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Experimental evidence for spatial correlation between F and H centres formed by exciton decay at low temperatures in KBr

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Abstract. Optical detection of electron paramagnetic resonance of F–H-centre pairs created by low-temperature x-ray irradiation of KBr was performed via the magnetic circular dichroism of the optical absorption (MCDA) whereby cross-relaxation (CR) effects between the H and F centres were detected in the MCDA of the F centres. A quantitative analysis of the CR effects yielded direct experimental evidence that all F and H centres are spatially correlated after their low-temperature formation with a separation of four lattice sites along the ⟨110⟩ directions. A theoretical analysis of the CR result yields an estimate of the F-centre formation time of 2 ps, in agreement with other experimental evidence, and also shows that the F–H separation obtained is the first stable F–H-centre pair configuration.

1. Introduction

The formation and the decay of excitons have been the subject of intensive studies in the alkali halides (for a recent comprehensive review see Song and Williams 1993a). Exciton decay causes a luminescence on the one hand, and on the other hand the formation of the fundamental trapped electron and trapped hole centres: F centres (electron trapped at an anion vacancy) and H centres, halogen$_2^-$ molecular ions on substitutional halogen sites. F–H pairs were formed during relaxation of the self-trapped exciton (STE) of the lowest energy as a result of the adiabatic instability against axial relaxation of the system (Song and Williams 1993a, Song and Baetzold 1993). Their formation happens in a time faster than the lifetime of the π and σ luminescence (Bradford *et al* 1975, Suzuki *et al* 1979). As was shown by Toyozawa (1974), there is no barrier against the hole relaxation, which is very fast (10^{-13}–10^{-12} s). Electrons move very fast in the conduction band before they are captured by a relaxed or an unrelaxed hole (Williams *et al* 1978). Thus, the total lifetime of the exciton decay is the sum of the lifetime of the electron, the relaxation time of the unrelaxed excited state to the relaxed excited state and the formation time of F- and H-centre pairs. When irradiating an alkali halide crystal with ionizing radiation, the formation of F–H pairs is the dominating process (Faraday and Compton 1965). The majority of the F centres formed decays in a very short time due to the recombination of close F–H centre pairs (Kondo *et al* 1969). At temperatures below 25 K the decay time is temperature independent, while above this temperature there is a thermally activated process with an activation energy of 20 meV (Kondo *et al* 1969). The simplest explanation for the decay of F–H-centre pairs

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in the first few microseconds is the assumption that F–H pairs are direct neighbours along a ⟨110⟩ direction and that those pairs that are stable at 4.2 K have a separation of at least two lattice spacings along a ⟨110⟩ direction, where they are localized separately. However, there is no direct experimental proof for such a spatial correlation between F–H-centre pairs created at 4.2 K, nor is it clear how far apart the pairs need to be in order to remain stable.

In this paper we report on experiments that for the first time give direct experimental evidence for a spatial correlation of F–H-centre pairs formed at 4.2 K in KBr. In the experiment optical detection of the electron paramagnetic resonance (EPR) of the correlated F and H centres is measured via the magnetic circular dichroism of the absorption (MCDA) whereby cross-relaxation (CR) effects between the correlated defects are used to deduce the spatial correlation (Koschnick *et al* 1992).

2. Experiment

The crystal used in this study was a particularly pure KBr crystal provided by G McDugle (Eastman Kodak Co.). It was irradiated with x-rays in the microwave cavity at 4.2 K for about 15 h in order to produce enough H centres. V_K centres were also generated simultaneously.

The experimental method used to detect a spatial correlation between F and H centres was that of optically detected electron paramagnetic resonance (ODEPR) via the MCDA with detection of CR effects (Koschnick *et al* 1992). This is briefly explained as follows.

The MCDA, which is the differential absorption of right and left circularly polarized light, propagating along an external magnetic field, is proportional to the spin polarization of the ground state of a paramagnetic Kramers defect within the approximation of a free atom or ion. For a system with a spin of $\frac{1}{2}$ the MCDA is proportional to the population difference of the two Zeeman levels. The change in spin polarization by EPR transitions can be monitored as a change of the MCDA of the defect (Ahlers *et al* 1983). If there is a sufficiently strong spin–spin interaction between the two paramagnetic defects to induce spin flip-flop processes between the two spin systems, then an EPR-induced change of the spin polarization of one defect can cause a change in the spin polarization of the other, which can be monitored as a change in its MCDA. Thus, if there is such a CR effect, then the EPR of one defect can be monitored in the MCDA of the other defect linked to it by CR. Such a link is expected if the two defects are sufficiently near to each other (see below). Another condition to observe the CR effects in the MCDA is that the EPR spectra of the two defects have a partial overlap to ensure energy conservation (for further details see Koschnick *et al* 1992).

The experiments were performed with a custom-built computer-controlled K-band MCDA/ODEPR spectrometer (25 GHz), which operated between 250 nm and 1700 nm at temperatures between 1.5 K and 300 K.

3. Experimental results

X-irradiations of the pure KBr crystal at 4.2 K produced H centres, F centres and V_K centres. Figure 1(*a*) shows the optical absorption bands of these centres according to the literature, and figure 1(*b*) the MCDA spectrum. It was shown recently that H centres have an MCDA superimposed on the high-energy flank of the F-centre absorption, which is caused by those H centres with their molecular axes perpendicular to the static magnetic field. Parallel H

centres have no MCDA in the spectral region between 1.0 and 3.4 eV (Spaeth *et al* 1993, Meise 1993). Figure 2, trace a shows the ODEPR spectrum of the perpendicular H centres measured at 2.4 eV together with an EPR spectrum calculated with the known $g_\perp$-value and assuming a hyperfine interaction constant $A_\perp$ of 5 mT (figure 2, trace b; for details see Spaeth *et al* 1993). At 2.4 eV one also measures F centres (see figure 1(*b*)), which therefore also appear in figure 2, trace a. The V_K centres, simultaneously present, have MCDA bands different from those of the H centres. This is seen in the 'MCDA tagged by EPR', a kind of excitation spectrum of the ODEPR lines (Ahlers *et al* 1983) (figure 1(*c*)). Thus, e.g. at 2.38 eV (520 nm) one can measure the H-centre EPR without inducing simultaneously the V_K-centre EPR. It is also seen that the H-centre MCDA band does not overlap with the low-energy flank of the F-centre MCDA. Therefore, when measuring the ODEPR at 2.0 eV (620 nm) at the low-energy flank of the F centres one should not detect any H-centre EPR.

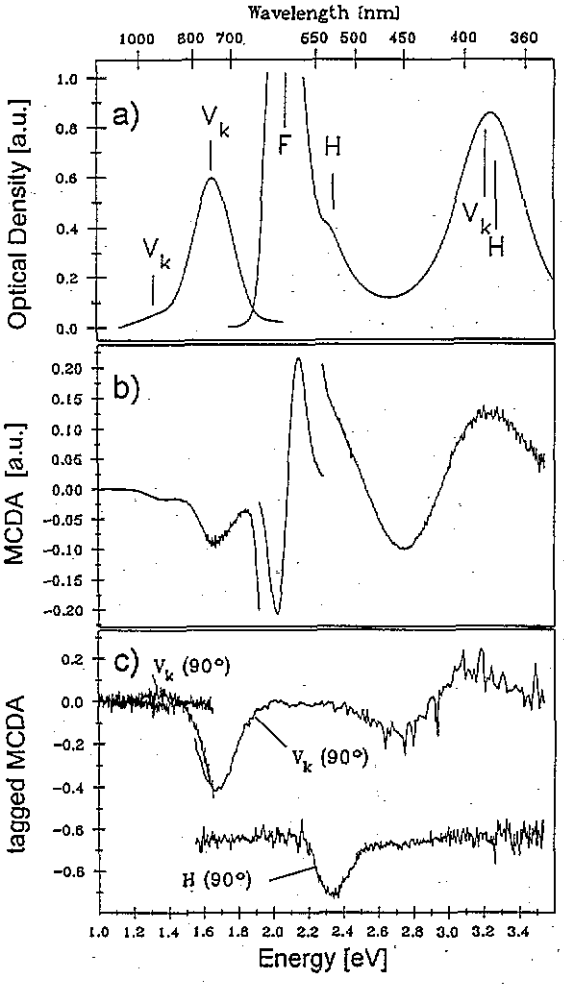

Figure 1. (*a*) Absorption of V_K, H and F centres in KBr x-irradiated below 20 K. (*b*) MCDA spectrum of KBr x-irradiated at 4.2 K *in situ*, measured at 1.5 K; magnetic field, 2 T. (*c*) Tagged MCDA spectra of V_K and H centres in KBr; $B_0 \parallel [100]$.

In figure 3 the results of the ODEPR measurements at 2.0 eV (low-energy flank of the F centre) and at 2.38 eV (H-centre MCDA) are shown. At 2.38 eV both the F-centre and the H-centre EPR lines appear (trace a) due to the overlap of the two MCDA bands. However,

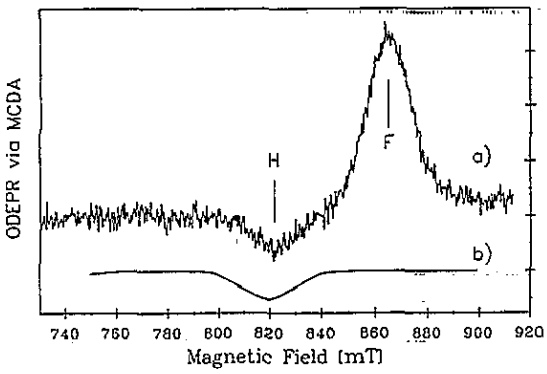

Figure 2. Trace a, ODEPR spectrum of KBr x-irradiated at 4.2 K *in situ*, measured at 1.5 K; microwave frequency, 23.8 GHz; phonon energy, 2.4 eV; $B_0 \parallel [100]$. Trace b, EPR simulation of H centres in KBr with their axes perpendicular to B_0; $A_\perp = 5$ mT; $g_\perp = 2.074$; half width of HF lines, 5 mT.

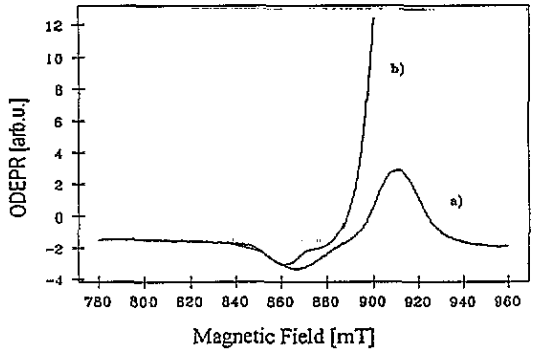

Figure 3. ODEPR spectra of pure KBr x-irradiated at 4.2 K *in situ* for about 15 h, measured at 1.6 K; microwave frequency, 24.5 kHz. Trace a, ODEPR via the H-centre MCDA at 2.38 eV (520 nm); trace b, ODEPR via the F-centre MCDA at 2.0 eV (620 nm).

at 2.0 eV no H-centre EPR should appear. The fact that it does shows the presence of a CR effect. A change in the H-centre spin polarization is transferred to the F-centre spin polarization (Meise *et al* 1993).

The effects of polarization transfer are also seen in time-resolved measurements. Figure 4(*b*) and (*c*) shows the temporal behaviour of the MCDA of F- and H-centre MCDA bands after switching off the microwaves that had induced the F-centre and H-centre EPR transitions, respectively. The MCDA bands reach thermal equilibrium with the characteristic spin-lattice relaxation times T_1 for the F and H centres ($T_{1F} = 20$ s, $T_{1H} = 2$ s at 1.5 K). When inducing the H-centre EPR and monitoring it in the F-centre MCDA, the temporal behaviour is approximately the same as inducing the F-centre ODEPR directly. The CR effect also changes its sign at 845 mT when changing the field position within the H-centre EPR line. This effect is demonstrated in figure 5(2), where the CR effect is measured for the H-centre field position at 837 mT (figure 5(2), trace a) and at 846 mT (figure 5(2), trace b). The vertical bars indicate the measured effects. Due to the light-induced F–H-centre recombination, the measurements were performed with very weak light with the consequence of a rather low signal-to-noise ratio. The CR signals follow the shape of the F-centre MCDA (figure 5(1), trace a), but at 845 mT, at the peak of the H-centre EPR line, it changes sign. For $B > 845$ mT the F-centre MCDA decreases; for $B < 845$ mT it increases.

Upon warming the crystal to 28 K for about 5 min, a thermally stimulated luminescence is observed because of a partial recombination of F and H centres. However, the CR effects were completely lost. This means that the spatial correlation between F and H centres is lost because of the fact that H centres could move away in a thermally stimulated diffusion.

A close proximity of F and H centres after their low-temperature generation could also

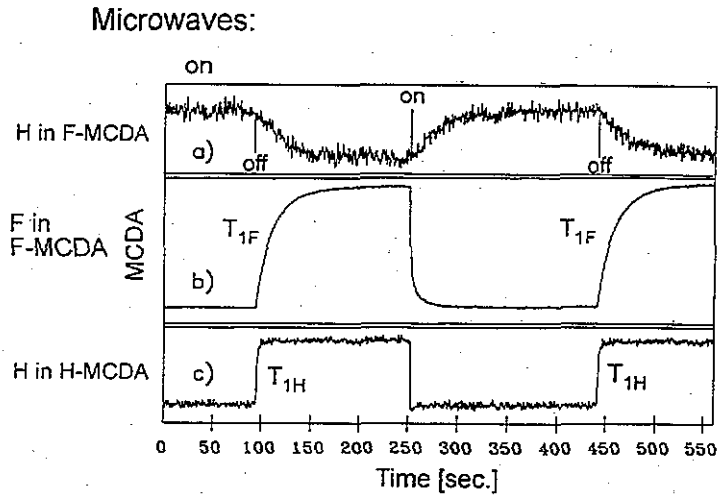

Figure 4. Time-resolved measurement of the ODEPR effect after switching on and off the microwaves: (*a*) behaviour of the MCDA of the F centers when inducing the H-centre EPR (CR); (*b*) behaviour of the MCDA of the F centres when inducing the F-centre EPR (T_{1F}); (*c*) behaviour of the MCDA of the H centres inducing the H-centre EPR (T_{1H}).

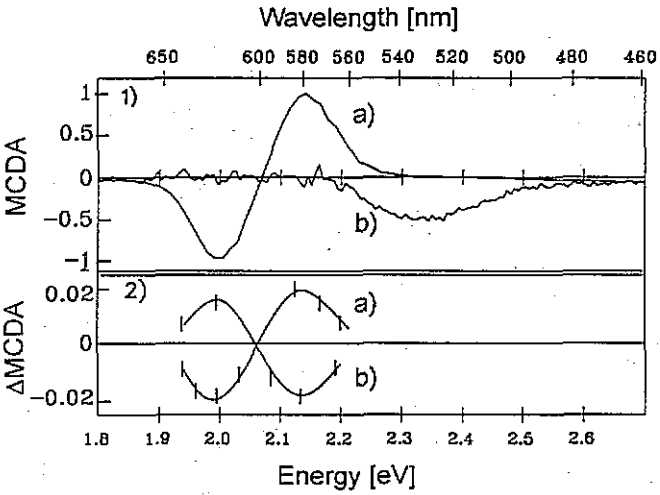

Figure 5. (1) Trace a, MCDA spectrum of the F centres; trace b, MCDA spectrum of the H centres. (2) Trace a, CR effect exciting the H-centre resonance at $B_0 = 837$ mT, measured as a function of the photon energy; trace b, as above, but exciting the H-centre resonance at $B_0 = 846$ mT.

show up in the conventional EPR spectra, since a spin–spin interaction could be seen either as an additional line splitting or as a line-broadening effect. We therefore measured the EPR spectrum of parallel centres at 5 K after x-ray generation of H centres at 10 K, a temperature where the CR effect is not yet destroyed. Figure 6 shows a section of the EPR spectrum: the lowest-field superhyperfine line for $I_1 = I_2 = \frac{3}{2}$. There are three lines due to the combination of the two Br isotopes ^{79}Br and ^{81}Br as indicated in figure 6 (^{79}Br has 50.69%

abundance, $g_I = 1.404\,27$ and ^{81}Br has 49.31% abundance, $g_I = 1.5137$). All single lines have a peak-to-peak width of 0.30 mT. Upon warming the crystal for 5 min to 30 K and cooling again to 5 K for the measurement, the line width did not change measurably, but a portion of the signal was lost because of F–H-centre recombination.

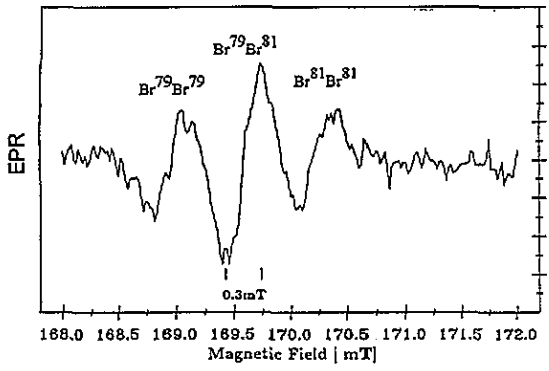

Figure 6. Conventional EPR spectrum of KBr x-irradiated at 10 K *in situ* for about 5 h, measured at 5 K; microwave frequency 9.4 GHz. The HF transition $\Delta m_s = 1$, $m_I = 3$ is shown.

4. Discussion

4.1. Cross-relaxation effects

For an estimate of the spatial correlation between F and H centres one can perform a quantitative calculation of the CR effects and compare with the experiment. The CR probability between two spin systems assuming a dipole–dipole interaction is given by (Bloembergen *et al* 1959)

$$R_{ij} = \hbar^{-2}|H_{ij}|^2 g_{\alpha\beta}$$
$$|H_{ij}|^2 = g_i^2 g_j^2 \beta^4 (3 - \cos^2 \Theta_{ij})^2 / r_{ij}^6 \qquad (1)$$
$$g_{\alpha\beta} = \int g_\alpha(\nu') g_\beta(\nu')\, \mathrm{d}\nu'.$$

$g_{\alpha\beta}$ is the overlap integral of the shape function of the EPR lines of both defect types, α and β, which can be determined experimentally from the EPR spectra. The indices i and j characterize the individual defect of each type taking part in the CR and having a distance r_{ij} and an angle Θ_{ij} between the connection line and the magnetic field. β is the gyromagnetic ratio in the CGS system and g_i, g_j are the electronic g factors. The dynamical behaviour of the spin polarization of a paramagnetic defect can be calculated by a set of rate equations describing the occupation of the Zeeman levels. The occupations are influenced by EPR transitions and spin-lattice relaxations. If two different spin systems are coupled by CR, additional terms due to CR enter the rate equations, which become non-linear. For the CR effects between F centres and Eu^{2+} activators in the x-ray storage phosphor system BaFBr:Eu the rate equations have been described in detail (Koschnick *et al* 1992). We have performed an analogous calculation here. In figure 7 the energy-level scheme is shown for the CR between F and H centres. All transitions and relaxations that were used to calculate

the CR effect quantitatively are indicated. Because of energy conservation during a spin-flip-flop process only those H centres whose total nuclear spin I is equal to three couple via CR to F centres. In principle the two central Br nuclei of an H centre can couple to a total spin of 0, 1, 2 and 3. In all calculations effects due to the two different isotopes of ^{79}Br and ^{81}Br are neglected. We further assumed that the total spin of three does not change within the CR time τ_{CR}. τ_{CR} is approximately R_{ij}^{-1}. To explain the change in sign of the CR effect (see figure 5(1)) we had to introduce 'forbidden' spin-lattice relaxations with $\Delta m_s = \pm 1$ and $\Delta m_I = \pm 1$ besides allowed spin-lattice relaxations $\Delta m_s = \pm 1$, $\Delta m_I = 0$ and weak nuclear spin relaxations $\Delta m_s = 0$ and $\Delta m_I = \pm 1$.

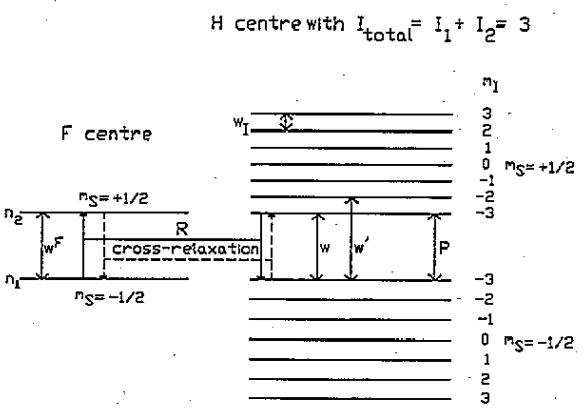

Figure 7. Energy-level scheme for the CR between F and H centres in KBr. The arrows indicate possible relaxations. The CR process is a spin-flip-flop process, which is caused by a coupling of the Zeeman levels of the F centre to the $m_I = -3$ levels of the H centre.

The following experimental parameters were used: $T = 1.5$ K, $T_{1F} = 20$ s, $T_{1H} = 2$ s. For details of the rate equations and calculations of the CR effects see the article by Spaeth *et al* (1993).

With the CR probability R_{ij} as a fit parameter the CR effect on the MCDA of the F centres was calculated and compared with experiment. In figure 8 the open triangles are the calculated effect and trace a the experimental result, while trace b shows the ODEPR line of the H centres for comparison (see section 3). The obtained value of R_{ij} can be interpreted with (1) assuming a certain spatial correlation between the F and H centres, as follows.

(i) After low-temperature generation all F and H centres are correlated with one separation between them. In this case the observed CR effect of about 5% of the ODEPR of the F centres can be explained by assuming a separation of $r_{F,H} \simeq 20$ Å.

(ii) Only a fraction of the F and H centres is correlated. Then the separation between the correlated pairs must be smaller than 20 Å to explain the experimental observations. If, for example, the separation was 14.1 Å (three halogen separations along [110]), 20% of the pairs must be correlated, and 80% must have a separation of five or more halogen sites in the [110] direction.

However, the dipole–dipole interaction between the unpaired F-centre electron and the hole of the H centre would be about 0.7 mT for the 20% correlated pairs with 14 Å separation: this would have been seen in the EPR spectrum as a line-splitting effect, which was not observed. For a separation of 18.6 Å this interaction is only 0.3 mT and thus smaller than the half widths of the EPR lines.

Therefore we conclude that approximately all F–H pairs have the same separation of four halogen spacings along ⟨110⟩, which seems to be the stable F–H pair configuration (figure 9). We have no information about the orientation of the molecular axis of the H centres relative to the F–H connection line.

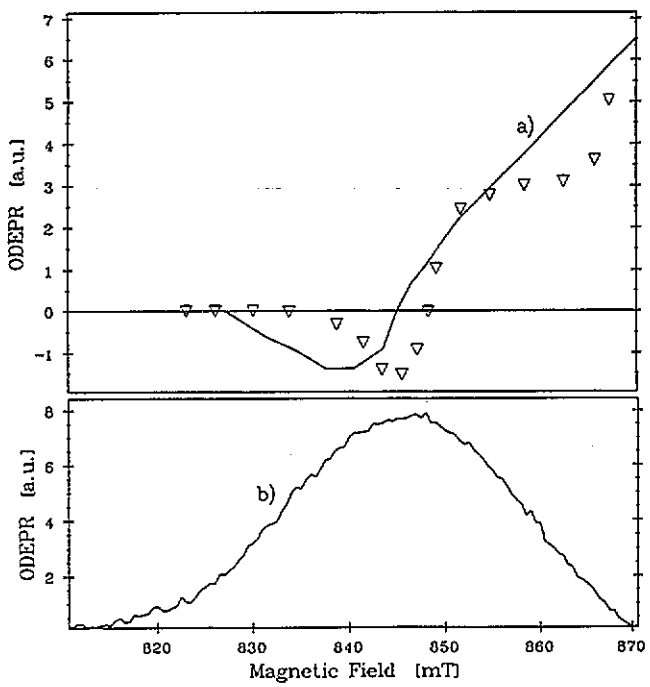

Figure 8. Trace a, experimental CR effect measured in the low-energy flank of the F-centre MCDA; open triangles, CR effect calculated with the rate equations described in the text; trace b, ODEPR spectrum of H centres in KBr for comparison.

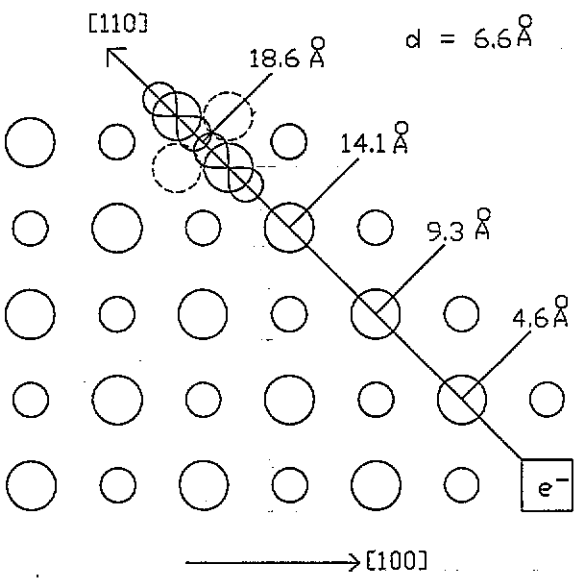

Figure 9. Model for the spatial correlation of F- and H-centre pairs as estimated from the CR. The orientation of the H centre cannot be inferred from the experiments.

4.2. Estimate of the F–H separation from exciton decay

Recent works strongly indicate that the relaxed STE is axially off-centre such that the electron and hole do not occupy a common centre. As such it should be viewed as equivalent to a primitive F–H pair. Well separated and therefore stable F–H pairs are further down on the common actiabatic potential energy surface (APES). A geometrically ideal first-neighbour F–H pair is unlikely to exist when the interaction between the electron and hole is considered. Such species are indeed one of the possible configurations of the STE and they usually recombine radiatively or non-radiatively. From theoretical calculations of both approximate and *ab initio* Hartree–Fock methods, as well as from a careful analysis of the parameters of the spin Hamiltonian (Song *et al* 1990), it appears that in KBr the relaxed STE is at a separation of about 5 Å between the hole and electron, which is between one and two lattice spacings along ⟨110⟩. Associated with this axial relaxation is an energy gain (lowering) of about 1 eV (Song *et al* 1989, Song and Baetzold 1992) relative to the on-centre configuration, which provides enough kinetic energy to be utilized in propelling the hole (localized on the H centre) further from the electron (localized on the F centre). This mechanism is believed to be at the origin on the F–H pair formation at very low temperature (Song *et al* 1989). Also, energetic halogen atom desorptions with kinetic energies as large as about 1 eV are observed in the alkali halides in which the efficient low-temperature F-centre formation is observed (Szymonski 1990).

Here we present a qualitative description of the observed correlated pairs in KBr with a separation of about 20 Å (fourth NN). We assume that the covalent bond-switching event that propels the H centre along a ⟨110⟩ axis (the same as the replacement sequence) can be approximated as a projectile motion of a halogen atom that is initially given a kinetic energy of about 1 eV. A damping mechanism linear to the velocity is assumed, and contributes to slowing down the process. When the residual kinetic energy has reached about 0.1 eV, it is assumed that the process comes to an end and results in the correlated F–H pairs. This limit of 0.1 eV is about the potential barrier height of H-centre thermal diffusion (see e.g. Song and Williams 1993b). With this model an elementary calculation shows that in the case of KBr, the process takes about 1.8 ps to reach a separation of about 20 Å (the fourth NN along ⟨110⟩). The energy loss at successive F–H separations is 0.18, 0.32, 0.24 and 0.16 eV, respectively.

This description is obviously crude and qualitative. We know, for example, that some fraction will lose all its energy earlier and decay radiatively as a relaxed STE at a shorter separation. Assuming that the energy loss is accounted for in terms of emitted LO phonons, each step would represent about 10 LO phonons. Taking the initial kinetic energy of 1 eV as an upper limit, the time required to reach the fourth NN found here, 1.8 ps, would be a lower limit. This range of time seems not unreasonable when compared with the F-centre formation time in KBr of 2 ps after the electron–hole pair creation (Williams *et al* 1990). Tokizaki *et al* (1991) have observed in their sub-picosecond studies in NaCl that after the relaxed STE is excited to higher excited states, F centres appeared in about 3 ps.

If the separation were five lattice spacings along ⟨110⟩, the total separation time would be 2.3 ps, and for three spacings 1.3 ps. Within this estimate of the displacement time of H centres for the third, fourth and fifth lattice spacings we cannot safely discriminate between them when comparing to the formation time of F centres.

From the relaxation between the electron–hole separation and the radiative lifetime of the triplet STE in KBr (Song and Chen 1989) we have estimated the lifetimes for different F–H separations.

For the separation of four lattice spacings along ⟨110⟩ the lifetime is found to be in the range of 10^4–10^6 s depending on the value taken for the recombination energy, assumed to

be 2 eV and 0.5 eV, respectively. Thus this F–H pair separation corresponds to a stable pair configuration. However, assuming as the electron–hole separation three lattice spacings along ⟨110⟩, the lifetime varies between 10 s and 10^3 s for the same range of recombination energies. This result shows that three lattice spacings do not correspond to a stable F–H pair configuration. Thus our experimental results do agree very well with the theoretical predictions of the exciton decay mechanism explaining the F–H pair creation.

5. Conclusions

The present work establishes for the first time the stable F–H pair separation in KBr at low temperature to be four lattice spacings along ⟨110⟩ before thermally activated diffusion of the H centres destroys this correlation. Using results of previous theoretical work on the STE in KBr the estimate of the F-centre formation time as well as the lifetime of the correlated F–H pair yields results consistent with the experimental results obtained from very different kinds of approach: CR spectroscopy, EPR spectroscopy and time-resolved optical spectroscopy. Thus a consistent picture emerges for the F–H pair formation through the STE decay.

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