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LETTER TO THE EDITOR

Optical detection of exciton EPR in fluorite crystals

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Abstract. Irradiation of alkaline earth fluorides with x-rays produces a strong fluorescence band in the ultraviolet. This band shows pronounced polarization effects when the crystals are placed in a magnetic field. EPR experiments on excited states using optical detection show that perturbed excitons with the molecular configuration of an H centre contribute to the fluorescence.

Considerable progress has been made recently in our understanding of excited states of the self-trapped exciton in alkali halide crystals (see the preceding letter (Call *et al* 1975), henceforth referred to as I, for references). The basis for this advance has been the observation of EPR in a $^3\Sigma$ -type state of the exciton. This exciton may be envisaged as arising from the trapping of an electron into an excited state of the V_K centre giving a complex which may be represented as $(V_K + e)$. EPR measurements show that the $^3\Sigma$ -type state has a molecular configuration similar to that of the V_K centre.

In the present work we report results of measurements of exciton EPR in crystals with the fluorite structure. The experimental techniques were similar to those used for alkali halides (see I). The excitons are created by irradiating crystals at helium temperatures in a microwave cavity with x-rays and EPR is detected by monitoring microwave-induced changes in either the intensity of polarized components of fluorescence, or the total intensity of fluorescence, as the field B of a superconducting magnet is varied.

It was shown by Beaumont *et al* (1970) that under x-irradiation crystals of CaF_2 , SrF_2 and BaF_2 emit a strong fluorescence band at 280, 298 and 310 μm respectively. They also showed that recombination luminescence of the V_K centre (arising from decay of $V_K + e$) occurs in the same spectral region and they concluded from lifetime and polarization studies that the recombination band was due to a transition of the type $^1\Sigma \rightarrow ^1\Sigma$. Our investigations show a large magnetic polarization of the UV fluorescence band for the three materials, suggesting that the band cannot be due entirely to a transition of the $^1\Sigma \rightarrow ^1\Sigma$ type. Guided by this result we have detected EPR in an excited state of the emitting centre and results of measurements on SrF_2 are shown in figure 1. We conclude from these measurements that there are at least two different centres contributing to the UV fluorescence band.

There are two fine-structure transitions in figure 1, each with a four-line hyperfine structure (HFS) and analysis shows that we are dealing with an $S = 1$ electronic state coupled to two inequivalent fluorine nuclei. Although detailed angular plots of the spectrum are not possible, because of lack of intensity when the external magnetic field is not oriented

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along a $\langle 111 \rangle$ direction (see I), it is nevertheless clear that the largest fine structure and hyperfine structure develop with $B \parallel [111]$. The H centre in alkaline earth fluorides is aligned along $\langle 111 \rangle$ and shows a hyperfine interaction with two inequivalent nuclei (Hayes *et al* 1974). It follows that the polarized emission in the UV band arises from an exciton with the molecular configuration of an H centre rather than a V_K centre (the principal axis of the V_K centre in alkaline earth fluorides is aligned along $\langle 100 \rangle$ and its EPR spectrum shows a hyperfine interaction with two equivalent nuclei (Beaumont *et al* 1970)).

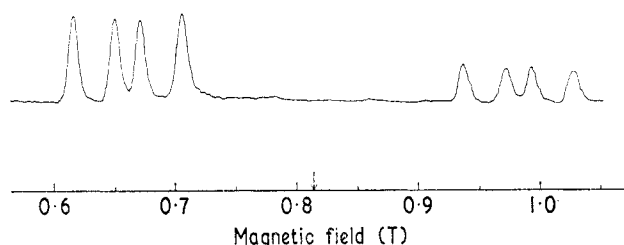


Figure 1. EPR of a triplet state of an exciton in SrF_2 at 1.6 K ($B \parallel [111]$, $\nu = 22.84$ GHz, microwave modulation frequency 180 Hz). Resonance was detected by microwave-induced changes in the total intensity of the 298 nm fluorescence band. The arrow indicates $g = 2$.

The limited angular investigations of the EPR spectrum that have been made show that the symmetry of the centre is less than axial and suggest that the polarized fluorescence is emitted by a centre of the type $(\text{H} + \text{e})$ perturbed by a neighbouring defect. To label our EPR spectrum we take $[111]$ as a principal (z) axis; the orthogonal (x, y) axes are chosen to be $[110]$ and $[11\bar{2}]$ in the perpendicular plane. We use the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D [S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \sum_i \mathbf{I}^i \cdot \mathbf{A} \cdot \mathbf{S}^i \quad (1)$$

where $S = 1$ and the summation covers two fluorine nuclei, each with $I = \frac{1}{2}$. The parameters of (1) are given in table 1 for CaF_2 , SrF_2 and BaF_2 ; the general precision is not high because of the limitations of the angular data. It should be emphasized that only one of the 'natural' axes for the centre has been experimentally established.

Table 1. Parameters of the EPR spectra of perturbed excitons in alkaline earth fluorides

Crystal	g_z	$g_x \approx g_y$	$D(\text{G})$	$E(\text{G})$	$A_z^1(\text{G})$	$A_z^2(\text{G})$	$A_x^1 \approx A_y^1(\text{G})$	$A_x^2 \approx A_y^2(\text{G})$
CaF_2	1.992	~ 2.00	+1552	~ -587	588	286	~ 349	~ 297
SrF_2	1.982	~ 1.98	+1588	~ -954	547	341	~ 379	~ 288
BaF_2	1.985	~ 1.98	+1397	~ -1164	539	368	~ 329	~ 336

Comparison of the hyperfine parameters of table 1 with those for the H centre (Hayes *et al*) shows that the A_z^i are close to one half of the corresponding parameter for the H centre, and this is consistent with a change from $S = \frac{1}{2}$ to $S = 1$ (the hyperfine parameters for the two centres scale in the same way from CaF_2 to SrF_2 to BaF_2). A similar relationship holds between a triplet state of the self-trapped exciton in alkali halides and the V_K centre (Marrone *et al* 1973). However, our EPR spectrum is different from the alkali halide case to the extent that we have a relatively large E value (table 1) indicating a major perturbation of $(\text{H} + \text{e})$.

It seems that in our EPR spectrum we are observing effects directly relevant to the radiolysis process in fluorites. Here intrinsic mechanisms of radiolysis are very inefficient (Call *et al* 1974) and the triplet we observe may be a result of production of close H-F pairs with a rapid subsequent production of $(H + e)$ in an excited state and also an anion vacancy. Restoration of the lattice to an undamaged state would follow as a consequence of exciton decay and recombination of the resulting interstitial ion with the vacancy.

We shall present a more detailed description of our experiments and a full discussion of their relevance to radiolysis at a later time.

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