Experimental Evidence for the Aggregation of Photostimulable Centers in BaFBr:Eu^{2+} Single Crystals by Cross Relaxation Spectroscopy

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Spatial correlation between the activator ion Eu^{2+} and electron and hole traps generated by x irradiation is thought to play a decisive role in the photostimulated emission process of the storage phosphor BaFBr:Eu^{2+}. We report the first direct experimental evidence for correlations among F centers, hole centers, and Eu^{2+} obtained by measuring cross relaxation effects in optically detected paramagnetic resonance. BaFBr treated with the known procedures for removing oxygen still retains 50 ppm or more of O^{2-}. This ion is critically involved in the formation of F and hole centers.

Barium fluorobromide doped with Eu^{2+} is an important storage phosphor in which x-ray produced images are stable in the dark at room temperature [1–3]. Its dynamic range for image formation of over 5 orders of magnitude makes it superior to conventional x-ray films for many applications in medicine, crystallography, and biochemistry. For readout, the phosphor is optically stimulated, frequently with a He-Ne laser (633 nm), leading to a Eu^{2+} emission at 390 nm. Until now, the mechanisms of the storage and readout processes have not been understood, preventing improvements in the efficiency of the phosphor material and providing a challenging fundamental problem of defect interactions. There is agreement that electron and hole traps are involved in the process, the former being F centers on either the Br$^-$ or F$^-$ sublattices (BaFBr crystallizes with the PbFCl structure [4,5]). There are controversial views about the nature of the hole centers and the F center production mechanism. Takahashi et al. [6] proposed that, upon x irradiation, Eu^{2+} is ionized to Eu^{3+} and the free electron is subsequently captured by an existing Br$^-$ vacancy to form an F(Br$^-$) center [7]. von Seggern and co-workers [8,9], however, argued that high-energy radiation creates free excitons which decay near Eu^{2+} to form an F-H pair (the H center is a Br$_2^-$ ion occupying a Br$^-$ site [10]). They assumed that the vacancies needed to form F centers are created by the irradiation process. The F-H center production is thought to be analogous to the process known in the alkali halides. From a study of the temporal dependence of the photostimulated luminescence (PSL), von Seggern et al. [8] claimed that the hole trap, the electron trap, and the Eu^{2+} activator must be in close proximity, a conclusion arrived at independently by Hangleiter et al. [11] from the temperature dependence of the PSL effect. This model is unusual, since short trapped-electron–trapped-hole distances normally lead to rapid recombination.

In this Letter we present the first direct experimental evidence that the irradiation-created electron centers, hole centers, and Eu^{2+} activators are correlated and not statistically distributed, by detecting cross relaxations among them using optically detected electron paramagnetic resonance (ODEPR). We identify electron and hole centers created at low temperature and at room temperature, and show that the model of Takahashi et al. [6,7] is not correct. In all previous work, the essential role of the ubiquitous oxide impurity as a hole trap at room temperature and a source of Br$^-$ vacancies for F-center formation was overlooked. In the presence of oxide, an F-(Br$_2^-$-V_k) center mechanism is dominant, rather than an F-H pair mechanism as proposed by Rüter et al. [9] (in a V_k center a hole is shared by two adjacent halide ions [12]).

Single crystals of BaFBr:Eu^{2+} were grown by the Bridgman method in graphite crucibles coated with pyrolytic graphite. Some crystals were deliberately doped with ^{17}O-enriched (40%) BaO.

Experimental evidence for the correlation of the various defects is obtained from the magnetic circular dichroism of the optical absorption (MCDA) and MCDA-detected ODEPR. The MCDA is the differential absorption for left- and right-polarized light propagating along a static magnetic field. It is proportional to the spin polarization of the ground state of a paramagnetic Kramers defect. Upon inducing EPR transitions in the ground state the spin polarization can be diminished. This is monitored as a decrease of the MCDA [13].

In Fig. 1 the MCDA is shown for a BaFBr crystal containing 100 ppm Eu^{2+}, as doped in the melt, following its exposure to x rays at room temperature. At low photon energy two MCDA bands are measured which are caused by F(Br$^-$) and F(F$^-$) centers, as was shown previously by ODEPR and optically detected electron-nuclear double resonance (ODENDOR) [14,15]. The MCDA spectrum associated with the 4f-5d transition of Eu^{2+} appears at 4.5 eV. The spectral region between approximately 3 and 4 eV is a superposition of MCDA signals from at least two defects, one of which was identified as being O$^-$ on an F$^-$ site (see also below) [16].

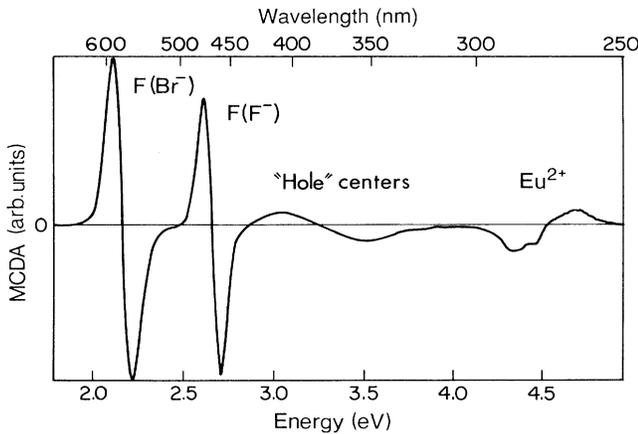Figure 2, curve a, shows the MCDA spectrum from a

FIG. 1. MCDA of BaFBr: 100 ppm Eu^{2+}, x irradiated at 300 K, measured with $B = 3$ T parallel to c at 1.5 K. The O^{2-} content was of the order of 50 ppm.

FIG. 2. MCDA vs magnetic field at 1.5 K for $BaFBr:Eu^{2+}$ measured under continuous microwave irradiation of 24 GHz. Curve a: at 285 nm prior to x irradiation; 100 ppm Eu^{2+}. Curve b: at 590 nm [in the $F(Br^-)$ band] after x irradiation at 300 K; 10 ppm Eu^{2+}.

crystal doped with 100 ppm Eu^{2+} measured at 285 nm, i.e., in the Eu^{2+} transition, at 1.5 K as a function of the magnetic field under continuous microwave irradiation of 24 GHz. The continuous MCDA increase with field reflects the thermal equilibrium magnetization (Brillouin function [17]). The dips and peaks are caused by EPR transitions of the paramagnetic Eu^{2+} ion ($[Xe]4f^7$; $S = \frac{7}{2}$). The expected seven fine-structure lines are measured in the high-field region [18]. The corresponding forbidden transitions with $\Delta m_s = \pm 2$ are seen at lower field. There is a remarkable change of sign in the allowed ODEPR lines compared to the forbidden signals, which all have the expected negative sign. This phenomenon is not influenced by the light intensity, i.e., it is not due to optical pumping effects [19]. It can be explained by a "forbidden" spin-lattice relaxation within the Eu^{2+} Zeeman levels which connects $\Delta m_s = \pm 2$ states faster than those with $\Delta m_s = \pm 1$. This effect does not appear in the forbidden EPR transitions where only $\Delta m_s = \pm 2$ states are connected by the microwaves. Details of the Eu^{2+} spin-lattice relaxation will be published elsewhere [20]. The effect of an anomalous spin-lattice relaxation on the sign of the EPR lines can only show up in optical detection where the total spin polarization of the ground state is measured. In conventional EPR one measures only the absorption of the microwave quanta which induce an EPR transition [20].

Figure 2, curve b, shows a similar result to that in Fig. 2, curve a, but after the crystal was x irradiated at 296 K. The optical wavelength is set to 590 nm, i.e., into the $F(Br^-)$ band. The crystal was doped with 10 ppm Eu^{2+}. As well as the EPR line from $F(Br^-)$ centers, which occurs at about 880 mT, the Eu^{2+} fine-structure transitions are seen due to a cross relaxation (CR) effect. CR is possible if the EPR spectra of two defects overlap and if there is a sufficiently strong spin-spin interaction to induce spin flip-flop processes between the two spin sys-
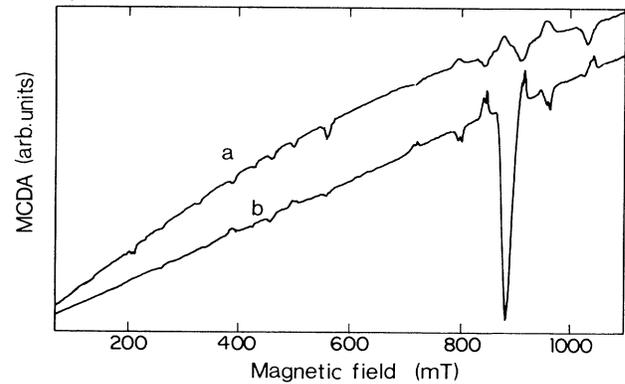
tems [21]. The $Eu^{2+} + \frac{1}{2}$ to $-\frac{1}{2}$ transition and the F-center transition overlap to a large extent. The spin-spin interaction causing CR is, however, weak so that neither the F center spectrum nor the Eu^{2+} fine-structure splitting is affected.

A CR effect is seen if the CR rate R_{CR} is an appreciable fraction of the spin-lattice relaxation rate R_{rel}. For $F(Br^-)$ centers at 1.5 K, R_{rel} is 0.1 s^{-1} [20]. An R_{CR} value exceeding 0.05 s^{-1} should give a measurable effect. In order to estimate whether a CR effect could be observed for a statistical distribution of $F(Br^-)$ centers (concentration about 10^{16} cm^{-3}) and the Eu^{2+} activators, we have assumed that a dipole-dipole interaction causes the spin flip-flop processes [21]. For 10 ppm Eu^{2+}, less than 5% of the F centers will, on average, have a Eu^{2+} ion closer than 60 Å. For this distance, R_{CR} is only 0.005 s^{-1}. We have clearly observed the CR effect between F centers and Eu^{2+} for a dopant concentration as low as 5 ppm (6.5×10^{16} cm^{-3}). Therefore, F centers and Eu^{2+} activators must be present in a correlated fashion after x irradiation. A CR effect caused by a statistical distribution would only be seen if the Eu^{2+} concentration exceeded 100 ppm. However, the Eu^{2+} and F centers cannot be nearest neighbors since the dipole-dipole interaction in this case would have caused measurable effects on the shapes of the respective EPR spectra. The details of the CR effects seen in Fig. 2, curve b, are fully understood on the basis of the appropriate rate equations, and will be published elsewhere [20]. A CR effect from the F centers was not observed in the Eu^{2+} MCDA, which is explained by the fact that the spin-lattice relaxation time of Eu^{2+} at 1.5 K is 30 times shorter than that of the F center and that a population change between the $m_s = \pm \frac{1}{2}$ states in Eu^{2+} has a smaller influence on its total spin polarization, to which eight levels contribute ($S = \frac{7}{2}$). It is the total spin polarization that is measured by the MCDA technique. The spin po-

larization of the F center, which has only two Zeeman levels, is much more sensitive to changes in their occupancy. Furthermore, the concentration of Eu^{2+} is much higher than that of the F centers so that their influence on the total Eu^{2+} MCDA must be relatively small.

EPR measurements of a crystal doped with ^{17}O-enriched BaO after x irradiation at room temperature and ODEPR measurements in the MCDA bands peaking at 405 and 350 nm (see Fig. 1) gave the spectra arising from an O^- hole center in Figs. 3 and 4, respectively. The hyperfine interaction with ^{17}O ($I = \frac{5}{2}$) is resolved in both spectra. The EPR spectrum also shows a partly resolved superhyperfine structure. Electron-nuclear double resonance (ENDOR) and ODENDOR investigations unambiguously showed that the O^- ion occupies a regular F^- site [16]. The oxide precursor to the O_F^- impurity center is always present in nominally pure BaFBr, whether or not it is doped with Eu^{2+}. The accepted procedures for eliminating oxide impurities from alkali and alkaline-earth halides were meticulously applied in our experiments, but they failed to prevent substantial O^{2-} contamination in all of our samples [22]. Strong O_F^- signals were always observed following x irradiation of these crystals and their concentration was estimated to be of the order of 10^{18} cm^{-3}. The asymmetric shape of the ODEPR spectrum of O_F^- (Fig. 4, curve a) is due to the superposition of an ODEPR line with negative sign peaking at 890 mT. The MCDA of this species is superimposed on that from O_F^-. The origin of this center is not known. Figure 4, curve b, shows the ODEPR spectrum obtained by setting the optical wavelength into the $F(Br^-)$ band at 590 nm in an ^{17}O-containing crystal after its x irradiation at 300 K. Clearly, a CR to the O_F^- center is seen. Since both $F(Br^-)$ and O_F^- centers have concentrations of the same order of magnitude, i.e., 10^{16} cm^{-3}, a CR effect can only be seen if these centers are spatially correlated. CR effects between O_F^- and Eu^{2+} were also observed.
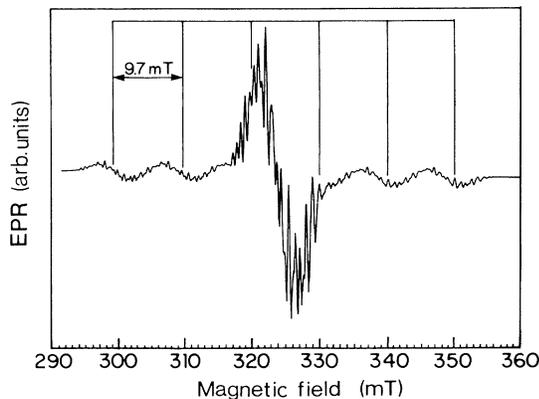
In crystals that contained comparatively low levels of oxide contamination, both $F(Br^-)$ and $F(F^-)$ centers were produced by x irradiation. At higher oxide levels, there was a large enhancement of $F(Br^-)$ center production. CR effects with Eu^{2+} were found for both F centers in BaFBr.

X irradiation below 120 K produces $Br_2^- \text{-} V_k$ centers and $F(Br^-)$ centers. The optical absorption of the $F(Br^-)$ centers (Fig. 1) is redshifted by 0.05 eV, indicating that their environment is perturbed. No $F(F^-)$ or O_F^- centers are formed below 120 K. The ODEPR of the $F(Br^-)$ centers can be measured in the $Br_2^- \text{-} V_k$ bands; the production of these centers occurs in a correlated way. Upon warming to 120 K, about half of the $Br_2^- \text{-} V_k$ and $F(Br^-)$ centers recombine giving a thermal luminescence between 2.2 and 3.0 eV. The remaining $Br_2^- \text{-} V_k$ centers diffuse through the crystal and a substantial fraction react with oxide impurities and form perturbed O_F^- centers. The O_F^- MCDA band around 3 and 4 eV (see Fig. 1) is redshifted by 0.07 eV. The $F(Br^-)$ MCDA band remains perturbed, but the redshift is only 0.04 eV after annealing to 120 K. Upon warming above 200 K, the $F(Br^-)$ MCDA band shifts to the position seen in additively colored BaFBr, where ENDOR established that the $F(Br^-)$ center is in a regular environment [23]. Also, the O_F^- band shifts to the position observed in BaFBr after x irradiation at room temperature. Thus, the O^{2-} precursor must be incorporated into the crystal at an F^- site and be charge compensated by a spatially correlated bromide vacancy. F centers are created by a radiation-induced electron-hole pair formation in which the electron is trapped in the bromide vacancy associated with O^{2-}, causing a redshift of the optical absorption. The hole is trapped as a nearby V_k center in the bromide sublattice. After warming to 120 K, $F(Br^-) \text{-} O_F^-$ pairs are formed which are stable up to

FIG. 3. EPR spectrum of O_F^- centers in BaFBr doped with BaO enriched to 40% in ^{17}O measured for B parallel to c at 10 K and 9.15 GHz.
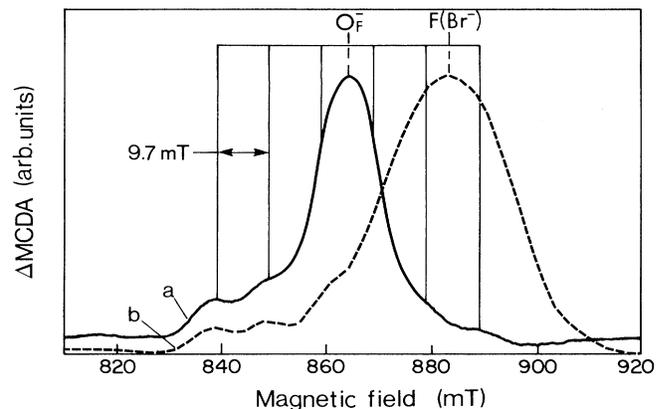

FIG. 4. Curve a (solid): ODEPR spectrum of ^{17}O-enriched O_F^- centers, measured at 405 nm, 24 GHz, and 1.5 K. Curve b (dashed): ODEPR spectrum measured at 590 nm showing cross relaxation between O_F^- and $F(Br^-)$ centers.

200 K. Thus, these results imply that the charge compensating vacancy becomes mobile at temperatures above 200 K when it is occupied by an electron. This mobility of F centers above 200 K was previously inferred from the observation of a replenishment effect in the photostimulated luminescence [11]. Corroborating this result, our ENDOR investigation showed that the O_F^- center formed at room temperature by x irradiation has a regular local environment—the vacancy has diffused away [16].

There are other hole centers formed as products of the $Br_2^- \text{-} V_k$ center decay that have yet to be identified. It is, however, clear that they have weak MCDA spectra above 2.5 eV. From F-center bleaching experiments, it is not yet clear which of these hole centers formed by $Br_2^- \text{-} V_k$ decay are involved in the PSL process.

The observation that below 250 K in relatively oxide-free material no $F(F^-)$ centers can be produced implies that their formation involves thermal activation.

In conclusion, the CR spectroscopy shows that irradiation-produced F centers, O_F^- centers, and Eu^{2+} activator ions are spatially correlated with each other although their local environments, as far as can be determined by ENDOR spectroscopy, are regular. We think that this spatial correlation is not a strict and rigid one, but it has certain statistical features. Probably there are enough "triple configurations" among F, hole, and Eu^{2+} centers to make the PSL process possible without thermal activation, as was observed by von Seggern and co-workers [8,9]. The PSL replenishment effect, observed after exhaustion at low temperatures and subsequent warming [11], shows that this correlation is not fortuitous. At this stage we can only speculate on the reason for the correlation. It could be the result of a combination of local lattice distortions around the smaller substitutional Eu^{2+} ion and the unusual double-layered structure of the BaFBr system.

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