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D. L. Sastry and K. V. S. Rama Rao

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D. L. Sastry and K. V. S. Rama Rao

Department of Physics, Indian Institute of Technology, Madras 600 036, India

The paramagnetic defect centers observed in $Sr(BrO_3)_2 \cdot H_2O$ single crystals γ irradiated at 300 K are identified as pseudo V_k centers of the type (A) $(^bBr{-}^aBrO_2)^-$ and (B) $(^bBrO_3{-}^aBrO_2)^-$. Both these centers occur at one site each. A comparison of the experimentally observed direction cosines with those calculated from the crystal structure shows that the separation between the secondary bromine (^bBr) and primary bromine (^aBr) nuclei is 0.366 nm in the case of radical (A) and 0.369 nm in the case of radical B. In addition, O_3^- and O^- paramagnetic centers and a BrO^- diamagnetic center have also been observed in the crystals γ irradiated at 300 K. After γ irradiation at 77 K, BrO_3^{2-} centers occuring at two magnetically inequivalent sites were observed. Thermal and UV light bleaching effects on these centers are discussed.

INTRODUCTION

Radiolysis of alkaline earth bromates have been studied extensively by chemical analysis method.[1,2] There have been no detailed investigations using the technique of electron spin resonance (ESR) spectroscopy on the nature of paramagnetic radicals produced in the single crystals of these compounds. However, some of the alkaline earth bromates were studied in the form of frozen aqueous glasses after γ irradiation at low temperatures in order to identify bromine containing paramagnetic radicals which are comparable to known oxy radicals of chlorine.[3] But the information obtainable from such studies is limited due to the inherent difficulties present in interpreting the spectra of randomly oriented species. Besides, detailed ESR investigations of γ irradiated single crystals of bromates were confined only to $KBrO_3$.[4-6] Among divalent bromates only $Zn(BrO_3)_2 \cdot 6H_2O$ was studied after γ irradiation at 300 K for the detection of BrO_2 radicals.[7] It is interesting to note that no bromine containing radicals were observed in monovalent bromates like $NaBrO_3$[8] after γ irradiation at 300 K whereas chlorine containing radicals were observed in similar chlorates.[9,10] There have been extensive ESR studies on irradiated single crystals of divalent chlorates[11-15] and the results obtained in similar divalent bromates can be expected to show interesting differences. The present studies on the single crystals of $Sr(BrO_3)_2 \cdot H_2O$, γ irradiated at 300 and 77 K are expected to help not only in understanding the nature of paramagnetic defect centers formed in this lattice in particular but also the possible radiation damage mechanisms present in the alkaline earth bromates, in general.

EXPERIMENTAL

Commercially available $Sr(BrO_3)_2 \cdot H_2O$ of 99.99% purity supplied by Cerac, U.S.A. was used in all the studies. The single crystals were grown by slow evaporation of the aqueous solution over silica gel. Deuterated single crystals were similarly grown from a solution of the dehydrated substance (complete dehydration temperature is 120 °C)[16] in heavy water of ~98% purity. Well formed single crystals with prominent

(110) and (1$\bar{1}$0) faces were obtained. A ^{60}Co γ-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 temperature variation studies. A vacuum oven with ± 2 °C accuracy for thermal bleaching and a mercury lamp with a UV filter for optical bleaching were employed. A Cary-14 spectrometer was used for recording the optical absorption spectra at 300 K. For verification, some of the ESR spectra were also recorded on an AEG Q-band spectrometer employing 100 KHz field modulation.

ESR spectra were recorded by rotating the single crystals about three mutually perpendicular directions (i) [001], (ii) [110]*, which is perpendicular to (110) face, and (iii) a direction which is mutually perpendicular to the former two and which is denoted as III in this paper. DPPH g value of 2.0036, was used as an internal standard for evaluating the g parameters.

The crystal structure of this substance is not known. Therefore, intensity data of the diffracted x-rays were collected on a computer automated Enraf Nonius CAD 4 diffractometer using Mo K_α radiation for solving the crystal structure of $Sr(BrO_3)_2 \cdot H_2O$.

CRYSTAL STRUCTURE

Preliminary studies have shown that these crystals belong to a monoclinic class with four molecules per unit cell.[17] The space group is $C_{2/c}$ and the unit cell dimensions are $a = 1.2703$, $b = 0.7609$, $c = 0.9375$ nm, and $\beta = 135.71°$. The atomic positions were obtained by the usual heavy atom technique and least squares refinement employing full matrix diagonalization.[18] The final agreement factor (R) obtained was 0.12 after using isotropic temperature factors. Corrections for absorption and extinction were not applied in the refinement of the structure in the present studies. The positions of the individual atoms and their isotropic temperature factors are given in Table I. Figure 1 shows the projection of unit cell of this crystal. The structure of $Sr(BrO_3)_2 \cdot H_2O$ seems to be very similar to that of

TABLE I. Atomic positions and isotropic temperature factors (B) in $Sr(BrO_3)_2$ $\cdot H_2O$.

| Atom | Fractional coordinates | | | |
	x	y	z	$B^0(nm^2)$
Sr	0	0.399	0.75	0.072
Br	0.245	0.226	0.301	0.024
O_1	0.425	0.167	0.483	0.097
O_2	0.239	0.413	0.391	0.130
O_3	0.225	0.297	0.118	0.114
O_w	0	0.075	0.75	0.249

$Ba(BrO_3)_2 \cdot H_2O$.[19] However, BrO_3^- geometries in the two structures show large differences as can be seen from Table II. The possible reason for this discrepancy is supposed to be due to a slight error in the location of one of the oxygen atoms of $Ba(BrO_3)_2$. This observation has also been borne out in the calculations of the quadrupole coupling constant of the BrO_3^- ions in the two crystals using the CNDO/2 method of MO calculations.[20,21]

RESULTS

Irradiation at 300 K

For ESR studies at X-band frequencies large single crystals of the dimensions $7 \times 6 \times 4$ mm were subjected to prolonged γ irradiation for 20 to 30 h. The crystals developed purple coloration and the spectra recorded revealed the presence of several paramagnetic defect centers. These centers are identified as A, B, C, and D as is shown in Fig. 2. Of these, A and B are identified as bromine containing centers from the presence of characteristic nuclear hyperfine interaction due to ^{81}Br and ^{79}Br ($I = 3/2$ for both). Each of A and B centers is supposed to contain a primary bromine nucleus (^aBr) which gives rise to a major hyperfine interaction

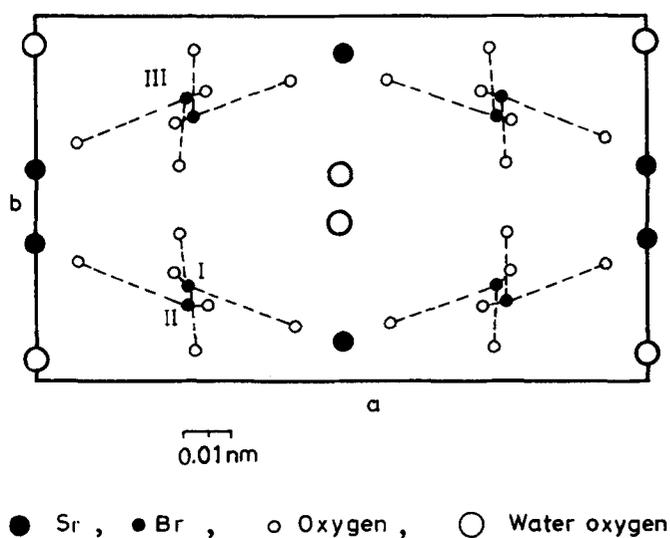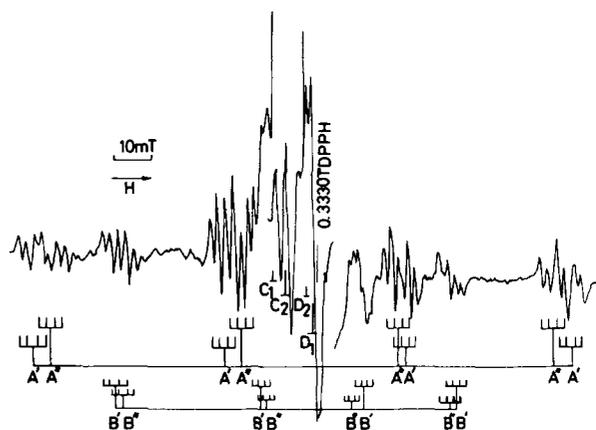FIG. 2. X-band ESR spectrum at 300 K of $Sr(BrO_3)_2 \cdot H_2O$ single crystal γ irradiated at 300 K. H lies in (001) plane at an angle 40° from III. Primes and double primes indicate ^{81}Br and ^{79}Br transitions, respectively.

and a secondary bromine nucleus (^bBr) which gives rise to a minor hyperfine interaction. Each of ^{81}Br and ^{79}Br hyperfine transitions of A and B centers corresponding to ^aBr is further split into four lines due to the hyperfine interaction from ^bBr. Owing to the superposition of the resulting eight lines, a pattern of bunches containing five to six lines can be seen. However, the ^{81}Br and ^{79}Br hyperfine transitions corresponding to ^bBr could not be resolved as the linewidths are large ($\approx 12 \times 10^{-4}$ T) and the ^bBr hyperfine splitting is small ($\approx 20 \times 10^{-4}$ T). The spectra recorded in the deuterated crystals were essentially the same except for a slight narrowing of the lines. Similarly, the spectra obtained at the Q-band frequencies were also the same as those obtained at X-band and the spacings between different lines in the "bunches" corresponding to A and B remained constant. These observations confirm that these bunches are hyperfine lines and arise from the presence of a secondary bromine nucleus in A and B centers. The primary bromine and the secondary bromine hyperfine interactions exhibit considerable second order effects due to large magnetic dipole and electric quadrupole moments of the bromine nuclei. The centers C and D do not exhibit any bromine nuclear hyperfine interaction and probably contain only oxygen nuclei (since $I = 0$ for O^{16}). All the centers were extremely stable when the irradiated crystals were stored in the

FIG. 1. Projection of the crystal structure of $Sr(BrO_3)_2 \cdot H_2O$ on (001) plane.

● Sr , ● Br , o Oxygen , ○ Water oxygen

0.01 nm

TABLE II. Comparison of BrO_3^- structure in $Sr(BrO_3)_2 \cdot H_2O$ and $Ba(BrO_3)_2 \cdot H_2O$.[a]

Bond lengths and bond angles	$Ba(BrO_3)_2 \cdot H_2O$	$Sr(BrO_3)_2 \cdot H_2O$
$Br-O_1$ (nm)	0.142	0.164
$Br-O_2$ (nm)	0.152	0.166
$Br-O_3$ (nm)	0.172	0.169
O_1-Br-O_2	132.9°	103.5°
O_1-Br-O_3	100.24°	102.4°
O_2-Br-O_3	108.5°	103.9°

[a]Calculated from Ref. 19.

dark. But A and B centers were completely bleached when subjected to 4 to 5 h of UV bleaching or thermal bleaching for one hour at 343 K. The intensities of the lines due to C and D remained constant in both the cases. Optical absorption spectra were recorded in thin transparent single crystals (5×3×1 mm) irradiated for nearly 10 h. Two prominent bands, one around 350 nm and the other in the region 450–475 nm were observed as can be seen from Fig. 3.

Irradiation at 77 K

Single crystals of the dimension 3×2×2 mm were irradiated for 6 to 7 h at 77 K. The crystals developed a deep bluish coloration and ESR spectra were recorded at X-band. Two paramagnetic centers E_1 and E_2 each obviously containing a bromine nucleus were observed as can be seen from Fig. 4. These spectra are also characteristic of large second order effects. The hyperfine interaction for these centers is much larger than that observed for the primary bromine nucleus of A and B centers observed at 300 K. Besides E_1 and E_2 centers differ markedly from A and B in the absence of the hyperfine interaction from a secondary bromine nucleus.

Calculation of ESR parameters

The ESR spectra of A and B centers (considering only the ^aBr hyperfine interaction) and E_1 and E_2 centers can be described by the following Hamiltonian in which the nuclear Zeeman interaction is neglected:

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

A preliminary estimate of the principal g and A values and their direction cosines was obtained by Schonland's
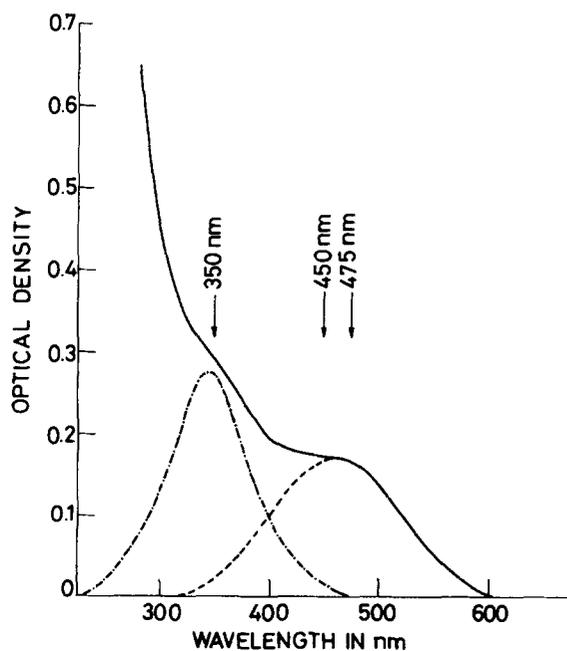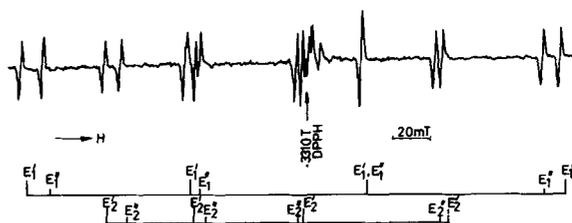

FIG. 4. ESR spectrum at 77 K of $Sr(BrO_3)_2 \cdot H_2O$ single crystal γ irradiated at 77 K. H lies in (001) plane along [110]* direction. Primes and double primes indicate ^{81}Br and ^{79}Br transitions, respectively.

procedure.[22] These parameters were used in the second order perturbation formulas given by Keitzers et al.[23] 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 principal values of ^bBr superhyperfine (SHF) interaction of A and B centers second order effects observed in this interaction due to the large quadrupole coupling constant and magnetic moment of the bromine nucleus were neglected for convenience in computation. The maximum and minimum average splittings were obtained by least square fitting and the principal shf values and their direction cosines were obtained by Schonland's procedure.[22]

The angular variation of the field positions corresponding to the ^aBr hyperfine interaction and the average shf splittings due to ^bBr are shown in Fig. 5 in the case of A and B centers. The angular variation of the field positions corresponding to E_1 and E_2 centers are shown in Fig. 6. Only one site was observed for A and B centers whereas E_1 and E_2 are identified as the same center trapped at two magnetically inequivalent sites. The parameters of all the bromine containing radicals observed in the present studies are given in Tables III and IV.

IDENTIFICATION

Centers A and B

The centers are characterized by highly anisotropic principal g and A (^aBr) values. The natures of these values are very much similar to that of well known ClO_2 radicals. These centers are supposed to be mainly BrO_2 radicals from a comparison of the present data with those reported for this radical in other matrices (Tables III and IV). The signs were assigned following the earlier convention adopted for 19 valence electron radicals. Though A and B are essentially the same centers there are differences in their principal g, A (^aBr) and A^{shf} (^bBr) values. These differences are attributed to the presence of a secondary bromine nucleus (^bBr). The value of the p/s ratio (a_p^2/a_s^2) depends on the amount of hybridization in the molecular orbital on the atom giving rise to nulear hyperfine interaction.[9] The value obtained for ^bBr shf interaction in the case of

FIG. 3. Optical absorption spectrum recorded at 300 K in the single crystal of $Sr(BrO_3)_2 \cdot H_2O$ γ irradiated at 300 K.
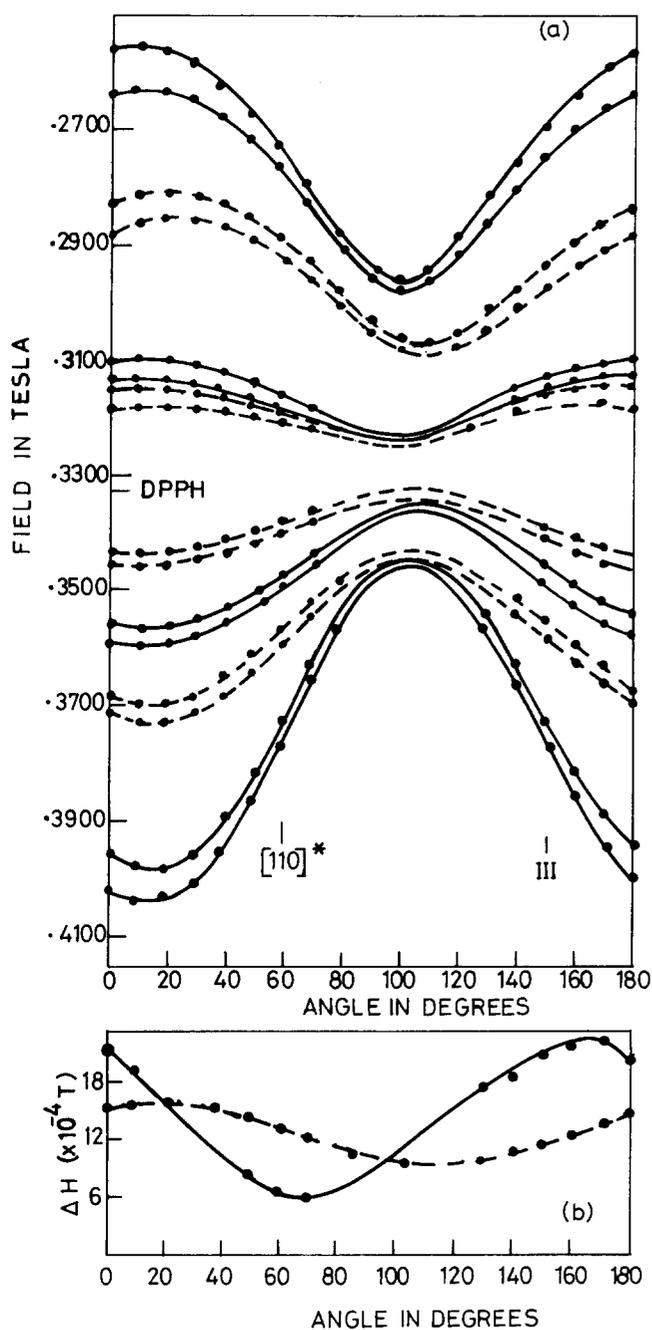
FIG. 5. Angular variation of the line positions of A (—) and B (- - -) centers at 300 K in $Sr(BrO_3)_2 \cdot H_2O$ single crystals γ irradiated at 300 K. H lies in (001) plane. (i) ^aBr hyperfine transitions; and (ii) ^bBr hyperfine splitting (ΔH).

radical A was greater than 17 and was less than eight in the case of radical B. This shows that there is no possibility of any hybridization on the ^bBr in the case of radical A, whereas such a possibility exists in the case of radical B. Since ^bBr shf interaction in the case of radical A seems to be caused by the involvement of essentially π orbitals, the perturbing fragment containing ^bBr in this case is supposed to be Br^- and the radical A is identified as $(^bBr-^aBrO_2)^-$. Similarly, since there seems to be considerable involvement of s and p orbitals of ^bBr in giving rise to the shf splitting in the

case of radical B, the perturbing fragment in this case is supposed to be BrO_3^- which contains an sp^3 hybridized molecular orbital on Br. Since there is no other suitable alternative this center is supposed to be $(^bBrO_3 - ^aBrO_2)^-$.

Radicals C and D

These species obviously contain only oxygen atoms. Detailed analysis for these centers was not carried out. The line positions of both these radicals are highly anisotropic and it can be seen from their ESR spectra that these radicals occupy at least two magnetically inequivalent sites each. The centers C and D with their g values varying between 2.000 to 2.065 and 2.002 to 2.017 have been, respectively, assigned to be O^- and O_3^- in the present studies.

Centers E_1 and E_2

These centers are characterized by nearly axial principal g and A values, a large quadrupole coupling constant and a large asymmetry parameter ($\eta = 0.4$). From the nature of their spin Hamiltonian parameters (Tables III and IV), these centers have been identified as BrO_3^{2-} radicals trapped at two magnetically inequivalent sites.

DISCUSSION

The formation of BrO_3^{2-} centers after γ irradiation at 77 K is similar to the identification of these centers in
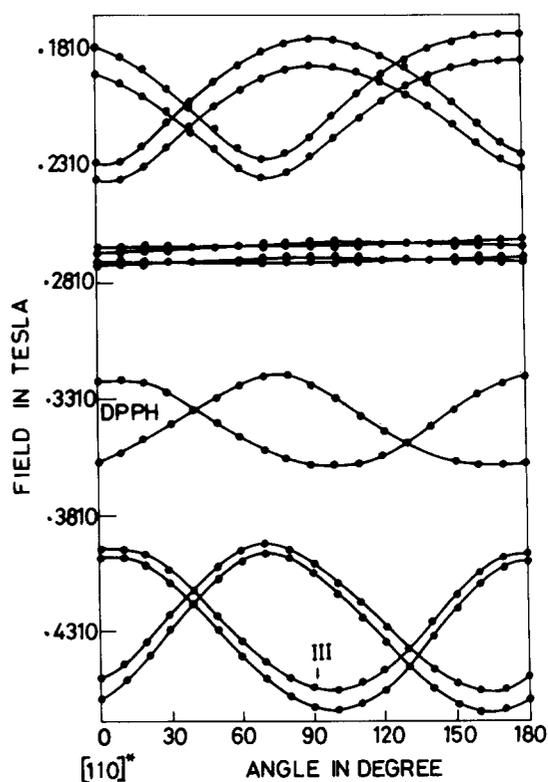

FIG. 6. Angular variation of the line positions at 77 K of E_1 and E_2 centers in $Sr(BrO_3)_2 \cdot H_2O$ single crystals γ irradiated at 77 K. H lies in (001) plane.

TABLE III. Principal g and A values for ^{81}Br of paramagnetic centers observed in $Sr(BrO_3)_2 \cdot H_2O$ along with those of BrO_2 and BrO_3^{2-} observed in other matrices.

Center	Matrix[a]	Principal g values				Principal A values ($\times 10^{-4}$ T)				Ref.
		g_{xx}	g_{yy}	g_{zz}	g_{av}	A_{xx}	A_{yy}	A_{zz}	A_{iso}	
BrO_2	$Zn(BrO_3)_2 \cdot 6H_2O$ (300)	1.981	2.055	2.046	2.027	450	−130	−110	70	7
BrO_2	$Zn(BrO_3)_2 \cdot 6H_2O$ (300)	2.005	2.056	2.068	2.042	483	−172	−121	63.3	3
BrO_2	$KBrO_4$ (100)	1.9958	2.0515	2.0299	2.026	325	−103	−115	34	27
BrO_3^{2-}	$KBrO_3$ (77)	2.008	2.038	2.00	2.015	430	480	800	570	5
A	$Sr(BrO_3)_2 \cdot H_2O$ (300)	1.997	2.065	2.022	2.028	535	−132	−60	114	Present studies
B	$Sr(BrO_3)_2 \cdot H_2O$ (300)	2.012	2.058	2.028	2.032	371	−145	−93	44	...do...
E_1	$Sr(BrO_3)_2 \cdot H_2O$ (77)	2.007	2.041	2.001	2.016	490	490	844	608	...do...
E_2	$Sr(BrO_3)_2 \cdot H_2O$ (77)	2.005	2.042	2.000	2.016	500	495	862	619	...do...

[a]Temperature (K) at which studies were made is indicated in the brackets.

$KBrO_3$ single crystals x irradiated at low temperatures. However, the present observation of $(^bBr-^aBrO_2)^-$ (A) and $(^bBrO_3-^aBrO_2)^-$ (B) centers at 300 K is interesting since such an observation has not been reported earlier in monovalent or divalent bromates. However, the chlorine analog for center A was detected in $KClO_3^9$ after γ irradiation at 300 K. In those studies, the unperturbed ClO_2 centers were also observed unlike in the present case in which the unperturbed BrO_2 was not observed. A comparison of the observed and calculated direction cosines shows that the maximum A^{shf} of ^bBr for A agrees to within 15° with the direction of a vector connecting the two bromine atoms (I and II in Fig. 1) separated by 0.366 nm. Similarly, the maximum A^{shf} of ^bBr of B is found to agree to within 18° with the direc-

tion of a vector joining two bromine atoms (I and III in Fig. 1) separated by 0.369 nm. The intensities of the ESR lines due to the center A were observed to be slightly more than those of the center B indicating that the probability for the formation of center A is more than that of the center B. On the whole, the large radiation dosage required to produce A and B indicates their formation in low yields when compared to C and D which are oxygen containing species. A comparison of the center A with $(^bCl-^aClO_2)^-$ is shown in Table V which indicates interesting similarities between these two centers. The involvement of a heavy molecule like $^bBrO_3^-$ in the formation of B may be the reason for a larger change in its g_{xx} value when compared to that of A (Table III). The reduced hyperfine interaction of the

TABLE IV. Quadrupole coupling constants for ^{81}Br of A, B, E_1, and E_2 centers along with those of BrO_2 and BrO_3^{2-} and the principal shf coupling constants and their direction cosines for A and B.

Center	Matrix[a]	$\lvert e^2 q_{zz} Q \rvert$	η	Principal values of ^bBr SHF interaction ($\times 10^{-4}$ T)	The direction cosines with respect to [001], [110]* and III directions			Ref.
BrO_2	$KBrO_4$ (100)	372	0.9	···	···			27
BrO_3^{2-}	$KBrO_3$ (77)	570	0.26	···	···			5
A $(^bBr-^aBrO_2)^-$	$Sr(BrO_3)_2 \cdot H_2O$ (300)	360	0.7	$A_{xx}=28$ $A_{yy}=6$ $A_{zz}=6$	0.68 b b	−0.697 b b	−0.234 b b	Present studies
B $(^bBrO_3-^aBrO_2)^-$	$Sr(BrO_3)_2 \cdot H_2O$ (300)	365	0.7	$A_{xx}=23$ $A_{yy}=11$ $A_{zz}=11$	0.41 b b	−0.687 b b	0.657 b b	...do...
E_1 (BrO_3^{2-})	$Sr(BrO_3)_2 \cdot H_2O$ (77)	420	0.4	···	···			...do...
E_2 (BrO_3^{2-})	$Sr(BrO_3)_2 \cdot H_2O$ (77)	420	0.4	···	···			...do...

[a]Temperature at which studies were made is indicated in the brackets.   [b]Do not possess any significance.

TABLE V. Comparison of $(^bCl-^aClO_2)^-$ and $(^bBr-^aBrO_2)$ centers.

Centers	g_{av}	A_{iso}^a $(\times 10^{-4}$ T)		Unpaired electron spin density		p/s (a_p^2/a_s^2)	a_X-b_X distance
				a_s^2	a_p^2		
$(^bCl-^aClO_2)^{-b}$	2.0127	^aCl	22	0.01	0.68	68	$^bCl-^aCl$
		^bCl	5.3	0.003	0.085	26	$=0.365$ nm
$(^bBr-^aBrO_2)^-$	2.028	^aBr	114.0	0.0136	0.86	64	$^bBr-^aBr$
		^bBr	13.3	0.0015	0.026	17	$=0.366$ nm

^{a}Values correspond to ^{35}Cl and ^{81}Br. ^{b}Reference 9.

center B when compared to that of A may also be due to a considerable transfer of unpaired electron density on to the oxygen atoms of $^bBrO_3^-$. Both the centers $(^bBr-^aBrO_2)^-$ and $(^bBrO_3^--^aBrO_2)^-$ can be considered to be electronically similar to the V_k centers. Here the $^aBrO_2$ part behaves like an electron excess center and ^bBr or $^bBrO_3^-$ part becomes a hole like center. The large increase in the hyperfine coupling constant of $^aBrO_2$ part of $(^bBr-^aBrO_2)^-$ can be supposed to be due to a spin polarization mechanism as in the case of $(^aCl-^bClO_2)^-$.[9]

The BrO^- radical is supposed to give an optical absorption band around 330 nm[1,2,24] hence the optical absorption peak observed around 350 nm is supposed to be due to the presence of this center in the single crystals irradiated at 300 K. Both O_3^- and BrO_2 radicals are supposed to give an optical absorption peak around 460 nm.[25,26] The observation of an optical band in the 450–475 region in the present studies may be due to both O_3^- as well as BrO_2 part of the radicals A and B. However, any shift in the optical band position of BrO_2 due to the perturbing nuclei probably lies within the width of this band. In order to verify this observation unfortunately optical absorption spectra could not be recorded using the single crystals in which radicals A and B were thermally or optically bleached as the crystals lose their transparency after the decay of A and B. The extreme stability of C and D centers to thermal or optical bleaching is also in accordance with the observation that these are O^- and O_3^- centers since similar centers observed in $Ca(ClO_3)_2$ were found to exhibit such stability.[12] The BrO_3^{2-} centers formed at 77 K were found to gradually decay with thermal bleaching. These centers could be completely bleached around 210 K but no features corresponding to A and B centers could be detected in the ESR spectra as small crystals had to be used for low temperature experiments and also the relative yield of A and B centers is very low. However, when large single crystals subjected to prolonged irradiation at 77 K were warmed to 300 K and studied, the ESR spectra recorded were found to be same as those obtained after irradiation at 300 K. Since BrO_3^{2-} is an electron excess radical it is natural to expect a charge compensating species like BrO_3 to be present. Since no such species were observed, the charge compensation at 77 K might be taking place through the formation of other hole type center like BrO, the ESR spectra due to which cannot be detected even at 77 K owing to its fast spin lattice relaxation similar to that

of ClO.[9] Owing to lack of facilities, ESR experiments at low temperatures at Q-band frequencies were not carried out. Such experiments are expected to give a detailed understanding of the influence of the second order effects arising from the presence of secondary as well as the primary bromine nuclei on the ESR spectra of $(^bBr-^aBrO_2)^-$ and $(^bBrO_3-^aBrO_2)^-$ centers. Besides further interesting information regarding the geometric models of these new centers can be obtained by O^{17} substitution or ENDOR studies.

ACKNOWLEDGMENT

[1] J. W. Chase and G. E. Boyd, J. Phys. Chem. 70, 1031 (1966).

[2] T. Anderson, J. R. Byberg, and T. Olsen, Trans. Faraday Soc. 62, 2409 (1966).

[3] K. V. S. Rao and M. C. R. Symons, J. Chem. Soc. A 147 (1972).

[4] A. Begum, S. Subramanian, and M. C. R. Symons, J. Chem. Soc. A 1970, 916.

[5] J. R. Byberg and B. S. Kirkegaard, J. Chem. Phys. 60, 2594 (1974).

[6] J. R. Byberg, S. J. K. Jensen, B. S. Kirkegaard, J. Chem. Phys. 61, 138 (1974).

[7] M. A. Collins, M. M. Cosgrove, and G. P. Betteridge, J. Phys. B 240 (1976).

[8] M. A. Collins and M. M. Cosgrove, J. Chem. Phys. 52, 989 (1970).

[9] R. S. Eachus, P. R. Edwards, S. Subramanian, and M. C. R. Symons, J. Chem. Soc. A 1968, 1704.

[10] F. T. Gamble, J. Chem. Phys. 42, 3542 (1965).

[11] D. Suryanarayana and J. Sobhanadri, J. Phys. C 7, 3770 (1974).

[12] D. Suryanarayana and J. Sobhanadri, J. Magn. Reson. 16, 274 (1974).

[13] D. Suryanarayana and J. Sobhanadri, Mol. Phys. 28, 1127 (1974).

[14] D. Suryanarayana and J. Sobhanadri, J. Chem. Phys. 61, 2827 (1974).

[15] E. C. de Silva, I. C. L. Torriani, N. F. Leite, C. E. Hennies, C. Evora, and H. Varges, Phys. Status Solidi 97, 441 (1979).

[16] Handbook of Physics and Chemistry, edited by N. A. Lange (McGraw-Hill, New York, 1966).

[17] D. L. Sastry and K. V. S. Rama Rao, Z. Kistallogr. 152, 353 (1980).

[18] G. H. Stout and C. H. Jensen, X-ray Structure Determination (McMillan, London, 1968).

[19] G. Kartha, Proc. Indian Acad. Sci. A 38, 1 (1953).

[20]A. Valli and K. V. S. Rama Rao, J. Chem. Phys. **79**, 4113 (1983).

[21]A. Valli, Ph. D. thesis, Indian Institute of Technology, Madras, India, 1981.

[22]D. S. Schonland, Proc. Phys. Soc. London **73**, 788 (1959).

[23]C. P. Keijzers, G. F. M. Paulussen, and E. de Boer, Mol.

Phys. **26**, 973 (1973).

[24]G. E. Boyd and L. C. Brown, J. Phys. Chem. **74**, 3490 (1970).

[25]C. Ramanastry and Y. V. G. S. Murthy, Indian J. Pure Appl. Phys. **2**, 35 (1965).

[26]O. Amichai and E. Trenin, J. Phys. Chem. **74**, 830 (1970).

[27]J. R. Byberg, J. Chem. Phys. **55**, 4867 (1971).