

SOME MOLECULAR ASPECTS OF IMPURITY AND INTRINSIC EXCITATIONS IN ALKALI HALIDES

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ABSTRACT

A discussion of various molecular aspects of the properties of usual impurity centres in alkali halides and of the intrinsic electron excitations in these crystals, connected mostly with the formation of the quasi-molecular system Hal_2^- (self-trapped hole), is presented.

IMPURITY EXCITATIONS

To a certain extent a crystal may be considered as a gigantic molecule. Translational symmetry certainly leads the theory of ideal crystals aside from the traditional concepts of the theory of molecules. In the case of the impurity centre in a crystal the situation is different. It is already intuitively clear that here the main role is played by the impurity itself and its nearest crystal surroundings, whilst the symmetry of the system becomes a point one, as in the case of molecules[†]. Therefore from the very beginning molecular ideas have played an essential role in the elaboration of the microscopic theory of impurity centres in ionic crystals.

The first such quantum mechanical investigations¹⁻⁷ were devoted to the calculation of the relative location of adiabatic potentials of impurity electron states in the space of vibrational coordinates of the quasi-molecule in the crystal consisting of an impurity and a certain number of neighbours. The foundations of the quasi-molecular model of the vibrations of the impurity centre were further developed from the viewpoint of the dynamical theory of crystal lattices with a defect⁸. After the required difference of adiabatic potentials in the space of quasi-molecular vibrations is calculated (simple and effective methods developed in the theory of molecules can be used), it is possible to introduce the normal coordinates of the crystal with a defect (by means of a linear transformation) and to investigate the shape^{9, 10} of the optical spectra.

The electronic states of the centre were built in the LCAO scheme and the interactions between ions were calculated by the methods analogous to those of Löwdin¹¹. The latter include an orthogonalization of the wave functions of ions with overlapping electronic densities, and already in this

[†] In this article we will consider the general case of the centres giving deep impurity levels with expressed individuality.

respect optically active electronic states are not completely impurity states. Such calculations have shown, e.g. in the case of KCl-Tl, that the non-point contributions, connected with the finite size and overlapping of ions, are essential for the energy of their interactions. The calculated absorption and emission spectra were in reasonable agreement with the experimental spectra.

Further, it was necessary to find a more flexible description of optically active states of the impurity centre to allow for the formation of covalent bonds between the activator and the surroundings. This implies the use of molecular orbitals formed from the states of the impurity and its neighbours. In the mentioned investigations¹⁻³ the degree of mixing of the functions of neighbours with the impurity functions was determined uniquely by overlap integrals, but in the MO method this degree is found by variational methods and deviation of the charges from ionic values becomes possible.

The first work directed towards developing the MO theory for the KCl-Tl type centres was carried out by Sugano¹². The main result of this work lies in the establishment of useful relationships between the characteristics of the A, B and C absorption bands. However, the MO character of the theory is not essential for obtaining these relationships.

In an experimental work of Dreybrodt and Silber¹³ some indication was obtained for the first time that even in the ground state the localized hole in the KCl-Tl centre 'lives' on a MO, embracing essentially the neighbouring Cl⁻ ions. Parallel to this, it was demonstrated theoretically that Tl⁺ strongly perturbs neighbouring Cl⁻ ions¹⁴, so that 'induced' localized levels, some of which must mix with the impurity levels, arise from their states.

An important drawback of the above-mentioned investigations was (and is also frequently at present) the fact that they did not supply information about the full structure of the energy spectrum of the crystal with an impurity, i.e. about the location of impurity levels relative to energy bands and the distortion of band states. A method which allows the development of the corresponding theory, taking into consideration also the mentioned covalent effects, is Green's function method for localized perturbations^{15,16}. This method was developed^{17,18} by making use of the quasi-atomic functions of the LCAO-type basic set. In the case of the crystal with an impurity in the node $R(l) = 0$ the one-electron equation

$$[H_0 + V(r)] \psi(r) = E\psi(r), \quad H_0 = -\frac{\hbar^2}{2m} \Delta + V(r) \quad (1)$$

is written, where V is the periodic potential of the ideal lattice, and V' is the perturbation potential. The wave function is presented in the form

$$\psi(r) = \sum_{\alpha=1}^{s'} C_{\alpha}(0) |0\bar{\alpha}\rangle + \sum_l \sum_{\alpha=1}^s C_{\alpha}(l) |l\alpha_0\rangle \quad (2)$$

where $|l\alpha_0\rangle$ and $|0\bar{\alpha}\rangle$ are the quasi-atomic functions of the host and the impurity.

The substitution of equation 2 reduces equation 1 to the form

$$EC_{\alpha}(l) = \sum_{l',\beta} H_{\alpha\beta}^{(0)}(ll') C_{\beta}(l') + \sum_{l',\beta} W_{\alpha\beta}(ll') C_{\beta}(l') \quad (3)$$

It is possible to give to the elements of the perturbation matrix \hat{W} a clear physical meaning, if one forgets for a moment about the non-orthogonality of atomic functions and uses for V' the difference of the atomic potentials of the impurity and the substituted ion. $W_{\alpha\alpha}(00)$ is the difference of the atomic levels of the impurity and the substituted ion, renormalized by the field; $W_{\alpha\beta}(00)$ describes the difference in the value of the splitting of these levels by the crystal field; $W_{\alpha\beta}(l0)$ is the change in resonance integrals; and $W_{\alpha\alpha}(ll)$ is the shift of the levels of matrix atoms due to the impurity. The non-orthogonality may be taken into account by the Löwdin method¹¹.

Let $s = s'$ (this is not in principle), then the solution of equation 3 has the form

$$C_{\alpha}(l) = \sum_{\substack{LL' \\ \beta\gamma}} G_{\alpha\beta}(lL; E) W_{\beta\gamma}(LL) C_{\gamma}(L) \quad (4)$$

$$G_{\alpha\beta}(ll) = \sum_{k,n} \frac{C_{\alpha}^{(0)*}(l) C_{\beta}^{(0)}(l')}{E - E_n(\mathbf{k})} \quad (5)$$

Here $E_n(\mathbf{k})$ and $C_{\alpha}^{(0)}(l)$ are the eigenvalues and eigenfunctions of the matrix $H_{\alpha\beta}^{(0)}(ll')$. Indices L and L' number the atoms in a small region where the perturbation acts. Supposing that $l = L$ on the left-hand side of equation 4 we obtain a system of equations for determining localized levels ($E \approx E_n(\mathbf{k})$). These equations may essentially be simplified by forming linear combinations from $C_{\alpha}(l)$, transforming according to irreducible representations of the symmetry group of the crystal with the defect. The method permits a calculation of the probability amplitudes of the location of an electron on every lattice site in the given state.

The localized levels may be divided into three groups: pure impurity levels, induced levels and mixed levels. The first two types correspond to the cases where the representations are generated only by the wave functions of the impurity or only by the functions of the nearest neighbours, respectively: the third type corresponds to the case of repeated representations, one of which is generated by the impurity functions and the others by the functions of the host atoms.

Using the described method, the localized levels for the ground state of the system KCl-Tl were calculated¹⁷. A two-band model was used, including the 3p functions of Cl^- and the 4s functions of K^+ . The parameters of the perturbation potential were determined partially on the basis of existing calculations, and partially by means of semi-empirical formulae which are well known in the MO-LCAO method. The calculated location of energy levels is shown in *Figure 1*. Levels A_{1g} are the mixed ones; the other levels are induced. The upper A_{1g} level represents the ground state for optical transitions. The coefficients at the 6s function of Tl^+ , and at the A_{1g} combination of the 3p functions of Cl^- in the full wave function, corresponding to the upper A_{1g} level, are equal to 0.548 and -0.724 , respectively. For the lowest A_{1g} level they equal 0.806 and 0.588, respectively (normalization with respect to the whole crystal). The spin-orbital interaction and also many-electron effects need to be included in the theory for the calculation of the excited states in a similar manner.

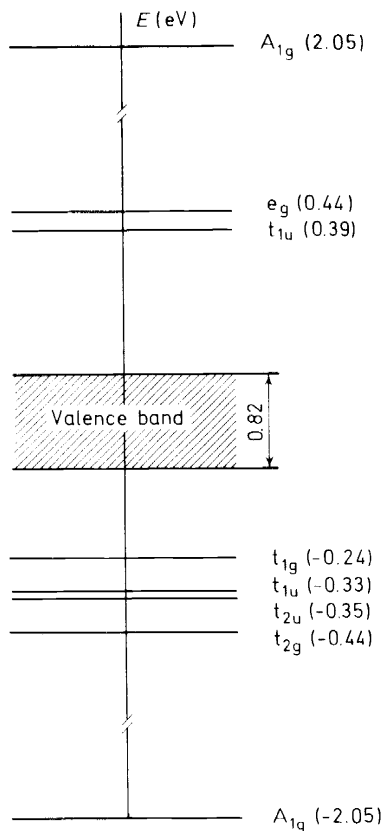


Figure 1. Localized energy levels of the impurity centre for KCl:Ti in the ground state. Figures in brackets represent the distance from valence band edges

An analogous calculation was made for the KCl-Eu²⁺ centre with C_{2v} symmetry (the centre includes a charge-compensating vacancy), and the distortion of the lattice by the defect was taken into account¹⁷⁻¹⁹. The calculation was made for the ground state (5s, 5p and 4f functions of Eu²⁺ were included) of the centre and the excited state (4f⁰5d¹) for the lattice configuration which is in equilibrium for the ground or excited electronic state. Table 1 shows the energies of the localized levels of the ground state relative to the valence band edges.

Energy levels, determining the optical spectrum of this centre, are almost pure impurity levels and are situated below the valence band. The observed splitting (from 5d levels) of the optical absorption band is well represented as the difference between certain B₁ and B₂ levels. Especially interesting is the existence of the induced level A₁ (1.59) which explains the observed possibility for the localization of a hole in the region of the centre. At first sight such a possibility seems improbable because of the excess of positive

Table 1. The energies of the localized levels for the ground state of the KCl-Eu²⁺ (C_{2v}) centre relative to the valence band edges

Symmetry of states	Energy (eV)
A ₁	+ 1.59
	- 0.62
	- 0.68
A ₂	- 0.71
	- 2.13
B ₁	- 0.54
	- 1.93
	+ 7.43
B ₂	- 0.59
	- 1.25

activator charge; but according to the described results the trapping of the hole on the neighbours of Eu²⁺ is possible.

Thus, the whole system of energy levels of the impurity centre may be much more complicated than it is usually considered to be. This is especially important in the consideration of the kinetic processes. On the other hand, calculations have shown that together with the relaxation process of the lattice (after excitation) the system of local levels of the centre may undergo drastic changes.

During recent years the so-called cluster method has become popular for solving such problems, which implies a direct application of the MO-LCAO method to the quasi-molecule 'impurity plus a certain number of neighbours'. From the methodical point of view it is a part of Green's function method. The perturbation operator is similar in both cases but the secular equations are different. The main drawback of this approach at present lies in the fact that it is not clear which of the levels are local, i.e. where the band edges are situated (and how intraband states are perturbed). Despite this, the semi-empirical calculation of optical KCl-Tl bands with this method²⁰ is of interest. A good experimental agreement was obtained for the location of A, B and C absorption bands²⁰. However, this seems to be partly due to the compensation of some uncertainties (the application of the Wolfsberg-Helmholtz formula without varying coefficient k , and of the Mulliken population analysis are doubtful, the value of the overlap integral $S_{\sigma} = \langle 6p_x | z_1 \rangle$ raises some questions, etc.). It seems that the degree of covalency of the Tl⁺ bonds with ligands (the charge at Tl⁺ obtained was equal to +0.85), was somewhat over-estimated²⁰. It is doubtless that in such calculations the latest results accumulated in the quantum chemistry of inorganic complexes should be used. At the same time one has to bear in mind, however, that the parametrization of these methods has been carried out on molecules and that the application of them to crystals needs to be critically analysed. Analogous ideas are being intensively developed in the theory of the complexes of rare earth and transition elements³⁸. It should be stressed that in the case of considerable covalency in activator bonds with ligands one should apply the notion 'complex' with great care, since unlike true com-

plexes the coupling of this 'complex' with the rest of the crystal is not weaker than the coupling within itself. The role of covalent bonds increases as the host anions become heavier.

A cluster calculation of the NaCl-Cu system has been carried out²¹. The extended Hückel method with the self-consistent charge was used. The obtained degree of covalency of the Cu^+-Cl^- bond was considerable. It should be noted that in comparison with the free ion, the energy of the $d^{10} \rightarrow d^9s$ transition in NaCl-Cu increases, contrary to the $6s^2 \rightarrow 6s6p$ case of KCl-Tl. In this the covalent effects and the absence of orthogonalization restrictions on the overlap of some of the d orbitals with their neighbours play an important part. A special role of the covalent bonds of d electrons with their neighbours and the deformability of the d shell was also revealed in the studies on the dynamics of AgCl and AgBr lattices^{2,3}. A qualitative interpretation of the spectrum of the KCl- Ag^+ centre in the scheme of molecular orbitals is proposed by Dultz²⁴. A number of further examples are also known where it is not possible to give even a qualitative explanation of the structure of the absorption spectrum without including the MO picture for the centre. One such case is the interstitial U_2 centre whose electronic states cannot be described as the states of H^0 perturbed (and slightly mixed) by the rest of the crystal^{25,26}. The interpretation of the absorption spectrum of CsI- Tl^+ requires the application of ideas about the covalent bonds of thallium with its surroundings²⁷.

F-aggregate colour centres (M, R, N centres) also serve as good examples of quasi-molecular centres in ionic crystals. Their properties are determined to a considerable extent by the molecular orbitals for electrons in the field of the corresponding clusters of anion vacancies. The theory of these centres in the scheme of valence bonds was worked out in detail by Evarestov^{28,29}. The 'molecular individuality' of such centres increases as their vacancy framework becomes more complicated and it is especially revealed by a considerable decrease of the half-width of spectral bands in comparison with the F centre.

A very interesting analogue of the molecular phenomenon is the Jahn-Teller effect for degenerate electron states of the centres. This effect has been demonstrated for impurity centres^{30,31}. In the case of the so-called 'statical' effect a low-symmetric distortion of the surrounding lattice arises, and in the case of the 'dynamical' effect a non-adiabatic coupling of the electronic motion with non-totally symmetric vibrations occurs.

Three-fold degenerate excited states of the KCl-Tl type centres usually undergo the Jahn-Teller effect and the centre is tetragonally distorted. In this connection it is possible to explain the detailed structure of absorption bands, polarization properties of the emission, the influence of external fields, and uniaxial stresses, in particular, on spectral bands^{32,33}. Also a number of subtle properties of the emission spectra can be explained but the question about the origin of the long-wave emission band remains unanswered.

So it should be concluded that molecular aspects in the theory of impurity centres appear to be essential both in the methodical and physical sense. On the other hand, it is necessary to stress that in the theory of impurity centres (from the solid state viewpoint) the theory of the shape of vibronic

spectra^{9, 10}, radiationless transitions^{9, 34}, resonant Raman scattering^{35, 36}, etc. is worked out in detail. In the theory of polyatomic molecules analogous problems are obviously present because of the interaction of electronic transitions with all the vibrations of the molecular core. In the theory of impurity centres these problems seem to have been elaborated far more thoroughly at present, and the overtaking of a number of corresponding results on true molecular objects is topical. This conclusion is arrived at, for example, if one compares the present state of the theory of radiationless transitions in molecules³⁷ with the situation in the theory of impurity centres³⁴.

INTRINSIC EXCITATIONS

As a matter of fact, any elementary excitation of the crystal to a certain extent represents a defect in it. The molecular aspect is essential even for such elementary excitations as holes and excitons in alkali halide (ideal) crystals. The main physical reason for this is the relatively small electronic radius of the hole and a strong electron-phonon interaction in these systems.

The models of a free exciton were built long ago using the Heitler-London scheme. Thus, for example, in the Dykman model^{39, 40}, developed by Overhauser⁴¹, the hole component of the exciton is localized on the anion ($X^0(np)^5$), and the electronic function is built as the linear combination of s functions of neighbouring cations. In a series of papers by Tolpygo and Kudykina⁴² a more general model is examined. It is shown that the maximum density of the electronic charge is formed on two cations, adjacent to the central nucleus, which lie in the direction of the actual p function of the hole. Such an exciton has the symmetry D_{4h} (instead of O_h in the Dykman model). The D_{4h} model gives the lowest energy for the exciton when the translational symmetry of the crystal is taken into account†.

One of the fundamental properties of alkali halide crystals (during recent years it has been discovered that a number of ionic crystals with halides in the role of anions behave in this way⁴³⁻⁴⁵) is the tendency to form molecular bonds between the anion with a hole in the valence p shell and one of the neighbouring anions: $X^0 + X^- = X_2^-$. The ground state of X_2^- , $\sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^4$; ${}^2\Sigma_u^+$ is bonding and the stable configuration corresponds to the mutual approach of these two nuclei in comparison with their positions in a rigid lattice. The axial relaxation of the lattice takes place simultaneously. The structure of the so-called V_k centre is established by Känzig⁴⁶. The hole is well localized on a pair of anions. The crystal field is essential and is revealed through the anisotropy of the g factor and the hyperfine interaction⁴⁷ constants.

The excited anion (exciton in the excitation model⁴⁸) also forms a quasi-molecule, $X^{-\star} + X^- \rightarrow X_2^{-\star}$, analogous to the excimers of rare gases or their crystals⁴⁹. In such a system there is a rich set of molecular terms, containing a hole in one of the configurations of the V_k centre, and a trapped

† In these calculations, however, the contribution of the $(n+1)s$ and $(n+1)d$ states of the central anion which, according to the band structure calculations, must be essential, is not taken into consideration.

electron ($V_k + e$ centre). The lowest of the possible electron configurations is:

$$(\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np) [\sigma_g (n+1) s], {}^{1,3}\Sigma_u^+$$

containing two 'extra' bonding electrons. Therefore the V_k centre forms a very deep trap for the electron. The binding energy is 2–3 eV⁵⁰, while in the case of a free exciton the value of ~ 0.5 eV is typical. The ground state of X_2^{2-} , $\sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^2$; ${}^1\Sigma_g^+$, is unstable and the molecule dissociates after de-excitation with a return to the ideal lattice configuration.

The model of the $V_k + e$ centre was proposed by Tolpygo⁵¹ for a free exciton, the semiquantitative theory of the $V_k + e$ centre was elaborated by Wood⁵², and the quantum mechanical theory was developed by Kudykina and Tolpygo⁴².

In both cases under study (V_k and $V_k + e$) a strong non-cubic distortion of the lattice takes place and as a result of this the energy of the system decreases. At the same time electronic excitation 'goes out of resonance' and is transformed from the band excitation to the local excitation of the lattice. These self-trapped excitations are analogues of a one- or two-fold ionized impurity molecule with one difference. the molecular bond may jump over onto a new pair of neighbouring anions, one of which belongs to the previous quasi-molecule. This corresponds to the jump diffusion⁵³ which in the case of holes is connected with a potential barrier of ~ 0.3 eV, since together with the hole the local lattice distortion must also be transferred. In the case of the jump diffusion of the self-trapped exciton the barrier is somewhat lower but the diffusion path is restricted by the short lifetime of the exciton⁵⁴.

The main source of data on the basis of which the theory of self-trapped excitons is developed, is the emission of non-activated crystals. The luminescence of self-trapped excitons is identified in iodides, bromides and chlorides of alkali metals (Li, Na, K, Rb, Cs)^{55–57}. A considerable axial relaxation gives the exciton emission a large Stokes' shift (from 1.4 eV in NaI to 5.4 eV in KCl). The smaller the ionic radius of the anions the more they approach each other in the equilibrium $V_k + e$ configuration. As a rule, there are two emission bands: a short wavelength band with σ -polarization (along the molecule axis) and a long wavelength band with π -polarization^{58, 59}. σ -Luminescence has a short decay time of ~ 1 –3 ns⁶⁰. In the case of π -luminescence τ has a wide range depending upon the crystal⁶¹, and in iodides it also depends upon the temperature^{62–65}.

At the excitation in the long wavelength exciton absorption band only the long wavelength band appears in the emission spectrum. the short wavelength band appears at the excitation to higher exciton states^{57, 66, 67}. In recombination luminescence of $V_k + e$ the whole spectrum is revealed.

There have been a number of attempts to interpret the optical transitions in self-trapped excitons. Among these Kabler's representations^{43, 61} have played the most important role. They have been supported by lifetime^{63, 65} and magneto-optical^{68, 69} measurements. The origin of the lowest odd-parity levels of X_2^{2-} according to Kabler is given in Figure 2. The lowest excited state is a triplet (${}^3\Sigma_u^+$) and the transition to the ground state (${}^1\Sigma_g^+$) is forbidden by multiplicity: the spin-orbital interaction mixes to the ${}^3\Sigma_u^+$ state the components of the ${}^1\Pi_u$ state with $|M_j| = 1$. The matrix element of the

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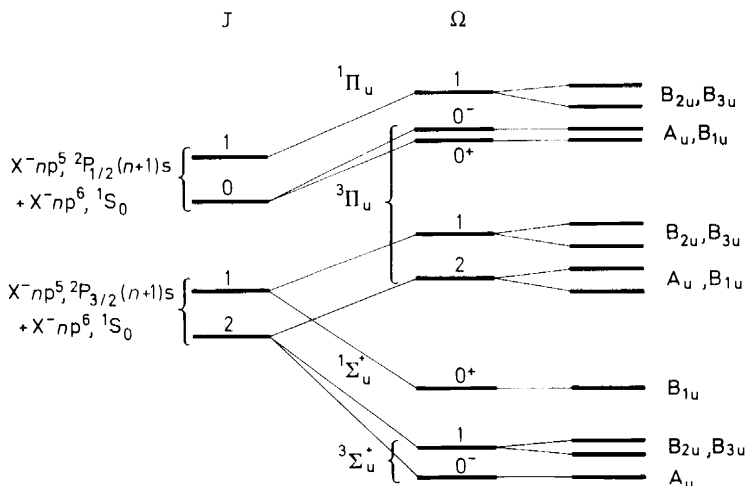


Figure 2. Origin of the low energy odd-parity excited levels of a self-trapped exciton ($V_k + e$ centre). States for separated atoms (with strong spin-orbital coupling) are on the left, states for the diatomic molecule (symmetry $D_{\infty h}$) are at the centre and those for the crystal (point symmetry D_{2h}) are on the right

transition increases in the anion series $\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ and also depends upon the distance between the Σ and Π states. The probabilities of radiative transitions change on a large scale (from 10^7 s^{-1} in NaI to $2 \times 10^2 \text{ s}^{-1}$ in RbCl).

Figure 3 shows schematically the states involved in the formation of the long wavelength band of the exciton luminescence.

The $^3\Sigma_u^+$ state in the NaCl-type lattice (D_{2h} symmetry) gives rise to levels of the type A_u , B_{2u} and B_{3u} . The lowest level A_u is metastable. Optical transitions are allowed from the B_{2u} and B_{3u} levels. The splitting between them, which can be detected only by means of the Faraday rotation⁶⁸ for emission, is $\sim 10^{-6} \text{ eV}$ in the zero field. The splitting between the A_u and $B_{2,3u}$ levels in iodides is $\sim 0.5 \text{ meV}$ and is easily determined by emission decay measurements. At low temperatures in the case of pulse excitation the

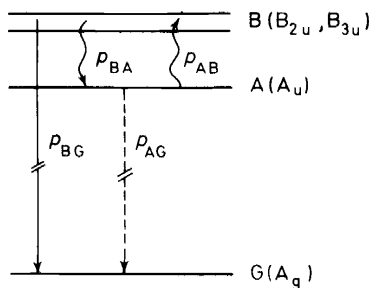


Figure 3. States and transitions in the self-trapped exciton which determine the kinetics of the long wavelength emission band

kinetics correspond to the non-equilibrium population of levels: two components with different decay times τ are observed.

The temperature dependence of decay times enables one to calculate the probabilities (p) of radiative and non-radiative transitions and also initial populations of the levels. Table 2 gives data for KI and NaI (p in s^{-1} and splittings in eV) obtained by us. The non-radiative transition probabilities are denoted by $p_{AB} = p_{AB}^0 \bar{n}$ and $p_{BA} = p_{BA}^0 (1 + \bar{n})$ with $\bar{n} = [\exp(E_{AB}/kT) - 1]^{-1}$.

Table 2. Probabilities of radiative and non-radiative transitions of $V_k + e$ centres in KI and NaI from lifetime measurements. Notations from Figure 3

Crystal	p_{BG} (s^{-1})	p_{AG} (s^{-1})	p_{AG}^0 (s^{-1})	p_{BA}^0 (s^{-1})	E_{AB} (eV)	E_{BG} (eV)
KI	1×10^6	$< 10^3$	2×10^6	1×10^6	0.7×10^{-3}	3.35
NaI	9×10^6	2×10^4	7×10^4	3.5×10^4	0.5×10^{-3}	4.20

The magnetic field mixes the triplet components and this leads to the change of τ in accordance with experiment. If the field is parallel to the molecular axis then the level-crossing leads to the resonance anomalies in the lifetime and magnetic circular polarization dependences^{6,9}.

The short wavelength emission band was initially connected with the singlet $^1\Sigma_u^+$, originating from the same atomic configuration $p^5s(\frac{3}{2}, \frac{1}{2})$, $J = 1$. However, a number of circumstances contradict such an interpretation. This band is not excited in the corresponding exciton absorption band^{57, 67}, and the calculated matrix element is too large when compared with the lifetime data⁶⁰. There exist some higher singlet states with B_{1u} symmetry, which are able to produce short wavelength emission with the σ -polarization. Such states arise, in particular, if one takes into account the possibility of localization of the electron on neighbouring cations.

Kudykina and Tolpygo⁴² examined the D_{2h} model (an exciton consists of two anions and ten cations) in which a rich set of singlet states (besides triplet ones) with the required symmetry are found. Only some of these states have sufficiently low energy. The theory of the $V_k + e$ centre needs developing; it is also necessary to take into consideration the axial relaxation of the lattice and to find an explanation for some of the complications in the emission aspect of iodides^{60, 65}.

Three possibilities for the origin of a self-trapped exciton in a crystal are: (i) the recombination of a free (or tunnelling) electron with the V_k centre; (ii) the axial relaxation of a free exciton (formed, e.g., by light or an electron impact); and (iii) direct optical creation. In the first case all the excited states of the system contain a hole shared between two anions, in the second case the exciton enjoys some time in the 'one-nucleus' state before the excited quasi-molecule is formed; and the third possibility has a negligibly low probability because of the smallness of the matrix element in phonon functions.

The similarity of emission spectra in the first and second cases of excitation has historically served as a very important argument in the establishment of the self-trapped exciton model^{52, 59}. There are, however, a number of

experimental facts which show that the obtained excited states, at least in iodides, are not totally identical. In connection with this there are some interesting theoretical studies of the evolution of the exciton state from the atomic state to the molecular one (e.g. Wood⁵² or the investigation by Mulliken of the diatomic rare-gas molecules⁷⁰).

It is known that if electrons are recombined with oriented V_k centres the emission is polarized. The polarization of luminescence was also searched for in the optical creation of excitons by polarized light^{62, 71}, but the result was negative. It is as if the exciton 'forgets' about its initial orientation, either in the free state ('rotation' of the hole function during migration) or in the course of vibrational relaxation through intermediate states. It should be noted, however, that the conditions for observing polarization are rather unfavourable in the f.c.c. alkali halide crystals and one can hardly expect the degree of polarization in the optical creation of excitons to be more than 5 per cent.

In the case of optical excitation the exciton emission is quenched with decreasing temperature^{62, 72}. It is probable that at low temperatures the exciton has to overcome the activation barrier of 0.015 eV in NaI⁷² and 0.010 eV in KI⁶⁷ on its way to the self-trapped state. This hypothesis is supported by the fact that simultaneously with the quenching of the self-trapped exciton emission the efficiency of the energy transfer to impurities increases, especially in KI-Tl to Tl⁺ ions⁷³. This may be related to the increase of migration of non-relaxed excitons.

In connection with the barrier problem it is interesting to mention that in the diatomic rare-gas molecules a number of potential curves, connecting the states of separate atoms with molecular states, pass a maximum⁷⁰. They correspond to the so-called promoted orbitals that have higher quantum numbers n in the united atom than in the separated atoms (e.g. $5p^56s(\frac{3}{2}, \frac{1}{2})$, $J = 1 \rightarrow 0_g^+ \rightarrow \sigma_u 5p7p\sigma$ in Xe₂^{*}; see Figure 2, Ref. 70).

If the exciton exists 'behind the barrier' for quite a long time, one may expect the appearance of edge emission from free or partially relaxed exciton states at low temperatures. The corresponding measurements on KI and NaI have not given positive results. If edge emission exists its yield does not exceed 0.3 per cent of that of the self-trapped exciton which is close to unity at moderately low temperatures. Consequently, the lifetime of the exciton in the non-relaxed state hardly exceeds 10^{-11} s. This time seems to be too short for relaxation by means of the sequence of one-phonon scattering processes, but is sufficient for distances exceeding $\sim 10^2$ - 10^3 lattice constants. It may be supposed that the reason for the absence of edge emission is the migration of excitons to lattice defects, leading to the emission of another spectral composition (observed in experiment) or to the radiationless annihilation of excitons.

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