The influence of oxide impurity on the generation by x-irradiation of F centres in BaFBr

F K Koschnick†, J-M Spaeth† and R S Eachus‡

† University of Paderborn, Warburger Strasse 100, 4790 Paderborn, Federal Republic of Germany
‡ Eastman Kodak Company, Research Laboratories, Rochester, New York 14650-2021, USA

Abstract. Using magneto-optical and optically detected electron paramagnetic resonance methods, it is shown that in BaFBr single crystals grown using standard procedures the ubiquitous oxide impurity is primarily responsible for the x-irradiation-induced formation of $F(Br^-)$ centres. The bromide vacancy formed to charge compensate O^{2-} is implicated in the direct trapping of electrons. $F(F^-)$ centres are also produced by irradiation, probably by an exciton collapse process requiring thermal activation. Cross relaxation measurements show that many of the $F(F^-)$ and $F(Br^-)$ centres are spatially correlated, more than expected on statistical grounds. The relevance of these results to the use of rare earth-activated BaFBr materials as storage phosphors is discussed.

1. Introduction

Storage phosphors are materials capable of storing images produced by the absorption of x-radiation, making them important systems for medical diagnostic applications. BaFBr doped with divalent europium ions is a particularly useful material in this area (Stevels 1975, Luckey 1975, Kotera 1980, Amemiya 1988, Sonoda 1983). The precise mechanism by which the image is produced in BaFBr is a subject of conjecture, and much experimental work has been focused on the nature and generation by x-irradiation of trapped electron and hole centres (Takahashi et al 1984, 1985, von Seggern 1988a,b, Hangleiter 1990). It is generally agreed that F centres, electrons trapped at either bromide ($F(Br^-)$) or at fluoride ($F(F^-)$) vacancies, are involved in the imaging process as the electron storage centres. In order to optimize the efficiency of the imaging process through the intelligent variation of the phosphor composition, it is necessary to understand the mechanisms by which the F centres are formed.

It has been clearly demonstrated by electron paramagnetic resonance spectroscopy (EPR) that the oxide is a ubiquitous impurity in BaFBr which greatly influences the formation of the hole storage centres in this material (Koschnick 1991, Eachus 1991a,b). In this paper we show that the generation of $F(Br^-)$ centres is also mediated by the presence of O^{2-}, while the production of $F(F^-)$ centres is unaffected by the presence of this anion. $F(Br^-)$ centres can be generated at very low temperatures whereas the formation of $F(F^-)$ centres is thermally activated and irradiations must be performed near room temperature to enable their production. It is also shown that at room temperature both types of F centres are produced with spatial correlation.

2. Experimental details

2.1. Crystal growth

BaFBr single crystals (see figure 1 for structure) were grown by the Bridgman–Stockbarger method from a stoichiometric mixture of $BaBr_2$ and BaF_2. The BaF_2 (Merck Optipure) was purified by zone refining in vitreous carbon crucibles and $BaBr_2$ (W G McDugle, Eastman Kodak Company) was dried under vacuum and treated with $SiBr_4$ to remove oxygen according to standard procedures that have been successfully applied in the growth of oxygen-free alkali halides (Rosenberger 1972). Nearly transparent single crystals of excellent quality were obtained. However, these crystals still contained oxygen impurities in the concentration range of $3–5 \times 10^{17}$ cm^{-3}. Oxygen is incorporated primarily as oxide which is believed to substitute for fluoride with charge compensation provided by a bromide vacancy (Eachus 1991a,b). Henceforth we shall refer to these samples as 'normally grown crystals'. BaFBr crystals containing less than 10^{16} cm^{-3} of oxide impurities were prepared by W G McDugle, Eastman Kodak Company. For these samples, the starting materials for crystal growth were handled in dry, oxygen-free environments and dissolved oxygen was removed from the BaFBr melt by bromine treatment. These crystals, called 'oxygen-free', were finally grown under electronic grade argon. Some of these crystals were then regrown doped with BaO. Samples for spectroscopic studies were cut with a wire saw and orientated by Laue back reflection. F centres were produced by *in situ* x-irradiation at room temperature or at 4 K (50 kV, 40 mA, 3–10 min).
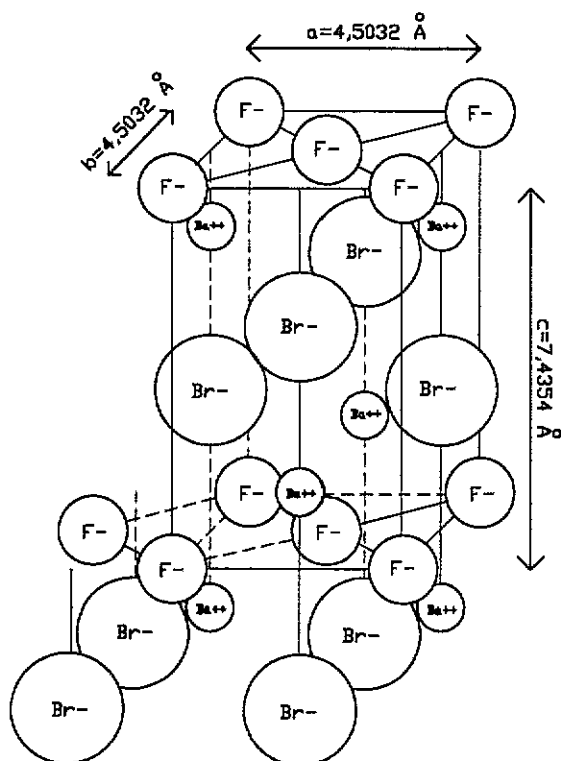

Figure 1. Crystal structure of BaFBr.

2.2. *Optically detected magnetic resonance measurements*

The magnetic circular dichroism of the absorption (MCDA), which is the differential absorption of right and left circularly polarized light, was measured in a custom built, computer controlled spectrometer. Optically detected EPR was measured as a microwave produced change of the MCDA (Mollenauer 1972). For optically detected electron nuclear double resonance (ODENDOR), an additional RF excitation was applied to the sample (Hofmann 1984). The MCDA experiments were usually performed at 1.5 K at fields up to 4 T, whereas ODEPR and ODENDOR spectra were measured at 1.5 K and 24 GHz and in an RF range from 0.5 to 200 MHz.

3. Experimental results

3.1. *The production of F centres*

Figure 2 is the MCDA spectrum obtained from a normally grown crystal (i.e. contains oxygen at a concentration of about 10^{17} cm^{-3}) of BaFBr irradiated *in situ* at 4.2 K and measured with E perpendicular to the c-axis. The MCDA bands peaking at 1.28 and about 3.4 eV are due to Br$_2^-$–V$_k$ centres. This is shown by measuring the ODEPR spectrum in either of the two bands. Figure 3 is the ODEPR spectrum measured in the 3.4 eV band for B parallel to the c-axis. The same spectrum was obtained from the 1.28 eV MCDA band. The dotted lines in figure 3 are a simulation of the V$_k$ EPR spectrum using the g-matrix and hyperfine splitting data determined by conventional EPR (Hangleiter 1990). The simulation was performed in first-order perturbation theory. A slight misorientation of the crystal caused a further splitting of the hyperfine structure since, by this misorientation, the equivalence of the four out-of-plane V$_k$ centre orientations Hangleiter 1990) was lifted. The agreement between the measured and simulated spectra in the field range between 700 and 860 mT confirms that the two bands at 1.28 and 3.4 eV in BaFBr are from the out-of-plane V$_k$ centre and thus identify, for the first time, its optical absorption transitions. According to the experience in alkali halides, two bands are expected within the molecular orbital representation of their ground and excited states. Neglecting spin–orbit coupling, two transitions are dipole allowed (Stoneham 1985): $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ is the UV transition while $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ is the IR transition. The corresponding two transitions in KBr are found to be at 3.22 and 1.5 eV (Delbecq 1961) which are similar to the values obtained here. There is a corresponding similarity between the EPR hyperfine and g data obtained from the V$_k$ centres in KBr (Schoemaker 1973) and BaFBr (Hangleiter 1990). The splitting of the IR band due to spin–orbit coupling in KBr is not observed with the MCDA technique in BaFBr.

The broad EPR line peaking at 880 mT in figure 3 is due to F(Br$^-$) centres (Koschnick 1992). It is surprising that this F centre EPR line can be measured in the MCDA of the V$_k$ centre. The explanation for this observation is that there is a cross relaxation between the F(Br$^-$) and V$_k$ centres indicating that there is a spatial correlation between them (see also section 4.1 for further discussion).

The MCDA band with a derivative structure around 2.1 eV is due to F(Br$^-$) centres. When measuring the ODEPR spectrum in this MCDA, the same EPR line as that discussed above peaking at 880 mT ($g_\parallel = 1.98$) is obtained. In ODEPR, the linewidth of about 20 mT is broadened due to saturation effects compared with the conventional EPR spectrum obtained from additively coloured material (12 mT) (Koschnick 1992).
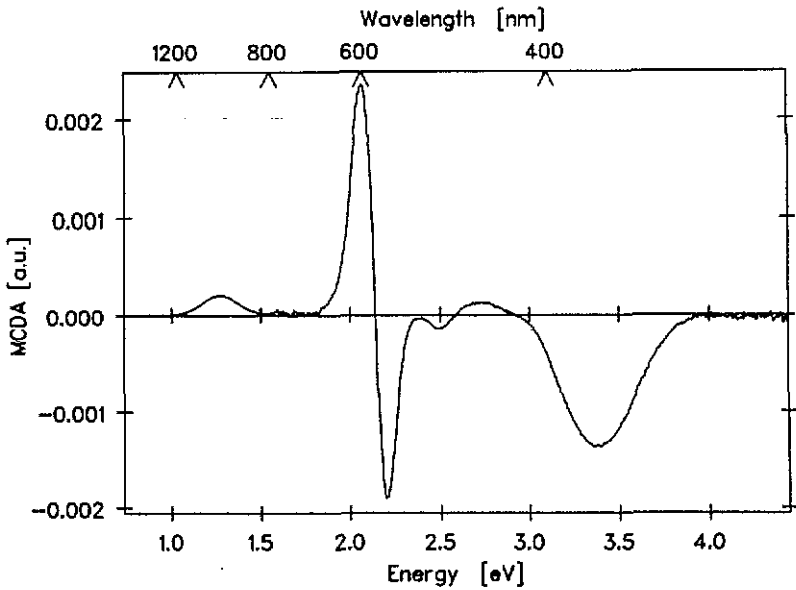
Figure 2. MCDA spectra of perturbed F(Br$^-$) centres and Br$_2^-$-V$_k$ centres, $B =$ 3000 mT, $T = 1.5$ K, x-irradiation at $T = 4.2$ K.
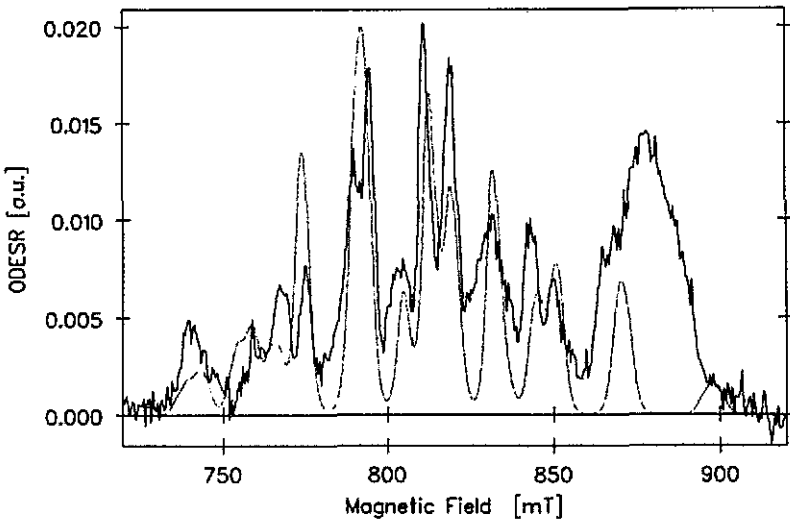

Figure 3. ODEPR spectrum of Br$_2^-$-V$_k$ centres, microwave frequency 24 GHz, $T = 1.5$ K. The calculated spectrum is also shown (see text).

Saturation broadening is unavoidable in ODEPR due to the measurement technique. It is also seen in ODEPR measurements on the F(Br$^-$) centre in additively coloured crystals. From the EPR spectrum, one would conclude that isolated F(Br$^-$) centres are created by x-irradiation. However, comparison of the precise spectral position of the MCDA from the F(Br$^-$) centre in figure 2 with that of F(Br$^-$) centres created by additive colouration shows that in the x-irradiated crystal the zero crossing point of the derivative-like signal is shifted by about 50 meV to a lower energy. This indicates

that the peak position of the $F(Br^-)$ centre absorption is shifted by about 50 meV to lower energy, an observation which is known from the alkali halides as being typical behaviour for perturbed defects such as F_A centres (Fowler 1968).
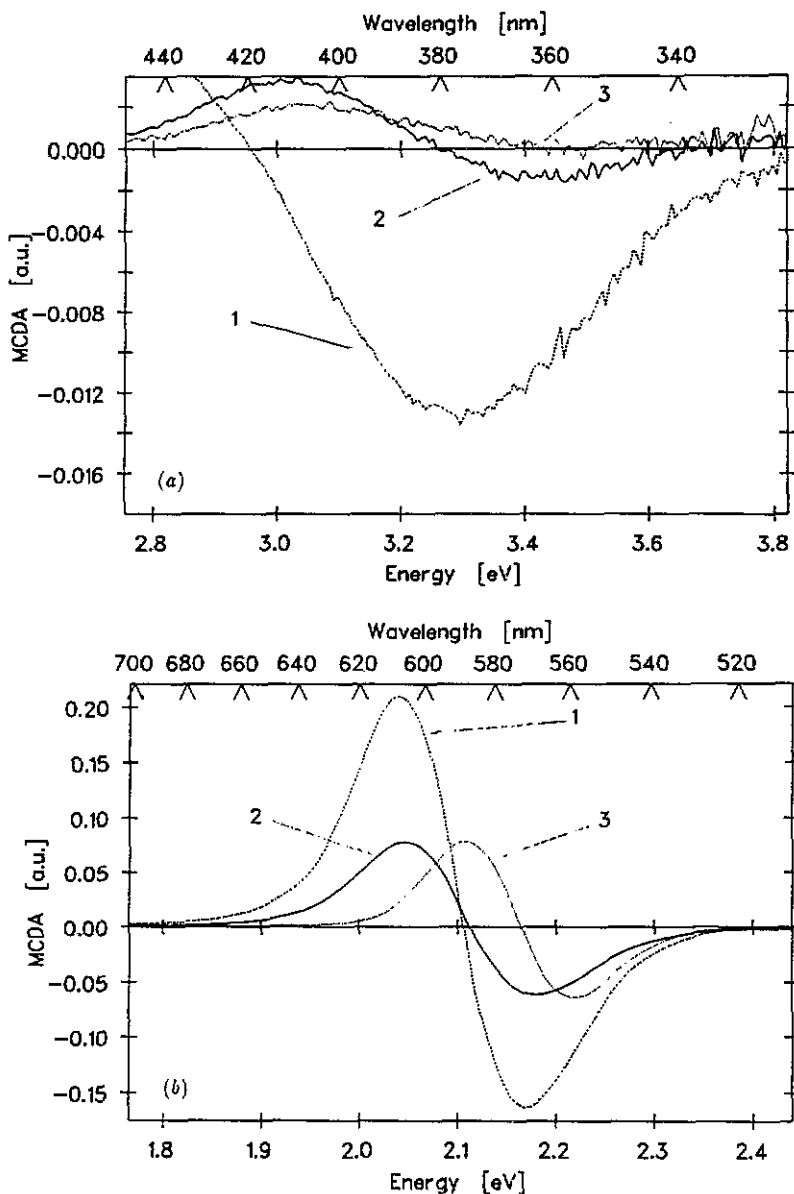

Figure 4. (*a*) Decay of $Br_2^- - V_k$ centres after annealing: curve 1, MCDA spectrum after x-irradiation at 4.2 K; curve 2, MCDA spectrum after warming to 120 K; curve 3, MCDA spectrum after warming to 200 K. (*b*) Change of the MCDA spectrum of $F(Br^-)$ centres after annealing: curve 1, MCDA spectrum after x-irradiation at 4.2 K; curve 2, MCDA spectrum after warming to 120 K; curve 3, MCDA spectrum after warming to 200 K.

Upon warming the irradiated crystal to 120 K, the $Br_2^- - V_k$ centres decay resulting

in the disappearance of their MCDA (curve 1 in figure 4(a)) and the appearance
of a new MCDA in the same spectral region (curve 2, figure 4(a)). The decay of
the V_k centre can also be observed in conventional EPR (Hangleiter 1990). The
MCDA of the perturbed $F(Br^-)$ centres decays to about half of its original intensity
(figure 4(b)), and its position shifts slightly by about 10 meV to higher energy. A
thermal luminescence peaking at about 2.7 eV is associated with the decay of these
centres (figure 5). $F(Br^-)$ centres and mobile V_k centres must recombine to give
rise to this thermal emission. Those V_k centres which do not recombine with $F(Br^-)$
centres must decay by a different mechanism. Curve 2 in figure 4(a) is almost
identical to the MCDA which was previously identified as being from O_F^- centres, but
it is spectrally shifted by 70 meV to a lower energy. Upon warming further to about
200 K the MCDA of the F centre shifts to the normal position for isolated $F(Br^-)$.
Simultaneously curve 2 in figure 4(b) shifts to the precise position where the O_F^-
centres created at room temperature have their MCDA indicating that the mobile V_k
centres also react with oxide impurities (Eachus 1991a,b). With this second annealing
step a second thermal luminescence is observed at 2.7 eV, but the intensity is reduced.
Thus some $F(Br^-)$ centres recombine with the O_F^- centres. The observation that the
perturbed $F(Br^-)$ centres have now become isolated centres, as judged by the spectral
position of the MCDA band, indicates that a thermal dissociation between the F centres
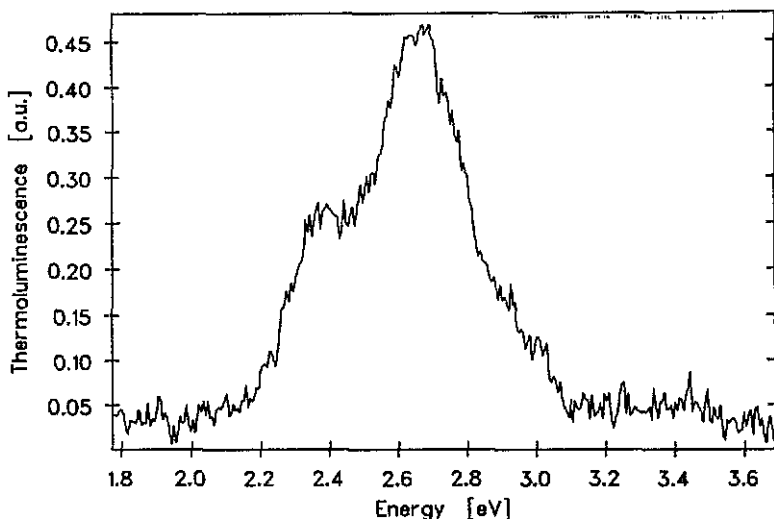and their perturbing defects has occurred.

Figure 5. Thermoluminescence of normally grown BaFBr at $T = 120$ K, x-irradiation
at $T = 4.2$ K.

In normally grown BaFBr $F(F^-)$ centres have only been produced by x-irradiation
near to room temperature. Apparently their formation needs a thermal activa-
tion. Figure 6 shows the concentration of $F(F^-)$ and $F(Br^-)$ centres produced
by x-irradiation at room temperature in normally grown material as a function of
x-irradiation time. There is a striking difference between the $F(F^-)$ and $F(Br^-)$
production. $F(Br^-)$ centres are produced at a very high rate at the beginning of
irradiation and saturate very quickly, while the creation of $F(F^-)$ centres is almost
monotonic. The decrease in the $F(Br^-)$ concentration at longer times is probably
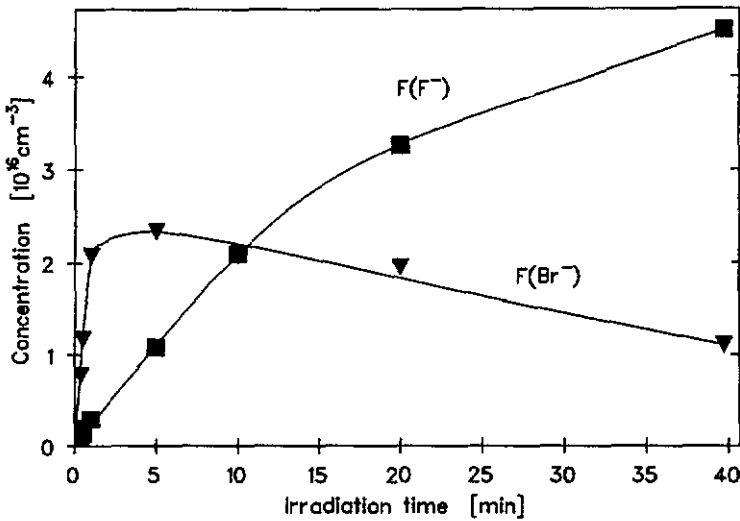
Figure 6. Production of $F(Br^-)$ and $F(F^-)$ centres against x-irradiation time at room temperature.

due to their thermal decay (see next section).

Investigation of F centre production as a function of the oxide content shows that the oxide greatly enhances the production of $F(Br^-)$ but has little or no effect on the yield of $F(F^-)$. For example, in a crystal with a very low oxide content we obtained only 20% of the saturation value of $F(Br^-)$ obtained in normally grown material, while in an oxide-rich sample (about 200 mppm O^{2-}) the yield was about 15 times higher than that in the 'oxide-free' sample. The concentration of $F(F^-)$ was much higher (an order of magnitude after sufficient radiation exposure) than that of $F(Br^-)$ in the 'oxide-free' material and its relative concentration in the oxide-containing crystals depended on the level of oxide incorporation. It should be noted that the concentration of F centres was determined from their optical absorption bands using the Smakula formula (Fowler 1968) and an oscillator strength of $f = 0.8$ for both centres.

3.2. The optical and thermal stability of F centres ·

$F(Br^-)$ and $F(F^-)$ centres have different thermal stabilities at room temperature. A normally grown crystal was x-irradiated at room temperature and then held in the dark for one week, at which time almost all of the $F(Br^-)$ centres had disappeared while about 20% of the $F(F^-)$ remained. This is in agreement with calculations of the stability of F centres in BaFBr (Baetzold 1987) according to which $F(F^-)$ centres are more stable.

The optical bleaching of F centres is a critical step in the readout of the x-ray produced image in BaFBr, therefore we investigated the optical properties of these centres in some detail. A normally-grown crystal irradiated at room temperature and containing both $F(Br^-)$ and $F(F^-)$ centres (figure 7(a), curve 1) was bleached by irradiation in the $F(Br^-)$ band at 2.15 eV at 1.5 K. Its MCDA decreased to about half of its original value (figure 7(a), curve 2), while that of the $F(F^-)$ centres increased by about 10% (figure 7(a), curve 2). Note that the MCDA of the O_F^- centres does not change at all. The MCDA remaining after bleaching at 2.15 eV is slightly
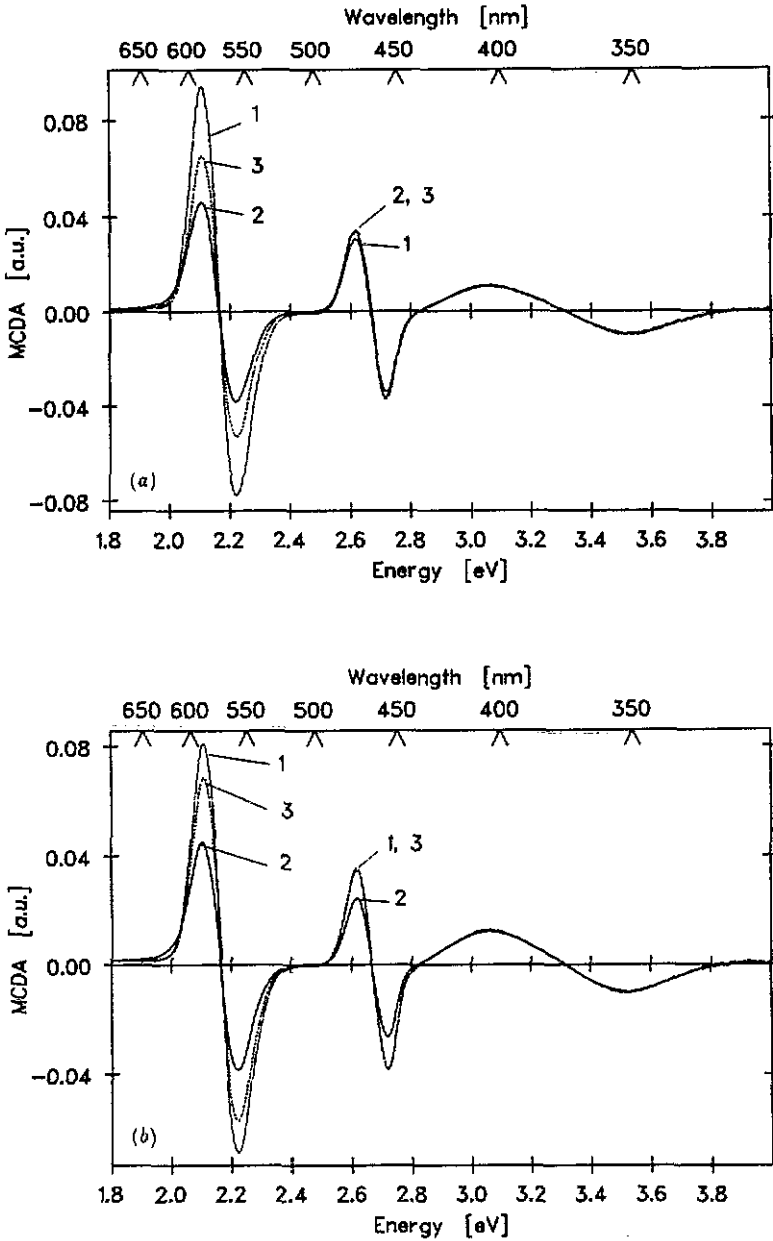
Figure 7. MCDA spectrum of BaFBr x-irradiated at room temperature, $B = 3000$ mT, $T = 1.5$ K. (a) curve 1, before bleaching; curve 2, after bleaching into the F(Br$^-$) absorption band at 1.5 K; curve 3, after warming to room temperature. (b) Curve 1, before bleaching; curve 2, after bleaching into the F(F$^-$) absorption band at 1.5 K; curve 3, after warming to room temperature.

broadened in the low energy wing. A measurement of the MCDA as a function of field and temperature (Mollenauer 1972) showed that this low-energy wing is due to diamagnetic defects. After warming the crystal to room temperature, the increased number of F(F$^-$) centres remains, while the concentration of the F(Br$^-$) centres

recovers to about 70% of the value before bleaching and the diamagnetic centre contribution to the low-energy wing of the MCDA disappears. A different picture was obtained when bleaching in the F(F$^-$) centre band at 2.65 eV at 1.5 K. The MCDA of F(F$^-$) centres only decreased by 30% (figure 7(b)) while, surprisingly, that of the F(Br$^-$) centres decreased by 50%.
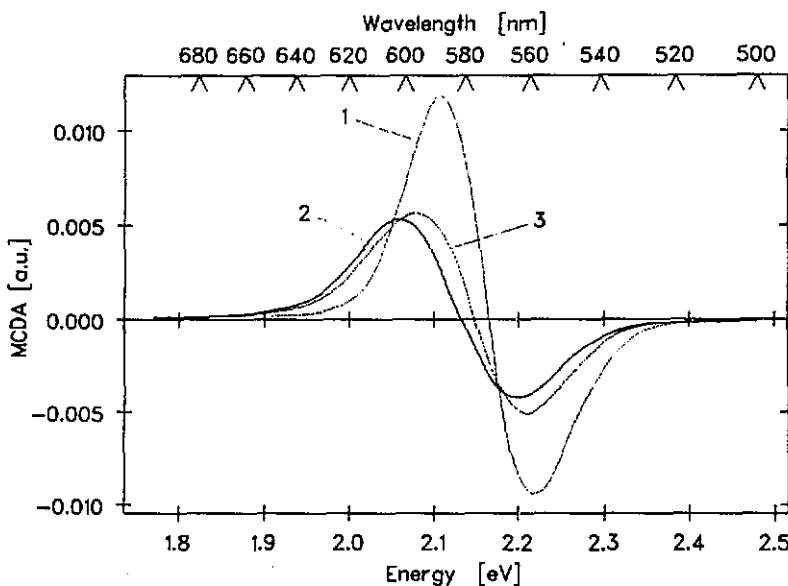

Figure 8. Change of the MCDA spectrum of F(Br$^-$) centres in oxygen-doped BaFBr after bleaching at 1.5 K: curve 1, before bleaching; curve 2, after bleaching into the high-energy flank of the F(Br$^-$) absorption band at 1.5 K; curve 3, after bleaching into the low-energy flank of the F(Br$^-$) absorption at 1.5 K.

The low-temperature bleaching experiments on x-irradiated samples of the oxygen-doped crystals clearly showed the effects of a mixed population of F(Br$^-$) centres, those formed from vacancies closely associated with the perturbing defect (which we will reveal later to be the oxide) and those produced from free, unperturbed vacancies. When bleaching the F(Br$^-$) centres at low temperature, perturbed F(Br$^-$) centres are created and the MCDA is shifted towards the low-energy side (see figure 8, curve 2). The resulting MCDA is probably a superposition of signals from perturbed and unperturbed centres. Irradiation at 1.5 K into the low-energy flank has the effect of transforming some of the perturbed centres back into the unperturbed structure showing the higher energy MCDA (figure 8, curve 3). This procedure is fully reversible at 1.5 K. The perturbed centres are not stable at room temperature. After warming the crystal to room temperature, a loss of about 30% in the MCDA signal from F(Br$^-$) centres was noted, a similar behaviour to that observed in the normally grown material.

3.3. Spatial correlation of F(F$^-$) and F(Br$^-$)

When measuring ODENDOR by setting the optical wavelength into the MCDA of the F(F$^-$) centres, a surprising effect was discovered. For the magnetic field position

in the high-field flank of the F(Br⁻) EPR line, where there is no overlap with the F(F⁻) EPR line ENDOR lines of the F(Br⁻) centre could be measured as an RF- and microwave-induced decrease of the MCDA of the F(F⁻) centres fairly efficiently. Figure 9 shows in the lower trace the ENDOR lines of the F(Br⁻) centres measured in this way. For comparison, figure 9(*a*), trace 2 shows the ENDOR lines measured in the MCDA of the F(Br⁻) centre itself for the same crystal and orientation ($B \parallel c$). Both sets of ENDOR lines are the same. It is known from the investigation of the optical properties of the two F centres that the F(Br⁻) centres have a high-energy transition overlapping the MCDA at 2.65 eV from the F(F⁻) centres. Therefore, this observation could be due to an optical transition into the higher excited states of the F(Br⁻) centres. In order to verify this interpretation, we have measured the excitation spectrum of the ODENDOR lines, the so-called MCDA-tagged by ENDOR (Ahlers 1983). In this experiment, one sets the double resonance condition for one particular ENDOR line, varies the optical wavelength and monitors the appearance of the MCDA. The result of such an experiment (figure 9(*b*)) clearly reproduces the MCDA of the F(Br⁻) centres, which is trivial, but also that of the F(F⁻) centres. Therefore, the observed effect is not due to the higher F(Br⁻) transition, but rather due to a cross relaxation. Such a cross relaxation between the two F centres was detected in both normally grown and oxygen-free crystals. In oxygen-rich crystals, we could not generate sufficient F(F⁻) centres in order to produce this effect. The observation of this cross relaxation clearly signifies that both F centres are produced with spatial correlation (see later).

4. Discussion

4.1. The mechanism for the generation of F centres

As is well known from colour-centre research on the alkali halides, there are two principal routes for the formation of F centres in halide materials. One involves the collapse of an exciton at a lattice anion to produce an interstitial halogen atom and a correlated F centre; with thermal activation these defects can separate (Hayes 1980). The second mechanism involves trapping of free electrons at pre-existing anion vacancies to form F centres, with a corollary production of V_k centres. Our observation that the generation of F(Br⁻) centres is correlated with the presence of oxide impurities suggests that we are dealing predominantly with the latter formation process. At low temperature, x-irradiation produces perturbed F(Br⁻) centres as seen in the low-energy shift of the MCDA. Appearently the charge-compensating vacancies of the O^{2-} ion are in the bromide sub-lattice and spatially correlated to the impurity which presumably substitutes for an F⁻ ion. This latter conclusion is based upon the observation that, upon warming, the oxide reacts with the mobile $Br_2^- - V_k$ centres to produce O_F^- as was shown previously by EPR and ENDOR (Eachus 1991a,b). When the spatially correlated bromide vacancy becomes an F centre, and thus neutral, it can diffuse away from the oxide centre at temperatures above 200 K and forms the isolated F(Br⁻) centre which shows the same MCDA as that produced in the additively coloured material. The reduced low-energy shift of the MCDA observed at 120 K may be the effect of a superposition, such that some F centres are near to an O⁻ ion rather than to an O^{2-} ion. From the shift in the MCDA towards lower energy at low temperature, one can conclude according to Mollwo–Ivey's law, that the lattice
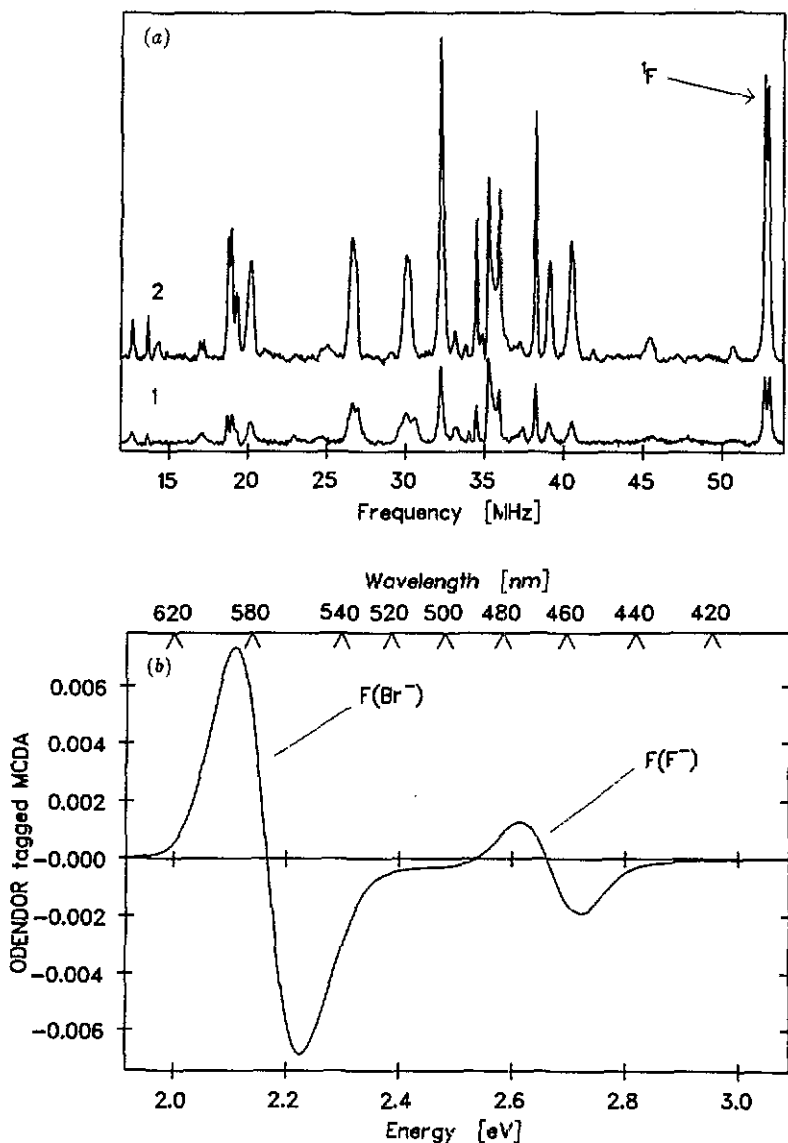
Figure 9. (*a*) Curve 1, cross relaxation ODENDOR of F(Br$^-$) centres detected via the F(F$^-$) MCDA, $T = 1.5$ K, $B = 888$ mT; curve 2, ODENDOR spectrum of F(Br$^-$) centres as a comparison. (*b*) ODENDOR tagged MCDA spectrum measured via an ODENDOR line due to the first fluorine shell of the F(Br$^-$) centre, $B = 888$ mT, $T = 1.5$ K, frequency of the RF field 52.65 MHz (arrow in figure 9(*a*)).

volume available for the F(Br$^-$) centre is greater for the defect produced by low-temperature irradiation. Thus, we infer that the vacancy is adjacent to the oxide impurity at low temperatures. The mechanism that we propose for the formation of the F(Br$^-$) centre at low temperature is supported by the observation of the cross relaxation between the Br$_2^-$–V$_k$ centres and the F(Br$^-$) centres. From a simple estimate of the classical dipole–dipole interaction between the Br$_2^-$–V$_k$ hole and the F centre electron spin, we can estimate the minimum distance between the two centres

to be about 8 Å. Had they been closer to each other, splittings in their EPR spectra would have been observed from the dipole–dipole interaction. That means that the V_k centre is in the next or next-but-one unit cell of the lattice with respect to the $F(Br^-)$ centre. To the best of our knowledge, the direct correlation between the V_k and F centre as a pair centre when a vacancy is available for trapping the F electron has never been demonstrated so clearly.

The thermal luminescence observed at 2.7 eV is identical to a luminescence which can be excited at 4.6 eV in unirradiated, oxide-containing BaFBr and which is due to a triplet emission from the excited oxide centre (Meise 1992). The broad recombination luminescence of F and V_k centres which peaks at 4.1 eV may excite this oxide triplet emission directly. It was recently suggested that the 2.7 eV emission was intrinsic to BaFBr (Crawford 1991), but we have clearly demonstrated here its association with the ubiquitous oxide impurity.

At low temperatures, only a few $F(F^-)$ centres can be produced by a direct electron trapping mechanism because there are apparently few F^- vacancies present in the material. No V_k centres were observed in the fluoride sublattice. Our bleaching experiments at low temperature of the $F(Br^-)$ centres showed that these small number of fluoride vacancies can be filled with electrons liberated from the $F(Br^-)$ centres. Since the ionization of the photoexcited $F(Br^-)$ centre is a thermally activated process with an activation energy of 35 ± 5 meV (Thoms 1991) irradiation at 1.5 K will not produce free conduction band electrons. Thus, we must conclude that the F^- vacancies must be located in close proximity to the $F(Br^-)$ centres for photoexcited electron transfer to take place by tunnelling. It remains an open question why the reverse photoelectron transfer does not occur when irradiating in the $F(F^-)$ absorption band. Probably the relaxed excited state (RES) of $F(F^-)$ is too low in comparison with that of the $F(Br^-)$ centre and prevents the back tunnelling process. This interpretation is in contradiction to a recently proposed energy level scheme (Iwabuchi 1991) which places the RES of $F(F^-)$ within 1.3 meV of the conduction band in BaFBr.

The production of $F(F^-)$ centres at room temperature without any saturation effects suggests that in this case the F–H mechanism operates, however, that the separation of the fluorine interstitial and the F centre require thermal activation. Since we have been unable to detect them optically or by EPR spectroscopy, the H centres are clearly unstable at room temperature.

4.2. Spatial correlation between F centres

From the investigation of the luminescence properties of the F centres (Koschnick 1992) evidence was found that energy transfer between $F(F^-)$ centres and $F(Br^-)$ centres and *vice versa* must occur in order to explain the luminescence excitation spectra at low temperature. This pointed to a spatial correlation between the two types of F centres beyond statistical probabilities, considering that their concentrations were both of the order of 10^{16} cm^{-3}.

Direct evidence for a spatial correlation was also found here from the observation of the cross relaxation effects described in section 3.3. In the cross relaxation process, spin polarization is transferred from one spin system to another by spin flip–flop processes. The cross relaxation effect which enabled us to measure the ODENDOR lines of the $F(Br^-)$ centres indirectly via the MCDA of the $F(F^-)$ centres can be explained with the fact that the change of the spin polarization of the ground state of the $F(Br^-)$ centres, which are induced by the ODENDOR effect, is transferred via

the cross relaxation to the ground state polarization of the F(F$^-$) centres. A quantitative analysis of this effect is difficult because of the complicated processes involved. However, a simple estimate can be obtained in order to obtain an approximate idea about the form of the spatial correlation between the two F centres.

Since energy must be conserved, cross relaxation can only happen between paramagnetic centres, the EPR spectra of which at least partly overlap. The probability for a spin flip–flop process between two spins i and j, neglecting angular parts, is approximately given by (Bloembergen 1959)

$$R_{ij} \approx \hbar^{-2} \beta^4 g_{\alpha\beta} / r_{ij}^6 \tag{1}$$

where, in equation (1), it is assumed that the g factors of the two defects are approximately two and that the spins of the interacting defects are $\frac{1}{2}$, r_{ij} is the distance between two spin vectors i and j, β is the gyromagnetic ratio of the electron and $g_{\alpha\beta}$ is the overlap integral of the two form functions g_α and g_β of the two EPR lines of the defect species α and β taking part in the cross relaxation:

$$g_{\alpha\beta} = \int g_\alpha(\nu) g_\beta(\nu) \, \mathrm{d}\nu. \tag{2}$$

In order to measure the effects of cross relaxation, the inverse of R_{ij} must be of the same order as the spin–lattice relaxation time T_1 of the F(F$^-$) centre. Since the cross relaxation must open a competing channel to the spin–lattice relaxation of the F(F$^-$) centre:

$$T_1(F(F^-)) = 1/R_{21} \tag{3}$$

where R_{21} is the transition probability of a spin flip–flop process from an F(Br$^-$) centre (2) to an F(F$^-$) centre (1). It follows from equations (1) and (3) for the distance between the two interacting F centres:

$$r_{12} \leqslant \sqrt[6]{\hbar^{-2} \beta^4 T_1 g_{\alpha\beta}}. \tag{4}$$

The overlap integral between the two normalized form functions of the EPR lines from the two F centres transformed to frequency from the field dependence was determined numerically to be 4×10^{-10} s. The spin–lattice relaxation time T_1 of the F(F$^-$) centre was measured to be 8 s at 1.5 K by observing the recovery of its MCDA after switching off the saturating microwaves. From equation (4) it then follows that r_{12} is approximately 20 Å. This distance is an order of magnitude smaller than the average distance between two F centres of about 200 Å which one would have for a purely statistical distribution between the F centres based on their concentrations of 5×10^{16} cm^{-3}. Thus the observation of cross relaxation between the F(F$^-$) and F(Br$^-$) centres can only be explained by a spatial correlation between the two types of F centres. This estimate cannot determine if all of the F centres are correlated or only part of them.

The minimum distance between the F centres can be estimated from the fact that there is no measurable splitting in their ODEPR spectra from a dipole–dipole interaction between their unpaired electrons. This is corroborated by the observation that the ODENDOR spectra of F(Br$^-$) centres show an unperturbed symmetry out to the fifth ligand shell (Koschnick 1992). This again suggests that their separation exceeds 7 Å. Thus, taking all of the evidence into account, the separation between the two F centres seems to be in the range of 7–20 Å, which means that they are separated by one or two unit cells.

5. Conclusions

F(Br$^-$) centres are known to be the important electron storage centres involved in the imaging process in practical Eu^{2+}-doped BaFBr phosphors. It is, therefore, vital to understand the mechanism responsible for their formation and the effects of lattice composition and structure on this process. It seems that the decisive role of the oxide impurity for the formation of F(Br$^-$) centres has not been recognized in the past. Our experience with the materials described in this paper indicates that the yield of F(Br$^-$) centres decreases dramatically as the oxide impurity is removed from BaFBr. It is quite conceivable that no F(Br$^-$) centres would be formed by x-irradiation of the ultra-pure (oxide-free) material. This would imply that the exciton collapse mechanism does not operate in the bromide sublattice, while it seems to be the dominant mechanism to create F(F$^-$) centres on the fluoride sublattice. One can only speculate about the reason. A possibility is that the collision sequence that must occur to separate the halide interstitial from the F centre is linear and, therefore, most facile within the fluoride plane. In the double-layer of bromide planes, the collision sequence must involve either an interplanar, non-collinear motion or an intraplanar diffusion along the a (b) direction. The latter seems improbable due to the large separation between the bromide ions while the former requires a change in the collision direction and is, therefore, less facile. Diffusion between the F$^-$ and Br$^-$ planes will be prevented by the confining planes of barium cations.

Since, in practice, the x-ray generated image in a storage phosphor is read out by the stimulation of electron–hole recombination using 633 nm light, the formation of F(Br$^-$) centres is a pre requisite for the use of BaFBr in this application. Thus, the inadvertent incorporation of the oxide impurity is vital for this material to function as a storage imaging system. Note, however, that we have already demonstrated that the oxide impurity also acts as an efficient hole trap in BaFBr. It has been clearly shown that Eu^{2+} does not trap holes to become Eu^{3+} during x-irradiation of this material (Hangleiter 1990). It remains to be determined whether or not Eu^{2+} competes with oxide for the stabilization of holes by some other mechanism in order for the phosphor to function.

The observation of spatially correlated F centres by cross relaxation implies that an energy transfer can occur between them by a dipole–dipole mechanism. If the correlation between the two F centres is triggered by the oxide impurity, the europium impurity might also cause a correlation between the irradiation induced defects within the distance required for dipole–dipole energy transfer. Preliminary cross relaxation results from Eu^{2+}-doped BaFBr support these speculations (Koschnick 1991).

References

Ahlers F J, Lohse F, Spaeth J-M and Mollenauer L F 1983 *Phys. Rev.* B **28** 1249
Amemiya G and Miyahara J 1988 *Nature* **336** 89
Baetzold R C 1987 *Prog. Surf. Sci.* **26** 213
Bloembergen N, Shapiro S, Pershan P S and Artman J O 1959 *Phys. Rev.* **114** 445
Crawford M K and Brixner L H 1991 *J. Luminescence* **48** & **49** 37
Delbecq C J, Hayes W and Yuster P H 1961 *Phys. Rev.* **121** 1043
Eachus R S, McDugle W G, Nuttall R H D, Olm M T, Koschnick F K, Hangleiter Th and Spaeth J-M 1991 *J. Phys. C: Solid State Phys.* submitted
Fowler W B 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic)

Hangleiter Th, Koschnick F R, Spaeth J-M, Nuttall R H D and Eachus R S 1990 *J. Phys. C: Solid State Phys.* **2** 6837
Hayes W 1988 *Contemp. Phys.* **21** 451
Hofmann D M, Meyer B K, Lohse F and Spaeth J-M 1984 *Phys. Rev. Lett.* **53** 1187
Iwabuchi G, Kinnemoto Ch, Takahashi K and Shionoga S 1991 *J. Luminescence* **48 & 49** 481
Koschnick F K, Spaeth J-M, Eachus R S, McDugle W G and Nuttal R H D 1991 *Phys. Rev. Lett.* **67** 3571
Koschnick F K, Hangleiter Th, Spaeth J-M and Eachus R S 1992 *J. Phys.: Condens. Matter* **4** 3001
Kotera N, Eguchi S, Miyahara J, Matsumoto S and Kato H 1980 *US Patent 4,239,968*
Luckey G W 1975 *US Patent 3,859,527*; 1983 revised 31847
Meise W and Spaeth J-M 1992 to be published
Mollenauer L F and Pan S 1972 *Phys. Rev.* B **6** 772
Rosenberger F 1972 *Ultrapurity-Methods and Techniques* ed M Zief and R Speights (New York: Marcel Dekker) pp 3–69
Schoemaker D 1973 *Phys. Rev.* B **7** 786
Sonoda M, Takano M, Miyahara J and Kato H 1983 *Radiology* **148** 833
Stevels A L N and Pingault F 1975 *Philips Research Reports* **30** 277
Stoneham A M 1985 *Theory of Defects in Solids* (Oxford: Clarendon Press)
Takahashi K, Kohda K, Miyahara J, Kanemitsu Y, Amitani K and Shionoya S 1984 *J. Luminesc.* **31 & 32** 266
Takahashi K, Miyahara J, Shibahara Y 1985 *J. Electrochem. Soc.* **132** 1492
Thoms M, von Seggern H, Winnacker H 1991 *Phys. Rev.* B submitted
von Seggern H, Voigt T, Knupfer W, Lange G 1988 *J. Appl. Phys.* **64** 1405
von Seggern H, Voigt T and Schwarzmichel K 1988 *Siemens Forsch.-u. Entwickl.-Ber.* **17** 124