Alpha and Gamma Bands in Alkali Halides

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(Received 29 March 1963)

This is a calculation of the effect produced by a nearby vacancy on the energy of the transition of an electron from a negative ion in an alkali halide crystal to a neighboring positive ion ("charge transfer" model of the exciton). Some, but not all, of the results agree satisfactorily with experimental observations of the α and γ bands. The evaluation of certain "dipole" lattice sums of interest in other problems as well as this one is reported in the Appendix.

THE so-called "fundamental absorption band" in alkali halides is generally assumed to result from the creation of an exciton, and the so-called alpha and gamma bands, which are observed on the long-wavelength side of the fundamental absorption,[1,2] have been attributed to that same transition perturbed by a nearby negative-ion vacancy. The position of the alpha band was first calculated by Bassani and Inchauspé[3] on the basis of the "charge-transfer" model of the exciton (defined in the paragraph below and also in the caption for Fig. 1) for the configuration of vacancy, positive ion, and negative ion shown in Fig. 1(a). The formalism was extended to arbitrary configurations by Tsertsvadze[4] and evaluated numerically by him for the configuration shown in Fig. 1(b). Klick and Patterson[2] have suggested that the configuration shown in Fig. 1(d) would provide a reasonable model for the gamma band, and the calculation for this configuration is reported in the present note. We also discuss the effects to be expected from other possible configurations.

Let an electron on a negative ion (called ion number 1) be transferred to a neighboring positive ion (called ion number 2). The energy of this transition is affected by the presence nearby (in a position called number 3) of a negative ion vacancy. Let $h\nu$(free) be that energy when no such vacancy is present (fundamental absorption) and let $h\nu$(pert.) be the energy if such a vacancy is present at position number 3, and let $\Delta E = h\nu(\text{free}) - h\nu(\text{pert})$. Then[4]

$$\frac{\Delta E}{e^2} = \frac{1}{a}\left\{ C - R - \left[\frac{A}{2}M_- + S_+ M_+' + S_- M_-'\right]\right\}. \quad (1)$$

Here the first term, C, describes the Coulomb energy, the second the repulsive energy, viz., $R = \alpha_M \rho/6a$ if sites 2 and 3 are nearest neighbors and 0 otherwise, and the bracket the energy of the induced dipoles. Two of the quantities involved in Eq. (1) are constants: the Madelung constant $\alpha_M = 1.7455$ and the square of the charge on the electron, $e^2 = 14.39$ eV cm. The other quantities that appear in that equation are one of two

kinds: some that depend only on the host lattice $(a, \rho, M_-, M_+', M_-')$ and some that depend on the relative position of ions $1, 2, 3 (A, C, S_+, S_-)$. Consider first the former. a is the distance between nearest neighbors, ρ is a quantity of dimensions length appearing in the expression for the repulsive energy, and M_-, M_+', and M_-' are quantities related to the dielectric properties of the components of the lattice which are defined in Ref. 3 and can be quantitatively computed from data given in the book of Mott and Gurney.[5] Turning now to the quantities which depend on the relative positions of ions 1, 2, 3, the definitions are

$$C = r_{23}^{-1} - r_{13}^{-1},$$

$$A = r_{23}^{-4} + r_{13}^{-4} - 2r_{23}^{-2}r_{13}^{-2}\cos(r_{13}, r_{23}),$$

$$S_+ = \sum_{+\text{ions}}{}''' f_{23}{}^i - \sum_{+\text{ions}}{}''' f_{13}{}^i, \quad (2)$$

$$S_- = \sum_{-\text{ions}}{}''' f_{23}{}^i - \sum_{-\text{ions}}{}''' f_{13}{}^i,$$

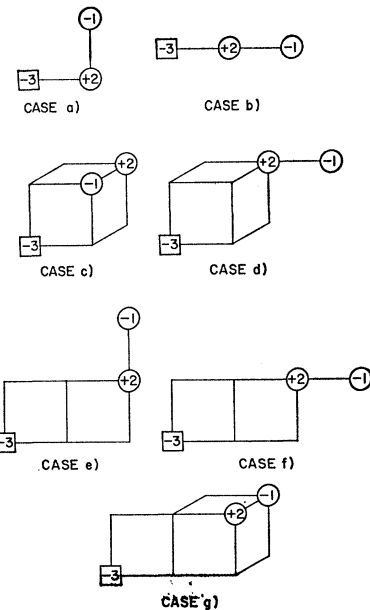where $f_{23}{}^i = r_{2i}^{-2}r_{3i}^{-2}\cos(r_{2i}, r_{3i})$ and r_{3i} is the distance

Fig. 1. The charge-transfer model for the exciton involves transfer of an electron from a negative ion (labeled by number 1 in the figure) to a positive ion labeled number 2. In this paper the effect on the energy of this transition of a negative-ion vacancy (number 3) in various nearby positions is calculated. The figure shows the various configurations that are discussed in the text.

[1] C. J. Delbecq, P. Pringsheim, and P. Yuster J. Chem. Phys. 19, 574 (1951).
[2] C. C. Klick and D. A. Patterson, Phys. Rev. 130, 1269 (1963).
[3] F. Bassani and N. Inchauspé, Phys. Rev. 105, 819 (1957).
[4] A. A. Tsertsvadze, Fiz. Tverd. Tela 3, 336 (1961) [translation: Soviet Phys.—Solid State 3, 241 (1961)].

[5] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1938), Chap. 1.

TABLE I. The first seven columns give ΔE as calculated for the seven configurations defined by Fig. 1. The last two columns give ΔE as observed experimentally (Ref. 2).

	ΔE (in eV)							Observed band	
	Calculated-case								
	a	b	c	d	e	f	g	α	γ
NaCl	0.49	0.81	−0.28	0.17	0.15	0.21	0.09	0.80	⋯
KCl	0.51	0.83	−0.26	0.18	0.15	0.19	0.08	0.81	0.20
KBr	0.47	0.78	−0.25	0.17	0.14	0.19	0.07	0.67	0.23
KI	0.42	0.69	−0.23	0.15	0.13	0.18	0.07	0.60	⋯

between ion i and ion 3, etc., and the summations are over all positive- or negative-ion sites (as indicated) except that the sites 1, 2, and 3 are omitted (as suggested by the triple prime).

We have done quantitative calculations for seven cases which we have called cases a, b, c, d, e, f, and g. These seven cases are distinguished by different relative positions of ions 1, 2, 3, and are defined by Fig. 1. The results are shown in Table I, together with the experimental observations[2] that they are supposed to be related to. The calculated values reported in the first two columns disagree with previously published values[3,4] —slightly in case a and rather sharply in case b. We have traced this discrepancy to the use of different numbers for the lattice sums involved in the quantities S_+ and S_- and discuss it in Appendix I. It is worth mentioning that the lattice sums whose values are reported there are of interest in other physical problems as well. The observed values for the α band, which are taken directly from Klick and Patterson,[2] also differ from earlier published values, but only because different positions for the first absorption peaks were used before.

In the calculations, cases a and b involve transitions of an electron to the nearest positive neighbor of the vacancy; case d involves a transition to the second-nearest positive neighbor of the vacancy, and cases e, f, and g involve transitions to its third-nearest positive neighbor. These six cases exhaust all possible transitions to these three positive sites in which the electron moves *toward* the vacancy. (Case c, in which the electron moves *away from* the vacancy, is included largely in order to show explicitly that such transitions lead, as expected, to negative ΔE's which would put the absorption on the other side of the edge and, therefore, make it unobservable.) The fourth positive neighbor of the vacancy, the nearest one that is left out, is located at sites (300), etc., and the ΔE's arising from transition to these may be expected to be small (and experimentally unobservable on account of their closeness to the absorption edge).

Agreement between theory and experiment may be described as incomplete. Case b agrees satisfactorily with the alpha-band data, and cases d, e, and f with the gamma-band data; but the effects from case a have not

been observed. To be sure, we have not actually calculated the transition probabilities for any of the transitions, and it is possible that such a calculation might show the probability for case a to be very small; but the most naive, purely statistical, estimate points in the other direction. For case a, there are twelve negative "1" atoms about each vacancy, and the electron on each has two positive "2" atoms adjacent to it, so that $12 \times 2 = 24$ separate "case a" transitions are possible for each vacancy; by contrast in case b there are only 6 negative "1" atoms about each vacancy, and the electron on each of them has only one positive "2" atom adjacent to it, so that only $6 \times 1 = 6$ separate "case b" transitions are possible. Statistically, therefore, the probability of the unobserved "case a" transition is four times as large as that of the observed "case b" transition. This ratio remains unchanged if we slightly refine this argument by taking account of the fact that transitions will be induced only by light with a component polarized in the direction in which the electron is to move (for unpolarized light, for example, this merely reduces the number of possible transitions by $\frac{2}{3}$—in both cases).

It may be possible to improve agreement further by refining the details of the calculations, at the cost of greater complexity, without abandoning the somewhat specialized "charge transfer" model for the exciton. For details of the assumptions involved and refinements possible, the reader should consult the paper by Bassani and Inchauspé.[3] Although the present calculation has, generally speaking, improved agreement between theory and experiment, it cannot claim to provide completely convincing evidence for the correctness of either the overall theory of the method of computation.

APPENDIX I

The numerical work involved in computing the quantities $S_\pm$ in (1) can be reduced to evaluation, for various values of i, j, k, of lattice sums

$$T_{\text{even}}{}^{ijk} = \sum\sum\sum{}'' \quad f^{ijk}(l,m,n), \tag{3}$$
$$|l+m+n|=\text{even}$$

with $f^{ijk}(l,m,n) = r^{-2}r_-^{-2}\cos(r,r_-) = 2^{-1}r^{-3}r_-^{-3}[r^2+r_-^2 - (i^2+j^2+k^2)]$, $r^2 = l^2+m^2+n^2$, $r_-^2 = (l-i)^2 + (m-j)^2 + (n-k)^2$, the double prime indicating omission of points $r = 0$ and $r_- = 0$; and of $T_{\text{odd}}{}^{ijk}$ defined analogously. To speed convergence, the quantities T were not summed directly, but evaluated as follows. Omitting indices

and subscripts irrelevant for present purposes, we write

$$T= \sum_{\text{all space}}'' f$$

$$=\left[\sum_{r\leq R}'' + \sum_{r>R}\right]f \quad \text{[provided } R \text{ is chosen greater} \\ \text{than } (i^2+j^2+k^2)^{1/2}]$$

$$=\sum_{r\leq R}'' f + \sum_{r>R} (f-r^{-4}) + \sum_{r>R} r^{-4}$$

$$T=\sum_{r\leq R}'' f + \sum_{r>R} (f-r^{-4}) + \left[\sum_{\text{all space}}' - \sum_{r\leq R}'\right]r^{-4}. \quad (4)$$

We now choose $R=10$ and define

$$\left. \begin{array}{c} \sum_{r\leq 10}'' f = W, \\[4pt] \sum_{\text{all space}}' r^{-4} = A, \\[4pt] \sum_{r\leq 10} r^{-4} = B; \end{array} \right\} \quad (5)$$

then, with neglect of $\sum_{r>10} (f-r^{-4})$, we can write (4) as

$$T=W+(A-B)$$

or, restituting the subscripts and indices,

$$\begin{aligned} T_{\text{even}}{}^{ijk} &= W_{\text{even}}{}^{ijk} + (A_{\text{even}} - B_{\text{even}}), \\ T_{\text{odd}}{}^{ijk} &= W_{\text{odd}}{}^{ijk} + (A_{\text{odd}} - B_{\text{odd}}). \end{aligned} \quad (6)$$

Of these quantities, the A's are known from the work of Jones and Ingham[6] (done analytically by what is usually called Ewald's method); they are $A_{\text{even}} = 6.334\,58$ and $A_{\text{odd}} = 10.197\,74$. The B's were evaluated numerically on the NAREC computer and found to be $B_{\text{even}} = 5.709\,218\,766\,6$ and $B_{\text{odd}} = 9.564\,363\,607\,4$. The W's were also evaluated numerically for thirteen sets of (i,j,k) and are listed in Table II. The T's were then computed from (6) and also put in Table II. The reader will observe that omitting the second term in (4) was equivalent to replacing f in (3) by r^{-4} outside the sphere of radius $R=10$; the error induced by this can be shown to be at most of order R^{-4}. [Had (3) been evaluated directly inside a sphere of radius R, and the points outside omitted, the error would have been of

[6] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) A107, 636 (1925).

TABLE II. The lattice sums
$$T_{\text{even (odd)}}{}^{ijk} = \underset{\substack{\text{all space} \\ |l+m+n| = \text{even(odd)}}}{\sum\sum\sum}{}'' \quad f^{ijk}(l,m,n)$$
and
$$W_{\text{even (odd)}}{}^{ijk} = \underset{\substack{l^2+m^2+n^2 \leq 10, \\ |l+m+n| = \text{even(odd)}}}{\sum\sum\sum}{}'' \quad f^{ijk}(l,m,n),$$
with f defined by Eq. (3), and points $(l,m,n,) = (0,0,0)$ and $(l,m,n) = (i,j,k)$ omitted.

ijk	$W_{\text{even}}{}^{ijk}$	$W_{\text{odd}}{}^{ijk}$	$T_{\text{even}}{}^{ijk}$	$T_{\text{odd}}{}^{ijk}$
100	5.116 108 251 2	5.108 089 417 7	5.7415	5.7415
110	3.649 258 238 8	4.095 104 007 1	4.2746	4.7285
111	3.133 469 930 4	3.125 450 183 0	3.7588	3.7588
200	2.598 588 965 8	2.135 646 475 0	3.2240	2.7690
210	2.168 934 682 3	2.160 916 353 0	2.7943	2.7943
211	1.947 518 730 3	1.961 774 141 3	2.5729	2.5952
220	1.566 829 053 5	1.619 507 228 3	2.1922	2.2529
221	1.478 109 887 5	1.470 085 862 2	2.1035	2.1035
300	1.447 991 434 3	1.439 983 496 3	2.0734	2.0734
310	1.369 263 033 5	1.330 108 493 7	1.9946	1.9635
222	1.190 244 071 2	1.191 114 948 5	1.8156	1.8245
321	1.052 413 788 0	1.050 690 531 3	1.6778	1.6841
400	0.949 221 791 8	0.924 124 131 1	1.5746	1.5575

order R^{-1}.] As a check, we also ran two of the T-sums in a larger sphere, of radius $R=15$, and found agreement to six decimal places; we, therefore, feel safe quoting four decimals for the T's. The fact, apparent from Table II, that $T_{\text{even}}{}^{ijk} = T_{\text{odd}}{}^{ijk}$ when $i+j+k=$ odd also follows directly from the symmetry of the sums.

The T's shown in Table II for $(ijk) = (100)$, (110), and (200) differ from numbers given for the same quantities in some earlier papers.[7,8,4] I am grateful to Dr. J. R. Reitz and Dr. E. S. Rittner for attempting, though unsuccessfully, to help me trace the source of the discrepancies. Case (a) of Table I involves the T^{100} and T^{110} sums, and on account of these discrepancies, our results for case a are about 4% lower than those of Bassani and Inchauspé.[3] Case b involves the T^{100} and T^{200} and for the same reason our results for case b are about 2 or 3 times as high as those of Tsertsvadze.[4]

The quantities $S_{\pm}$ of (2) were computed from Table II. Each of them contains the difference between two T's, and since in subtracting two even T's, or two odd T's the terms $A-B$ in (6) cancel out, the W's alone were sufficient for the calculations and the T's did not have to be used explicitly.

[7] R. A. Hutner, E. S. Rittner, and F. K. duPre, J. Chem. Phys. 17, 204 (1949).
[8] J. R. Reitz and J. L. Gammel, J. Chem. Phys. 19, 894 (1951).