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Orientalional disorder in the high temperature phase of KClO_4

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Résumé. — Un monocristal de la phase à haute température de KClO_4 a été étudié par diffraction de neutrons, à 325 °C et 420 °C. L'analyse du facteur de structure des réflexions de Bragg conduit à la fonction statique de densité de probabilité d'orientation. La position des maximums de cette fonction montre que les ions ClO_4^- ont des orientations privilégiées de symétrie T_d , avec deux positions possibles. Ce résultat est comparé avec ceux d'articles antérieurs. On suggère aussi que les ions pourraient effectuer des rotations non instantanées autour des axes quaternaires du cube.

Abstract. — Neutron diffraction experiments have been performed on a single crystal of the high-temperature phase of KClO_4 at 325 °C and 420 °C. The analysis of the structure factor of Bragg reflections leads to the static orientational probability density function. The positions of the maxima of this function show that ClO_4^- ions have preferred orientations of T_d symmetry, with two possible positions. Comparison is made of this result with previous papers. It is also suggested that the ions could reorient between the two potential wells mainly by non-instantaneous rotations around the four-fold axes of the cube.

1. Introduction.

It has been known for many years that potassium perchlorate, KClO_4 , exhibits a transition between two crystallographic phases. Below $T_{tr} = 310$ °C, the structure is orthorhombic [1] (D_{2h}^{16} -Pnma) and is face-centered cubic [2] (O_h^5 -Fm3m) above T_{tr} . The transition has all the characteristics of a first-order transition between an ordered and an orientationally disordered phases : strong hysteresis, important volume change (11 %) of the unit cell at the transition. In the cubic phase, the ClO_4^- ions are disordered (a situation usually referred to as ODIC : orientational disorder in crystals), and reorient dynamically between several orientations.

One possible approach to study this kind of disorder is to determine the static orientational probability density function $P_0(\Omega)$ [3]. This function

represents the probability for an ion to be in a given orientation with respect to the symmetry elements of the crystal, and thus gives the symmetries and the number of the potential wells between which the ions can reorient. Its maxima usually correspond to orientations such that the ion and the crystal have two or more symmetry elements in common. For a tetrahedron in a cube, there are four such possible point groups [4] : T_d with 2 different orientations, D_{2d} with 6 orientations, C_{3v} with 8 orientations, C_{2v} with 12 orientations.

In 1983, two papers gave different results concerning the most probable orientation of the ClO_4^- ions in the disordered phase : Toupry *et al.* [5] concluded, from Raman scattering experiments, that $P_0(\Omega)$ should have maxima corresponding to orientations C_{3v} . Klein *et al.* [6] obtained, from a molecular dynamics simulation, T_d orientations in agreement with Pistorius' assumption [2]. This contradiction lead us to measure $P_0(\Omega)$ by the most direct method, that is through a neutron diffraction experiment, because the structure factor of Bragg reflections contains directly $P_0(\Omega)$, as we will see in section 3.

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2. Experiment.

The structure of the high-temperature phase of KClO_4 has been determined from experiments performed on the four-circles diffractometer 5C2 on the hot source of the Orphée reactor at Léon Brillouin Laboratory ⁽¹⁾ (CEN-Saclay). The wavelength of the incident neutron beam is 0.832 Å. Two crystals have been used. They were grown by the silica gel technique and have been provided by Venkateswara Rao [7]. They were of excellent optical quality and showed, during the experiment, very small mosaicity in the room temperature phase.

The first crystal was heated very slowly (0.5 °C per minute). During heating, two Bragg reflections of the orthorhombic phase have been recorded repeatedly. These two reflections had been chosen in the following way : Toupry *et al.* had proposed a relationship between the structures of the two phases, namely a_{orth} and b_{orth} are parallel to the diagonals of a face of the cube and such that $a_{\text{orth}} \approx a\sqrt{2}$ (a = parameter of the cubic cell) and $b_{\text{orth}} \approx a/\sqrt{2}$, c_{orth} being parallel to an edge of the cube with $c_{\text{orth}} \approx a$. If their hypothesis had been correct, one of the two reflections chosen, $(040)_{\text{orth}}$ should have remained in the cubic phase, becoming $(440)_{\text{cub}}$, while the other $(333)_{\text{orth}}$ should have disappeared at the transition. It happened that the result did not correspond to their hypothesis : the $(333)_{\text{orth}}$ reflection disappeared and a Bragg reflection was detected very close to the original position of $(040)_{\text{orth}}$. But this reflection was found to be, not a (440) , but a (333) reflection of the cubic phase. We also checked that the crystal was no more a single crystal and was made of at least two crystals.

The second crystal was heated much faster (10 °C per minute). Again two reflections $(040)_{\text{orth}}$ and $(333)_{\text{orth}}$ were followed during heating and both disappeared at the transition temperature. In the cubic phase, the crystal broke into four crystals, one of them much larger than the others. None of these four crystals had an orientation which could be deduced from the scheme proposed by Toupry *et al.*, and these orientations were also different from those found in the first crystal. In neither case, a simple relation could be found between the orientations of the crystals.

This means that the transition occurs with a complete reconstruction of the structure in an unpredictable way with respect to the low-temperature structure. Such effect is usual when there is no possible group theory relationship between the two phases i.e. when one structure cannot be considered as a subgroup of the other, or when the two structures are not subgroups of a real or hypothetical mother structure. This is the case, for instance, in

the reconstructive transition from the f.c.c. to the b.c.c. structure. On the contrary, in the present case, Pnma is a subgroup of Fm3m. We are here in the less usual case where the strong first order character of the transition impedes, when passing from the less symmetric to the more symmetric phase, any relationship between the two structures. It may be possible to relate the reconstructive nature of the transition and the increase of the transition temperature when the rate of heating decreases : this temperature was, indeed, 320 °C for heating at 10 °C per minute and 390 °C for heating at 0.5 °C per minute.

We made a refined structure analysis, using the largest of the four crystals, and recorded Bragg reflections at 325 °C and 420 °C. As always in ODIC crystals, very few reflections have been recorded (32 independent reflexions) due to the fast decrease of intensity when the wave vector increases.

3. Structure of the high-temperature phase : first model.

We first checked that the structure of KClO_4 in the high temperature phase was indeed face-centered cubic. The cell parameter was found to be $a = 7.522 \pm 0.002$ Å at 325 °C and increased up to $a = 7.58 \pm 0.01$ Å at 420 °C.

The mean positions of the K and of the Cl atoms are fixed by symmetry and will not be refined. The ClO_4^- tetrahedron is supposed to be regular so that the knowledge of the mean position of one oxygen atom or of the direction and the length of one Cl-O bond is sufficient to determine the structure. The now well known method of Press and Hüller [3] was used to calculate the structure factor $F(\mathbf{Q})$ of the Bragg reflections, which includes the static orientational probability density function $P_0(\Omega)$; Ω represents the Euler angles associated with the rotation which brings the crystal axes in coincidence with the molecular axes. $P_0(\Omega)$ can be expanded on the basis of functions $R_{\lambda\lambda'}^l(\Omega)$ (cubic rotators) adapted to the symmetries of the ion and of the crystalline site :

$$P_0(\Omega) = \frac{1}{8\pi^2} \sum_{l,\lambda,\lambda'} (2l+1) A_{\lambda\lambda'}^l R_{\lambda\lambda'}^l(\Omega). \quad (1)$$

The structure factor is a sum of two terms : one for K^+ ions including the Debye-Waller factor $\exp(-W_{\text{K}^+}(\mathbf{Q}))$, the other is the product of the Debye-Waller factor for ClO_4^- ions, $\exp(-W_{\text{ClO}_4^-}(\mathbf{Q}))$, of a phase term due to the choice of origin on K^+ , and of a rotational term $F_{\text{rot}}(\mathbf{Q})$:

$$F(\mathbf{Q}) = f_{\text{K}^+} \exp\left(-\frac{1}{2} Q^2 \langle u_x^2 \rangle_{\text{K}^+}\right) + \exp(i\mathbf{R}_{\text{Cl}} \cdot \mathbf{Q}) \times \exp\left(-\frac{1}{2} Q^2 \langle u_x^2 \rangle_{\text{ClO}_4^-}\right) \cdot F_{\text{rot}}(\mathbf{Q}). \quad (2)$$

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In this formula

- $\mathbf{Q}$ is the scattering vector ;
 f_n is the scattering cross-section of the atom n ;
 $\langle u^2 \rangle$ is the isotropic mean displacement of an ion
 $= 3 \langle u_x^2 \rangle$;
 $\mathbf{R}_{\text{Cl}}$ is the position of the Cl atom if the origin is
 taken on K^+ .

From [3],

$$F_{\text{rot}}(\mathbf{Q}) = f_{\text{Cl}} + 4 f_0 \left[4 \pi \sum_{l, \lambda} c_{\lambda}^l J_l(Q\rho) K_{\lambda}^{l*}(\mathbf{Q}) \right] \quad (3)$$

where

- $J_l(Q\rho)$ is the spherical Bessel function of order l
 ρ is the Cl-O distance
 K_{λ}^l is a cubic harmonics
 c_{λ}^l is the orientational probability density of
 the oxygen atoms in the reference frame of
 the crystal. It can be expanded, with the
 help of equation (1), as :

$$c_{\lambda}^l = \sum_{\lambda'} A_{\lambda\lambda'}^l b_{\lambda'}^l \quad (4)$$

where $b_{\lambda'}^l$ is the orientational probability density of
 the oxygen atoms in the molecular reference frame :

$$b_{\lambda'}^l = K_{\lambda'}^l(\theta_0, \phi_0) \quad (5)$$

where θ_0, ϕ_0 are the spherical angles defining the
 direction of one oxygen atom in the molecular
 frame.

Finally,

$$F_{\text{rot}}(\mathbf{Q}) = f_{\text{Cl}} + 4 f_0 \times \left[4 \pi \sum_{l, \lambda, \lambda'} A_{\lambda\lambda'}^l b_{\lambda'}^l J_l(Q\rho) K_{\lambda}^{l*}(\mathbf{Q}) \right] \quad (6)$$

Using these formulas, the structure factor is easily
 calculated : $K_{\lambda}^l(\mathbf{Q})$, $J_l(Q\rho)$ and $b_{\lambda'}^l$ are either tabu-

lated [8, 9] or calculated from the structure of the
 ion. $A_{\lambda\lambda'}^l$ and $\langle u_x^2 \rangle$ are adjusted as parameters so
 that $|F(\mathbf{Q})_{\text{calc}}| = \sqrt{F^2(\mathbf{Q})_{\text{obs}}}$. Then the knowledge
 of the maxima of $P_0(\Omega)$ is straightforward.

The distance Cl-O was first refined and was found
 to vary between 1.47 Å and 1.51 Å depending on the
 total number of parameters. It was then fixed at
 1.5 Å, an average value compatible with the esti-
 mated standard deviations obtained in the first set of
 refinements. The last least-squares fit was performed
 with 9 parameters (a normalization factor, $4 A_{\lambda\lambda'}^l$,
 $2 \langle u^2 \rangle$, and 3 correlation factors defined at the end
 of this paragraph), which is the number of par-
 ameters used in the second model (see paragraph
 (5)). Table I gives the result at 325 °C, with a
 reliability factor $R_w = 4.6\%$ ($R = 8.7\%$).

Because of the invariance of $P_0(\Omega)$ with respect
 to the symmetry operations of the site group and of
 the molecular group [10], only a few $A_{\lambda\lambda'}^l$ are not
 equal to zero. In the case of ClO_4^- ions (symmetry
 T_d in site O_h), the first non zero coefficients are :
 $A_{11}^4, A_{11}^6, A_{11}^8, A_{11}^{10}$ and so on. A_{11}^0 is taken to be equal
 to 1 (normalization condition).

4. Discussion of the first model.

Table II gives the values of the coefficients fitted in
 the calculation of the structure factor of KClO_4 at
 325 °C and 420 °C. They are all positive or nearly
 equal to zero. This is a strong indication that the
 ClO_4^- ions have preferred orientations with T_d
 symmetry, with two possible positions, because
 when the coefficients are calculated for a $P_0(\Omega)$
 corresponding to one of the ideal positions recalled
 in the introduction, they are found to be [11] all
 positive (and equal to 1) only for T_d orientations.

The values obtained for the non zero coefficients
 are, nevertheless, smaller than they would be in the
 ideal T_d case, which means that the disorder is more

Table I. — Comparison between the structure factors : F_{obs} : observed ; σ_{obs} : standard deviations ;
 $P_0(\Omega)$: calculated from the first model ; 32f : calculated from the second model.

hkl	F_{obs}	σ_{obs}	$[P_0(\Omega)]$	[32f]	hkl	F_{obs}	σ_{obs}	$[P_0(\Omega)]$	[32f]	hkl	F_{obs}	σ_{obs}	$[P_0(\Omega)]$	[32f]
111	13.32	0.45	13.47	13.45	440	5.97	0.15	6.13	5.99	642	2.26	0.13	1.83	2.26
200	14.73	0.50	14.77	14.78	531	3.22	0.13	3.01	3.17	553	0.92	0.12	0.68	1.09
220	9.12	0.22	8.54	8.94	600	4.11	0.14	4.17	4.00	731	1.31	0.12	0.90	1.40
311	0	0.09	0.47	0.73	442	5.29	0.15	5.13	5.17	800	2.45	0.13	2.2	2.38
222	7.58	0.18	7.51	7.67	620	3.94	0.14	3.93	4.09	733	0	0.15	0.35	0.83
400	0.80	0.21	1.20	0.91	533	2.37	0.12	1.99	2.37	644	1.53	0.14	0.97	1.28
331	2.95	0.08	3.26	3.03	622	3.55	0.14	3.23	3.57	820	1.57	0.14	1.48	1.79
420	4.29	0.09	4.64	4.29	444	2.74	0.14	2.66	2.97	822	1.35	0.12	1.03	1.39
422	5.72	0.11	6.05	5.72	711	2.30	0.11	1.98	2.26	660	1.42	0.12	1.08	1.33
511	0.81	0.08	1.28	1.14	551	2.08	0.11	1.68	2.11	751	0	0.15	0.41	0.73
333	4.15	0.09	4.28	4.11	640	2.82	0.11	2.59	3.01	R_w	=		4.6 %	2.3 %

Table II. — *Parameters of the first model.*

T	A_{11}^4	A_{11}^6	A_{11}^8	A_{11}^{10}	$(\text{\AA}^2)\langle u_x^2 \rangle_{K^+}$	$(\text{\AA}^2)\langle u_x^2 \rangle_{ClO_4^-}$
325 °C	0.44 ± 0.03	0.07 ± 0.02	0.45 ± 0.17		0.101 ± 0.006	0.093 ± 0.002
	0.44 ± 0.03	0.07 ± 0.02	0.43 ± 0.17	0.10 ± 0.18	0.101 ± 0.006	0.093 ± 0.002
420 °C	0.41 ± 0.03	0.05 ± 0.02	0.35 ± 0.19		0.119 ± 0.007	0.110 ± 0.003
	0.41 ± 0.03	0.05 ± 0.03	0.36 ± 0.20	-0.04 ± 0.24	0.119 ± 0.007	0.110 ± 0.003

complex : even if these orientations are preferred, an important fraction of the ions have, at a given time, different orientations.

Another way to check this result is to plot the stereographic projection of the Cl-O bond orientational probability, or more precisely, to compare this stereographic projection with that obtained for the ideal T_d case. As pointed out in [11], this is meaningful only as long as the expansion of the orientational probability density function of the ideal case is truncated at the same $l = 10$ value as in the $KClO_4$ case. Figure 1 is drawn, in such a way, for the ideal T_d case, and figure 2 for $KClO_4$ at 325 °C. In both figures, a strong maximum is found in the (111) direction and this confirms a preferred orientation with T_d symmetry. The main difference between figures 1 and 2 is that, in the (110) directions, $P_0(\Omega)$ is not zero in $KClO_4$; the fact that, at a given time, ClO_4^- ions can be found out of the potential wells indicates either that the disorder is dynamic and that the reorientations of the ions are not instantaneous, or that secondary potential wells exist in orientations of D_{2d} symmetry.

One way to check the second possibility is to examine $P_0(\Omega)$ as a function of φ , which is one of the three Euler angles (φ, θ, ψ) (with the usual

Fig. 2. — Stereographic projection of $KClO_4$ at 325 °C, in arbitrary intensity units.

definition [12]) which characterize the molecular orientation Ω . With $\theta = \psi = 0^\circ$, $P_0(\Omega)$ should have a maximum for $\varphi = 45^\circ$ (corresponding to D_{2d} orientation) in addition to the two maxima for $\varphi = 0^\circ$ and $\varphi = 90^\circ$ corresponding to the T_d orientations. Figure 3 shows $P_0(\Omega)$ versus φ for both

Fig. 1. — Stereographic projection of T_d , in arbitrary intensity units. Fig. 3. — Rotation of $P(\Omega)$ obtained from the first model around (100) axis of the crystal : (—) ideal T_d case ; (---) $KClO_4$ at 325 °C ; (.....) $KClO_4$ at 420 °C ; straight line = isotropy ; (■) $P(\Omega)$ obtained through the libration angles given by the second model at 325 °C ; (*) *idem* at 420 °C.

temperatures. The secondary maximum seen at 45° is not significant : it is an oscillation caused by the truncation, the curves for KClO₄ being below the curve drawn for the ideal T_d case, truncated, as above, for $l = 10$. Indeed, the expansion of the orientational probability density function is similar in this respect to a Fourier series expansion, well known artefact of which are periodic spurious maxima caused by truncation [11]. The figure shows that ions are present in every position intermediary between the two potential wells of T_d symmetry. The existence of an important orientational disorder, superimposed over the T_d orientation, is thus confirmed.

In order to check if a model of uniaxial reorientations around a four-fold axis common to the crystal and to the molecule could explain our results, we have calculated theoretical coefficients corresponding to a uniform distribution of molecules around this four-fold axis. Their values are $A_{11}^4 = 0.583$, $A_{11}^6 = 0.125$, $A_{11}^8 = 0.516$ and $A_{11}^{10} = 0.17$, as compared with $A_{11}^4 = 0.44$, $A_{11}^6 = 0.07$, $A_{11}^8 = 0.43$ and $A_{11}^{10} = 0.10$, found in KClO₄. The values are of the same order of magnitude and provide another indication that uniaxial reorientations of ClO₄⁻ ions can exist in this crystal.

At 420 °C, all results are similar, except that the maxima of $P_0(\Omega)$ along the (111) directions is less intense than at 325 °C and that the curve of figure 3 comes closer to the straight line corresponding to isotropy : when the temperature increases, disorder increases also and less and less ions are in their equilibrium positions at a given time.

Among the coefficients fitted, are the $\langle u_x^2 \rangle$ coefficients included in the Debye-Waller factor, corresponding to translation of K⁺ and of ClO₄⁻. At 325 °C, they are found to be : $\langle u_x^2 \rangle_{K^+} = 0.10 \text{ Å}^2$ and $\langle u_x^2 \rangle_{ClO_4^-} = 0.09 \text{ Å}^2$. At 420 °C, they are : $\langle u_x^2 \rangle_{K^+} = 0.12 \text{ Å}^2$ and $\langle u_x^2 \rangle_{ClO_4^-} = 0.11 \text{ Å}^2$. The values of $\langle u_x^2 \rangle_{ClO_4^-}$ can be compared to the Debye-Waller factor calculated from a Debye model :

$$\langle u_x^2 \rangle_{\text{Debye}} = \frac{1}{4\pi} \sqrt{\frac{3}{\pi}} \frac{a^2}{MV^2} RT \quad (7)$$

in which :

$$R = 8.32 \text{ J K}^{-1} \text{ mole}^{-1}$$

a is the cell parameter at temperature T

M is the molar mass of ClO₄⁻ ion

V is an average sound velocity, taken here to be about 3 300 m/s, which is the value found a few degrees above the transition, in the cubic phase of KCN [13], another orientationally disordered crystal.

$\langle u_x^2 \rangle_{\text{Debye}}$ is found equal to 0.020 Å^2 at $T =$

325 °C , and 0.024 Å^2 at $T = 420 \text{ °C}$. So, $\langle u_x^2 \rangle_{ClO_4^-}$ is approximately five times larger than $\langle u_x^2 \rangle_{\text{Debye}}$ and increases faster with temperature.

It is thus clear that a simple harmonic translational phonon contribution cannot explain these results. As usual in orientationally disordered crystals, the steric hindrance leads to an important coupling between the orientations of an ion and the positions of its neighbours, which masks completely the temperature dependent translation phonon contribution to the Debye-Waller factor.

On the other hand, one can also, following Press, Grimm and Hüller [14], look for the correlations between the translation and the orientation of the same ClO₄⁻ ion. This effect is induced by the neighbouring K⁺ ions, and can be expected to be much smaller than the previous one. Three coefficients of correlation, corresponding to the linear coupling between orientations and translations, were included into the fit ; they correspond to terms with $l = 3$ and $l = 7$. They were found to be equal to zero within the limit of accuracy, with no changes in the Debye-Waller factors for both temperatures.

5. Structure of the high-temperature phase : second model and discussion.

One of the assumption of the previous model is the rigidity of the reorienting ion. This is certainly a crude approximation in the case of ClO₄⁻ ions, and a contribution to the structure factor, due to anharmonicity, may be not negligible. If this is the case, one can hope to obtain a better refinement by calculating the structure factor in the way commonly used in crystallographers' atomic model and by introducing explicitly anharmonic coefficients in the development of the temperature factor of the atoms.

Then, the structure factor is equal to :

$$F(\mathbf{Q}) = \sum_{n=1}^6 f_n T_n(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{R}_n) \quad (8)$$

where the notations are the same as in (6) ; n is the number of atoms in the unit cell and $T_n(\mathbf{Q})$ is the temperature factor of atom n , and is the Fourier transform of the probability density function representing the time averaged displacement $\mathbf{u}_n$ of atom n from its equilibrium position. To a first approximation, this probability density function is a Gaussian function, but anharmonicity causes a deviation from the Gaussian shape. The general expression for a harmonic crystal is :

$$T_n(\mathbf{Q}) = \exp \left(-\frac{1}{2} \langle \mathbf{Q} \cdot \mathbf{u}_n^2 \rangle \right) .$$

By putting $\mathbf{Q} = 2\pi\mathbf{H}$

$$\mathbf{R}_n = \sum_i x_n^i \mathbf{a}_i \quad (\mathbf{a}_i \text{ is the unit cell edge})$$

and expanding $T_n(\mathbf{Q})$ up to the third order, the structure factor becomes :

$$F(\mathbf{H}) = \sum_{n=1}^6 f_n \exp \sum_{rs} (2 \pi i x_n^2 h_r - \beta_n^{rs} h_r h_s) \times \left(1 - \frac{4 \pi^3}{3} i \sum_{rst} c_n^{rst} h_r h_s h_t \right)$$

where

- h_r, h_s, h_t represent the Miller indices hkl ;
 β^{rs} are the anisotropic temperature factor coefficients ;
 c^{rst} are the anharmonic temperature factor coefficients ;
 β^{rs}, c^{rst} are invariant to pair wise interchange of the indices. So in the general case, there are six β^{rs} terms and ten c^{rst} terms for each atom n .

In the particular case of KClO_4 , the calculation was performed with the Prometheus program [15], starting from a few assumptions derived from the results of the first model : the crystal is face-centered cubic Fm3m (cell parameter = 7.522 Å), and the ClO_4^- ions have two preferred orientations corresponding to T_d symmetry. So, the positions of potassium and chlorine atoms are (000) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$, without any refinement ; the oxygen atoms are (xxx) and symmetry corresponding positions (model 32f [16]), with an occupation factor of 0.5 ; the distance Cl-O is thus indirectly fitted. As for the temperature parameters, because of the high symmetry of the crystal, the only non zero coefficients are one β_{K} coefficient for K^+ , $\beta_{\text{O}}^{\text{r}}$, $\beta_{\text{O}}^{\text{s}}$, $c_{\text{O}}^{\text{rrr}}$, $c_{\text{O}}^{\text{rrs}}$ and $c_{\text{O}}^{\text{rst}}$ for oxygen, and an isotropic factor for Cl [17] : $B = 8 \pi^2 \langle u^2 \rangle$.

In a first step, x , B_{Cl} , $\beta_{\text{K}}^{\text{r}}$, $\beta_{\text{O}}^{\text{r}}$, $\beta_{\text{O}}^{\text{s}}$, plus a normalization coefficient were fitted. This leads to six adjustable parameters, the values of which are given in table III, and the structure factor was obtained with a reliability factor R_w equal to 5.9 %.

The next step has been to introduce anharmonic coefficients for oxygen atoms, namely c^{rrr} , c^{rrs} and

c^{rst} . The weighted reliability factor decreased down to 2.3 %. The values of the parameters are given in the third and fifth rows of table III. They are significant but not easy to interpret except by a deformation of the thermal ellipsoid. The structure factors obtained for $T = 325^\circ\text{C}$, after fitting of the 9 parameters defined above, are listed in table I ; most of them are in better agreement with the observed F_{obs} than the structure factors derived from the first model with the same number of parameters (which is expected since the reliability factor is smaller) but no decisive conclusion can be drawn from this comparison, except that T_d orientation is confirmed.

Mean-square displacements can be calculated from the B and β 's coefficients. Their values are found to be (for 325°C) : $\langle u^2 \rangle_{\text{K}^+} = 0.103 \text{ Å}^2$ (as compared to 0.101 Å^2 in the first model), $\langle u^2 \rangle_{\text{Cl}} = 0.079 \text{ Å}^2$, $\langle u_{\parallel}^2 \rangle_0 = 0.118 \text{ Å}^2$ and $\langle u_{\perp}^2 \rangle_0 = 0.272 \text{ Å}^2$. ($\parallel$ and $\perp$ indexes refer to the Cl-O bond). At 420°C , $\langle u^2 \rangle_{\text{K}^+} = 0.116 \text{ Å}^2$ (0.119 Å^2), $\langle u^2 \rangle_{\text{Cl}} = 0.089 \text{ Å}^2$, $\langle u_{\parallel}^2 \rangle_0 = 0.134 \text{ Å}^2$ and $\langle u_{\perp}^2 \rangle_0 = 0.309 \text{ Å}^2$. From $\langle u_{\perp}^2 \rangle_0$, the librational angle is found to be $\approx 20^\circ$ at 325°C and $\sim 22^\circ$ at 420°C . These very high values are an indication that the disorder is not purely static and that the ClO_4^- ions have a strong tendency to reorient between their preferred mean positions. They are also larger than the resolution of the cubic rotator of order 10 used in the first model ($\sim 18^\circ$). To calculate the three coefficients of order 12 in the development of $P_0(\Omega)$, if it were reasonable, would probably not add more details to the results.

We have checked (Fig. 3) that if we assume as in the Prometheus program that $P(\Omega)$ is Gaussian, centered on the T_d orientations with halfwidths 20° and 22° , the resulting profiles agree very well with the o.p.d.f. expansion model in regions not too far from the equilibrium orientations. This confirms that both descriptions are consistent in those regions. The disagreement is large far from the equilibrium

Table III. — Parameters of the second model.

B_{Cl}	$\beta_{\text{K}}^{\text{r}}$	$\beta_{\text{O}}^{\text{r}}$	$\beta_{\text{O}}^{\text{s}}$	$c_{\text{O}}^{\text{rrr}} (\times 10^3)$	$c_{\text{O}}^{\text{rrs}} (\times 10^3)$	$c_{\text{O}}^{\text{rst}} (\times 10^3)$	$d(\text{Cl-O}) (\text{Å})$	T
5.858 ± 0.356	0.037 ± 0.003	0.074 ± 0.004	- 0.018 ± 0.002				1.316 ± 0.026	325 °C
6.202 ± 0.152	0.036 ± 0.001	0.077 ± 0.003	- 0.018 ± 0.001	-0.179 ± 0.033	0.033 ± 0.004	- 0.027 ± 0.006	1.264 ± 0.026	
7.019 ± 0.393	0.048 ± 0.004	0.075 ± 0.004	- 0.015 ± 0.001				1.326 ± 0.026	420 °C
7.051 ± 0.129	0.040 ± 0.001	0.087 ± 0.005	- 0.020 ± 0.001	- 0.204 ± 0.057	0.027 ± 0.005	- 0.023 ± 0.008	1.221 ± 0.026	

orientations because of the principle of Prometheus program and of the truncation of $P(\Omega)$ in the first model.

The distance Cl-O calculated in this second model is very short ($\sim 1.32 \text{ \AA}$) and unrealistic, as compared to $\sim 1.5 \text{ \AA}$ found previously and to the distances found in the low temperature orthorhombic phase, which vary from $1.4 \text{ \AA}$ to $1.44 \text{ \AA}$ (the ClO_4^- tetrahedron is slightly distorted in this phase). To find too short a distance is usual in this kind of model [17], and is due to the deformation of the thermal vibrational ellipsoid by anharmonicity. Moreover, because of the high values of $\langle u^2 \rangle_{\text{Cl}}$ and $\langle u^2 \rangle_{\text{O}}$, the mean instantaneous distance can vary considerably.

6. Conclusion and final remarks.

This experiment confirms the result obtained by Klein *et al.* by molecular dynamics simulation, concluding that ClO_4^- ions have preferred orientation of T_d symmetry in the high temperature phase of KClO_4 . These authors calculated values for the coefficients of order 4 and 6 of the symmetry adapted functions; once transformed into coefficients of the cubic rotators, those are: $A_{11}^4 = 0.366$, but $A_{11}^6 = 0.203$ which is much higher than our very small A_{11}^6 . This difference may come from the potential they used. The disorder is higher than that predicted by their force model, even at a few degrees above the transition temperature.

As for the experiment of Toupry *et al.*, our discussion of the phase transition explains their incorrect result: it was obtained from an analysis of the relative intensity of an internal mode of the ClO_4^- ion in two different scattering geometries. This leads to a direct measurement of A_{11}^4 , and they deduced an orientation of C_{3v} symmetry from a negative sign of this coefficient. As the Raman scattering geometries are related to the crystal axes, the method implies knowledge of the crystal orientation, which they had not. As we have seen in section 2, contrary to Toupry *et al.* assumption, this orientation cannot be predicted and several orientations may coexist. It is thus not possible to relate their measurements to our present and more refined knowledge of the structure and/or of the phase transition. One can simply conclude from the anisotropy they detected that, as in our experiments, their high temperature specimen was formed of a small number of crystallites.

Our experiment dealing with the static orientation probability density function, it is of course not possible to give definite conclusions about the dynamical aspect of the disorder. But, because of the presence of many ions in orientations of T_d symmetry and of quite a number of ions out of the potential wells, and also because our very small value of A_{11}^6 is consistent with the theoretical value of

A_{11}^6 calculated for a uniaxial rotation of a tetrahedron, we are tempted to conclude that, in KClO_4 , ions reorient mainly between their two potential wells by rotations around the (100) axes of the crystal. This is confirmed by figure 4 in which are drawn on a stereographic projection, the reorientational paths of an oxygen atom during rotations around the three four-fold axes of the crystal [18]. The relatively high probability of presence of oxygen atoms in the region (110) is clearly visible.

Fig. 4. — Theoretical reorientational paths of an oxygen atom during rotation around the three four-fold axes of the crystal.

A short comparison between the results obtained by the two methods used to analyse our data can now be made. Both models agree on the preferred orientation of the molecules (a fit assuming a D_{2d} orientation in the second model lead to a poor reliability factor) and on large oxygen motions perpendicular to the Cl-O bond. The first model strongly tends towards the reorientational process described above. The second model provides an estimate of the mean deviation of the Cl-O bond from its preferred orientation; this value is so large that the resolution ($l = 10$) of the first model turns out to be sufficient to describe our data. This is not always the case, as Depondt *et al.* have shown in the case of neopentane [19].

Before closing this section, let us point out that the present study stresses the importance of detailed structure analyses of the ionic ODIC phases. Indeed, though both KClO_4 and NaClO_4 , have the same f.c.c. structure in their plastic phase, the maximum of $P_0(\Omega)$ corresponds to a D_{2d} orientation in the latter case [20], contrary to the T_d orientation found here. From a purely steric point of view, one would

expect the Cl-O bond always to point towards the center of a potassium octahedron face, i.e. in the (111) direction. This is indeed the situation with the K^+ ion, but not with the smaller Na^+ ion, where a strong orientation translation coupling allows for a different preferred orientation. The same situation had already been encountered with the alkali

cyanides, and detailed numerical simulations [21] showed that, in the latter case, no simple interionic potential was able to reproduce, at once, the high and low temperature structures of these crystals. More work needs to be done to see if the situation is easier to model in the case of the ClO_4^- corresponding phases.

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