ESR of trapped centers in γ irradiated silver chlorates single crystals

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The paramagnetic centers O_3^-, ClO_2, and $(ClO_2-Cl)^-$ have been identified in irradiated $AgClO_3$ single crystals by X and Q band ESR experiments at room temperatures and by the optical absorption bands at 480 and 360 nm, characteristic of the first two centers, respectively. The ESR spectrum and its angular dependence show that the first two centers have two magnetically inequivalent sites per unit cell. The third center was clearly observed only at certain orientations. The data for ClO_2 show that the principal directions of the g and A tensors do not coincide; the two magnetically inequivalent sites have similar principal values of the g and A tensors related by a 90° rotation about the tetragonal crystal axis of symmetry, and can therefore be assumed to be chemically equivalent. It is found that the ClO_2 center is formed substitutionally in the ClO_3^- ion position, but that the ozonide O_3^- is not. The thermal annealing of the γ irradiated $AgClO_3$ has revealed an increase in the concentration of the O_3^- radical that seems to be connected with the simultaneous destruction of the ClO_2 center.

I. INTRODUCTION

The observation of trapped paramagnetic centers on gamma irradiated single crystals of many different sulphates, chlorates, and nitrates has already been published in earlier works.[1-8] While the identification of such centers was not too obvious at the beginning it seems now possible to give appropriate identification of these fragments with the additional information derived from experimental techniques other than ESR, like optical absorption, Raman scattering, annealing at high temperatures, and bleaching with ultraviolet (uv) light.

In this paper we shall report ESR experiments of the paramagnetic fragments trapped in gamma irradiated $AgClO_3$ single crystals. We have been able to identify different fragments like O_3^- (ozonide), ClO_2, $(ClO_2-Cl)^-$, and Cl-like (nonidentified) centers by performing ESR experiments at X and Q band, optical absorption and studies of the thermally induced evolution and disappearance of these radicals.

The main features obtained are that the ozonide fragment is not located at the place of the oxygen atoms in the ClO_3^- ion, but occupies two magnetically inequivalent sites per unit cell with the plane of the molecule rotated by approximately 55° from the plane of the three oxygens in the ClO_3^- ion[8] in the unirradiated $AgClO_3$. For ClO_2 it was found that the principal directions of the g and A tensors do not coincide: the axis associated with the largest eigenvalue of A makes an angle of approximately 7° with the direction of the minimal eigenvalue of the g tensor (cf. Table I). Although we have not yet completed the theory of this effect, it seems that the ClO_2 fragment occupies essentially the same position as the ClO_3^- ion does in the perfect crystal, and that the final effect of irradiation consists in the elimination of one given oxygen atom from the ClO_3^- ion, leaving the remaining of this group at essentially the initial position.

We believe that the two magnetically inequivalent ClO_2 sites that are found per unit cell are chemically equivalent, since they have approximately the same principal values of the g and A tensors; one can be obtained from the other by a 90° rotation around the tetragonal axis of the crystal.

It was not possible to measure the principal values for the g tensors and hyperfine tensor of the $(ClO_2-Cl)^-$ center, because of its poor intensity relative to the other centers.

The fourth center must be associated to a Cl-like fragment because the spectra shows four lines characteristic of an hyperfine interaction with a spin $I = \frac{3}{2}$ (^{35}Cl or ^{37}Cl in this case). The observed hyperfine and g tensors are isotropic for this fragment.

II. EXPERIMENTAL

The $AgClO_3$ single crystals were grown by slow evaporation at room temperature from a supersaturated aqueous solution. The starting materials were analytically pure reagents from K & K Laboratories and were further purified by recrystalization. The x-ray

TABLE I. Principal values and direction cosines of the g and A tensors for the two trapped sites of ClO_2 in $AgClO_3$ (X band).[a]

g and A tensors	Direction cosines		
	[110]	[$\bar{1}$10]	[001]
$g_x = 2.0041$	0.522 (59°)	−0.853 (149°)	−0.007 (90°)
$g_y = 2.0183$	0.014 (89°)	0.016 (89°)	−1.000 (180°)
$g_z = 2.0128$	0.853 (31°)	0.522 (59°)	0.020 (89°)
$g_{av} = 2.0117$			
A_1			
$A_x = 69$	0.615 (52°)	−0.788 (142°)	0.000 (90°)
$A_y = 11$	0.301 (73°)	0.234 (76°)	−0.924 (158°)
$A_z = 14$	0.729 (43°)	0.569 (55°)	0.381 (68°)
$g_x = 2.0043$	0.854 (31°)	0.521 (59°)	0.002 (90°)
$g_y = 2.0183$	−0.001 (90°)	0.004 (90°)	−1.000 (180°)
$g_z = 2.0132$	−0.521 (121°)	0.854 (31°)	0.004 (90°)
$g_{av} = 2.0119$			
B_1			
$A_x = 68$	0.790 (38°)	0.613 (52°)	−0.002 (90°)
$A_y = 12$	0.141 (82°)	−0.185 (101°)	−0.973 (167°)
$A_z = 8$	−0.597 (127°)	0.768 (40°)	−0.233 (103°)

[a]Hyperfine tensor values in $10^{-4}cm^{-1}$. $\Delta g_x = \pm 0.0006$; $\Delta g_y = \Delta g_z$ $= \pm 0.0010$. $\Delta A_x = \pm 1$; $\Delta A_y = \Delta A_z = \pm 5$ (see text).
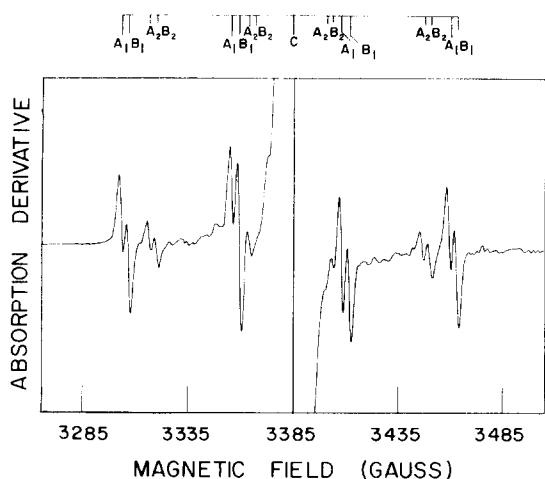
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FIG. 1. X band ESR spectra of γ-irradiated $AgClO_3$. The magnetic field lies on the (001) plane and at 37° from the [100] direction. Irradiation of all samples was performed at room temperature.

analysis shows that the single crystals grow along the [110] direction in two different shapes: a parallelepiped with faces perpendicular to the [110], [$\bar{1}$10], [001] directions or a trapezoidal shape with faces perpendicular to the crystallographic axis a, b, and c.[9] The structure of silver chlorate is tetragonal with eight molecules per unit cell (space group C_{4h}^5, $I4/m$).[10] The chlorate ion (ClO_3^-) consists of three oxygens arranged in an equilateral triangle with the chlorine atom slightly outside of the plane of the three oxygens, forming a flat pyramid.

The crystals were irradiated at room temperature from a ^{60}Co source with a total dose of 3 Mrad. The transparent crystals became dark brown after irradiation. The lifetime of the trapped paramagnetic centers was about 4 or 6 months.

The ESR experiments were done at room temperature in a conventional Varian E-line X and Q band spectrometer with 100 kHz rectangular and cylindrical cavities. The magnetic field was measured using proton and deuterium NMR resonances. The radio and X band microwave frequencies were measured with a digital counter within one part in 10^6, while an ESR signal from a standard pitch with a known g value was used to calibrate the Q band frequencies. At X band, a goniometer was used to mount the sample in the cavity to allow rotation of the crystal with respect to the magnetic field at intervals of 1° or 2°. At the Q band the magnet itself was rotated.

The optical absorption measurements were made on a Cary 14 spectrophotometer. For each crystal the data collection process consisted of (a) recording a background spectrum with a mask that was slightly smaller than the crystal, and (b) measuring the spectrum of the unirradiated crystal at $T \sim 4K$. For the low temperature measurements, the crystals were contained in a Sulfrian liquid helium cryostat.

Thermal annealing and uv-light bleaching were done with the sample mounted in the ESR cavity, so that

it was possible to monitor the ESR signal intensity as a function of temperature and time. In the former case a variable Temperature Control Varian which uses a nitrogen gas flux was used, and in the second case a 150 W mercury lamp together with a rectangular cavity with window was employed.

III. RESULTS

Figure 1 shows the X band ESR spectra for $AgClO_3$ irradiated with 3 Mrad. The magnetic field was on the (001) plane and at an angle of 37° from the [100] direction. In this spectrum the lines of three centers A, B, and C can be easily recognized, and in the "stick diagram" on top of Fig. 1, we have labeled with A_1, A_2 and B_1, B_2 the lines of what we shall call the A and B centers, respectively.

At this orientation, the spectra of the two centers A and B are nearly the same. The strong signal at the middle of the spectra, labeled C in the figure, has already been identified as the ozonide O_3^- fragment: the principal values and direction cosines of its g tensor are given in Ref. 8.

The two natural isotopes of chlorine (^{35}Cl and ^{37}Cl) have nuclear spin $I = \frac{3}{2}$, and we have therefore assigned the lines indicated by A_1, B_1, in Fig. 1 to a complex with ^{35}Cl, and those indicated by A_2, B_2, to a complex with ^{37}Cl. The relative intensities of these lines agree with the relative natural abundance 3 : 1, and their hyperfine separation ratio agree with the corresponding ratio 1 : 0.83 of the magnetic moments.

With the magnetic field still in the (001) plane but at different angles from [100], the two chemically equivalent complexes A and B give very different spectra, as can be seen in Fig. 2.

Figures 3 and 4 show the angular variation of the resonance field of the A_1 and B_1 lines at X and Q band, with the magnetic field again on the (001) plane. From this dependence it seems that the two trapped fragments A and B are chemically equivalent, but one of them is rotated by 90° with respect to the other, and are therefore magnetically inequivalent. For the ozonide center there is a direction in which the two sites are equivalent,
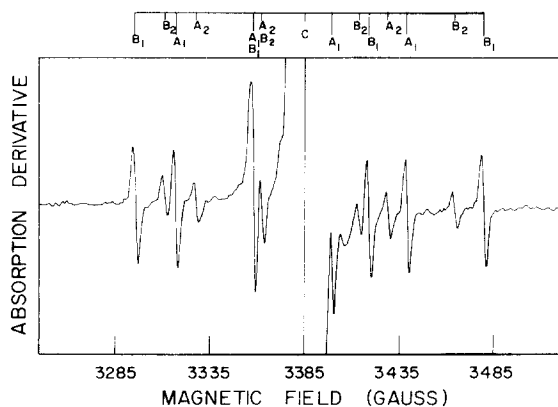

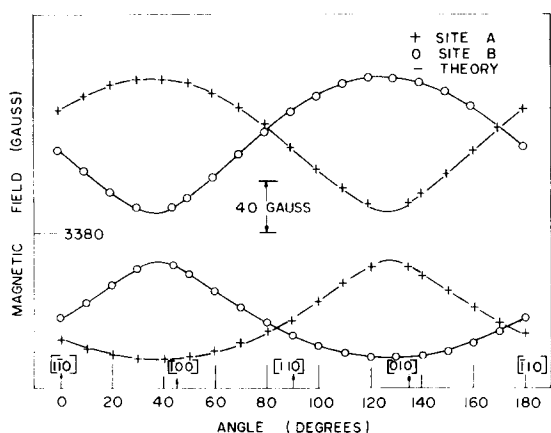FIG. 2. X band ESR spectra of γ-irradiated $AgClO_3$ at an arbitrary direction on the (001) plane.

FIG. 3. Angular variation of the resonance field of the hyper-fine lines for the two ClO_2 sites at the X band.

FIG. 5. X band ESR of 10 Mrad γ-irradiated $AgClO_3$ with the magnetic field on the (001) plane and at 38° from the [100] direction.

but we could not find such a direction for the A and B fragments. This is explained by the anisotropy of the g and A tensors, coupled with the fact that their principal axes do not coincide in the (001) plane and that there is not an axis of symmetry in this plane [nor a reflection plane perpendicular to (001)] that would transform fragment A into fragment B as it is discussed in a latter section.

To find the g and A tensor by Schonland's method, the ESR spectra were taken at three perpendicular planes (110), ($\bar{1}$10), and (001) and at a series of angles for each plane. The crystal was glued to the mounting rod for each set of measurements at a given plane, and the conventions described by Poole and Farach[11] were adopted to define the origin and sense for the measurements of the angles.[12] Several angles were measured for different planes. As it is indicated in Figs. 3 and 4, no measurements were taken at angles where the small hyperfine splitting made difficult the correct assignment of the A or B lines. The mounting method used could easily produce errors of a few degrees in the alignment of the measuring planes as well as in the origin of the angles.
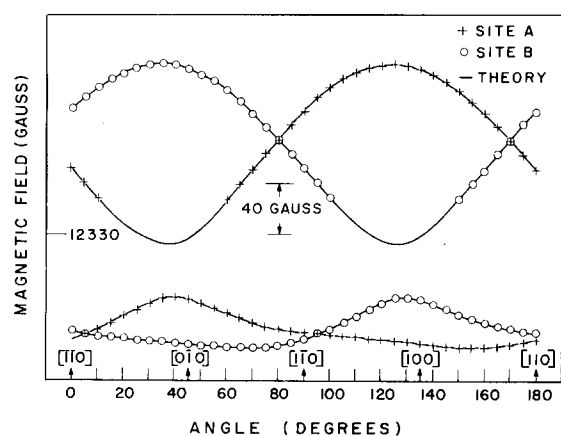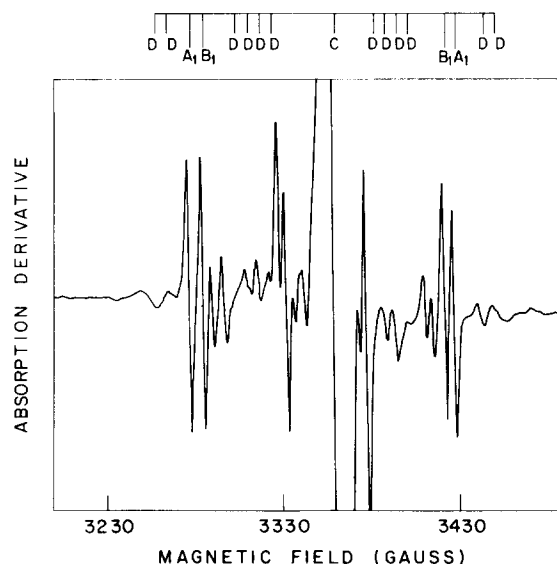
Figure 5 shows the ESR spectra at X band of a sam-

ple that was irradiated with 10 Mrad. The magnetic field was on the (001) plane and at an angle of 38° from the [100] direction. At this orientation the presence of an additional center D was clearly detected. It was not easy to follow the angular dependence of the resonance field for this fragment, because it has a very small intensity and it overlaps with the other resonances. It was observed that the spectrum follows approximately the same angular dependence of the fragments A and B, at least in the regions where it was clearly detected.

We named E a fourth center, with a characteristic Cl hyperfine interaction. It was observed when the magnetic field was in the planes (110) and (110), and in such orientation, where the hyperfine splittings of the other centers were small. In the regions where this center was clearly identified, the angular dependence of its spectrum was isotropic. Figure 6 shows a typical spectrum for this fragment and Table III gives its g

FIG. 4. Angular variation of the resonance field of the hyper-fine lines for the two ClO_2 sites at the Q band.
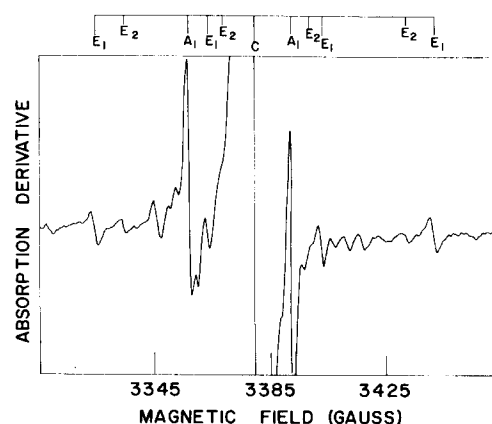

FIG. 6. X band ESR spectra of the γ-irradiated $AgClO_3$ when the magnetic field lies on the (110) plane 6° from the [001] direction.
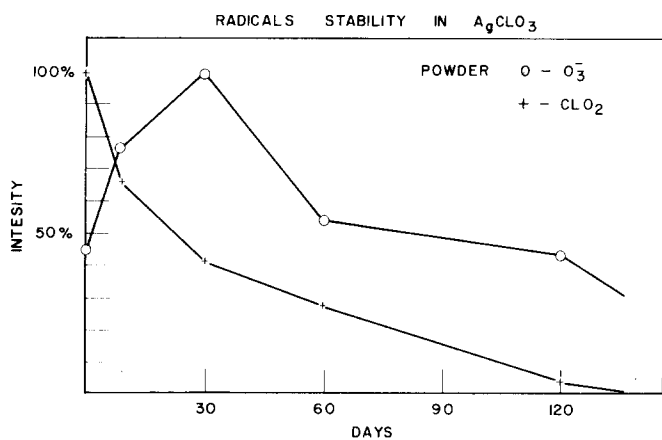
FIG. 7. Isothermal evolution at room temperature of the radicals. ClO_2 (A, B) and O_3^- (C). The O_3^- intensities were normalized relative to the initial intensity of the ClO_2 center.

factor and hyperfine parameter.

Figure 7 shows the isothermal behavior of the relative ESR intensity of the A, B, and C lines, for a powder sample which was irradiated with 3 Mrad. After irradiation the relative intensity of the A, B lines is clearly higher than that for the C line. It is interesting to note that while the relative intensity of the A, B lines goes down, that of the C line goes up, reaching a maximum at 30 or 40 days after the irradiation. After 4 months the A, B lines disappear completely, while the C line remains unchanged for a much longer time. The intensity of the sample coloring did not diminish, however. It was not possible to see what happens to the other fragments because they are obscured by the more intense A, B, and C spectra.
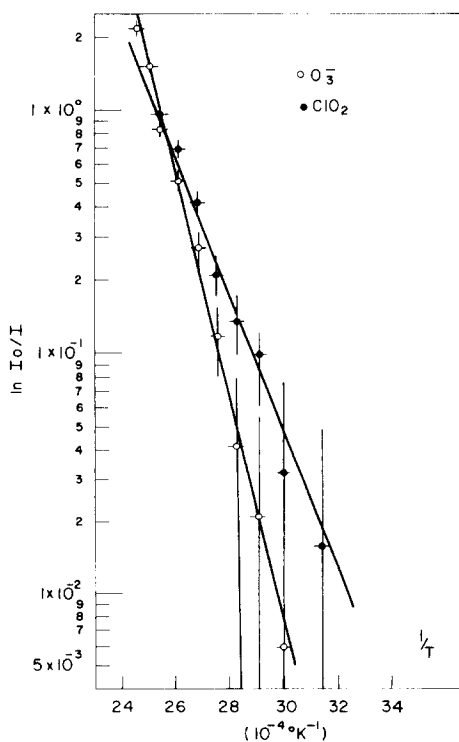

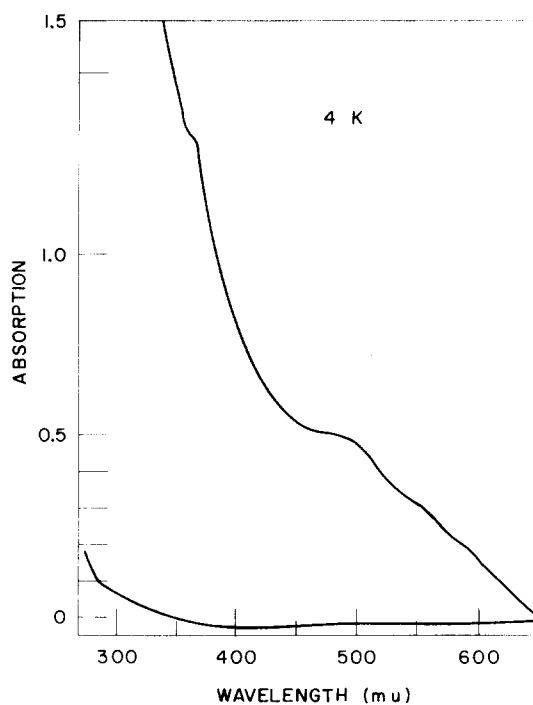FIG. 8. Arrhenius plot of the rate constant for ClO_2 and O_3^-.

FIG. 9. Unpolarized optical absorption spectra of nonirradiated and γ-irradiated $AgClO_3$ single crystal at liquid helium temperature.

Isochronal thermal annealing of the free radicals was performed on single crystals by increasing the temperature by steps of 10 °C and then heating during 5 min at each temperature. After each step the ESR spectra were taken at room temperature with the magnetic field on the (001) plane and at an orientation where the spectra had good resolution. The maximum temperature reached was 140 °C, because above this temperature the crystal breaks in small pieces. The radicals D and E could not be studied by this method because of their poor intensity. Although less pronounced, we have observed the same behavior that we found in the isothermal evolution of the powder samples, i.e., an initial increase in the C concentration with a simultaneous decrease of the A, B concentration. Assuming that the observed processes follow a first order kinetics, the activation energies (E) and frequency factors (ν_0) have been estimated. For A, B we have found $E = 0.57$ eV and $\nu_0 = 10^7$ sec^{-1}, and for C the values $E = 0.93$ eV and $\nu_0 = 10^{12}$ sec^{-1}. These values are similar to those obtained by Andersen et al.[13] in thermoluminescence experiments on irradiated $KBrO_3$ and $NaBrO_3$. The Arrhenius plot for A, B, and C is shown in Fig. 8.

The optical absorption spectrum with unpolarized light is shown in Fig. 9. This spectrum shows two absorption bands, one at 360 nm and another at 480 nm, which do not appear in the unirradiated or in the completely annealed $AgClO_3$ single crystals: we therefore attribute these two bands to the species A, B, and C observed in ESR.

As indicated above, we have also performed a bleaching experiment with uv light: We observed that the A

and B magnetic resonances were bleached out by illumination with this light. The intensity of the C center also decreased under illumination but rather more slowly. As the Hg lamp used had strong lines only in the 200–400 nm region, and only weak lines in the 500 nm region. This result seems to connect the 360 nm optical absorption to the ESR lines A and B.

IV. ANALYSIS

To derive the g and A tensors from the experimental measurements, we have used Schonland's method. First, the expressions that give the angular variation of the resonant fields according to this method were fitted by a least squares calculation to the set of measurements associated to each of the three planes. With the coefficients so derived, Schonland's method was applied and the g and A tensors obtained. As this method assumes only first order perturbation, we used the values obtained for g and A to correct for second order perturbations; Schonland's method was again applied and new g and A were then obtained. This process could be iterated, but in our case it was not necessary to iterate more than once, and even this first correction was less than 0.1%.

For the case of the C fragment, which was identified as the ozonide (O_3^-), there was no hyperfine splitting. To interpret the data the following spin Hamiltonian was used:

$$\hat{H} = g_{ij}\beta H_i S_j. \tag{1}$$

The experimental results and calculated parameters have been given in Ref. 8.

The fragments A and B show hyperfine splittings which are related to the ^{35}Cl and ^{37}Cl isotopes, and therefore it was necessary to add to Eq. (1) a hyperfine interaction term

$$\hat{H} = g_{ij}\beta H_i S_j + A_{ij} I_i S_j. \tag{2}$$

Even though the chlorine quadrupolar moment is rather large, we have neglected it for the following reasons: (a) the three hyperfine splittings between adjacent lines were equal to each other independently of the magnetic field orientation, and (b) no forbidden transitions ($\Delta m = \pm 1$, ± 2) could be seen at any orientation.

Tables I, II, and III show the principal values and direction cosines of the g and A tensor for the A, B, and E species. It was not possible to obtain hyperfine parameters for the fragment D because the corresponding ESR spectra had poor resolution.

An inspection of the A tensors obtained from the measurements in X band vs those obtained from Q band (cf. Table I and II) for A and B fragments, shows that the values of A_y and A_z as well as the directions of the principal axes associated to them vary rather strongly. After some calculations where we simulated orientation errors, we concluded that those large changes can be understood by the effect of (1) the impossibility of doing any accurate experiment at orientations where the total hyperfine splitting is given by these two small components of the hyperfine tensor, because of the presence of the very strong signal at the middle of the spectra coming from the C center, (2) misalignments of the planes in which the magnetic field was rotated with respect to the true (110), ($\bar{1}$10), and (001) planes, and (3) small errors in the determination of the origin of measurements of the angles of rotation of the magnetic field.

From the results of the calculations with simulated errors we feel confident that the values of g_x, g_y, g_z, A_x, and the directions of their associated principal axes given in Table I and II are essentially correct. With regard to A_y and A_z we can only say that they are smaller than A_x and of the order of magnitude of 10 G. From our measurements we cannot really say much about the direction of the principal axes to A_y and A_z.

V. DISCUSSION

By comparison of our ESR data with many other ESR experiments on chlorates and perchlorates like $KClO_3$, $KClO_4$, $NaClO_3$, $Ba(ClO_3)_2 \cdot H_2O$, and $Ca(ClO_3)_2 \cdot H_2O$, we have identified the paramagnetic centers A and B as ClO_2, the center C as O_3^-, the center D as $(ClO_2-Cl)^-$, and the center E as a Cl-like fragment.

Radicals A and B

There are several arguments that justify the assignment of the ClO_2 radical to the species A and B: (a) The ESR spectrum has the right number of lines, and both the g and A tensors agree fairly well with the values previously measured.[1,7] The small differences

TABLE III. g value and A tensor for the trapped sites of the E-specie in $AgClO_3$.[a]

	X band		Q band	
E_1	$g = 2.010$	$A = 36$	$g = 2.010$	$A = 38$
E_2	$g = 2.010$	$A = 30$	$\cdots$	$\cdots$

[a]Hyperfine tensor values in 10^{-4} cm^{-1}. $\Delta g = \pm 0.001$. $\Delta A = \pm 2$.

TABLE II. Principal values and direction cosines of the g and A tensor for the two trapped sites of ClO_2 in $AgClO_3$ (Q band).[a]

		Direction cosines		
	g and A tensors	[110]	[$\bar{1}$10]	[001]
A_1	$g_x = 2.0047$	0.516 (59°)	−0.856 (149°)	−0.032 (92°)
	$g_y = 2.0195$	0.011 (89°)	0.044 (87°)	−0.999 (187°)
	$g_z = 2.0139$	0.856 (31°)	0.515 (59°)	0.032 (88°)
	$g_{av} = 2.0127$			
	$A_x = 69$	0.613 (52°)	−0.790 (142°)	−0.030 (92°)
	$A_y = 9$	0.100 (84°)	0.115 (83°)	−0.988 (171°)
	$A_z = 14$	0.784 (38°)	0.603 (53°)	0.150 (81°)
B_1	$g_x = 2.0051$	0.846 (32°)	0.532 (58°)	0.024 (89°)
	$g_y = 2.0196$	−0.006 (90°)	0.055 (87°)	−0.998 (177°)
	$g_z = 2.0139$	−0.533 (122°)	0.845 (32°)	0.050 (87°)
	$g_{av} = 2.0129$			
	$A_x = 68$	0.791 (38°)	0.612 (52°)	0.019 (89°)
	$A_y = 14$	0.119 (83°)	−0.123 (97°)	−0.985 (170°)
	$A_z = 7$	−0.600 (127°)	0.781 (39°)	−0.170 (100°)

[a]Hyperfine tensor values in 10^{-4} cm^{-1}. $\Delta g_x = \pm 0.0004$; $\Delta g_y = \Delta g_z = \pm 0.0008$. $\Delta A_x = \pm 1$; $\Delta A_y = \Delta A_z = \pm 5$ (see text).

observed can easily be attributed to the difference in host crystal: in particular the presence of Ag^+ ions instead of Na^+ or K^+ ions could in principle be the reason for these different values. (b) The presence of an optical absorption band at 360 nm coupled to the bleaching that we have observed with uv light (see Sec. II above) seems to reinforce the assignment of the A and B center to the ClO_2 fragment.

It is of interest to know the orientation of the ClO_2 molecule in the irradiated crystal. Because the measured g and A tensors are not very different from those obtained in other irradiated crystals, we could use these values to define the orientation of the ClO_2 radical.

As usual, the smallest g and the maximum A would correspond to the direction perpendicular to the plane of the ClO_2 (x direction), while the maximum g would correspond to the line along the 2 oxygen atoms (y direction) and the intermediate g to the direction of the C_{2v} axis (z direction). Although for the Na and K salts the g and A tensors have colinear principal axis (p. a.) this is not true any more for the Ag salt, and the direction of the smallest g and that of the maximum A make an angle of approximately 7° between each other.

For a ClO_2 fragment with C_{2v} symmetry, the A and g tensors should be colinear, so we attribute the observed deviation to the breaking of the C_{2v} symmetry, either by low symmetry crystal fields or by covalent effects with the nearby Ag ions. It is well known that Ag ions are more easily affected by radiation than the Na or K ions, and this could produce a change in the environment of ClO_2 more marked for the Ag than for the Na or K salts. This argument is very speculative, and for simplicity we are currently studying only the effects of low symmetry crystal fields on the g and A tensors of ClO_2.

Since the relative difference between the g principal values (p. v.) is much smaller than that between the largest and any of the other two p. v. of A, the small off-diagonal matrix elements present both in the A and g tensors, because of the breaking of the C_{2v} symmetry, would relatively affect more the direction of the p. a. of the g tensor than those of the A tensor. If we accept that the ratio of the off-diagonal to diagonal matrix elements is similar for both the g and A tensors, then the direction of the p. a. of the g tensor would be much more affected by the low symmetry perturbation than that of the largest p. v. of the A tensor. If these perturbations are small, we can assume that the p. a. of the A tensor would be unaffected for our purposes. Although we have not proven that the perturbation is small, it seems a reasonable assumption, and we shall conditionally accept it until we can make a more precise estimate. We shall then assume that the plane of the ClO_2 fragment is perpendicular to the principal axis of A associated with the largest principal value of A. Using this criterion, we can say that the final effect of the radiation on the ClO_3^- ion in $AgClO_3$, is to always lose the same ($8h$) oxygen because the plane formed by the Cl ($8h$) and the two O's ($16i$) is perpendicular to the

principal axis associated with the largest principal value of the A tensor.

Radical C

We shall not go into details for this radical, since it has already been identified by us in Ref. 8. We shall only mention that it can be attributed to the ozonide (O_3^-) radical, since its average g value and the observed optical absorption band are characteristic for this fragment. However, it is worthwhile to mention that this radical is not oriented like the three oxygens in the ClO_3^- ion, since the direction cosine for its g tensor does not coincide with the direction cosines of the plane formed by the oxygen atoms in the ClO_3^- ion in the unirradiated $AgClO_3$.[14]

It is also worthwhile to add that an alternative interpretation of the data for the orientation of the O_3^- center, other than that given in Ref. 8, could be suggested. It is possible that as a final result of the irradiation, the oxygens $O(8h)$ occupy the hole created by the absence of the chlorine atom. In this case the O_3^- center will have its plane rotated by $-35°$ from the original orientation of the plane of the three oxygens in the ClO_3^- ion.

Radical D

We believe that in this fragment there are two chlorine atoms involved, because the spectra shows four groups of four lines which will correspond to the superhyperfine interaction of two chlorines ^{35}Cl–^{35}Cl or ^{35}Cl–^{37}Cl, both with spin nuclear $I = \frac{3}{2}$. Qualitatively, following Eachus et al.[1] we attribute the major splitting to ClO_2-like species and the minor one to Cl-like ion, but we cannot give a quantitative analysis due to the poor resolution and intensity obtained for this center.

Radical E

This center could not be identified completely, but our results show that it has isotropic g and A tensors (see Table III). The isochronal thermal annealing of this center, performed in the same way as for the A, B, and C fragments, shows no measurable change (less than 20%) in the intensity of the ESR lines up to the maximum temperature obtainable (140 °C, at which point the samples shatter), showing that the kinetics followed by this center are completely different than for the other fragments.

Stability and annealing of ClO_2 and O_3^-

Now we shall discuss shortly the stability and annealing of the centers ClO_2 and O_3^- obtained by ESR experiments.

The isothermal behavior at room temperature of the paramagnetic centers shows an increase in the O_3^- concentration (see Fig. 7), simultaneously with a decrease in the ClO_2 concentration. This O_3^- increase, that has been previously observed only in the cubic $NaClO_3$, could then be interpreted as the result of the simultaneous destruction of the ClO_2 fragment.[15]

The increase in the O_3^- concentration could be, in

part at least, attributed to the following reactions[1,3,16,17]:

$$ClO_2 + O^- \rightarrow (ClO_3^-)^*, \tag{A}$$

$$(ClO_3^-)^* + e^- \rightarrow Cl^- + O_3^- \tag{B}$$

or

$$ClO_2 + e^- \rightarrow (ClO_2^-)^*, \tag{C}$$

$$(ClO_2^-)^* + O^- \rightarrow Cl^- + O_3^-. \tag{D}$$

In these reactions the capture of an ion or an electron by a free radical leads to the formation of highly excited and unstable ions.[6,18] For steps (B) and (C) the heating of the crystal frees trapped electrons which interact with $(ClO_3^-)^*$ and ClO_2.

For the radical O_3^- the following reactions could be suggested:

$$O_3^- \rightarrow O_3 + e^-, \tag{E}$$

$$O_3 \rightarrow O_2 + O. \tag{F}$$

The oxygen molecule could diffuse towards the surface at these temperatures. These reactions like those proposed for the elimination of ClO_2 do not reconstitute the initial lattice. On the contrary they probably leave elastic distortions in the matrix which give rise to the large broadening of the ^{35}Cl NQR lines even after the disappearance of the O_3^-.[15]

VI. CONCLUSIONS

We believe that after gamma irradiation on silver chlorates three main paramagnetic centers are trapped at two magnetically inequivalent but chemically equivalent sites. Our ESR data together with additional experiments like thermal and light bleaching as well as optical absorption seem to be sufficient to identify them as ClO_2, O_3^-, and $(ClO_2-Cl)^-$.

For the fourth fragment observed we have been able to measure the g value and the hyperfine parameter, but no attempt to identify this center was made.

The ambiguity in the determination of the orientation of the ClO_2 fragment requires more theoretical work in order to understand why the principal directions of the

g and A tensors do not coincide. Our assumption that the principal direction associated with the large principal value of A is perpendicular to the plane of the ClO_2 fragment has to be taken with care.

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