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Radiation-produced electron and hole centres in oxygen-containing BaFBr: I. EPR and ODEPR studies

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Abstract. An O^- centre formed upon hole trapping by O^{2-} in x-irradiated BaFBr is long-lived at room temperature and has been detected by EPR below 30 K. It can also be produced in low concentrations by exposure of BaFBr to sub-bandgap (200–300 nm) radiation. The formation of $F(Br^-)$ centres at charge-compensating bromide ion vacancies is a corollary of the photoionization of O^{2-} . High concentrations of oxide have been successfully introduced into this material by doping with anhydrous BaO, including $Ba^{17}O$ for unambiguous identification of the O^- defect. Oxide addition and the formation of O^- produces a series of optical bands that have been assigned using a combination of optical and magneto-optical techniques. The influence of the material preparation conditions on the concentration of O^{2-} is discussed and possible mechanisms for the formation of O^- are proposed.

1. Introduction

Radiation damage in the alkali and alkaline earth halides is mediated by impurities, especially the ubiquitous oxide and superoxide anions. Oxide may substitute for halide or be incorporated interstitially and, thereby, become a Coulomb trap for excitons or mobile H or V_K centres. The products of these reactive trapping processes, namely paramagnetic O^- centres, have been studied extensively by EPR in the alkali halides (Sander 1962, 1964, Brailsford *et al* 1968, Brailsford and Morton 1969).

BaFBr crystallizes with the tetragonal PbFCl structure shown in figure 1 (Liebich and Nicollin 1977, Beck 1979). We are aware of no published experimental data regarding the defect structure of BaFBr. However, ionic conductivity measurements indicate Schottky disorder in the isostructural material BaFCl (Somaiah and Hari Babu 1983). Atomistic simulations predict Schottky-like defects, with barium and halide vacancies and the unusual feature of fluoride antisites (F^- substituting for Br^- or Cl^-) in these compounds (Baetzold 1987, 1988, 1991). If it is prepared by reaction at temperatures close to or above its melting point, the BaFBr produced on cooling is frequently non-stoichiometric with a slight excess of F^- (Stevens and Pingault 1975). Out-of-plane $Br_2^- V_K$ centres (Eachus and Nuttall 1988, Hangleiter *et al* 1990), $F(F^-)$ and $F(Br^-)$ (Takahashi *et al* 1984, Takahashi *et al* 1985, von Seggern *et al* 1988, Koschnick *et al* 1988, Koschnick *et al* 1990, 1991) are products of x-radiation damage.

The F centres can be stable in the dark for hours or days at room temperature, with the lifetime of $F(F^-)$ exceeding that of $F(Br^-)$ (Baetzold 1988, Takahashi *et al* 1985, Koschnick *et al* 1988, Koschnick *et al* 1991, Ye *et al* 1987). The $Br_2^- V_K$ centre is thought to diffuse above about 120 K (Eachus and Nuttall 1988, Hangleiter *et al* 1990) and is annihilated by a variety of processes that may include self-aggregation ($2Br_2^- \rightarrow Br_3^- + Br^-$ or $2Br_2^- \rightarrow Br_2 + 2Br^-$) (Baetzold 1991), reaction with impurities or recombination with F centres.

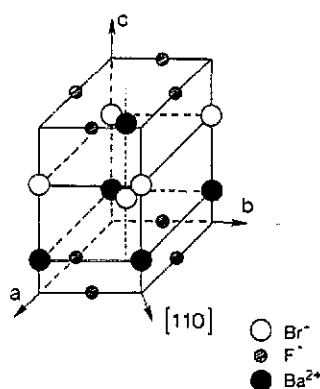


Figure 1. The structure of pure, stoichiometric BaFBr: $a = b \approx 4.503 \text{ \AA}$ and $c = 7.435 \text{ \AA}$ (Liebich and Nicollin 1977, Beck 1979).

This paper describes a study of the behaviour of an oxide impurity during the exposure of BaFBr to x- or UV-radiation. This defect functions as a deep hole trap during x-irradiation above 120 K and is weakly photoionized by UV light at room temperature. The resultant O^- centre has been detected by EPR and optically-detected EPR (ODEPR). The association of the EPR data with oxygen has been confirmed by doping with anhydrous BaO enriched to about 40% in the magnetic ^{17}O isotope ($I = 5/2$). Several absorption bands from the O^- centre were identified by ODEPR. An electron nuclear double resonance (ENDOR) investigation, presented in Part II of this series, showed that the O^- ion formed at room temperature occupies an F^- site in a regular lattice environment. Thus, the expected charge-compensating defect, assumed to be an anion vacancy formed upon the introduction of O^{2-} , diffuses away from the impurity above 200 K.

2. Experimental procedure

Single crystals of BaFBr were grown by the Bridgman method in graphite boats coated with pyrolytic graphite. These boats functioned as susceptors for a radio-frequency induction furnace. Mixtures of optical grade BaF_2 and refined $BaBr_2$ were first melted under high vacuum and then treated with high-purity bromine for several hours. Finally, ultra-pure carrier grade argon (Air Products) was passed over the molten material before crystal growth commenced. Neutron activation analyses of typical samples found that the only contaminants in concentrations greater than 3 ppm by weight were potassium and chlorine. However, this technique is not suitable for detecting low levels of oxygen impurities. Thus, we have no reliable estimates of the residual oxygen levels in our purified materials.

For oxide doping, anhydrous BaO was prepared from finely dispersed barium metal and oxygen at 650 °C. The barium metal was obtained from the controlled thermal decomposition of barium azide in high vacuum. For enrichment studies, 40% $^{17}\text{O}_2$ was used as the reactive gas. The finely dispersed BaO was mixed with vacuum-dried samples of BaFBr, melted under purified argon, and then cooled to produce polycrystalline material from which single-crystal samples were grown by the procedure described above.

Single crystals suitable for optical and EPR studies were cut from the boules with a diamond wire saw. The crystals cleaved easily perpendicular to the c axis. The a and b axes were identified by Laue x-ray back reflection measurements. The EPR measurements were made with a Varian E-12 X-band (9.15 GHz) spectrometer fitted with a Heli-TranTM continuous transfer cryogenic system (Air Products and Chemicals Ltd.) and a Lake-Shore Cryotronics DR93C temperature controller. Spectra were accumulated and analysed with a Macintosh II PC operating under the LabViewTM protocol (National Instruments, Inc.). X-irradiations were made using an Enraf-Nonius Diffractis 582 generator and Seifert SW60W tube operating at 40 KV and 40 mA, with the x-ray beam filtered through 4 mm Al. UV irradiations were performed with an Oriel 1 KW Hg-Xe lamp and appropriate narrow band interference filters. Optical absorption spectra were recorded with a Perkin-Elmer Lambda 9TM spectrophotometer. Magneto-optical and ODEPR spectra were measured with a computer-controlled, custom-built K -band ODEPR spectrometer, which was described previously (Ahlers *et al* 1983).

3. Results

3.1. X-irradiated BaFBr

Nominally pure BaFBr single crystals with a range of stoichiometries were studied. Within the compositional limits of $\text{BaF}_{0.95}\text{Br}_{1.05}$ to $\text{BaF}_{1.05}\text{Br}_{0.95}$, identical results were realised from all of the samples.

When x-irradiation was performed at 77 K, EPR measurements confirmed the production of the out-of-plane $\text{Br}_2^- V_K$ centre (Eachus and Nuttall 1988, Hangleiter *et al* 1990). Optical absorption measurements made with $E_{\perp}c$ revealed the concomitant formation of the well-known $\text{F}(\text{Br}^-)$ centre through the detection of a broad absorption band centred at about 2.15 eV (Hangleiter *et al* 1990, Takahashi *et al* 1984, Takahashi *et al* 1985, Koschnick *et al* 1991, Ye *et al* 1987). No optical absorption from $\text{F}(\text{F}^-)$, which should appear as a doublet at about 2.65 eV with $E_{\perp}c$ (Hangleiter *et al* 1990, Ye *et al* 1987), was observed following irradiation at this low temperature. Curve a in figure 2 shows the magnetic circular dichroism of the absorption (MCDA) of an oxide-doped sample x-irradiated at 4.2 K and measured at 1.5 K with $B = 3T$ orientated parallel to the c axis. The MCDA is the differential absorption of right and left-circularly polarized light. The MCDA of a perturbed $\text{F}(\text{Br}^-)$ centre (see below) is seen around 2.1 eV and the broad band between approximately 2.9 and 3.8 eV results from the V_K centre. These identifications were made on the basis of results from ODEPR experiments that will be published elsewhere (Koschnick *et al* 1991). Annealing of the irradiated crystal to about 120 K activated the decay of the V_K centre, probably through a simple intraplanar diffusion process that is facilitated by the unusual bromide double-layered structure of BaFBr (see figure 1) (Eachus and

Nuttall 1988, Baetzold 1989). At 120 K, the MCDA from $F(\text{Br}^-)$ decreased in intensity by about 50%. The MCDA and EPR signals associated with the V_K centre vanished completely at this temperature. During the decay of the V_K centre, the MCDA of $F(\text{Br}^-)$ centres was shifted by about 0.01 eV to higher energy. After warming to room temperature, it shifted further by about 0.04 eV to higher energy and a new, weak MCDA appeared in the original spectral region for the V_K centre (figure 2, curve b), centred around 3.26 eV. The blue-shifted band is the same as that obtained from the isolated $F(\text{Br}^-)$ centre in additively-coloured BaFBr (Koschnick *et al* 1991), demonstrating that the $F(\text{Br}^-)$ centre produced by x-irradiation at low temperatures is in a perturbed environment. ODEPR was insensitive to this perturbation; it was only detected by the slight energy shift of the MCDA peak. The loss of some $F(\text{Br}^-)$ centres during annealing is the result of their recombination with mobile V_K centres. This process is associated with a strong thermal luminescence peaking around 2.6 eV.

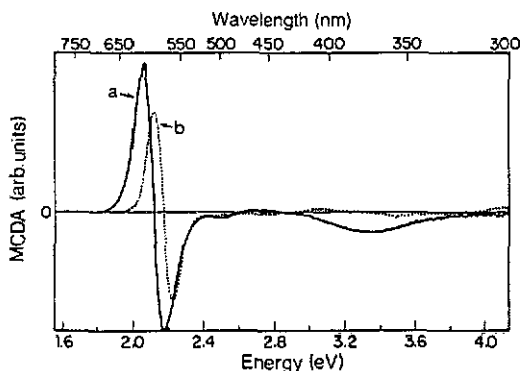


Figure 2. MCDA spectra obtained from a single crystal of O^{2-} -doped BaFBr with $B = 3.0$ T parallel to c . Curve (a): after x-irradiation at 4.2 K and cooling to 1.5 K. Curve (b): after x-irradiation at 4.2 K, annealing to 300 K and recooling to 1.5 K.

If a crystal was x-irradiated at temperatures below 140 K, annealed to 300 K, and then was cooled to about 50 K, a strong, new signal could be observed by EPR. At 50 K it was a broad, single line, but below 20 K it was resolved into a complex multiplet structure.

Figure 3 includes EPR spectra obtained from a single crystal of BaFBr after its exposure to x-radiation at 77 K for 300 s, annealing to 300 K and cooling to 10 ± 2 K. This material was not treated with bromine during crystal growth to remove residual oxygen impurity. Spectra with similar intensities were obtained from crystals exposed to x-rays for about 30 s at 300 K. The spectra in figure 3 were measured with the applied magnetic field parallel to a or b (figure 3(b)), or the four-fold crystal axis, c (figure 3(a)) (see figure 1 for orientations). The signals in figure 3 are assigned later to an O^- defect. Under the measurement conditions employed in these experiments, only weak, broad EPR signals could be resolved from the F centres observed optically.

Rotation data were obtained for the oxygen centre from the ab and ac planes. Only one symmetry site was observed; within the resolution of our experiment g was isotropic in the ab plane and slightly anisotropic in ac . The axially symmetric g matrix derived from these rotation data is included in table 1.

With B parallel to a or b , the spectrum was split into seven lines separated by 1.04 ± 0.05 mT (figure 3(b)). We tentatively attribute this septet to superhy-

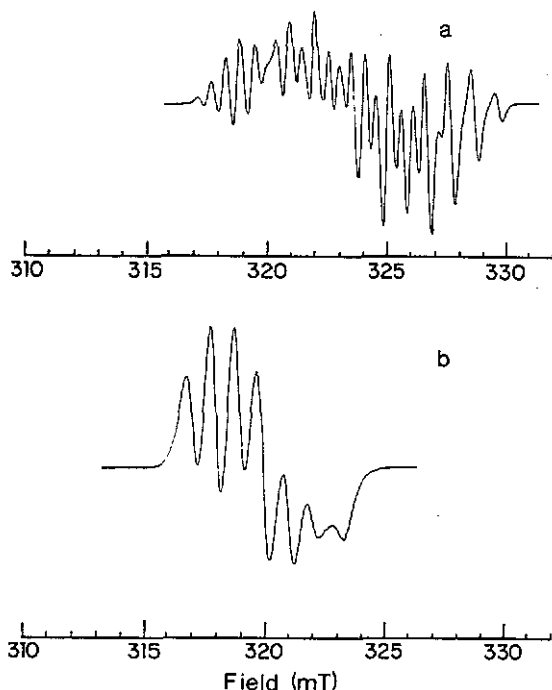


Figure 3. EPR spectra obtained from a single crystal of undoped BaFBr at 10 ± 2 K following 30 s exposure to x-rays at 300 K with (a) B parallel to c , and (b) B parallel to a (or b).

Table 1. EPR data for the O_F^- centre in BaFBr.

| g -matrix (± 0.0005) | ^{17}O Hyperfine Matrix |
|------------------------------|---|
| $g_{\perp} = 2.0419$ | $A_{\perp}/g\beta = 1.91 \pm 0.05$ mT |
| $g_{\parallel} = 2.0202^a$ | $A_{\parallel}/g\beta = 9.67 \pm 0.02$ mT |

^a The parallel principal direction was found to coincide with the c crystallographic axis.

perfine (SHF) interactions with two equivalent sets of bromine nuclei (^{79}Br : $I = 3/2$, 50.69%; ^{81}Br : $I = 3/2$, 49.31%), although it does not have the exact intensity distribution expected. The observed intensity distribution is the result of numerous secondary ^{19}F ($I = 1/2$, 100%), ^{135}Ba ($I = 3/2$, 6.59%) and ^{137}Ba ($I = 3/2$, 11.2%) SHF splittings buried within the septet structure, combined with unequal line separations and semi-forbidden transitions caused by bromine quadrupole interactions, as confirmed by the ENDOR investigations described in Part II. A similar seven-line spectrum was obtained from a rotation in the $c[110]$ plane (i.e., the plane containing the c and $[110]$ axes) at about 55° from the four-fold axis, but at this orientation the splitting was 1.18 ± 0.5 mT. This structure is again assigned to an interaction with two equivalent sets of bromine nuclei.

With B parallel to c , the EPR spectrum was asymmetric and consisted of at least 25 lines with no recognizable pattern (figure 3(a)). Finally, when B was parallel to $[110]$, the spectrum consisted of a single, symmetric line with halfwidth of about 3.8 mT. The

defect responsible for these EPR signals does not contain a central magnetic nucleus in high abundance, or a magnetic nucleus with a large nuclear moment. These conditions eliminate fluorine, bromine or barium as central nuclei. These spectra are not from F, H or V_K centres; therefore, an impurity ion is involved. Oxygen is the most reasonable candidate (Sander 1962, 1964, Brailsford *et al* 1968, Brailsford and Morton 1969).

Figure 4 shows EPR spectra obtained from a single crystal of BaFBr that was doped with 200 molar ppm of barium oxide enriched to about 40% with ^{17}O and x-irradiated at room temperature. The intensity of the EPR signals produced by x-irradiation was greatly enhanced by the oxide doping. With B parallel to c , additional features assigned to hyperfine splittings from a single ^{17}O nucleus could be clearly seen, but only at temperatures below about 20 K (figure 4(a)). Four of the ^{17}O lines are resolved at this orientation, the other two transitions being obscured by the central multiplet. At orientations with B in the ab plane, only the outermost features of the ^{17}O hyperfine structure could be resolved (figure 4(b)). Within the resolution of our experiment, the hyperfine matrix was found to be axially symmetric with A_{\parallel} along c . The principal values of the ^{17}O hyperfine matrix are included in table 1.

The O^- centre was stable at room temperature for several days, but it could be rapidly bleached by annealing to 500 K. Subsequent x-irradiation at 300 K regenerated O^- with about the same yield.

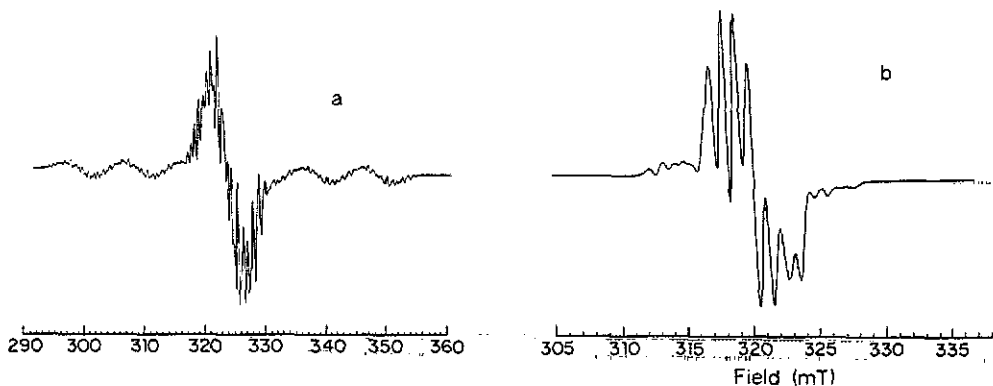


Figure 4. EPR spectra obtained from a single crystal of BaFBr doped with 200 ppm of BaO enriched to 40% ^{17}O obtained at 10 ± 2 K following 300 s exposure to x-rays at 300 K with (a) B parallel to c and (b) B parallel to a (or b).

Figure 5 shows the MCDA of a nominally pure BaFBr crystal after irradiation at room temperature. Both $F(\text{Br}^-)$ and $F(\text{F}^-)$ (Koschnick *et al* 1991, Koschnick *et al* 1990) centres are produced at this temperature, the latter giving rise to a symmetric band at 2.65 eV when measured at 1.5 K with B parallel to c . The MCDA in the region between 2.81 and 3.88 eV and crossing the baseline at 3.26 eV is the same as that shown in curve b of figure 2. An ODEPR spectrum similar to the EPR spectrum shown in figure 3(a) was measured when the optical wavelength was set at either 405 or 350 nm. The SHF structure observed in ODEPR was less well resolved than in conventionally detected EPR as a result of power broadening. A K -band ODEPR spectrum obtained from the same crystal as that used to generate the X-band EPR spectra of figure 4, is shown in figure 6. The same ^{17}O hyperfine splitting is observed as

that resolved in figure 4(a). At about 890 mT, an ODEPR signal is superimposed with opposite sign, causing an apparent asymmetry in the O^- ODEPR signal. This latter signal belongs to an as yet unknown defect. By obtaining the excitation spectrum corresponding to its ODEPR spectrum (MCDA tagged by EPR) (Ahlers *et al* 1983), five optical transitions could be identified for O^- with positions at 1.12 eV, 1.42 eV, 1.67 eV and two double bands at 3.26 eV and 4.35 eV, when measured at the peaks of the MCDA signals.

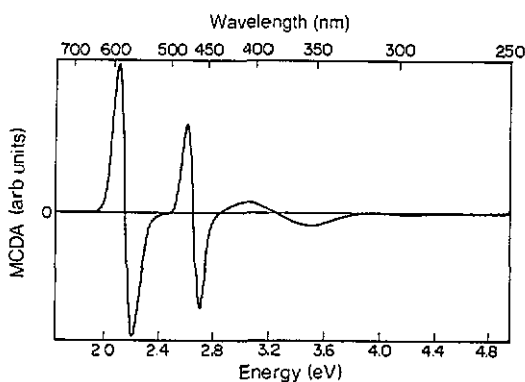


Figure 5. MCDA spectrum obtained at 1.5 K from a single crystal of undoped BaFBr (≤ 50 ppm O^{2-}) with $B = 3.0$ T parallel to c after x-irradiation at 300 K.

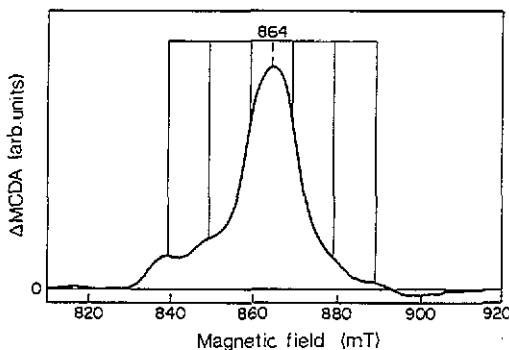


Figure 6. An ODEPR spectrum from a single crystal of x-irradiated BaFBr doped with 200 ppm BaO enriched to 40% ^{17}O . The spectrum was detected at 405 nm during excitation with 24.03 GHz microwave radiation at 1.5 K. B was orientated parallel to c .

An optical absorption spectrum measured at room temperature with $E \perp c$ from a single crystal of BaFBr doped with 200 molar ppm of barium oxide showed a symmetric absorption band centred at 4.98 eV whose intensity was greatly increased over that observed from a nominally pure crystal. This band, which must be associated with O^{2-} , decreased in intensity when the doped crystal was exposed to x-radiation, and several new absorption bands appeared at 3.26 eV, 2.15 eV [$F(Br^-)$], 1.53 eV, 1.26 eV and 0.95 eV (figure 7). All of these transitions were enhanced by oxide doping, but they could also be resolved in spectra from nominally pure samples after irradiation,

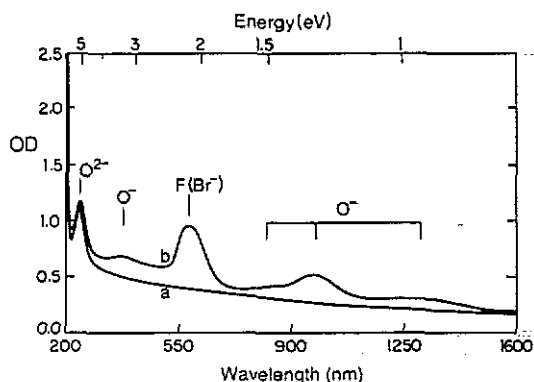


Figure 7. Optical absorption spectrum obtained from a single crystal of BaFBr doped with 200 ppm of BaO measured with $E_{\perp}c$ at 300 K. Curve (a): before exposure. Curve (b): after 300 s x-irradiation at 300 K. Optical density [$\log_{10}(\frac{I_0}{I})$, using standard symbols] is plotted.

along with a weak absorption from $F(F^-)$ at 2.65 eV. The radiation yield of $F(Br^-)$ was found to be proportional to the level of oxide doping.

Oxygen is a ubiquitous impurity in the alkali and alkaline-earth halides where it is extremely difficult to eliminate completely from melts by chemical treatment or evacuation (see for example Kanzig and Cohen 1959). The level of oxide contamination in BaFBr, as determined by EPR measurements on x-irradiated samples, was greatly reduced by exposing the molten material to a stream of purified argon saturated with bromine for several hours before crystal growth. This treatment was carried out in an extremely clean reactor to prevent recontamination by residual oxygen, since molten BaFBr has proved to be a very effective scavenger for this element.

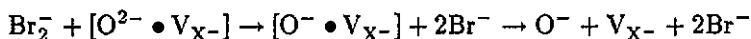
3.2. UV-irradiated BaFBr

The O^- centre was also found to result from UV-radiation of BaFBr crystals at room temperature, but the yield was substantially decreased from that produced by x-irradiation. The maximum concentration of this species resulted from exposure to 250 ± 25 nm light, in the region of the optical absorption spectrum which we attributed to absorption by O^{2-} . A low concentration of $F(Br^-)$ centres was detected optically following the photoionization of O^{2-} . This implies the presence of bromide vacancies prior to UV exposure, consistent with theoretical predictions (Baetzold 1987, 1988, 1991).

4. Discussion

The EPR and ODEPR spectra described in this paper are assigned to O^- , a stable trapped-hole state in BaFBr. The large increase in the radiation yield for this centre following deliberate O^{2-} addition and the observation of a single magnetic nucleus per centre in the ^{17}O enrichment experiments are consistent with this conclusion. It is also supported by the observation of this defect following x-irradiation only under conditions when the V_K centres formed at low temperatures could thermally diffuse (Eachus and Nuttall 1988, Hangleiter *et al* 1990). Charge compensation for the incorporation of the oxide impurity could be provided by interstitial cations, substitutional

M^{3+} impurities, or halide vacancies. In view of the restricted interstitial volume, compensation by barium interstitials is considered unlikely. The absence of significant concentrations of metal ion impurities makes compensation by anion vacancies most plausible. Thus, if we assume that charge compensation for the O^{2-} impurity centre introduced during crystal growth and occupying a halide site is provided by an anion vacancy, then the following reaction sequence is suggested:



where $\text{V}_{\text{X}-}$ represents either a fluoride or bromide vacancy. The symbolism $[\text{O}^{2-} \bullet \text{V}_{\text{X}-}]$ means a spatial correlation of the O^{2-} and the vacancy.

The observation of only $\text{F}(\text{Br}^-)$ and $\text{Br}_2^- \text{V}_K$ centres following x-irradiation at low temperatures implies that the F-centre generation proceeds via an electron-hole pair process in which the hole is captured by two adjacent bromide ions to form $\text{Br}_2^- \text{V}_K$ centres and the electron is captured by a bromide vacancy. It should be noted that no experimental evidence was found in EPR or ODEPR for the formation of F-H pairs, as recently suggested by Rüter *et al* (1990). The observation of a red shift for the $\text{F}(\text{Br}^-)$ optical band following x-irradiation at low temperatures (figure 2(a)) implies that the vacancy is either spatially correlated with an oxide impurity or with the V_K centre. Since the $\text{F}(\text{Br}^-)$ band remains red-shifted in a temperature regime where the V_K centre is observed to decay, and since the formation of $\text{F}(\text{Br}^-)$ is enhanced by oxide doping, the F-centre electron is believed to occupy the oxide's charge-compensating vacancy. Thus, $\text{V}_{\text{X}-}$ in the reaction above is a bromide vacancy, even in crystals prepared with an excess of Br^- . At room temperature, the F-centre must have been able to diffuse away from the O^- defect because the MCDA from the normal isolated $\text{F}(\text{Br}^-)$ centre is observed (Koschnick *et al* 1991). The fact that the $\text{F}(\text{Br}^-)$ centre is mobile at room temperature has important ramifications for discussions of radiation damage mechanisms in this system (Hangleiter *et al* 1990).

The observation of O^- by EPR following UV-irradiation of BaFBr and the concomitant formation of $\text{F}(\text{Br}^-)$ are consistent with the photoionization of O^{2-} and trapping of the electron in a charge-compensating vacancy. A similar process has been observed in KCl where F-centres were also produced upon photoionization of O^{2-} (Fischer and Gümmer 1966).

The charge-compensating bromide vacancies associated with O^{2-} are mobile at room temperature, as deduced from the unperturbed $\text{F}(\text{Br}^-)$ MCDA spectrum after warming to room temperature. There is no evidence from our experimental data obtained from UV-irradiated crystals for their continued association with the impurity following its ionization. Consistent with this observation, atomistic simulations have shown that intraplanar anion vacancy diffusion is particularly facile in materials with the PbFCl structure (Baetzold 1987,1988,1989).

In crystals containing low oxide concentrations, $\text{F}(\text{F}^-)$ centres are only produced by irradiation at room temperature. Since they are not formed at low temperatures, they must be created by a thermally activated process.

The location of the O^- defect in BaFBr is difficult to deduce from the EPR data alone. It is characterized by axially-symmetric g and A matrices with g_{\parallel} and A_{\parallel} parallel to the crystal four-fold axis. There was no site-splitting observed in the ac , ab or $c[110]$ planes, and SHF coupling to two equivalent bromine nuclei was observed with B directed along a or b . A multiplet pattern assigned as arising from coupling to two equivalent bromine nuclei was also observed at $55 \pm 2^\circ$ from c in the $c[110]$

plane. The spectrum at [110] was a broad single line and an asymmetric multiline structure of uncertain origin was observed along c .

There are two possible structural models whose symmetries are consistent with these magnetic resonance data. In the first, the O^- ion substitutes for F^- at a regular lattice position. In the second, the impurity is at an interstitial position. In each model the defect is surrounded by four structurally equivalent Br^- anions and four structurally equivalent Ba^{2+} cations in distorted tetrahedral configurations. When B is parallel to an edge of the approximate tetrahedron constituted by the four nearest bromide ion neighbours, they form two sets of magnetically equivalent pairs. This is the situation when B is parallel to either a or b , or at an angle θ to c in the $c[110]$ plane. At these orientations the EPR spectra should show major superhyperfine splittings from one pair of bromine nuclei, with splittings from the other pair possibly contributing only to the linewidth. This situation is realised in the intrinsic material when $\theta = 55.05^\circ$ for the interstitial site, and when $\theta = 31.42^\circ$ for the substitutional model. The experimental value of θ was $55 \pm 2^\circ$, suggesting an assignment to the former model *if* one assumes a relatively small lattice distortion occurs following incorporation of the impurity and that the unpaired electron is highly localized on oxygen. In Part II, however, we show from ENDOR that a substitutional site (figure 8) with a significant distortion of the anion environment is the correct assignment, a model that is supported by the results of atomistic simulations (Islam and Baetzold 1991).

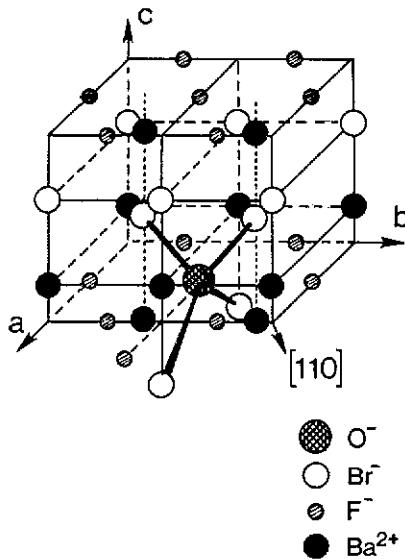


Figure 8. Structural model for the O_F^- centre in BaFBr.

The ^{17}O hyperfine interaction matrix can be analysed in order to address the question of the electronic ground state of the O^- defect. An estimate of the spin density on oxygen can be made from a comparison of the observed hyperfine splittings to those computed for unit orbital occupancy from self-consistent field wave functions (Atkins and Symons 1967). Taking $A_{\parallel} = a + 2b$ and $A_{\perp} = a - b$, in the usual notation, and assuming all possible sign combinations for the hyperfine splitting terms, we obtain

$a = 2.0$, $2b = 7.7$ mT ($A_{||}$ positive, A_{\perp} negative) and $a = 4.5$, $2b = 5.2$ mT (both signs positive) as physically reasonable solutions. The former results correspond to a total oxygen spin density of 0.75 (0.74 2p and 0.01 2s) and the latter to 0.53 (0.50 2p and 0.03 2s). In view of the small splittings assigned to $^{79/81}\text{Br}$ SHF couplings and the absence of resolved ^{19}F and $^{135/137}\text{Ba}$ structure, we favour the sign combination for the ^{17}O hyperfine splittings that leads to the larger estimate for the spin density on oxygen.

The experimental g matrix attributed to O^- is dissimilar from those previously obtained for this ion (Sander 1962, 1964, Brailsford *et al* 1968, Brailsford and Morton 1969, Nistor and Stoicescu 1971) and the related S^- (Vannotti and Morton 1968) in comparable systems. Although the S^- centre undergoes a static Jahn-Teller distortion in the alkali halides, its g matrix behaves as expected for a p_z orbital ground state ion (Bill *et al* 1980). Assuming a static, $p_x^2 p_y^2 p_z^1$ ground-state electronic configuration for O^- in BaFBr, two of the principal g values should be significantly larger than 2.0023, whereas one should be equal to or less than this value (Brailsford and Morton 1969, Vannotti and Morton 1968, Nistor and Stoicescu 1971). Experimentally, however, all three parameters well exceed the free electron value. One possible explanation is that the wavefunction derived for this electronic configuration (Brailsford and Morton 1969, Vannotti and Morton 1968, Nistor and Stoicescu 1971)

$$|\Psi^\alpha\rangle = A |p_x^\beta\rangle - iB |p_y^\beta\rangle + C |p_z^\alpha\rangle$$

is inappropriate (α , β represent spin up and spin down, respectively), and that the hole actually resides in a molecular orbital principally composed from the degenerate oxygen p_x and p_y atomic orbitals.

An alternative explanation follows arguments first proposed to account for the apparent g -shifts measured for O^- centres in Mg^{2+} - or Al^{3+} -doped SrTiO_3 (Schirmer 1968, Schirmer *et al* 1976). In each case, the three experimental values exceeded 2.0023. Schirmer and co-workers (1968, 1976) proposed that the p_z orbital rapidly resonated between two equivalent positions approximately 45° from z causing a partial averaging of two g values and an unexpectedly large positive Δg along z . Such a model for O^- in BaFBr would be consistent with the observed strong temperature dependence for the EPR spectrum: motional modulation completely obscures the ^{17}O hyperfine structure and bromine SHF splittings at temperatures above 20 K. At lower temperatures, residual dynamic motion of the O^- defect may still cause the $2p_z$ orbital to rapidly precess about z making g appear axial.

5. Summary

Oxide contamination of BaFBr introduces a deep hole trap. EPR, ODEPR and MCDA spectra have been obtained from a new O^- centre that is substitutional for F^- . It is formed most efficiently by the reaction of mobile $\text{Br}_2^- V_K$ centres with O^{2-} . The assignment of the EPR spectra to an oxygen-containing centre has been accomplished by doping with barium oxide enriched in the ^{17}O isotope. This centre can also be produced by photoionization at 250 nm. A comparison between the results of x-irradiations performed at room temperature and at low temperatures showed that F^- centres are preferentially produced on the bromine sublattice because of the presence of the charge-compensating bromide vacancies introduced by oxide doping.

Treatment of barium fluorobromide with bromine-containing carrier gases was found to greatly reduce or eliminate contamination by the O^{2-} precursor.

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