A paramagnetic Cl–O defect produced by x irradiation of KBr:ClO$_4^-$

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Experimental results on KBr:ClO$_4^-$ single crystals, before and after x irradiation at 77 K, are reported. Infrared and polarized Raman spectra show clearly that the perchlorate molecules are isolated in the KBr matrix and possess $T_d$ symmetry. EPR spectra, at 9.5 and 36 GHz, of irradiated crystals at 4.2 K indicate the formation of ClO$_4^-$ in trigonal symmetry. The g and $^{35}$Cl hyperfine tensors are found to be strictly axial and collinear. Temperature variation of the EPR spectra presented no motional averaging while uniaxial stress applied to the crystals yielded negative results. The structure of the ClO$_4^-$ molecule is discussed in terms of a trigonal Jahn–Teller effect and a probable dissociation into (ClO$_3^-$–O$^-$) complex.

INTRODUCTION

When single crystals of KClO$_4$ are exposed to x or γ irradiation, a number of paramagnetic defects identified as ClO$_4^-$, ClO$_3^-$, (ClO$_4$)$_2^-$, O$_2^-$, O$_2^-$ etc., are produced. These defects have been shown to arise from the trapping of holes and electrons at anion sites by distortion or fragmentation of ClO$_4^-$ ions. In particular, the EPR spectra of ClO$_4^-$ show strong deviation from tetrahedral symmetry with noncoincident $g$, $A$, and $Q$ tensors. The principal $g$ values of ClO$_4^-$ are consistent with those of a $g$ tensor from O$^-$ in orthorhombic fields while the principal $Q$ values of the Cl nucleus are those characteristic of ClO$_4^-$.

In view of these observations, it has been proposed that the ClO$_4^-$ defect is better described as a (ClO$_3^-$–O$^-$) complex. This complex is produced only by irradiating KClO$_4$ at or below 26 K. The large number of other associated defects produced thereby and the low symmetry of the crystal make it difficult, however, to conclude about the underlying physical mechanisms producing the observed structures. Further, the exact nature of the ground state for the unpaired electron on ClO$_4^-$ has not been elucidated conclusively so far. If the ClO$_4^-$ molecule had tetrahedral symmetry, it would be expected to have its unpaired electron in a triply degenerate $t_2$ orbital. However, there is no experimental evidence to corroborate these predictions of MO calculations. In contrast to the considerable amount of experimental work done on transition metal oxanions, rather little is known about the electronic structure of the corresponding tetroxides of nonmetals like ClO$_4^-$, SO$_4^-$, etc.

In the present investigation, we have studied the ClO$_4^-$ molecules isolated in KBr crystals before and after x irradiation by infrared, Raman, and EPR techniques. We have been interested in the molecular properties of tetrahedral anions, in particular the Jahn–Teller effect in their ground state. In view of our success in generating JT active molecules such as ReO$_4^-$, MnO$_4^-$ when isolated in alkalihalide matrices, we have attempted to matrix isolate the ClO$_4^-$ molecules in KBr crystals to produce a high symmetry ClO$_4^-$ species. The $T_d$ symmetry of this parent ClO$_4^-$ ion was established with the aid of IR and Raman experiments. Then, the radiation induced defects have been identified and characterized by EPR experiments at 9.5 and 36 GHz. We present these experimental results and discuss the possible molecular models.

EXPERIMENTAL

The single crystals of ClO$_4^-$:KBr crystals have been grown by slow evaporation of aqueous solutions. The concentration of the dopant, in the form of KClO$_4$, is typically 0.5 wt. % in the KBr solution. Optically transparent crystals have been cut and oriented for the IR and Raman measurements. IR spectra have been recorded on a Nicolet FT IR and Perkin–Elmer 597 spectrometers. Raman spectra were obtained with a laboratory assembled spectrometer consisting of a Spectra Physics argon ion laser, a Spex 1403 double monochromator and a Brookdeal photon counting system. The frequencies observed are within the error limits of $+/- - 2$ cm$^{-1}$. The EPR spectrometers (operated at 9.5 and 36 GHz), the irradiation and low temperature equipment have been described previously.

RESULTS AND DISCUSSION

IR and Raman spectra

Figure 1 shows the IR spectra of a KBr:ClO$_4^-$ single crystal at 300 K.

![FIG. 1. Infrared spectrum of KBr:ClO$_4^-$ single crystal at 300 K.](image)
crystal at 300 K while Fig. 2 shows the unpolarized and polarized Raman spectra of the same crystal. The frequencies of the bands are listed in Table I. We notice from Figs. 1 and 2 that the lines at (1110, 1120) and 640 cm$^{-1}$ are common to both IR and Raman spectra. Further, the polarized Raman spectra in Figs. 2(b) and 2(c) clearly indicate that these common lines belong to the same symmetry representation as they are observed only in the XZ polarization. Similarly, the other lines at 933, 945, and 472 cm$^{-1}$ pertain to the same symmetry in accordance with their polarization behavior. The splitting of the IR and Raman band at 1110 and 1120 cm$^{-1}$ (Figs. 1 and 2) is due to the presence of two isotopes of chlorine, $^{37}$Cl and $^{35}$Cl, with the natural abundance of 75.53% and 24.47%, respectively.

The nine vibrational modes of ClO$_4^-$ ion are distributed as $A_1 + E + 2T_2$, under the $T_d$ group. Of these, only the $T_2$ modes are IR active while all of them are Raman active. Further, the modes belonging to $T_2$ symmetry are allowed in the Raman XZ spectrum while those belonging to $A_1$ or $E$ are seen only in the Raman XX spectrum. Thus, the vibrations at (1110, 1120) and 640 cm$^{-1}$ are attributed to $T_2$ symmetry. The band at 640 cm$^{-1}$ is assigned to the "antisymmetric" bending mode while the band at (1110, 1120) cm$^{-1}$ is due to the antisymmetric stretching mode in agreement with the earlier data on pellets and on pure KClO$_4$ crystals. The other vibrations at 933, 472, and 945 cm$^{-1}$ which are seen only in the Raman XX spectrum belong to the $A_1$ or $E$ representation. The Raman line at 933 cm$^{-1}$ is indeed due to the totally symmetric stretching mode $v_1(A_1)$ while the Raman lines at 472 and 945 cm$^{-1}$ are attributed to the symmetric bending mode $v_2(E)$ and its overtone $2v_2$, respectively. As these vibrations do not involve the movement of the central Cl atom, the isotope effect is not expected to be seen here. These assignments are further confirmed by comparing them with the earlier data on pure KClO$_4$ and the solution spectra. Thus, we conclude that the observed IR and Raman spectra of ClO$_4^-$:KBr single crystals can be successfully interpreted if we assume a $T_d$ symmetry for the perchlorate ion. This means that the Cl–O bonds are aligned along the cube diagonals and each bond points along the direction that passes symmetrically between three nearest neighbors.

**EPR spectra**

Having established the site symmetry of ClO$_4^-$ in KBr, we now proceed to discuss the EPR results obtained after irradiating the as-grown crystals at 77 K. The EPR spectra recorded at 77 K show the presence of $v_4$(Br$_7^-$) centers of the matrix KBr while no lines associated with the impurity could be seen. Figure 3 shows the X band EPR spectra at 4.2 K along the three principal axes of the cube namely $C_4(001)$, $C_3(110)$, $C_2(111)$. Figure 4 shows the EPR spectra obtained at 36 GHz ($K_a$ band) under similar conditions at 4.2 K.

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**TABLE I. IR and Raman frequencies (in cm$^{-1}$) observed for KBr:ClO$_4^-$ at 300 K.**

<table>
<thead>
<tr>
<th>IR</th>
<th>Raman</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>933</td>
<td>$v_1(A_1)$</td>
</tr>
<tr>
<td>...</td>
<td>472</td>
<td>$v_2(E)$</td>
</tr>
<tr>
<td>1110</td>
<td>1110</td>
<td>$v_1(T_2)$ $^{37}$Cl</td>
</tr>
<tr>
<td>1120</td>
<td>1120</td>
<td>$v_1(T_2)$ $^{35}$Cl</td>
</tr>
<tr>
<td>640</td>
<td>640</td>
<td>$v_3(T_2)$</td>
</tr>
<tr>
<td>...</td>
<td>945</td>
<td>$2v_2(E)$</td>
</tr>
</tbody>
</table>

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**FIG. 2.** Raman spectrum of KBr:ClO$_4^-$ single crystal at 300 K. $\lambda_{ex} = 514.5$ nm. Laser power on the crystal = 0.6 W. (A) Unpolarized spectrum; (B) polarized spectrum with $z(xz)y$ geometry; (C) polarized spectrum with $z(xz)y$ geometry.

**FIG. 3.** X band EPR spectra of KBr:ClO$_4^-$ single crystal at 4.2 K after irradiation at 77 K. (i) $H||001$; (ii) $H||(110)$; (iii) $H||(111)$. The isotropic triplet marked by * is due to a free radical from irradiated silicon grease. The stick diagrams represent the spectra calculated from the parameters given in Table II.
when the static magnetic field $\mathbf{H}$ is oriented along the $C_4$ and $C_2$ axes. At both $X$ and $Ka$ bands, there are two sets of four lines when $\mathbf{H}$ is oriented along $C_2$ and $C_3$ axes while only one set of four lines is seen when $\mathbf{H}$ is along $C_4$. The fact that the four lines in each set arise from hyperfine interaction is clearly brought out by comparing the $X$ and $Ka$ band spectra. The lines are rather asymmetric in the $Ka$ band partly due to saturation and partly due to the mixed absorption and dispersion modes. They have widths of about 7 G at 4.2 K depending on the orientation of $\mathbf{H}$. It may be noticed from Figs. 3 and 4 that (i) the hyperfine spacings are not equidistant and (ii) the linewidths vary as a function of $m_I$. The linewidths have been found to be independent of temperature in the range 1.6–10 K. The $Ka$ band spectra showed, at certain orientations, resolved hyperfine structure due to the $^{35}\text{Cl}$ isotope also. On the contrary, no such isotopic splitting could be resolved at $X$ band frequencies. Besides, the EPR lines at both $X$ and $Ka$ bands also contain unresolved super-hyperfine interaction due to the nearby potassium nuclei ($I = \frac{1}{2}$) within their linewidths (see below). Angular dependence of the spectra has been studied by rotating the magnetic field in the (100) and (110) planes in order to determine the spin-Hamiltonian parameters and their orientation. As can be seen from Fig. 5, there are two quartets along any direction in the (100) plane except along (001). However, there are three quartets in the (110) plane except along $C_4$, $C_2$, and $C_3$ directions.

These EPR results have been analyzed by the spin-Hamiltonian

$$\mathbf{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}.$$  

Here, the quadrupole coupling term has been omitted due to its small magnitude, probably shifting the line positions by considerably less than the linewidths. The analysis proceeded as follows: The energies of the spin-Hamiltonian were evaluated by using the second order perturbation theory. The experimentally determined angular variations have been fitted to this expression using an optimization program. The best fit principal values of the $g$ and $A$ tensors have been determined and are presented in Table II. Within the limits of the experimental accuracy, they are found to be axial and collinear.

If the paramagnetic center has trigonal symmetry when isolated in a cubic host, one would expect the following criteria to be satisfied: (a) When the static magnetic field $\mathbf{H}$ is rotated in a (100) plane, the EPR spectrum consists of two groups of lines except along $C_4$ orientations. The spectrum along $C_4$ where all the sites become equivalent corresponds to $g_{57.4}$ while the two groups along $C_2$ correspond to $g_1$ and $g_{35.5}$. (b) When $\mathbf{H}$ is rotated in a (110) plane, one expects three groups of lines along any general direction. However, when $\mathbf{H}$ is parallel to $C_3$ axes, two groups of lines corresponding to $g_3$ and $g_{70.8}$ should be observed. The experimentally observed spectra (Figs. 3 and 4) and their angular dependencies (Fig. 5) agree well with these considerations. The orientation of the $g$ and $A$ tensors (Table II) indeed confirm the trigonal symmetry of the center.

Finally, a temperature variation study in the range 1.6–77 K has shown that EPR spectra disappear reversibly above about 10 K leaving no other lines associated with the impurity. Further, some EPR experiments have been performed under uniaxial stress applied externally to the crystals. These have indicated no significant changes in the EPR spectra.

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### Table II. Spin-Hamiltonian parameters at 4.2 K. Principal values of hyperfine tensor (in MHz) refer to $^{35}\text{Cl}$ nuclei.

<table>
<thead>
<tr>
<th>Principal $g$ values</th>
<th>Principal $A$ values</th>
<th>Direction cosines$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{xx} = g_1 = 2.0441 \pm 0.0005$</td>
<td>$A_{xx} = A_1 = 202$</td>
<td>0.4082, 0.4082, −0.8165</td>
</tr>
<tr>
<td>$g_{yy} = g_2 = 2.0441 \pm 0.0005$</td>
<td>$A_{yy} = A_2 = 202$</td>
<td>0.7071, −0.7071, 0.0</td>
</tr>
<tr>
<td>$g_{zz} = g_3 = 2.0037 \pm 0.0005$</td>
<td>$A_{zz} = A_3 = 230$</td>
<td>0.5774, 0.5774, 0.5774</td>
</tr>
</tbody>
</table>

$^*$Reference frame is the cubic $\{100\}, \{010\}, \{001\}$. 

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FIG. 4. $Ka$ band EPR spectra at 4.2 K. (a) $\mathbf{H}/(001)$; (b) $\mathbf{H}/(110)$.

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FIG. 5. Angular variation of the EPR spectra when the magnetic field is rotated in a (100) plane.

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TABLE III. Spin-Hamiltonian parameters of some Cl-O and oxygen centers in different lattices. Principal values of hyperfine and quadrupole tensors (in MHz) refer to $^{35}\text{Cl}$.

<table>
<thead>
<tr>
<th>Defect/matrix</th>
<th>$T(K)$</th>
<th>$g_{xx}$</th>
<th>$g_{yy}$</th>
<th>$g_{zz}$</th>
<th>$A_{xx}$</th>
<th>$A_{yy}$</th>
<th>$A_{zz}$</th>
<th>$Q_{xx}$</th>
<th>$Q_{yy}$</th>
<th>$Q_{zz}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\text{O}^-\text{ClO}_4^-$)/$\text{KClO}_4$</td>
<td>26</td>
<td>2.0415</td>
<td>2.0423</td>
<td>2.0014</td>
<td>185.8</td>
<td>180.9</td>
<td>213.8</td>
<td>-5.1</td>
<td>-4.5</td>
<td>9.6</td>
<td>2</td>
</tr>
<tr>
<td>$\text{ClO}_4^-$/KClO$_4$</td>
<td>26</td>
<td>2.0000</td>
<td>1.999</td>
<td>2.0063</td>
<td>-8.0</td>
<td>-11.0</td>
<td>70.0</td>
<td>9.0</td>
<td>-1.0</td>
<td>-8.0</td>
<td>1</td>
</tr>
<tr>
<td>($\text{ClO}_2^-$/KClO$_4$</td>
<td>26</td>
<td>2.0029</td>
<td>2.0062</td>
<td>2.0152</td>
<td>9.6</td>
<td>10.3</td>
<td>11.7</td>
<td>0.5</td>
<td>-0.5</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>$\text{ClO}_2^-$/KClO$_4$</td>
<td>300</td>
<td>2.0132</td>
<td>2.0132</td>
<td>2.0066</td>
<td>300.0</td>
<td>300.0</td>
<td>423.0</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{ClO}_2^-$/BaSO$_4$</td>
<td>300</td>
<td>2.0325</td>
<td>2.0255</td>
<td>2.0020</td>
<td>209.0</td>
<td>201.0</td>
<td>217.0</td>
<td>11</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\text{ClO}_2^-$/BaSO$_4$</td>
<td>300</td>
<td>2.0147</td>
<td>2.0147</td>
<td>2.0068</td>
<td>317.0</td>
<td>317.0</td>
<td>463.0</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{ClO}_2^-$/Ba( ClO$_3$)$_2$3H$_2$O</td>
<td>298</td>
<td>2.0071</td>
<td>2.0071</td>
<td>2.0043</td>
<td>324.0</td>
<td>324.0</td>
<td>441.0</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(OP$^-$)/CaF$_2$</td>
<td>77</td>
<td>2.0458</td>
<td>2.0458</td>
<td>2.0016</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O}^-$/CaF$_2$</td>
<td>4.2</td>
<td>2.1047</td>
<td>2.1047</td>
<td>1.9955</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O}^-$/SrCl$_2$</td>
<td>80</td>
<td>2.0650</td>
<td>2.0650</td>
<td>2.0032</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Thus, the center does not seem to reorient within the limits of detection and up to the highest stress accepted by the crystals ($<10^4$ dyn/cm$^2$).

**Identification and structure of the center**

From the ensemble of the results at $\chi$ and $K\bar{z}$ bands, we notice that the EPR spectra are attributable to a center with an unpaired electron ($S = 1$) interacting with a nucleus of spin $I = \frac{1}{2}$. The hyperfine interaction is characteristic of radicals containing a single chlorine atom. The isotopes $^{35}\text{Cl}$ and $^{37}\text{Cl}$ both have spin $\frac{1}{2}$, their natural abundance ratio being 3.07 and the ratio of their magnetic moments $^{35}\gamma /^{37}\gamma$ being 1.202. The relative intensities and the separation of the lines marked $^{37}\text{Cl}$ in Fig. 4 are consistent with these ratios and prove that the hyperfine interactions involve chlorine. The primary radiation induced defects in KBr:ClO$_4^-$ are essentially of the type ClO$_2^-$(electron trapped) and ClO$_4^-$ (hole trapped). The absence of any EPR lines other than those shown in Figs. 3 and 4 rule out the presence of radiation induced paramagnetic secondary defects like O$_2^-$, ClO$_2^-$, etc., at 4.2 K. Then, the relative magnitudes of the principal $g$ and $A$ values for ClO$_2^-$ are very different from those for ClO$_4^-$ (Table III). For example, in KClO$_4$, the Cl hyperfine interaction for ClO$_2^-$ lies in the range of 150--225 MHz while that for ClO$_4^-$ is much smaller (8--70 MHz). Also, we notice that $g_{xx} \approx g_{yy} > g_{zz}$ in ClO$_2^-$ while $g_{xx} \approx g_{yy} < g_{zz}$ in the case of ClO$_4^-$ species. By comparing Tables II and III, we find that the principal $g$ and $A$ values in the present case are closer to those observed for ClO$_2^-$ species.

It is indeed reasonable to consider a ClO$_2^-$ as the center responsible for the EPR spectra for the following additional reasons: The formation of $\gamma_x$ centers (hole type centers) is indicative of the creation of an electron excess center like ClO$_2^-$ at 77 K. Further, we never observed F centers within the sensitivity of the EPR spectrometer. The crystals, when warmed up to 300 K after x irradiation at 77 K, show bluish-green luminescence due to the recombination of $\gamma_x$ and ClO$_2^-$ centers. When the crystals were examined by IR and Raman after ClO$_2^-$ species was observed. These facts suggest that the perchlorate molecule has trapped an electron which recombines with the hole defects at $T > 77$ K. Such a process was also observed earlier in the case of ReO$_5^-$ and MnO$_4^-$ isolated in KBr crystals.

The observed trigonal symmetry of the presently reported center suggests two possible (although not totally distinct) models for its structure. Either, a strong Jahn-Teller effect distorts the molecule trigonally or the structure consists of two distinct entities: O$^-$ and ClO$_2^-$. We know that the parent ClO$_4^-$ has tetrahedral symmetry. Thus, the $T_2$ electronic ground state of the chlorate anion undergoes a JT effect. If such a model applies, then we have to start from this parent electronic state. The experimentally determined symmetry indicates then that a JT effect of the type $T_2 \otimes \tau_2$ is involved with an effective $\tau_2$ vibrational mode. In the strong coupling limit, this model predicts a fourfold degenerate vibronic ground state ($A_1 + T_2$) which gives rise to four possible trigonal distortions. If the corresponding adiabatic potential minima are deep, one observes a statically distorted trigonal complex. This model is in agreement with the following experimental facts: (1) Absence of any motional effects in EPR spectra and (2) absence of any effects under the influence of uniaxial stress applied to the crystal (along (001) and (111)).

The second possible structure consisting of the O$^-$ and ClO$_2^-$ entities is analogous to the one observed by Byberg in the KClO$_4$ matrix. He had indeed shown that trapping of an electron on a ClO$_4^-$ leads, in this host, to an immediate expulsion of O$^-$ when irradiated at 26 K. Some further support to the validity of this model for our center comes from the g tensor. Its principal values are characteristic of an O$^-$ ion in an axial field as was observed for instance in CaF$_2$ or SrCl$_2$ (Table III). The fact that in our case the $g$ and $A$ tensors are mutually parallel does not speak against this model because, unlike the situation in KClO$_4$, the symmetry of the problem here imposes mutually parallel tensors even if there are two neighboring entities. Additional support stems from the fact that the $\tau_0$ orbital of the ClO$_2^-$ is an antibonding orbital. Finally, there is also the known chemical evidence of the instability of the ClO$_2^-$ under even the weak reducing agents which favor such a complex. In spite of the fact that this second model is more likely than the first one, the JT effect is probably acting during the decomposition process. It is likely that the binding ($\leftrightarrow$ the restoring force) is not strong enough to provide for sufficiently deep minima in the adiabatic potential sheet.
This work has been supported by the Swiss National Science Foundation. One of us (Y.R.S.) wishes to thank Mr. D. Loy for his help in the computations.