

**ESR study of Cd(BrO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O single crystals  $\gamma$  irradiated at 300 and 77 K**

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# ESR study of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ single crystals $\gamma$ irradiated at 300 and 77 K

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In  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystals  $\gamma$  irradiated at 300 K,  $\text{BrO}_2$  and  $\text{O}_3^-$  centers are observed. A correlation between the ESR and optical absorption studies has revealed that the optical absorption band for  $\text{BrO}_2$  lies around 470 nm. After  $\gamma$  irradiation at 77 K, a complex defect center identified as  $\text{H} \cdots \text{BrO}_3 \cdots \text{HO}$  could be observed. The chemical inequivalence and the effect of thermal or UV light bleaching on the populations of these centers are discussed.

## INTRODUCTION

A program has been initiated in our laboratory to identify paramagnetic centers produced by  $\gamma$  irradiation in divalent bromates by the electron spin resonance (ESR) studies. We have reported earlier the new paramagnetic centers detected in  $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ <sup>1</sup> and  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ <sup>2</sup> after  $\gamma$  irradiation. In  $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ , the paramagnetic defect centers produced at 300 K have been identified to be  $V_k$  centers of the type  $(\text{Br}-\text{BrO}_2)^-$ , whereas  $\text{BrO}_3^{2-}$  centers have been detected when  $\gamma$  irradiated at 77 K. On the other hand, in  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ , no bromine containing paramagnetic radicals could be detected when  $\gamma$  irradiated at 300 K, whereas a complex radical of the type  $\text{BrO}_2^{2-} \cdot \text{H}_2\text{O}$  could be observed when  $\gamma$  irradiated at 77 K. In  $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,<sup>3</sup> Collins *et al.* reported the detection of  $\text{BrO}_2$  radicals after  $\gamma$  irradiation at 300 K. In the present work we report the paramagnetic centers detected in  $\gamma$  irradiated  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  at 300 and 77 K and these observations show interesting differences compared with the data reported earlier on other divalent bromates and also a comparable chlorate like  $\text{Cd}(\text{ClO}_3)_2$ .<sup>4</sup>

## EXPERIMENTAL

$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  was prepared in the laboratory by the double decomposition method by mixing hot aqueous solutions of  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$  and  $3\text{Cd}(\text{SO}_4) \cdot 8\text{H}_2\text{O}$ .<sup>5</sup> The insoluble precipitate of  $\text{BaSO}_4$  was removed by filtering the cooled solution containing highly soluble  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  which was purified by repeated crystallization. Good transparent single crystals with well formed (100), (010), (110), (210) faces were obtained by slow evaporation of the aqueous solution over silica gel. A <sup>60</sup>Co  $\gamma$ -ray source of 0.35 M rad/h was used for irradiation at 300 and 77 K. The ESR spectra were recorded mainly on a Varian E-4 X-band spectrometer employing 100 kHz field modulation. A Varian E-257 variable temperature accessory was used for the temperature variation studies. A vacuum oven with  $\pm 2^\circ\text{C}$  accuracy for thermal bleaching and a mercury lamp with a UV filter for optical bleaching were employed. A Carey-14 spectrophotometer was used for recording the optical absorption spectra at 300 K.

The ESR spectra were recorded in the three mutually orthogonal planes (001), (100), and (010) in steps of 5–10 deg. DPPH *g* value of 2.0036 was used as an internal standard for evaluating the *g* parameters.

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## CRYSTAL STRUCTURE

$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystals belong to orthorhombic class with space group  $P2_12_12_1$ .<sup>6</sup> There are four molecules per unit cell with the unit cell dimensions  $a = 12.495 \text{ \AA}$ ,  $b = 6.172 \text{ \AA}$ , and  $c = 9.24 \text{ \AA}$ . The *c* axis has been identified as the long axis of the crystal. The projection of the unit cell on (001) face is shown in Fig. 1. The  $\text{Cd}^{++}$  ion is surrounded by seven oxygen atoms, five of which belong to the neighboring  $\text{BrO}_3^-$  groups and two are water oxygens. There are crystallographically inequivalent  $\text{BrO}_3^-$  ions and water oxygens in the unit cell. The crystallographic inequivalence of  $\text{BrO}_3^-$  ions was also confirmed by NQR studies in this compound.<sup>7</sup> The geometries of the two crystallographically inequivalent  $\text{BrO}_3^-$  ions are described in Table I.

## RESULTS

### Irradiation at 300 K

No ESR spectra could be recorded before  $\gamma$  irradiation, but after irradiation for 6–7 h the crystals developed a reddish brown coloration and rich spectra spread over nearly 0.15 T revealing the presence of several bromine containing paramagnetic defect centers could be recorded. These spectra are extremely complex due to the overlapping lines from different magnetically and chemically inequivalent sites belonging to several paramagnetic centers. However, simple spectra could be obtained if the magnetic field was applied along one of the principal crystallographic directions. Figure 2 shows the paramagnetic centers, denoted by A, B, and C, observed when the magnetic field is parallel to the *C* axis. A and B centers are identified as bromine containing radicals from the characteristic nuclear hyperfine interaction from

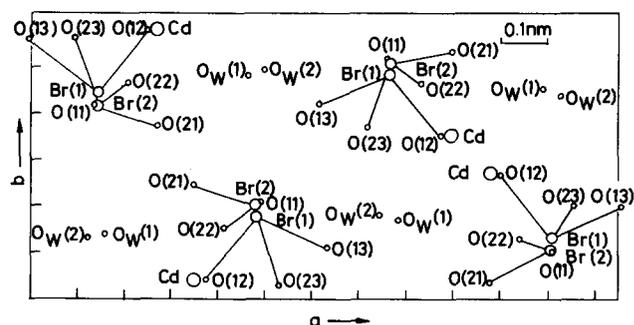


FIG. 1. Projection diagram of the unit cell of  $\text{Cd}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$  single crystal on the *c* plane.

TABLE I. Geometries of the two crystallographically inequivalent  $\text{BrO}_3^-$  ions.

	Bond length ( $\text{\AA}$ )	Bond angles (deg)
$\text{BrO}_3^- (1)$	$\text{Br}(1)-\text{O}(11)$ 1.68	$\text{O}(11)-\text{Br}(1)-\text{O}(12)$ 98.6
	$\text{Br}(1)-\text{O}(12)$ 1.70	$\text{O}(12)-\text{Br}(1)-\text{O}(13)$ 105.6
	$\text{Br}(1)-\text{O}(13)$ 1.65	$\text{O}(13)-\text{Br}(1)-\text{O}(11)$ 102.0
$\text{BrO}_3^- (2)$	$\text{Br}(2)-\text{O}(21)$ 1.66	$\text{O}(21)-\text{Br}(2)-\text{O}(22)$ 106.1
	$\text{Br}(2)-\text{O}(22)$ 1.63	$\text{O}(22)-\text{Br}(2)-\text{O}(23)$ 104.4
	$\text{Br}(2)-\text{O}(23)$ 1.68	$\text{O}(23)-\text{Br}(2)-\text{O}(21)$ 101.0

$^{81}\text{Br}$  and  $^{79}\text{Br}$ . The center C does not exhibit any bromine nucleus hyperfine interaction and probably contains only oxygen nuclei. All the centers were stable for several weeks when the irradiated crystals were stored in the dark. But when subjected to thermal bleaching at 363 K for 30 min or bleaching with UV light for 2 or 3 h, both A and B centers could be completely bleached. However, the intensities of the lines due to C center remained constant in both the cases. The optical absorption spectra recorded in the irradiated crystals showed two prominent bands, one around 470 nm and another 330 nm as can be seen from Fig. 3. The 470 nm band initially decreased in intensity because of thermal or UV light bleaching. However, even after prolonged bleaching, the intensity of the 470 nm band could not be completely bleached but remained constant at a particular value.

#### Irradiation at 77 K

After  $\gamma$  irradiation for 6 to 7 h at 77 K, ESR spectra spread over 0.2–0.25 T exhibiting the presence of several complex paramagnetic centers could be recorded and can be seen from Fig. 4. The two centers designated as D and E

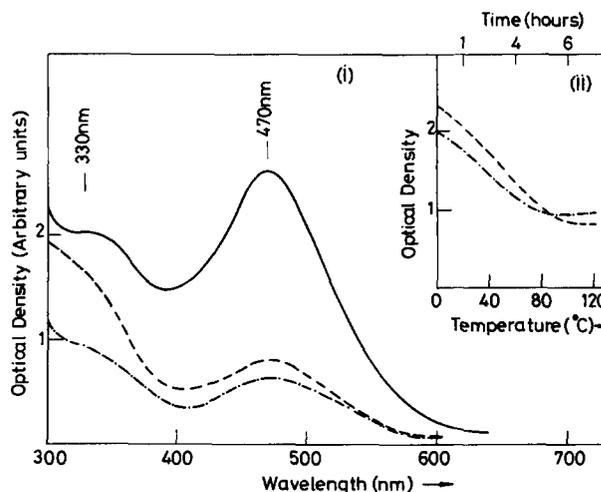


FIG. 3. (i) Induced optical absorption spectra recorded at 300 K in  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystal  $\gamma$  irradiated at 300 K.  $\leftrightarrow$  After 10 h of irradiation,  $\dashrightarrow$  After 10 min of thermal bleaching at 80 °C,  $\dashleftarrow$  After 6 h of UV bleaching.

could be identified as bromine containing paramagnetic defect centers from the characteristic  $^{81}\text{Br}$  and  $^{79}\text{Br}$  hyperfine lines. They were further split into a maximum of four lines. This probably reflects superhyperfine (SHF) interaction due to two protons ( $I = 1/2$ ) of water of hydration. The two protons were found to be inequivalent in all the three planes of rotation since the splittings which can be attributed to each proton remained different. For certain orientations of the crystal, the splittings disappeared, probably because the SHF interaction at these orientations was less than the line width ( $\sim 1.0$  mT). Under the effect of thermal bleaching D and E centers were unstable and completely decayed when the crystals were warmed to above 198 K. When the crystals

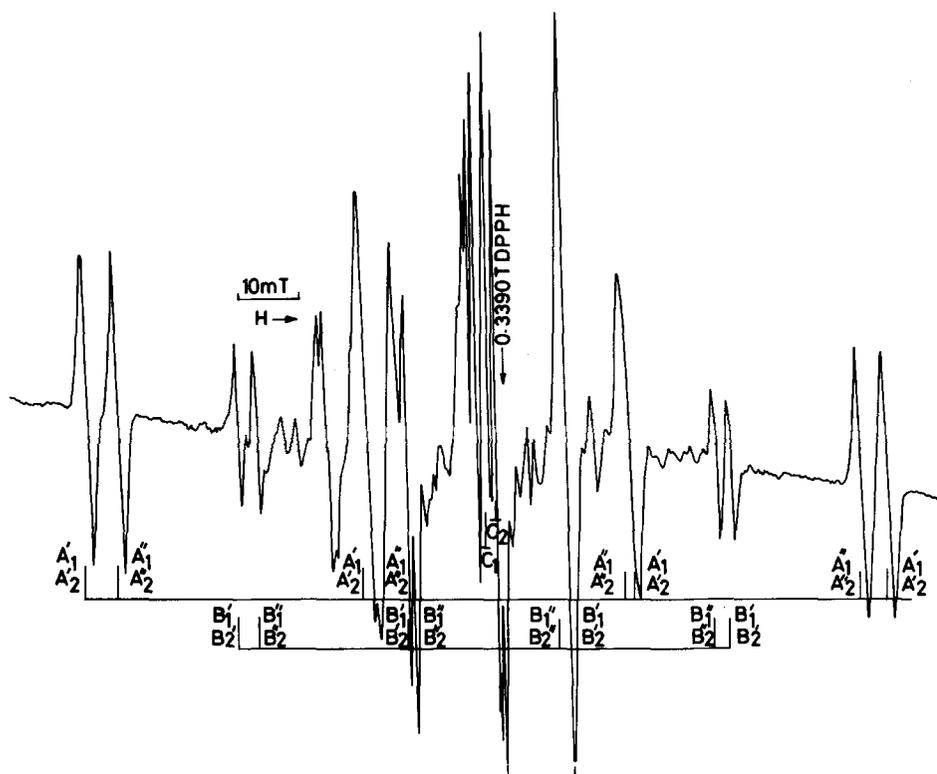


FIG. 2. ESR spectrum at 300 K in  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystals  $\gamma$  irradiated at 300 K. The field lies parallel to (001) axis.

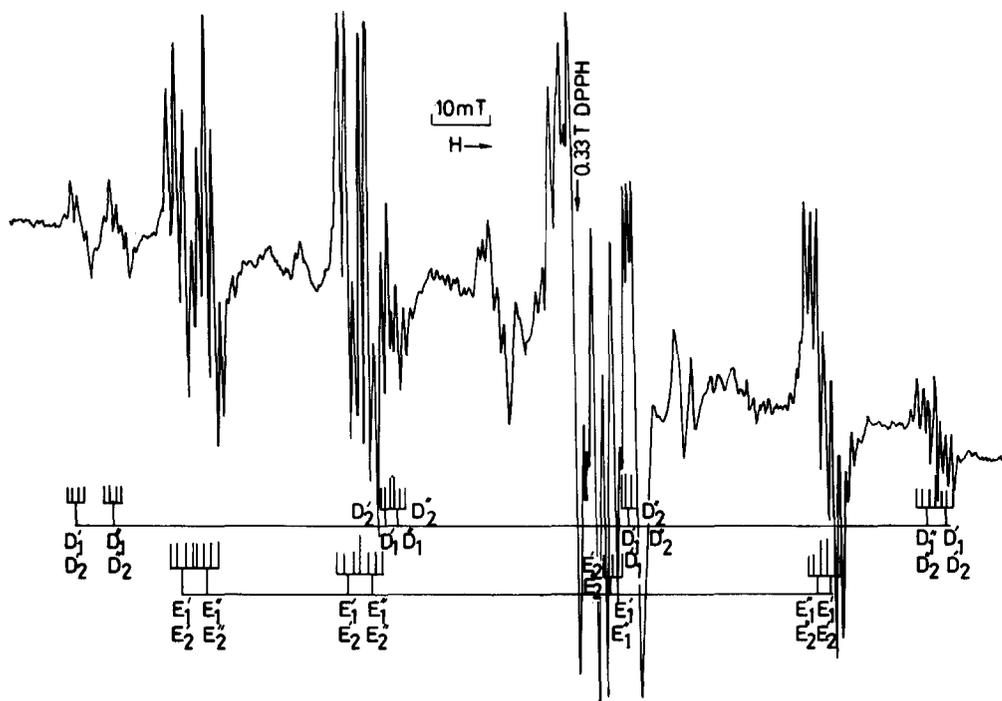


FIG. 4. ESR spectrum of  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystal recorded at 77 K after  $\gamma$  irradiation at 77 K. The field lies in (100) plane.

were warmed to 300 K, the spectra recorded were same as those obtained in the single crystals after  $\gamma$  irradiation at 300 K.

#### CALCULATION OF ESR PARAMETERS

The ESR spectra of A, B, D, and E centers can be described by the following Hamiltonian in which the nuclear Zeeman interaction is neglected:

$$\mathcal{H} = \beta H g s + S A I + I Q I$$

A preliminary estimate of the principal  $g$  and  $A$  values and their direction cosines was obtained by Schonland's procedure.<sup>8</sup> These parameters were used in the second order perturbation formulas given by Keitzers *et al.*<sup>9</sup> to obtain refined principal  $g$  and  $A$  values. An estimate of the quadrupole coupling constants was also made by introducing these values to improve the agreement between the observed and calculated positions of the allowed hyperfine transitions. In evaluating the spin Hamiltonian parameters of D and E centers, the proton SHF interaction was neglected. The angular variation of the field positions corresponding to the Br hyperfine interaction of the A and B centers are shown in Fig. 5 and those of D and E are given in Fig. 6. It can be seen that each one of these centers occurs at two magnetically inequivalent sites. The spin Hamiltonian parameters of the bromine containing radicals of the A, B, D, and E centers are given in Table II.

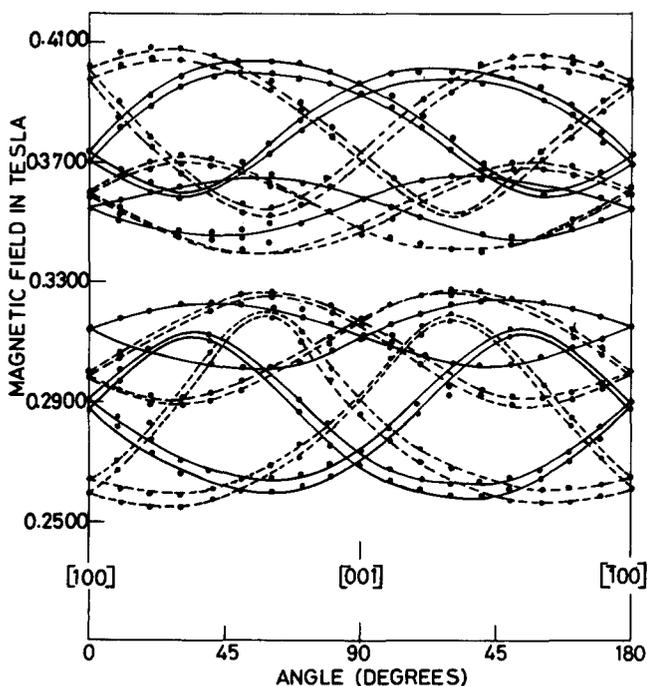


FIG. 5. Angular variation plot of the field positions of  $\text{BrO}_2$  radicals observed at 300 K in  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystal after  $\gamma$  irradiation at 300 K. The field lies in (010) plane.

#### IDENTIFICATION

##### Centers A and B

These centers are characterized by large  $g$  and  $A$  anisotropy and a large asymmetry parameter ( $\eta \approx 0.7$ ). From the nature of the spin Hamiltonian parameters A and B could be easily identified as  $\text{BrO}_2$  radicals. But the spin Hamiltonian parameters for these two centers are slightly different and the direction cosines of their principal  $g$  values are not related to those of A by crystallographic symmetry rotations. Besides, these centers are characterized by different decay behavior under the effect of thermal or UV light bleaching as can be seen from Fig. 7. Hence, A and B centers are identified as  $\text{BrO}_2$  radicals trapped at two chemically inequivalent sites and they must have obviously been formed by the dissociation of the crystallographically inequivalent  $\text{BrO}_3^-$  ions.

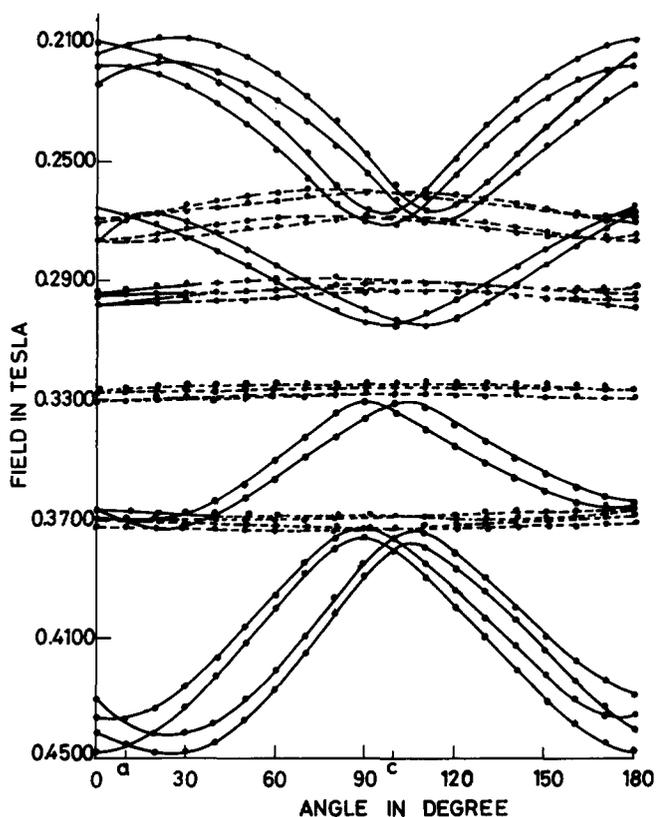


FIG. 6. Angular variation plot of  $\text{BrO}_3$  radicals recorded at 77 K in  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  single crystal after  $\gamma$  irradiation at 77 K. The field lies in (010) plane.

### Center C

The center C obviously contains only oxygen atoms. The line position of this radical is highly anisotropic and it can be seen from the ESR spectra that the radical is trapped at two magnetically inequivalent sites. The  $g$  value of this center is found to be between 2.002 and 2.018. This center

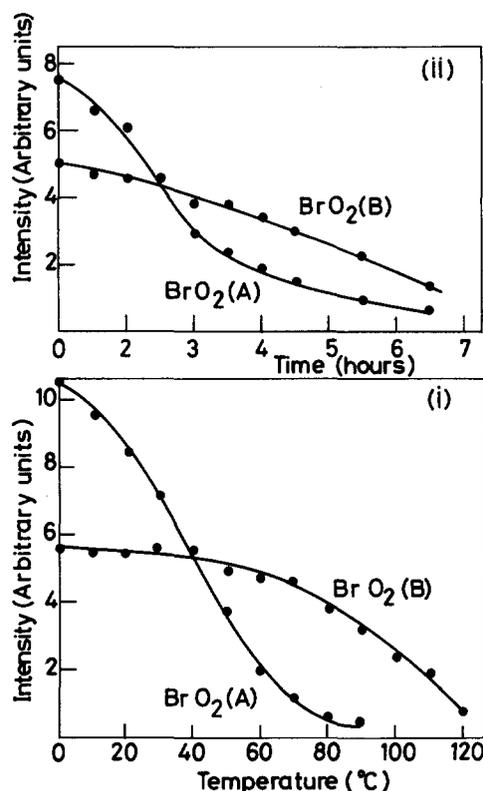


FIG. 7. Bleaching characteristics of ESR transition of A and B radicals; (i) after 30 min of thermal bleaching at each temperature, and (ii) after UV bleaching at 300 K at equal intervals of time (1 h).

was found to be extremely stable to thermal or UV light bleaching and has been identified to be  $\text{O}_3^-$  center.

### Centers D and E

These centers are characterized by a large isotropic component of the  $A$  tensor and the  $g_{11}$  is nearly equal to the

TABLE II. ESR parameters for  $^{81}\text{Br}$  of paramagnetic defect centers observed in  $\gamma$  irradiated  $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$  along with those reported for  $^{81}\text{BrO}_2$  and  $^{81}\text{BrO}_3$  in earlier studies.

Radical	Lattice <sup>a</sup>	Principal $g$ values			Principal $a$ values ( $\times 10^{-4}T$ )				$ e^2qQ $ MHz	$\eta$	Ref.
		$g_{xx}$	$g_{yy}$	$g_{zz}$	$A_{xx}$	$A_{yy}$	$A_{zz}$	$A_{iso}$			
$\text{BrO}_2$	$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ (300)	1.981	2.055	2.046	450	-130	-110	70	...	...	15
$\text{BrO}_2$	$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}^b$ (300)	2.005	2.056	2.068	483	-172	-121	633	...	...	3
$\text{BrO}_2$	$\text{KBrO}_4$ (100)	1.9958	2.0515	2.0299	325	-103	-115	34	372	0.9	16
$A$ ( $\text{BrO}_2$ )	$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ (300)	2.002	2.052	2.034	475	-125	-140	70	360	0.8	Present
$B$ ( $\text{BrO}_2$ )	$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ (300)	1.998	2.061	2.040	430	-105	-105	68	365	0.7	Present
$\text{BrO}_3$	$\text{KNO}_3 \cdot \text{KBrO}_3$ (77)	2.024	2.024	2.004	580	580	819		222	$\approx 0$	11
$D$ ( $\text{BrO}_3$ )	$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ (77)	2.033	2.035	2.002	440	440	640		210	0	Present
$E$ ( $\text{BrO}_3$ )	$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ (77)	2.031	2.032	2.005	450	450	670		220	0	Present

<sup>a</sup> The temperature of study is indicated in the bracket.

<sup>b</sup> Poly crystalline samples.

free spin value. These radicals exhibit the near axial symmetry of the well known ClO<sub>3</sub> radicals. Hence these radicals are supposed to be BrO<sub>3</sub> which is also a 25 valence electron radical like ClO<sub>3</sub>.<sup>10</sup> However, the parameters of the *D* and *E* radicals show slight differences and therefore they are supposed to be two chemically inequivalent BrO<sub>3</sub> radicals. Their chemical inequivalence was also reflected in the different decay characteristics of these radicals under thermal bleaching. Besides, there is a considerable reduction in the principal *A* values of these centers when compared to those of BrO<sub>3</sub> radicals observed in KBrO<sub>3</sub>·KNO<sub>3</sub> single crystals.<sup>11</sup> This indicates a considerable reduction in the unpaired electron spin densities  $a_s^2$  or  $a_p^2$  residing in the bromine 4*s* and 4*p* orbitals, respectively. It has been mentioned that there are two inequivalent protons interacting with these radicals and the maximum SHF splittings due to these two are around 35 and 15 G, respectively. Thus there must have been a considerable transfer of unpaired electron density in the bromine 4*s* and 4*p* orbitals. However, the *p/s* value (ratio of  $a_p^2$  to  $a_s^2$ ) remains around 4.0 indicating an *sp*<sup>3</sup> hybridizing molecular orbital on the bromine. Hence the present radicals can be considered as H...BrO<sub>3</sub>...HO type centers. The two nearest protons to the BrO<sub>3</sub><sup>-</sup> ion belong to two crystallographically inequivalent water molecules according to the crystal structure.

## DISCUSSION

### Orientation of the radicals

The principal *g* and *A* values are related to the BrO<sub>2</sub> molecular geometry in the same way as those of ClO<sub>2</sub> since these two radicals possess C<sub>2v</sub> symmetry with 19 valence electrons. The maximum *g* value of  $g_{yy}$  will be along 0–0 direction in BrO<sub>2</sub> and the minimum *g* value of  $g_{xx}$  will be perpendicular to the BrO<sub>2</sub> molecular plane. The intermediate *g* and *A* values lie along the C<sub>2v</sub> symmetry axis. From a comparison of the direction cosines of  $g_{yy}$  obtained from the experiment with those calculated from the crystal structure the following conclusions can be drawn regarding the orientations of A and B centers which are identified as BrO<sub>2</sub> radicals. The direction cosines (0.234, -0.3473, 0.908) calculated for O(21)–O(22) are in good agreement with the direction cosines (0.079, -0.276, 0.983) obtained for  $g_{yy}$  for BrO<sub>2</sub>(B) from the experiment. Hence this radical must have formed by the dissociation of Br(2)–O(23) bond which is 1.68 Å. Similarly the experimental direction cosines of  $g_{yy}$  of BrO<sub>2</sub>(A) (-0.574, 0.366, 0.733) are in good agreement with the values (-0.561, 0.35, 0.75) obtained from the crystal structure and therefore this radical must have formed by the dissociation of Br(1)–O(12) bond which is 1.70 Å.

For 25 valence electron radical like ClO<sub>3</sub> or BrO<sub>3</sub> with C<sub>3v</sub> symmetry the minimum principal *g* value lies along the C<sub>3v</sub> direction. From these considerations it could be seen that the centers D and E are formed at the BrO<sub>3</sub><sup>-</sup> (1) and BrO<sub>3</sub><sup>-</sup> sites, respectively.

### Stability of the radicals

It has been mentioned that both BrO<sub>2</sub>(A) and BrO<sub>2</sub>(B) are unstable to thermal as well as UV bleaching and the

decay characteristics of these two centers are different. Similar differences in the decay characteristics of BrO<sub>3</sub>(D) and BrO<sub>3</sub>(E) were formed. This inequivalence can be attributed to the crystallographic inequivalence of BrO<sub>3</sub><sup>-</sup> (1) and BrO<sub>3</sub><sup>-</sup> (2) ions and also to their different proton environments which can be seen from the distances of the water oxygens from the oxygen atoms of BrO<sub>3</sub><sup>-</sup> ions as given below:

$$\begin{aligned} O_w(2)-O(13) &= 1.87 \text{ \AA}, \\ O_w(1)-O(11) &= 3.06 \text{ \AA}, \\ O_w(2)-O(23) &= 2.91 \text{ \AA}, \\ O_w(1)-O(22) &= 2.94 \text{ \AA}. \end{aligned}$$

### Optical absorption at 300 K

Figure 3 shows the optical absorption spectrum recorded at 300 K in Cd(BrO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O single crystals after  $\gamma$  irradiated for 6 h at 300 K. The BrO<sup>-</sup> ion is supposed to give an optical band around 330 nm.<sup>12</sup> Hence the peak observed around 330 nm can be assigned to the presence of this diamagnetic radical in the irradiated single crystal. The band observed around 470 nm can be attributed to BrO<sub>2</sub> radicals which can be said from the earlier investigations on BrO<sub>2</sub> (in solution) and O<sub>3</sub><sup>-</sup> radicals, which given an optical absorption peak around 460 nm as can be seen from Table III. By a comparison of the bleaching characteristics of this band with those of BrO<sub>2</sub>(A) and BrO<sub>2</sub>(B) radicals, this band is assigned to BrO<sub>2</sub> radicals. The fact that this band is unaffected after certain amount of bleaching either thermally or by UV light indicates that there may be another radical whose optical absorption band lies in the same regions. This radical is supposed to be O<sub>3</sub><sup>-</sup> and evidence is also obtained for the presence of this radical from the ESR spectra recorded after BrO<sub>2</sub>(A) and BrO<sub>2</sub>(B) radicals were completely bleached out. Though the optical absorption for BrO<sub>2</sub> was reported earlier in solution, it is for the first time that its optical absorption around 470 nm was confirmed through the correlation of ESR and optical absorption studies.

Since BrO<sub>2</sub>(A) and BrO<sub>2</sub>(B) are chemically inequivalent

TABLE III. Optical absorption (O.A.) diffuse reflectance (D.R.) band position of oxy-radicals of bromine (n.p. neutron irradiated powder,  $\gamma$  aq.  $\gamma$ -irradiated aqueous solution,  $\gamma$  p.  $\gamma$ -irradiated powder, F.P. Flash photolysis).

Lattice	Band Position (nm)					Ref.
	BrO <sup>-</sup>	BrO	BrO <sub>2</sub>	BrO <sub>2</sub>	O <sub>3</sub> <sup>-</sup>	
KBrO <sub>3</sub> n.p.TC (D.R.)	330		285		450	17
NaBrO <sub>3</sub> n.p. (D.R.)	330				450	17
Sr(BrO <sub>3</sub> ) <sub>2</sub> $\gamma$ aq. (O.A.)	330				450	18
Cs(BrO <sub>3</sub> ) <sub>2</sub> $\gamma$ p. (D.R.)	330					
Solution (F.P.) (O.A.)		350		475		19
Solution (F.P.) (O.A.)					(340–360)*	20
Cd(BrO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	330			470	470	Present

\* Transient species.

species, they can be expected to give optical absorption peaks at slightly different wavelengths. However, no such splittings of the 470 nm could be observed in the optical absorption spectra recorded even at 77 K, probably because such splitting lies within the width of the optical absorption band due to BrO<sub>2</sub> and O<sub>3</sub><sup>-</sup> centers.

### RADIATION DAMAGE MECHANISMS

The radiation damage mechanisms in this crystal seems to be different from those present in other divalent bromates and also chlorates. In comparable Cd(ClO<sub>3</sub>)<sub>2</sub> single crystals  $\gamma$  irradiated at 300 K ClO<sub>2</sub> and Cl-ClO<sub>2</sub><sup>-</sup> centers were observed and V<sub>k</sub> (Cl<sub>2</sub><sup>-</sup>) centers were observed after UV bleaching.<sup>4</sup> Though ESR studies were carried out on several divalent chlorates they were mostly confined to irradiation at 300 K. In Sr(BrO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O or Ba(BrO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O single crystals.  $\gamma$  irradiated at 77 K essentially BrO<sub>3</sub><sup>2-</sup> radicals were observed.<sup>1,2</sup> However in a recent report on the ESR studies of KClO<sub>3</sub> single crystals irradiated at low temperatures it has been mentioned that in divalent chlorates like Sr(ClO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O or Ba(ClO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O after irradiation at 77 K ClO<sub>3</sub><sup>2-</sup> radicals could be observed.<sup>13</sup> Among chlorates ClO<sub>3</sub> was reported in NaClO<sub>3</sub> single crystals  $\gamma$  irradiated at 26 K.<sup>14</sup> Therefore the observations of BrO<sub>3</sub> and BrO<sub>2</sub> after irradiation at 77 or 300 K suggest that the radiation damage mechanisms in Cd(BrO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O are different from those of other divalent bromates and chlorates so far studied. The following radiation damage mechanisms can be proposed to be present in this lattice.

(i) Irradiation at 77 K.



Reaction (3) can be proposed since BrO<sub>3</sub><sup>2-</sup> centers not identified in this lattice. BrO is paramagnetic radical and is characterized by a fast spin lattice relaxation due to its degenerate ground state and hence cannot be observed even at 77 K, O<sub>2</sub><sup>2-</sup> is a diamagnetic radical.

(ii)  $\gamma$  irradiation at 300 K.



Since BrO<sub>3</sub> is unstable at 300 K, the primary product is supposed to decompose into BrO<sub>2</sub> or oxygen atoms. Reactions (5) and (6) can be proposed because the present experimental evidence suggests the presence of O<sub>3</sub><sup>-</sup> and also BrO<sup>-</sup>.

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