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ON THE LUMINESCENCE AND ABSENCE OF LUMINESCENCE OF *F* CENTERS*

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A model, proposed originally by Dexter, Klick and Russell, is used to explain the occurence or non-occurence of *F*-center luminescence in ionic crystals, in terms of a simple two-state configuration coordinate diagram. In this model, which works for all known cases, luminescence is quenched by a competing non-radiative process whenever the intersection of the ground and excited state curves lies below the energy reached in absorption in a vertical (Franck–Condon) transition. The criterion for the occurrence of luminescence is expressed as $\Lambda < \frac{1}{4}$, where Λ (= excited-state lattice-relaxation energy/optical-absorption energy) is a parameter, related to the relative displacement of the two curves, which can be inferred from data on the temperature dependence of the *F*-band line width. Thus the possibility of observing luminescence can be predicted from optical absorption data alone. It is found empirically that Λ for alkali halides with rocksalt structure is independent of lattice parameter, and the observed dependence of Λ on the ratio of ionic radii in terms of ion-size effects. Values of Λ range from 0.009 for CsF to 0.831 for LiI; NaCl with $\Lambda = 0.260$ is a marginal case for luminescence.

1. INTRODUCTION

IN MOST ionic crystals the general features of absorption and emission of light by *F*-centers are well established. The cycle is shown schematically in Fig. 1 for a model involving just two electronic states and a single configuration coordinate. At low temperatures the *F* center starts in its ground state, A. The mean lattice configuration, I, mimimizes the total energy in the electronic ground state. Optical absorption is dominated by the Franck–Condon transitions, without change of configuration. The excited *F*-center then relaxes rapidly by phonon emission from B to C, the lowest vibrational state associated with the

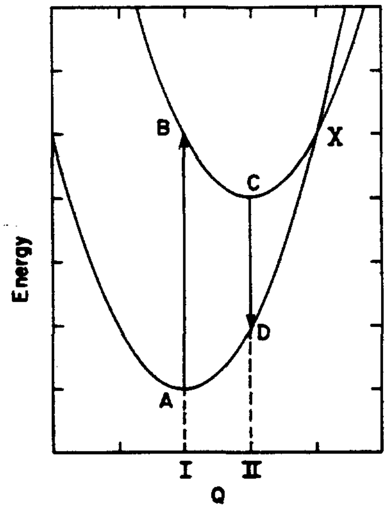

FIG. 1. Simple configuration-coordinate diagram to illustrate the absorption-emission cycle for *F*-centers. In this case $\Lambda = \frac{1}{4}$.

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excited electronic state. Emission occurs primarily by Franck–Condon transitions at the new configuration, II, and is followed by further phonon emission back to the initial state.

The foregoing model is oversimplified in two respects: the *F*-center electron is actually weakly coupled to very many modes of vibration, including modes of several symmetries;[1] a single configuration coordinate is justified only to the extent that the frequencies of the dominant modes are nearly equal.[2] Also, more than two electronic states are involved because of a near-accidental degeneracy of the 2*s* and 2*p* states.[3] Consequently, absorption and emission cannot both be described by a single configuration-coordinate diagram.[4]

Nevertheless, the simple two-state configuration-coordinate diagram accounts adequately for the gross features of absorption and emission for *F*-centers in NaF and NaCl; for the potassium, rubidium and caesium[5] halides; and for the one-electron *F*-centers in MgO and CaO. The scheme fails for the lithium halides, the alkaline-earth fluorides, NaBr and NaI, since no luminescence is observed in these cases.[6] In 1955, Dexter, Klick and Russell[7] presented a criterion for the occurrence of luminescence in terms of the possibility of quenching by an identifiable non-radiative transition. Their criterion was essentially speculative because of the paucity of data at that time; indeed, accurate data for *F*-center optical absorption have only recently become available for all alkali halides.[8]

We shal demonstrate that the occurrence of luminescence can be correctly predicted from available optical absorption data, using the criterion of Dexter *et al.*[7] We shall also show that the detailed theory of the *F*-center electronic structure correctly predicts the trends from host to host, and we shall suggest experiments by which it might be possible to observe emission in cases where it has proved elusive so far.

2. MODEL FOR RADIATIVE AND NON-RADIATIVE PROCESSES

The essential features of Dexter's model[7] are these:

(a) The non-radiative transitions which compete with luminescence are associated with the intersection of the configuration-coordinate curves of the ground and excited electronic states. No other electronic states (e.g. those associated with ionization of the *F*-center) are involved.

(b) The non-radiative transitions will only quench all luminescence if the system has an appreciable chance of passing through the vibronic states corresponding to the cross-over. This requires that the excited state reached in absorption lies above the cross-over. In terms of Fig. 1 B should lie above X. This figure is actually drawn to show the critical case where both radiative and non-radiative transitions are possible.

The first point follows from the standard approaches to non-radiative transitions with strong electron–lattice coupling.[9] The importance of the intersection arises naturally through the strong association at that point between vibronic states derived from the two electronic states. In simple models, this association is determined by the vibrational overlap integrals which occur in the transition probability. The second point results from the rapid lattice relaxation in the electronic excited state. When B lies above X, the system passes naturally through the vibronic states near X in the lattice relaxation following optical absorption. The thermal excitation of vibronic states higher in energy than B is very improbable at the low temperatures we have in mind. It should be noted that, for purposes of this model, it is a matter of indifference whether the configuration-coordinate curves actually cross or only nearly cross.[10] It is a postulate of Dexter's model that passage through point X results in complete quenching of the luminescence; a complete theoretical justification would be beyond the scope of this paper.

In dealing with a similar situation, exciton decay, Seitz[11] viewed the system as sliding from B to C along the upper curve in Fig. 1, and concluded that the exciton would decay radiatively unless the intersection of the two curves lay *between* B and C. However, it should be recognized that the configuration coordinate curve is actually the locus of classical turning points as a function of energy, and that in any given vibrational state the wave function extends between the corresponding turning points. Thus one cannot avoid the intersection simply by sliding down the opposite side of the curve.

3. PHENOMENOLOGICAL MODEL

The relative energies of the optically-excited state B and the cross-over X can be estimated from available data in several ways. For simplicity, we further restrict the two-state model by the assumption that both the ground- and excited-state energies depend parabolically on the configuration coordinate, with the same effective frequency. The assumption of equal frequencies is by no means essential, but availabale data do not seem sufficiently reliable to justify allowance for unequal frequencies. For example, Dawson and Pooley[8] find $\omega_e^2/\omega_g^2 = -0.2$ for KCl, while Klick, Patterson and Knox[4] find $\omega_e^2/\omega_g^2 = +1.4$ for the same compound; both groups used optical absorption data.

With these assumptions, the condition for luminescence to be observed becomes:

$$\Lambda = SE_{\text{phonon}}/E_{\text{abs}} \lesssim \tfrac{1}{4}. \tag{3.1}$$

Here E_{phonon} is the phonon energy, S is the Huang–Rhys factor and E_{abs} the mean energy for optical absorption.

Values of Λ calculated from data from the temperature dependence of the linewidth in absorption[8] are given in Table 1. Figure 2 shows appropriate configuration curves. It can be seen that the rule (3.1) correctly predicts the existence or absence of optical emission in all cases. The results are marginal for NaCl, but we shall show later that the value of 0.26 for Λ is consistent with significant emission; in any case, the value of Λ will have errors of a few percent. Unfortunately, no accurate linewidth results for the alkaline earth fluorides other than MgF_2 are available: the M_F band interferes with observation of the *F*-band in additionally-colored crystals, and fluorine interstitials cause large perturbations in irradiated crystals. Very crude estimates of Λ are possible, based on the smallest observed linewidths inferred from Faraday rotation results and the known phonon frequencies. These give values of Λ greater than 0.25, consistent with the observed absence of luminescence. An emission band in MgF_2 was originally attributed to *F*-center luminescence, partly on the basis of an incorrect calculation of the expected Stokes' shift.[12] However, it has not been possible to verify this assignment, which which now appears improbable.[13] Thus (3.1) seems to be a valid criterion for luminescence for *F*-centers in alkali halides of both structures, alkaline–earth oxides, and probably for alkaline–earth fluorides.

Table 1. Values of Λ and Λ'. The various hosts are placed in three groups, corresponding to Fig. 2. Errors of ± 5% are probably typical. Values of R, the ratio of anion to cation radius, are also shown for the alkali halides with rocksalt structure

				Luminescence	
Host	R	Λ	Λ'	Predicted	Observed
LiI	3.22	0.831		No	No
NaI	2.24	0.384		No	No
NaBr	2.00	0.375		No	No
LiCl	2.66	0.371		No	No
LiBr	2.88	0.358		No	No
LiF	1.96	0.323		No	No
BaF_2					No
SrF_2			Detailed parameters		No
CaF_2			not known; see text		No
MgF_2		0.348		No	No?*
NaCl	1.85	0.260	0.322	Yes	Yes[a]
KI	1.65	0.231	0.279	Yes	Yes[a]
KBr	1.47	0.223	0.278	Yes	Yes[a]
RbI	1.48	0.211	0.262	Yes	Yes[a]
KF	1.00	0.189	0.211	Yes	Yes[a]
KCl	1.36	0.188	0.235	Yes	Yes[a]
RbCl	1.22	0.182	0.232	Yes	Yes[a]
NaF	1.36	0.175	0.275	Yes	Yes[a]
RbF	0.90	0.173	0.224	Yes	Yes[a]
RbBr	1.32	0.162	0.265	Yes	Yes[a]
CsI		0.077	0.285	Yes	Yes[a]
CsBr		0.019	0.268	Yes	Yes[a]
CsCl		0.018	0.211	Yes	Yes[a]
CsF	0.80	0.009	0.122	Yes	Yes[a]
MgO		0.260	0.184	Yes	Yes[b]
SrO		0.070	0.080	Yes	Yes[c]
CaO		0.046	0.054	Yes	Yes[b]

* See text.

[a] FOWLER W.B., *Physics of Color Centers*, Appendix B. Academic Press (1968).

[b] HUGHES A.E. & HENDERSON B., in *Point Defects in Solids* (Edited by CRAWFORD J.H. Jr. & SLIFKIN L.M.) pp. 381–484.

[c] HUGHES A.E. (private communication).

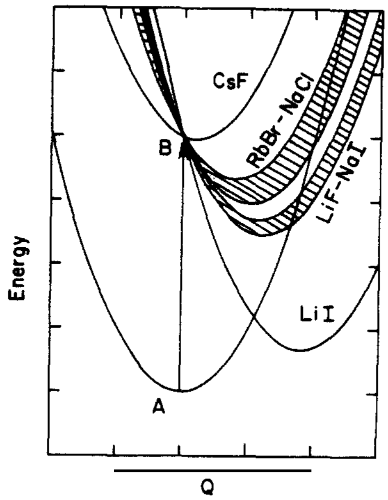

FIG. 2. Configuration-coordinate diagrams for *F*-centers in NaCl-structure alkali halides. The two shaded areas are $0.162 \leqslant \Lambda \leqslant 0.026$ and $0.323 \leqslant \Lambda \leqslant 0.384$; the cases $\Lambda = 0.009$ and $\Lambda = 0.831$, appropriate for CsF and LiI, respectively, are plotted separately.

There are several checks of our working assumption of a single coordinate and frequency. The original linewidth data[8] are consistent with one coordinate and one frequency, although slightly different frequencies seem appropriate in absorption and emission. But in no case does this difference cause any significant change in Λ. Nor does use of phonon energies derived, less accurately, from the shift in *F*-band energy with temperature change the predictions other than for NaBr and NaI. In these cases the shifts lead to anomalously small phonon energies, being about 1/2 (NaBr) and 1/20 (NaI) of those derived in other ways. Another check is to use emission energies and absorption energies when they are known. In our model the parameter

$$\Lambda' = (1 - E_{em}/E_{abs})/2 \qquad (3.2)$$

should equal Λ. As Table 1 shows, the trends in Λ and Λ' are almost identical, although Λ' is slightly larger, reflecting the inadequacy of a single configuration-coordinate diagram. While the reasons for the difference are not understood in detail, it is likely that they are related to Ham's observation[3] that the observed Stokes shift ($E_{abs} - E_{em}$) is much larger than that deduced from the stress response of the absorption band. Whatever the source of the discrepancy, it seems clear that Λ is the appropriate parameter to use in equation (3.1), rather than Λ', in that Dexter's model refers to the configuration-coordinate diagram for absorption. The vibronic structure of the relaxed excited state and the corresponding configuration-coordinate diagram for emission play no role in the criterion for luminescence, because the relaxed excited state is never achieved when luminescence is quenched.

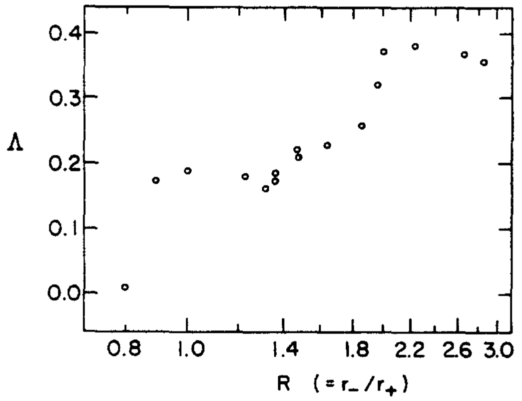

FIG. 3. Dependence of Λ on *R*, the ratio of the anion and cation ionic radii.

We also note that there is a substantial gap in Λ between those for which we expect to see luminescence and the others. This large gap means that the finite width of the *F*-band has little effect on the condition (3.1), except for NaCl, as will become apparent from the discussion in paragraph 5. This gap is indicated in Fig. 2, which also shows the anomalous nature of the LiI *F*-center.

4. ION-SIZE EFFECT

One important trend is apparent from Table 1: Λ increases with anion size and decreases with cation size. The dependence of Λ on the ratio of ionic radii, $R(= r_-/r_+)$, is shown in Fig. 3 for the alkali halides with rocksalt structure.

Note that there is no significant dependence on lattice parameter, *a*; for example, Λ is very nearly the same for NaF, KCl and RbBr, which have almost the same *R* but very different values of *a*. These observations suggest that the variation of Λ is governed by ion-size effects of the type discussed earlier by Buchenauer and Fitchen,[14] and by Bartram, Stoneham and Gash (BSG)[15] in connection with *F*-band energies.

It can be seen from Fig. 3 that Λ increases essentially monotonically with R, starting from a very small value for CsF, and that two plateaus are evident, only one of which is consistent with luminescence. The value of Λ for LiI is anomalous, as was its *F*-band energy in the treatment of BSG.[15]

5. DISCUSSION

The non-radiative mechanism considered here suggests that *F*-center luminescence can be observed in all cases provided one can populate the excited states with energy less than that of the crossover. Possible techniques include energy transfer from other centers, the exploitation of exciton decay, or, more simply, optical absorption from the red side of the *F*-band only. The fraction of the *F*-band area which can be used may be estimated from the known linewidths. Using a Gaussian fit to the lineshape, one finds that 26% of the *F*-band is suitable in NaCl (hence our earlier comment that luminescence is expected here even though Λ exceeds 1/4), that less than 10^{-5} of the band is suitable in LiF, and that negligible fractions are useful in other cases. Thus direct excitation is not expected to be efficient.

LiI is anomalous in many ways. Notable here is the very large difference in the configurations which minimize the total energy in the ground and excited electronic states. This difference should lead to a very long lifetime in the relaxed excited state, giving a system especially suitable for spin resonance and ENDOR.

Finally, we note that the radiative efficiency for *F*-centers in a number of hosts which do luminesce does not tend to unity at low temperatures.[16] One case is NaCl, and the anomaly may be a result of the processes we discuss here. But is almost certain that the competing non-radiative processes in the other cases (NaF, KF, RbF) are different in origin, and have much smaller transition probabilities.

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