Temperature dependence of the photostimulated luminescence of X-irradiate BaFBr:Eu^{2+}

Temperature dependence of the photostimulated luminescence of x-irradiated BaFBr : Eu²⁺

T Hangleiter†, F K Koschnick†, J-M Spaeth†, R H D Nuttall‡ and R S Eachus‡

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

Abstract. The temperature dependence of the luminescence from Eu^{2+} activators in BaFBr: Eu^{2+} photostimulated between 10 and 300 K in the optical absorptions of F centres produced by room temperature x-irradiation, revealed two thermally-activated processes. The photostimulated luminescence (PSL) increases sharply in intensity when excited between 60 and 100 K. After the low-temperature PSL is exhausted by continuous F centre excitation, it can be almost entirely regained by warming the crystal to 300 K. This thermal cycle can be repeated several times. It is shown by EPR that no Eu^{3+} is formed upon x-irradiation at 300 K. These results are explained with a model for the PSL mechanism which involves a loose aggregate of Eu^{2+}, F, and hole centres.

1. Introduction

The defects formed during the irradiation of alkaline earth fluorohalides have been of considerable interest because of their potential importance during the use of these materials in x-ray intensifying screens (Stevels and Pingault 1975) and storage phosphors (Luckey 1975, Kotera *et al* 1980). Europium-doped BaFBr has been used to prepare phosphor screens in which stable x-ray-produced images can be stored for long periods in the dark at 300 K. It is generally agreed that the image storage centres involve trapped electrons and holes, the former being F centres formed at one of two sites in this material: at fluoride vacancies to produce $F(F^-)$ and at bromide vacancies to produce $F(Br^-)$ (Takahashi *et al* 1984, 1985). Images are read by optical stimulation of electron–hole recombination which leads to emission at a wavelength determined by the rare-earth activator (390 nm, 3.19 eV, for Eu^{2+} in BaFBr) (Brixner *et al* 1980). This readout process erases the image record making the material reusable.

The fundamental mechanisms of image generation are not well understood. Takahashi *et al* (1984, 1985) have proposed a mechanism by which x-irradiation produces stable F centres and Eu^{3+}. Irradiation in the F centre absorptions produces electrons in the conduction band which subsequently recombine with Eu^{3+} producing the well-known Eu^{2+} luminescence (Luckey 1983, Brixner *et al* 1980).

In this paper we report on an EPR investigation of the effect of x-irradiation on the charge state of Eu^{2+} and on the temperature dependence of the photostimulated

luminescence (PSL) from Eu^{2+} excited by irradiation in the F centre optical absorptions. We show that a mechanism involving Eu^{3+} as the hole imaging centre is inconsistent with our results and we propose a new mechanism for the PSL effect.

2. Experimental details

2.1. Crystal growth and sample preparation

BaF_2 (Merck Optipur) was purified by zone refining in vitreous carbon crucibles. After drying under vacuum, $BaBr_2$ was treated with $SiBr_4$ in quartz crucibles to minimise contamination by oxygen-containing impurities. BaF_2 and $BaBr_2$ were mixed in stoichiometric quantities in a graphite crucible and melted at 960 °C in a high frequency furnace under an argon atmosphere. 100 ppm EuF_2 was added to the melt. BaFBr crystals with excellent optical quality were grown by the Bridgman–Stockbarger method.

The crystals were orientated by the Laue back reflection method and cut with a wire saw into $7 \times 6 \times 1 \ mm^3$ samples for optical measurements and into $5 \times 3 \times 1 \ mm^3$ samples for EPR measurements. The samples were irradiated with x-rays (50 kV, 40 mA) in darkness at room temperature (3–10 min) for optical measurements and at 77 K (4 hours) for EPR measurements.

2.2. Optical measurements

Absorption, luminescence and luminescence excitation spectra were measured with a single-beam spectrometer in which two 0.25 m double monochromators (Spex) were available for excitation and for luminescence. The samples were excited with either halogen or xenon lamps. UV-visible luminescence was detected using single photon counting with a photomultiplier. A germanium detector was used for the infrared emission. The excitation and luminescence spectra were corrected for the spectral response of the monochromator, for the lamp intensity, and for the detector sensitivity.

2.3. EPR measurements

EPR spectra were measured at the x-band on a Varian E-12 spectrometer equipped with an Air Products Heli-Tran™ continuous flow helium cryostat and a LakeShore Cryotronics DRC-93C temperature controller. For these experiments, the crystals were x-irradiated while immersed in liquid nitrogen or at room temperature in a light-tight enclosure.

3. Results

3.1. Optical measurements

Three types of defects were created in Eu-doped BaFBr by x-irradiation at room temperature. The absorption spectrum obtained for the electric field vector, E, perpendicular to the c axis showed the same bands at low temperatures as x-irradiated, undoped BaFBr: an $F(Br^-)$ band peaking at 2.15 eV, an $F(F^-)$ band centred at 2.65 eV
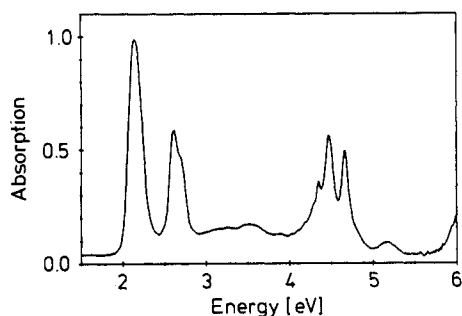
Figure 1. Optical absorption spectrum of BaFBr:Eu at 10 K after x-irradiation at room temperature.

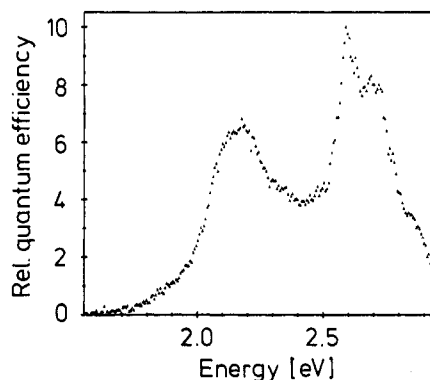Figure 2. Excitation spectrum of the photo-stimulated luminescence of Eu^{2+} (3.19 eV) measured at 10 K.

and an as yet unidentified band at 3.4 eV (figure 1). The assignment of the two bands at lower energy to electrons trapped in bromide and fluoride vacancies will be described in detail by Koschnick *et al* (1990). In the UV region the characteristic Eu^{2+} bands peaked at 4.36 eV (284 nm), 4.49 eV (276 nm) and 4.67 eV (265 nm). In both Eu^{2+}-doped and undoped BaFBr, two luminescence bands were observed at 0.91 eV (1.36 μm) and at 1.15 eV (1.08 μm) which could be excited by irradiation in the F centre absorption bands (Koschnick *et al* 1990). Since these results do not bear directly on the photostimulated luminescence results described here, they will be described in detail by Koschnick *et al* (1990).

Eu^{2+} luminescence at 3.19 eV (Brixner *et al* 1980) could be excited by irradiation in the F centre absorption bands. The excitation spectrum measured at 10 K of this photostimulated luminescence (PSL) is shown in figure 2. It shows all of the detailed structure observed in the F centre absorption spectrum (figure 1). Thus the photo-excitation of F centres is a prerequisite for the observation of PSL at low tempertures. This conclusion is in agreement with previous observations made at room temperature (Sonoda *et al* 1983, Takahashi *et al* 1984, 1985).

The PSL was found to have an unexpected strong temperature dependence as illustrated in figure 3. These data were obtained in the following way. The crystal was x-irradiated at room temperature and then cooled in the dark to 10 K. The PSL was then excited by irradiation in the centre of the $F(Br^-)$ band for about 3 seconds with low intensity light. The PSL was integrated during this period. The experiment was repeated at several temperatures while warming up the irradiated crystal from 10 K to room temperature. The experiment was repeated while ramping down the temperature. The intensity of the exciting light was so weak that, after a complete temperature cycle, the total PSL intensity was only 1–2% of that available. As can be seen from figure 3, the intensity increase on going from 60 to 100 K was about a factor of 10. The spectral energy shift of the PSL with temperature was so small that it remained within the spectral window of the detection. The broad absorption around 3.4 eV decreased in intensity with increasing temperature. Since the PSL overlaps this absorption region, this would cause an artificial increase in the PSL intensity. We estimate this would only be about 30% and would not account for the major intensity changes observed here. The region of figure
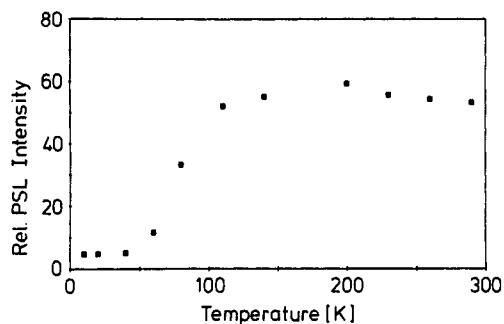
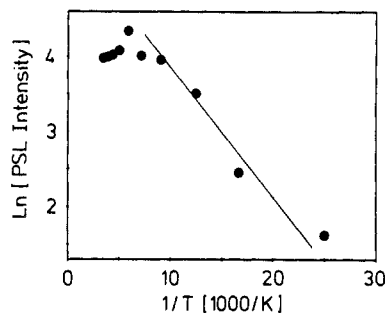**Figure 3.** Temperature dependence of the PSL intensity. For detail see text.

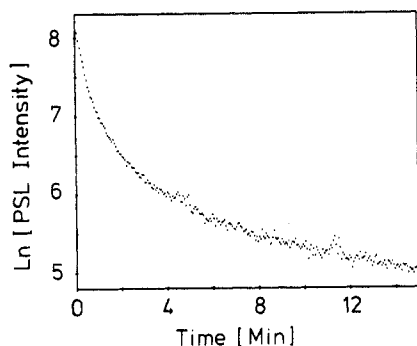**Figure 4.** Logarithm of the PSL intensity as a function of $1/T$.

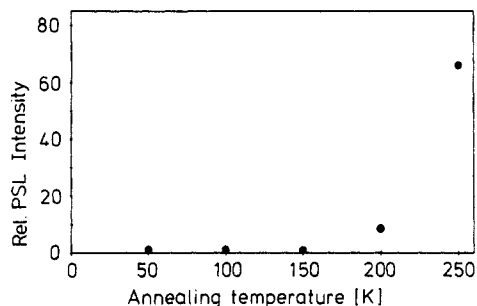**Figure 5.** Semilog plot of the bleaching effect of the PSL.

Figure 6. PSL intensity at 10 K as a function of the annealing temperature.

3 between 40 and 140 K is shown as a semilog plot versus $1/T$ in figure 4. It appears to be linear between about 40 and 90 K. An activation energy of about 15 meV was calculated from the slope of the line in this temperature region.

If the crystal was irradiated with monochromatic light in one of the F centre bands at 10 K, the PSL was almost completely exhausted after a few minutes of continuous excitation with a halogen lamp (de Leeuw *et al* 1987). The time dependence of this bleaching effect had fast and slow components (figure 5). This behaviour was observed at all of the temperatures studied. The time constants for the fast and slow components depended on the intensity of the exciting light, however, fast and slow components differing roughly by an order of magnitude were always observed. The time constants obtained from the data in figure 5 are 0.6 and 12 min when approximating the decay to only two time constants.

After continuous excitation at 10 K, the PSL intensity decreased to a very low residual value. Surprisingly, after subsequently warming the crystal to room temperature and recooling to 10 K, PSL could again be excited. Its intensity was about the same as that measured the first time at 10 K. This procedure of exhausting the PSL at low temperature, warming, recooling and re-exciting PSL could be repeated several times. For a more quantitative analysis of this effect the PSL was exhausted by excitation for a few minutes at 10 K before the crystal was annealed for 10 minutes at different temperatures and
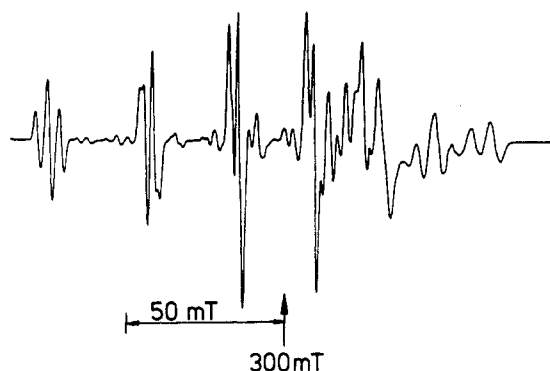
Figure 7. An EPR spectrum of the Br_2^- V_K centre in a single crystal of calcium-containing BaFBr exposed to x-rays at 77 K. The spectrum was measured at 40 K and 9.175 GHz with $B \parallel c$. The calcium impurity increased the yield of radiation-damage products, but did not affect the structure of the V_K centre.

then recooled to 10 K. As can be seen from the results in figure 6, the PSL could be restored after exhaustion at low temperature by warming above 150–200 K.

If the crystal was held at 200 K for a sufficient time, the original PSL intensity could be restored almost completely. Performing the experiment at 250 K accelerated the restorative effect. After each PSL-thermal restoration cycle, about 5–10% of the PSL effect was lost and a similar reduction in the intensity of the corresponding F centre absorption band occurred.

The exhaustion of the PSL by excitation in one of the F bands was found to influence the amount of PSL achievable from excitation in the other F band; an asymmetry in behaviour was observed for the two F centre bands. If the PSL was exhausted completely by continuous irradiation in the $F(Br^-)$ band (2.16 eV or 575 nm) at 10 K and then PSL was excited by irradiation in the $F(F^-)$ band (2.64 eV or 470 nm), only about half of the expected PSL intensity was obtained. However if the experiment was performed in the reverse order on a freshly irradiated crystal, then no PSL intensity could be excited by the final irradiation in the $F(Br^-)$ band.

3.2. EPR measurements

In this section we report EPR measurements on hole centres produced by x-irradiation between 8 and 77 K in pure and Eu^{2+}-doped BaFBr. The $F(F^-)$ and $F(Br^-)$ centres were not detected in conventional EPR experiments because of their low concentration and large linewidths. Fortunately, they can be measured by optically-detected EPR. A detailed analysis of their EPR spectra and their relationship to Eu^{2+} will be described in a forthcoming publication (Koschnick *et al* 1990). Figure 7 shows the EPR spectrum obtained at 40 K from a crystal of undoped BaFBr with B_0 parallel to the crystallographic c axis following its x-irradiation at 77 K. The spectrum is assigned to Br_2^- V_K centres.

The assignment of the V_K spectrum to a species containing two equivalent bromine nuclei is based on the distinctive hyperfine pattern from the two isotopes of bromine (^{79}Br: $I = 3/2$, 50.69%, $g_N = 1.404\,266$; ^{81}Br: $I = 3/2$, 49.31%, $g_N = 1.513\,706$). Three kinds of species form (^{79}Br–^{79}Br, ^{79}Br–^{81}Br, and ^{81}Br–^{81}Br), which have relative concentrations (1.0 : 1.94 : 0.94) determined by the natural abundances of the isotopes, and

Table 1. Principal values and directions of spin Hamiltonian parameters matrices for Br_2^- V_K centre† in BaFBr. The polar and azimuthal angles (θ, φ, respectively) are defined in the usual way in a right handed coordinate system defined by $x \equiv a$ and $z \equiv c$, where a and c are crystallographic axes (Liebich *et al* 1977). The angles marked by * were not varied. The presence of only four symmetry sites guarantees that the principal direction along (θ, φ) = $(90°, -45°)$ is exactly along that direction (Weil *et al* 1973).

Parameter matrix	Principal value		θ	φ
g	1	2.177 ± 0.002	34.8 ± 0.5	225.0^*
	2	2.170 ± 0.002	90.0^*	-45.0^*
	3	1.981 ± 0.002	55.2 ± 0.5	45.0^*
$\dfrac{A(^{81}Br)}{h}$ (MHz)	1	224 ± 10	35.8 ± 0.5	225.0^*
	2	203 ± 10	90.0^*	-45.0^*
	3	1225 ± 10	54.2 ± 0.5	45.0^*
$\dfrac{P(^{81}Br)}{h}$ (MHz)	1	-10 ± 20	70 ± 15	225.0^*
	2	-30 ± 20	90.0^*	-45.0^*
	3	40 ± 20	20 ± 15	45.0^*

† Principal values of g and A matrices for Br_2^- V_K centre in KBr for comparison to BaFBr data (Schoemaker *et al* 1973).

g		$\dfrac{A(^{81}Br)}{h}$ (MHz)	
	2.1629		215.2
	2.1623		214.7
	1.9839		1261.7

the isotopes.

To determine which of the various possible pairs of bromine ions form the observed Br_2^- centre, the orientation dependence of the EPR spectra was measured for the species in a single crystal at 40 K. An analysis of the orientation dependence gave the parameter matrices for a spin-Hamiltonian of the form

$$\mathcal{H} = \beta SgB + \sum_{i=1}^{2} (SA_i I_i + \beta_n I_i g_n B + I_i P_i I_i)$$

in which the terms have their usual meanings (Abragam and Bleaney 1970) and the index i denotes the two equivalent bromine nuclei. A computer program using exact diagonalisation of the spin Hamiltonian matrix was used, fitting 222 transitions from our independent crystal rotating to a mean field deviation of 0.5 mT. The principal values and directions of the resulting matrices are given in table 1. The presence of only four symmetry-related Br_2^- species, instead of the eight possible for D_4 point symmetry (Liebich and Nicollin 1977), restricts the principal directions of the H parameter matrices g, A_{Br} and P_{Br}, as indicated in table 1. (The quadrupole data could not be determined very precisely from the EPR line spectra.) Comparison of the principal directions obtained to internuclear directions in unperturbed BaFBr indicate that this centre is aligned parallel to the internuclear axis joining bromide ions in two different planes ($[\theta, \varphi]$ = $[55.05°, 45.0°]$). The large experimental linewidth at all of the orientations studied prevented resolution of superhyperfine splittings from adjacent nuclei. There are two possible models for this centre that must be considered. The first is an H centre in which a Br_2^- molecular ion is located at a single anion site with the internuclear axis parallel to

the out-of-plane Br–Br direction. This model is inconsistent with the EPR results, since the environments of the two bromide ions would be inequivalent. Also, by analogy with the H centre observed in KBr (Kanzig and Woodruff 1958), additional superhyperfine splittings from a third bromide ion would be expected. The second model is a V_K centre in which the trapped hole is shared equally between bromide ions in adjacent planes. In the latter model, the anions move off of their normal lattice positions, reducing the internuclear distance, in response to the increased bond strength from trapping the hole in an antibonding orbital. Atomistic simulations by Baetzold predict stable configurations for the Br_2^- H centre having internuclear axes parallel to either a or b. On the other hand, the most stable V_K centre is predicted (Baetzold 1990, 1988, Baetzold *et al* 1987) to have an out-of-plane Br_2^- configuration that is fully consistent with the structural data in table 1. In this model, the calculated bond length is 2.92 Å, reduced from the normal lattice distance of 3.89 Å (Baetzold 1987). The structures previously assigned to V_K centres in SrFCl (Bill *et al* 1969) and BaFCl (Yuste *et al* 1975) are similar. The footnote to table 1 also includes the principal values of the g and A matrices reported for Br_2^- V_K centre in KBr for comparison to the current data and to support our assignment.

Eu^{2+} ($4f^7$, $^8S_{7/2}$) provides a strong EPR signal that is easily detected between 4 and 300 K, whereas Eu^{3+} ($4f^6$, $^7F_0$) gives no EPR spectrum. (Abragam and Bleaney 1970). The spectrum shown in figure 8(a) is identical to that published previously for Eu^{2+} substituting for Ba^{2+} in BaFBr (Nicollin *et al* 1978). There are seven fine structure transitions, each of which shows twelve hyperfine features from the two magnetic isotopes of europium (^{151}Eu: $I = 5/2$, 47.9%; ^{153}Eu: $I = 5/2$, 52.1%). The field orientation for this spectrum was chosen so as to reduce the overlap of the V_K and Eu^{2+} spectra. Figure 8(b) shows the spectrum after irradiating the Eu^{2+} containing crystal with x-rays at 77 K for four hours. The asterisks mark the positions of the prominent V_K centre lines. The concentrations of V_K and Eu^{2+} centres are of the same order, about 10 ppm, as inferred from the line intensities. After warming the crystal to room temperature, the V_K centres decay (figure 8(c)). However, within experimental error, the Eu^{2+} EPR spectrum remained completely unchanged. This shows that the V_K centres do not decay at the europium sites to produce Eu^{3+}.

4. Discussion

Takahashi *et al* (1984, 1985) have proposed a model for radiation damage and the PSL process in BaFBr:Eu^{2+} in which x-irradiation produces Eu^{3+} ions and conduction band electrons which are trapped to form F centres. Von Seggern *et al* (1988a, b) argued that direct Eu^{2+} ionisation produces $F(F^-)$ and $F(Br^-)$ centres and mobile holes, the latter being trapped by the rare-earth activator to produce stable Eu^{3+}. Irradiation in the F centre absorption bands ionises these defects, the resultant mobile electrons being trapped by Eu^{3+} with PSL resulting from relaxation of the resultant excited Eu^{2+} state. The general features of this simple model have received wide acceptance.

Our EPR experiments show clearly that the mobile hole centres, either mobile V_Ks or secondary hole species, are not captured by Eu^{2+} to produce stable Eu^{3+} centres. In the Takahashi model it is assumed that only one carrier is mobile during the PSL which can account for only a single activation process. The results of our low-temperature PSL experiments (figures 3 and 4) in which a thermally-activated process was observed would be consistent with this model and an activation energy of 15 meV would be reasonable
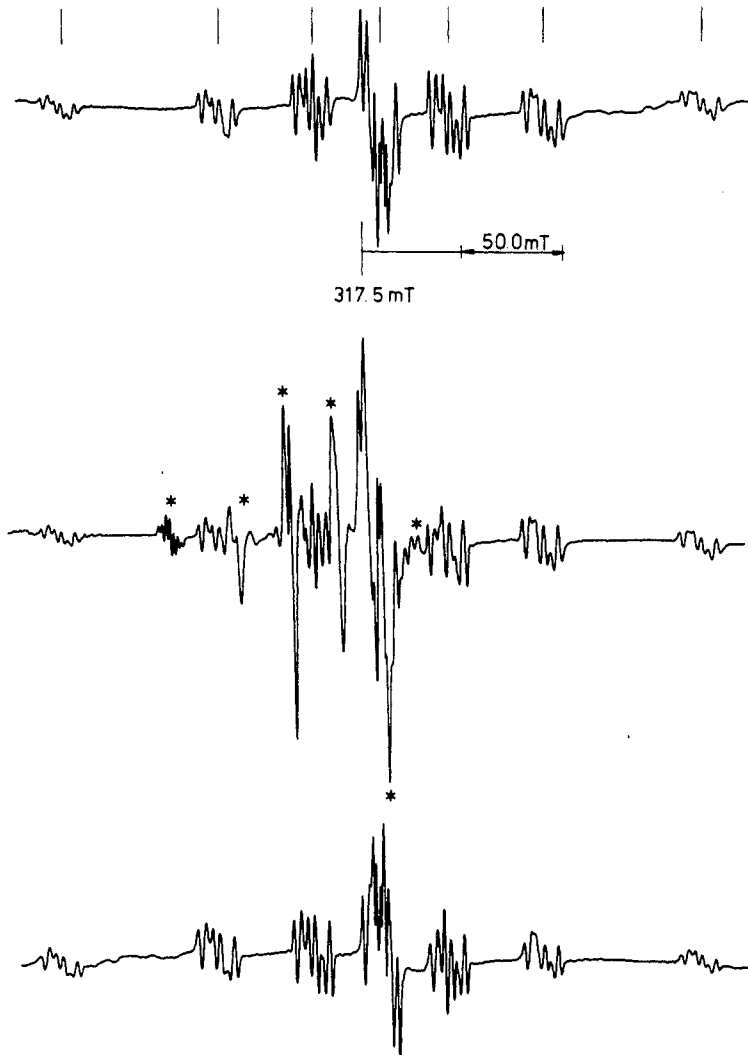
50.0 mT

317.5 mT

Figure 8. EPR spectra measured at 40 K from a BaFBr single crystal doped with about 10 ppm Eu^{2+}. The crystal orientation was chosen to reduce overlap between the V$_K$ and Eu^{2+} spectra. (a) before irradiation (the vertical bars indicate the Eu^{2+} lines); (b) after 4 hours x-irradiation at 77 K (the stars indicate the V$_K$ centre lines), (c) after subsequent warming to 300 K.

for the thermally-assisted ionisation of excited F centres to produce mobile conduction band electrons. However, the results of the thermal cycling experiments represented in figure 6 are difficult to reconcile with the Takahashi model. The stimulation of PSL by continuous F-band excitation at low temperatures should eventually exhaust all of the $F(F^-)$, $F(Br^-)$, and Eu^{3+} centres. The observed regeneration of PSL active centres by annealing above 150 K (figure 6) implies a source of electrons and/or holes that cannot be involved in PSL below this temperature.

Furthermore, recent luminescence studies (Sun *et al* 1987, 1988) of BaFBr doped with Eu^{2+} and Eu^{3+} have also shown that divalent europium has in fact no propensity to

react with V_K centres produced by x-radiation and Eu^{3+} has a high cross-section for electron trapping. Eu^{3+} would, therefore, be a powerful recombination centre in this material. We conclude from all of this evidence that the Takahashi model for the PSL process, that is a recombination between the F centre electrons and Eu^{3+}, is incorrect.

We propose the following alternative model to explain the effects of temperature on the PSL process in BaFBr : Eu^{2+}. Since Eu^{3+} is not the hole bearing centre, an alternative hole centre must exist which upon recombination with an F centre electron transmits the recombination energy to the rare-earth activator. The basic assumption of our model is that there is a propensity for the F centres and the room-temperature-stable hole centres, which must exist as the product of the decay of mobile V_Ks, to associate with the Eu^{2+} activators. There is evidence for such an association from recent magneto-optical and optically-detected ESR studies. A detailed description of this work is beyond the scope of this publication (Koschnick *et al* 1990). Upon x-irradiation isolated F centres, isolated hole centres, aggregates of Eu^{2+} and F centres and Eu^{2+} and hole centres, and a low concentration of 'triple aggregates' between Eu^{2+} holes and F centres are formed. These aggregates are not considered to be pair- or triple-defects with discrete configurations: rather they are visualised as centres in which the Eu^{2+}–F/hole are weakly bound resulting in a range of separations between the rare-earth ion and the two intrinsic radiation-damage products. Therefore, at a given temperature there is a dynamic equilibrium between isolated F and hole centres and these aggregated states. At low temperature this equilibrium is frozen in.

Irradiation in the F absorption bands causes immediate recombination of the electron–hole pairs in the triple aggregates. Energy transfer to the associated Eu^{2+} stimulates the well known 390 nm emission of the rare-earth ion. These triple aggregates are responsible for the fast components in the low-temperature, time-resolved PSL experiments.

The observation of a slow component in the PSL bleaching process at low temperatures is explained as being due to the excitation of F centres at intermediate distances; they are not close enough to Eu^{2+}–hole pairs to be considered as triple aggregates but they are sufficiently close for them not to behave as isolated defects. An implicit assumption is that the excited F centre electron has a finite diffusion range. If this was not so, all of the hole centres would be bleached by recombination upon F centre excitation. The observation of an increased PSL intensity above 60 K is interpreted to be the result of an increased range for excited F electrons through thermally activated conduction band motion so that more distant F centres contribute to the recombination with Eu^{2+}–hole aggregates.

Since PSL can be observed with slow and fast time constants down to temperatures as low as 10 K, where no anion vacancy motion can take place, it is clear that the ionised electron and not the F centre migrates to recombine with the hole centre.

After the supply of F(X$^-$)–Eu^{2+}-hole triple aggregates is exhausted by recombination at low temperatures, annealing above 150 K initiates the diffusion of both hole- and F centres. The equilibrium distribution between europium-associated and isolated centres is re-established and PSL can once again be stimulated at low temperatures.

Unfortunately, the nature of the room-temperature-stable hole centre is not yet known. As can be seen from figure 8(*c*), no new EPR spectrum could be detected at 40 K after the thermally-induced decay of the Br$_2^-$ V_K centre. The stable hole centre is expected to be paramagnetic. Therefore, further work at lower temperatures applying other magnetic resonance techniques with higher sensitivity, such as ODMR, is currently underway in an attempt to identify this species.

The observation that no PSL can be excited in the $F(Br^-)$ band at 10 K after PSL excitation in the $F(F^-)$ band suggests that both centres are excited simultaneously by 470 nm light. Indeed the $F(Br^-)$ centre has a second absorption band in the spectral region where the $F(F^-)$ centre absorbs (Koschnick *et al* 1990). The fact that, after exciting PSL in the $F(Br^-)$ absorption, the PSL achievable by subsequent excitation in the $F(F^-)$ band is only partly diminished after prolonged irradiation, means that there is no optical transition of the $F(F^-)$ centre superimposed on the main $F(Br^-)$ absorption band. It appears that electrons excited from $F(Br^-)$ centres find triple aggregates containing $F(F^-)$ centres. This suggests that the two types of F centres are not randomly produced, but that they are spatially correlated. Further evidence for this conclusion will be given by Koschnick *et al* (1990).

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