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A theoretical basis for the Rabin–Klick criterion in terms of off-centre self-trapped-exciton relaxation

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Abstract. Rabin and Klick showed empirically that low-temperature F-centre formation in alkali halides is easy or hard depending on whether the value of a geometric ratio S/D is greater or less than 0.45. We show that a similar correlation holds between the ease of F-centre formation at low temperature and the value of a parameter $\Delta E_2/(\Delta E_1 + \Delta E_2)$, where ΔE_1 and ΔE_2 are the calculated energies of odd-parity relaxation of the self-trapped exciton (STE) in modes that do not involve halogen pair translation and do involve halogen pair translation, respectively. These are the local relaxation modes used previously in calculation of the potential curves for on-centre–off-centre motion of the STE, and the values of ΔE_1 and ΔE_2 are obtained directly from such calculations for 12 alkali halides in the present work. The energy barrier that inhibits low-temperature F-centre formation is found to be comparable to the barrier already associated with thermally activated defect formation. That is, the barrier height against defect production does not change greatly from one side of the Rabin–Klick diagram to the other, in contrast to what was held to be the case in previous interpretations of the S/D parameter. What changes is the division of available STE relaxation energy between the productive and non-productive modes. This picture provides a unifying account of both thermally activated and low-temperature defect production in the alkali halides. Furthermore, this description of the Rabin–Klick diagram is based on a model in which low-temperature as well as high-temperature F-centre formation occurs on the lowest adiabatic potential surface connecting the STE π-luminescent state and the F–H pair.

In 1960, Rabin and Klick [1] plotted the x-ray dose per F centre created at 4.2 K in various alkali halides versus a parameter S/D. Here S is defined as the separation of two adjacent halide ions along a $\langle 110 \rangle$ row minus twice the halide-ion radius, i.e. the 'excess space' measured between hard spheres placed at the ion positions. D is the diameter of the halogen atom. In crystals with $S/D \geqslant 0.45$, i.e. KBr, LiF, KCl, and NaF in their study, F-centre formation proceeds with high efficiency at low temperature. In crystals with $S/D < 0.45$, i.e. NaCl, KI, and NaBr in their study, the F-centre production efficiency at 4.2 K decreases sharply with decreasing S/D, falling to a value for NaBr three orders of magnitude smaller than for the crystals with $S/D > 0.45$.

Rabin and Klick proposed the parameter S/D as a geometric measure of space available for the insertion of an interstitial halogen atom to form an H centre. It is reasonable that in crystals with less space available to receive the H centre, F-centre formation should be discouraged. In [1] the threshold value $S/D \simeq 0.5$ was characterised in the following way: if one imagines a row of hard spheres with spaces $S = 0.5D$ between

them, then by pushing one such sphere against its neighbour on one side, a space of length D is opened up on the other side. This allows just enough space along the close-packed $\langle 110 \rangle$ direction to accommodate the neutral halogen atom that is ejected to form the F centre. This is the geometric or static rationale for the Rabin–Klick criterion.

Townsend [2] presented data for a wider range of crystals, showing that the rule is obeyed at least approximately by virtually all alkali halides. He offered a somewhat different justification of the Rabin–Klick rule, based on ability of the lattice to support focused collision sequences. That is, Townsend suggested that as the distance S between the halide-ion 'hard-sphere' surfaces decreases, the ions on the close-packed row act more as a *bonded* unity of large effective mass; hence little momentum would be transferred from the moving halogen atom to propagate a collision sequence. (In the absence of bonding of the ions by interaction with the rest of the lattice, a row of identical hard spheres in contact provides optimal energy and momentum transfer, however.) In addition, Townsend pointed out that a halogen atom having a small diameter D can more easily pass between the nearest pair of adjacent alkali metal ions. Hence large values of S/D should favour F-centre production by a focused collision sequence.

Both of the geometrical rationalisations reach a similar conclusion: that an open lattice relative to the halogen atom size, characterised by $S \geqslant 0.5D$, is more receptive to the interstitial halogen and to its propagation by collision sequences. Basically, the barriers are believed to be smaller in the more favourable case.

However, with quite modest amounts of thermal energy, i.e. activation energies of order 100 meV, the crystals with $S/D < 0.45$ form F centres with high efficiency also. Furthermore, the crystals with $S/D \geqslant 0.45$ have similar thermally activated stages of F-centre formation, with roughly the same activation energies [3, 4, 5], in addition to the low-temperature process. It has thus been suggested that the thermally activated process is universal in alkali halides, and that the group with $S/D \geqslant 0.45$ simply have an additional temperature-independent channel [5]. The 'available space' argument of Rabin and Klick should inhibit thermally activated defect formation in crystals with $S/D < 0.45$, but it evidently does not. What seems to be inhibited is only the low-temperature process, which in any of the current models is driven by at least 1 eV of STE relaxation energy, and thus should be even less affected by 'available space' than the thermally activated process. This is really a dilemma if one insists on explaining the Rabin–Klick diagram in terms of a defect formation barrier that becomes prohibitive at one end of the diagram, because the thermal activation barrier does not change that much from one end of the diagram to the other. The key must be in how effectively the stored STE energy is used to displace the H centre over barriers that are comparable to those deduced from thermal activation. This is what we want to examine.

In this work, we present energy curves representing the potential surface along which the STE relaxes from 'on-centre' to 'off-centre' configurations. These curves were calculated using a method developed earlier by us [6]. The excited electron (F centre) is treated following the extended-ion approximation, while the hole (V_k or H centre) is represented by a CNDO code. The two parts are consistently interfaced so that the total energy of the system is obtained as the H centre diffuses away from the F centre. Figure 1 shows the potential curves calculated for NaF–RbF, NaCl–RbCl, NaBr–RbBr, and for NaI–RbI. In each panel of the figure, the relaxation is divided between two configuration coordinates. The panels depict displacement along coordinate axes $\tilde{Q}_2$ and Q_2 as occurring in two orthogonal planes, the $\tilde{Q}_2$ plane projecting out of the page. $\tilde{Q}_2$ indicates the odd-parity relaxation of ions surrounding the X_2^- core, while the X_2^- is artificially held in the 'on-centre' V_k position. Even-parity relaxation along Q_1, the 'hole self-trapping'

coordinate, has already occurred and is not shown in these diagrams. Q_2 is the coordinate representing off-centre motion of the X_2^- core toward the π-luminescent STE and/or F–H pair [6, 7]. The range of Q_2 varies from $Q_2 = 0$ to about $Q_2 \simeq 12$ (in au), and covers up to the second-nearest-neighbour F–H pair separation. The energy drop associated with relaxation along $\tilde{Q}_2$ is denoted by ΔE_1, while the energy drop associated with relaxation along Q_2 is denoted ΔE_2—that is to say, ΔE_2 is the energy difference between $Q_2 = 0$ and the first minimum along the Q_2 axis. As described in [7], the energy ΔE_2 can be transferred to kinetic energy of motion toward larger Q_2, i.e. toward larger F–H separation. Thus Q_2 is the 'productive' mode of the STE off-centre relaxation, in terms of producing F centres. In contrast, the energy ΔE_1 expended in relaxation along $\tilde{Q}_2$ is mostly wasted as far as defect formation is concerned.

According to this mechanism for low-temperature F-centre formation, there are two groups of alkali halides. Group I comprises NaCl, NaBr, NaI, KI, and RbI and group II comprises NaF, KF, RbF, KCl, RbCl, KBr, and RbBr. There is much more energy available in the 'productive' channel ΔE_2 in the second group (group II) than in group I. Quite generally, the ratio $\Delta E_2/(\Delta E_1 + \Delta E_2)$ tends toward larger values in crystals that exhibit efficient F-centre formation at low temperature. The calculated curves also verify that the barrier against thermal diffusion of the H centre away from the F-centre site (i.e. thermally activated defect formation) remains quite small, of the order of a few hundred meV, in all the crystals regardless of the value of S/D. Both of these aspects are in quite good agreement with data. The H-centre diffusion along a $\langle 110 \rangle$ direction should be understood in terms of quantum chemical 'bond-switching' of the molecule ion X_2^-; we use this simulation in the present work. Because of the large size of I_2^-, we encountered some difficulties in evaluating the energies with small values of Q_2. especially for NaI and KI. This is seen in figure 1. We understand that this is the result of our trying to draw the potential surface at fixed values of Q_2 in a region where there is strong coupling to the $\tilde{Q}_2$ mode.

The alkali fluorides are the extreme cases of large S/D and efficient low-temperature F-centre production. Our calculated curves are in excellent agreement with this, indicating by far the largest ΔE_2 in these materials. The alkali iodides, at the other extreme of small S/D and minimal low-temperature F-centre production, exhibit small calculated ΔE_2 values. KCl had a surprisingly small ΔE_2 value from the calculations, but is not inconsistent with the overall behaviour. To illustrate the trend, we plot the common logarithm of the average energy required per F centre formed at 4.2 K, from [2], against the parameter $\Delta E_2/(\Delta E_1 + \Delta E_2)$, in figure 2. In terms of this parameter, the threshold value for efficient F-centre production seems to be quite small, in the neighbourhood of 0.10. The critical 'barrier' corresponding to ΔE_2 at threshold is a few hundred meV, i.e. very similar to the thermal activation barrier. In this picture, if there is sufficient energy of relaxation available in the 'productive' STE relaxation mode Q_2 to overcome the barrier for H-centre motion that has already been found to characterise thermally activated F-centre production, then F centres can be produced even at low temperature. We believe this is the only reasonable way to account for both low-temperature and thermally activated F-centre formation in terms of a single energy barrier.

We have not attempted to derive ΔE_2 or $\Delta E_2/(\Delta E_1 + \Delta E_2)$ in terms of S/D. ΔE_2 is the result of a self-consistent calculation and there is a firm basis for regarding it as the primary parameter. Although it is reasonable that the calculated relaxation path should go more readily along channels favoured by geometrical factors such as S/D, we have not attempted to establish a quantitative connection. The fact that the Rabin–Klick trend has been successfully described in the context of the model presented in [7] for
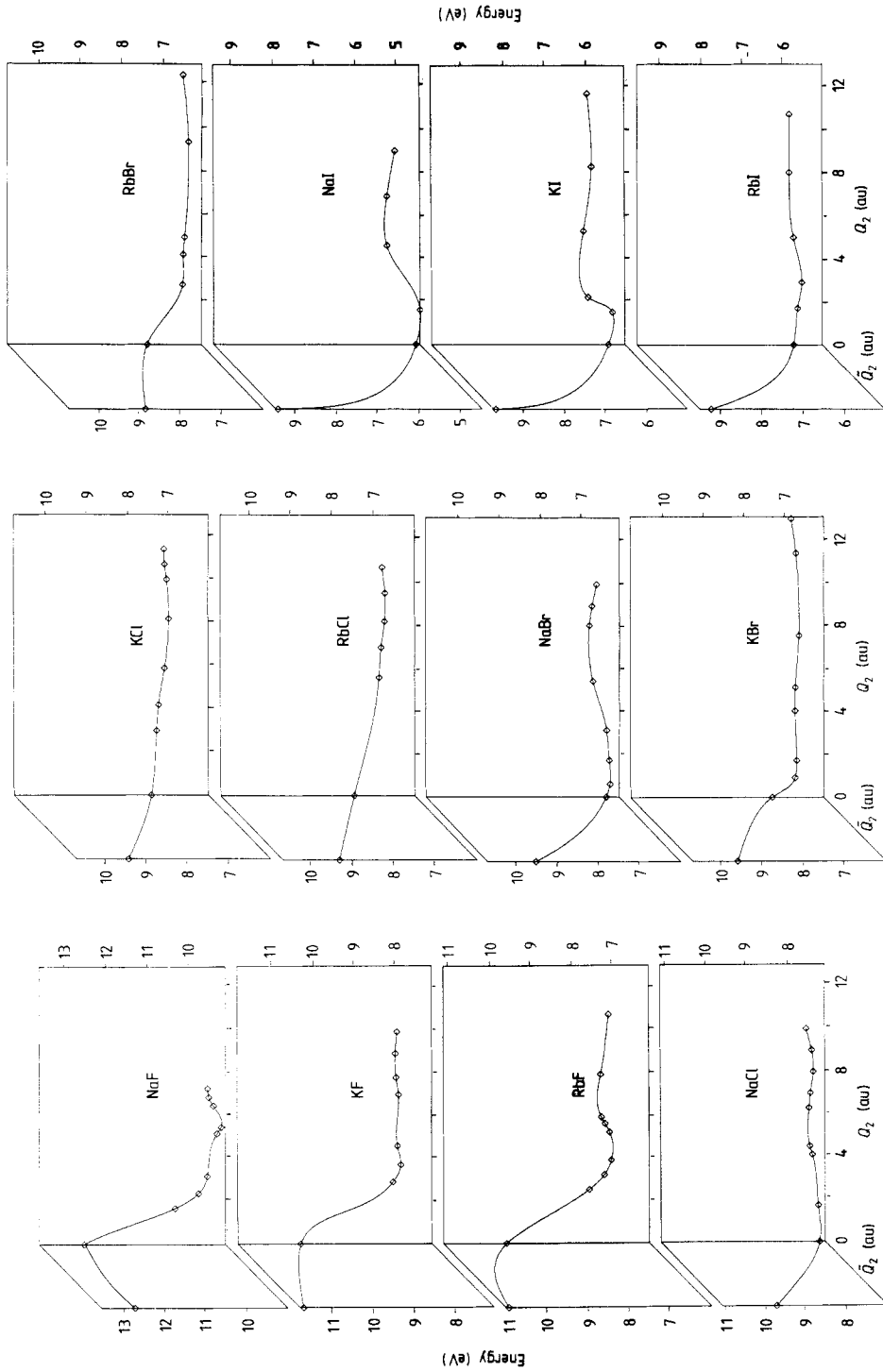
Figure 1. Energy surfaces of the STE–(F–H) system along the two coordinate axes $\tilde{Q}_2$ and Q_2.

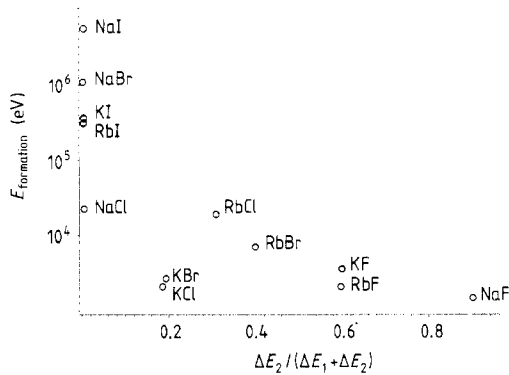**Figure 2.** The energy required to form one F centre ($E_{formation}$) versus $\Delta E_2/(\Delta E_1 + \Delta E_2)$.

low-temperature F-centre formation during off-centre relaxation of the STE seems to us to offer further verification of the mechanism.

Acknowledgments

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