction correction of the best-fitting models, *viz* models *A* and *B* in space group $P6_3/mmc$, are given in Table 3.* Refinements of models *A* and *B* in the other possible space groups give no significant lowering of the final discrepancy indices and are not

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* All crystallographic calculations were carried out on the Leiden University IBM 370/158 computer using a set of computer programs written or modified by E. W. M. Rutten-Keulemans and R. A. G. de Graaff of the X-ray and Electron Diffraction Section.

* Lists of structure factors and thermal parameters obtained at 430 and 470 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36178 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

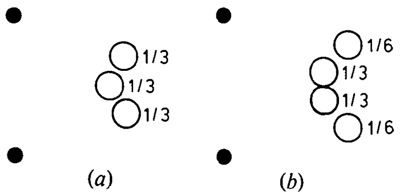

Fig. 2. Schematic picture of models (*a*) *A* and (*b*) *B* with the numbers representing the occupation numbers of the different Cl^- ion positions.

Table 2. *Discrepancy indices of* α-$CsCuCl_3$ *at* 430 K (*first row*) *and* 470 K (*second row*)

(*a*) The values found with isotropic thermal parameters for the Cl^- ion. (*b*) The values with anisotropic thermal parameters for the Cl^- ion.

Model	$R_w^{(a)}$	$R^{(a)}$	Number of parameters$^{(a)}$	$R_w^{(b)}$	$R^{(b)}$	Number of parameters$^{(b)}$
A	2·05	2·17	9	1·87	2·07	12
	2·30	1·90		2·21	1·84	
B	2·05	2·18	10	1·86	2·07	13
	2·28	1·88		2·19	1·82	
C	8·08	6·73	8	6·62	5·48	11
	9·89	7·22		7·51	5·56	
D	11·28	9·52	7	7·84	6·41	8
	13·87	9·96		9·89	6·73	
E	8·08	7·45	9	6·03	5·44	12
	10·33	8·17		6·58	5·61	

Table 3. *Positional parameters of* α-$CsCuCl_3$ *at* 430 K (*first row*) *and* 470 K (*second row*)

		x	y	z	b_{eq}*	Model
Cs	2(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	4·70 (3)	*A*, *B*
		$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	4·95 (1)	
Cr	2(*a*)	0	0	0	3·82 (4)	*A*, *B*
		0	0	0	3·92 (2)	
Cl(1)	12(*k*)	0·1603 (3)	−0·1603 (3)	0·2998 (4)	3·81 (4)	*A*
		0·1605 (1)	−0·1605 (1)	0·2986 (3)	3·96 (3)	
	12(*k*)	0·1603 (3)	−0·1603 (3)	0·2994 (9)	3·80 (5)	*B*
		0·1605 (1)	−0·1605 (1)	0·2979 (5)	3·95 (3)	
Cl(2)	6(*h*)	0·1407 (5)	−0·1407 (5)	$\frac{1}{4}$	3·81 (4)	*A*
		0·1398 (3)	−0·1398 (3)	$\frac{1}{4}$	3·96 (3)	
	12(*k*)	0·1406 (5)	−0·1406 (5)	0·2576 (64)	3·80 (5)	*B*
		0·1394 (3)	−0·1394 (3)	0·2594 (25)	3·95 (3)	

* $b_{eq} = (8\pi^2/3)$ trace $\tilde{U}$.

reported. After averaging the reflections hkl and $\bar{h}\bar{k}\bar{l}$, refinements of all parameters converged for $CsCuCl_3$ at 430 K to R_w = 2·05% and R = 2·17% (148 independent and 139 non-observed reflections) and for $CsCuCl_3$ at 470 K to R_w = 2·29% and R = 1·89% (208 independent and 78 non-observed reflections) in models *A* or *B*. The final discrepancy indices of the different model refinements are listed in Table 2. The positional parameters are in Table 3.

Discussion

The basic principle is to refine the structure in which the Cl^- ions are described with an isotropic thermal parameter, as was found in a non-Jahn–Teller distorted structure, such as $CsMgCl_3$ (McPherson *et al.*, 1970). To check the thermal behaviour of the Cl^- ions in β-$CsCuCl_3$ (with an ordered Jahn–Teller distortion) we also determined the structural parameters at 400 K. The positional parameters were found to be the same as those reported by Schlueter *et al.* with R_w = 2·42% and almost isotropic thermal motion of the Cl^- ions (Crama, 1980). For instance, a refinement in which the Cl^- ions were described as moving isotropically also resulted in a small R index: R_w = 3·42%. Therefore, it can be concluded that the static Jahn–Teller effect is not responsible for large anisotropic thermal motion of the Cl^- ions.

As was found for $CsCrCl_3$ and $CsCrI_3$, models *A* and *B* describe the crystal structure of α-$CsCuCl_3$ in the best way, as they have the lowest R indices and describe the real thermal motion of the Cl^- ions as approximately isotropic, just as has been found in β-$CsCuCl_3$. A difference Fourier analysis of the results shows no distinct peaks larger than the standard deviation.

In these kinds of models, the different Cl^- ion parts are split up over a distance of ~0·35 Å. These small distances mostly lead to high correlations between the thermal parameters and the z parameters of the Cl^- ion sites. Nevertheless, the only correlation in model *A* larger than 0·6 is between the x parameter of Cl(2) and the scaling factor (0·74).

No indication of the structural properties of the β phase can be found in the α phase. Also, no differences between the refinements at the temperatures 430 and 470 K can be found. We conclude that $CsCuCl_3$ also has a disordered Jahn–Teller distorted structure like $CsCrCl_3$ and $CsCrI_3$ and no softening of a mode with the **k** vector $0,0,2\pi/3c$ can be found.

Although from the X-ray refinements no definite choice can be made between models *A* and *B* from the R indices, it is clear that the Jahn–Teller contribution to the pseudo thermal motion of the Cl^- ions can be subtracted from the other contributions. From the positional parameters of model *B* it can be seen that this model approximates model *A*; therefore, the disorder of the local Jahn–Teller effect is most probably described by model *A*, *i.e.* disorder of elongated $CuCl_6$ octahedra with pseudo $4/mmm$ (D_{4h}) symmetry. This disorder of the elongation contributes to an additional configurational entropy (S) content. This entropy contribution is responsible for the disappearance of the static or ordered Jahn–Teller distorted structure of β-$CsCuCl_3$ when the temperature is high enough (423 K). The average picture of the disordered $CuCl_6$ octahedron described by model *A* is shown in Fig. 3. Now that we have found a disordered

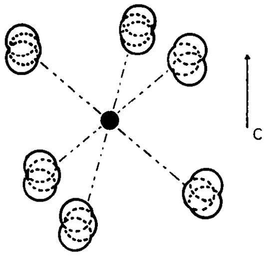

Fig. 3. The average picture of a $CuCl_6$ octahedron as described by model *A*. The *c* axis of the unit cell is indicated.

Jahn–Teller distorted structure in α-$CsCrCl_3$, α-$CsCrI_3$ and α-$CsCuCl_3$, we can also generalize that the high-temperature structures of $RbCuCl_3$, $CsCrBr_3$, *etc.*, are isostructural.

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The Structure of Dimercury(I) Aluminium(III) Fluoride Dihydrate

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Abstract

Single crystals of $Hg_2AlF_5.2H_2O$ are tetragonal with $a = 9{\cdot}353\ (5)$, $c = 7{\cdot}241\ (6)$ Å, *I4cm*, $Z = 4$, $D_c = 5{\cdot}86$ Mg m^{-3}. The final $R = 0{\cdot}0365$ ($R_w = 0{\cdot}0391$) for 383 independent reflections. The network of *trans* chains of AlF_6 octahedra parallel to the *c* axis is closely related to similar arrangements found in $Cs_2MnF_5.H_2O$ and several $M^I_2AlF_5.H_2O$ compounds. Between the chains, the structure contains the quasi-linear $[H_2O-Hg-Hg-OH_2]^{2+}$ cation, with an Hg–Hg distance of 2·511 (1) Å and equivalent Hg–O distances of 2·144 (9) Å. Cooperative hydrogen bonding is discussed.

Introduction

Only very few crystal structures of fluorinated compounds containing Hg^I are known: Hg_2F_2 (Grdenić & Djordjević, 1956), $Hg_2SiF_6.2H_2O$ (Dorm, 1971). The present work on $Hg_2AlF_5.2H_2O$ forms part of a research programme on inorganic fluorinated compounds containing monovalent mercury.

Preparation

Single crystals were prepared in HF (5 *M*) solutions at 423 K under 15 MPa from Hg_2F_2 and AlF_3 in

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