PHYSICAL REVIEW VOLUME 105, NUMBER 3 FEBRUARY 1, 1957

Position of the α and β Bands in Alkali-Halide Crystals†

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(Received October 2, 1956)

The traditional model of the exciton is used to determine the positions of the α band and the β band relative to the first maximum of the fundamental absorption bands. The β band is considered to be due to an exciton created in the immediate vicinity of an F center and the α band to an exciton created in the immediate vicinity of a negative-ion vacancy.

Simple assumptions are made in performing the calculations of the energy required to create the exciton. The results obtained agree satisfactorily with the available experiments.

I. INTRODUCTION

THE experimental evidence concerning the appearance of an absorption band in the tail of the fundamental absorption band when a large number of halogen vacancies are present in the crystal suggested that this absorption band, which is called the α band, is due to an exciton which is created in the vicinity of an halogen ion vacancy.[1] The β band, which appears in the tail of the fundamental absorption when a large number of F centers are present in the crystal, has been attributed to an exciton created in the vicinity of an F center.[1] Since such excitons are localized at specific points of the lattice where the imperfections are present, the related absorption coefficients are of the same order of magnitude as those associated with the bands due to color centers and are smaller than the fundamental absorption coefficients by several orders of magnitude. In contrast with the excitons responsible for the fundamental absorption these excitons have no ability to migrate about the crystal. A critical discussion of the properties of the α and β bands can be found in the review article by Seitz.[1]

The model used by Von Hippel, de Boer, Mott, and others[2] to determine the position of the first and the second fundamental absorption peaks in alkali-halides crystals can be also used to determine the positions of the α band and the β band relative to the first absorption maximum. The model has been recently revived by Overhauser, who has used it to explain the occurrence of many components in the fundamental absorption band.[3] It amounts essentially to looking at the crystal from an atomic standpoint. The exciton is considered as an excited state of the crystal in which a valence electron from one halogen ion has been transferred to one of its nearest alkali ions. In this framework the three different situations of a free exciton, an exciton trapped at an F center, and an exciton trapped to a negative-ion vacancy are illustrated by Figs. 1, 2, and 3, respectively.

In all cases the change in energy involved in the creation of the exciton can be evaluated by considering the following cycle: first, a negative ion and one of the nearest neighboring positive ions are extracted from their lattice positions indicated in the figures by the numbers 1 and 2. Next, the valence electron is transferred from the halogen ion to the alkali ion so that two neutral atoms result. Finally, the neutral atoms are brought back into their original lattice positions in the crystal. The total work required is, for the different cases:

$$h\nu\ (\text{free exciton}) = {}^1W_- + {}^1W_+{}^{[-]} + E - I + \Omega_1, \tag{1}$$

$$h\nu\ (\beta\ \text{exciton}) = {}^2W_- + {}^2W_+{}^{[-]} + E - I + \Omega_2, \tag{2}$$

$$h\nu\ (\alpha\ \text{exciton}) = {}^3W_- + {}^3W_+{}^{[-]} + E - I + \Omega_3. \tag{3}$$

In these formulas, W represents the energy required to extract an ion from the crystal and the different subscripts and superscripts refer to the negative or the positive ions and to the configurations represented by Figs. 1, 2, and 3. The symbol E represents the electronic affinity of the halogen atom, and I the ionization energy of the alkali atom. The symbol Ω represents the energy required to bring the newly formed neutral atoms into their original lattice positions in the crystal. The contribution to this energy of the halogen atom is small because its dimensions are small and the atom does not interact with the surrounding ions. On the contrary, the metal atom is large compared with the lattice distance, and the valence electron must be

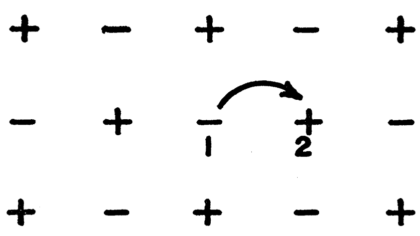

FIG. 1. Schematic representation of an exciton as the transfer of a valence electron from halogen ion 1 to alkali ion 2.

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† This research was supported by the Office of Naval Research.

[1] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952); W. Martienssen, Z. Physik **131**, 488 (1952); W. Martienssen and R. W. Pohl, Z. Physik **133**, 153 (1952); W. Martienssen, Nachr. Akad. Wiss. Göttingen **111** (1952); F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[2] J. H. de Boer, *Electron and Emission Phenomena* (Cambridge University Press, New York, 1935); A. Von Hippel, Z. Physik **101**, 680 (1936); N. F. Mott, Trans. Faraday Soc. **34**, 500 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1938).

[3] A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

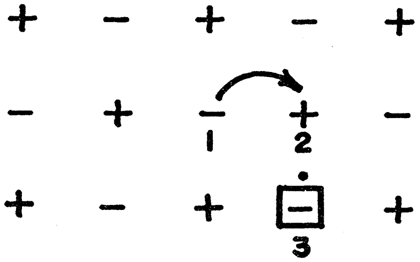

FIG. 2. Schematic representation of a β exciton. One electron is transferred from halogen ion 1 to alkali ion 2 in presence of the F-center 3.

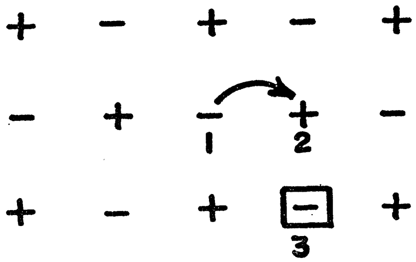

FIG. 3. Schematic representation of an α exciton. One electron is transferred from 1 to 2 in presence of the negative-ion vacancy 3.

shared between six positive ions giving a non-negligible energy. Unfortunately it is impossible to evaluate Ω in any simple way which would take into account the detailed atomic and electronic structure of the lattice. It will be assumed that its value for the α exciton and the β exciton is the same as in the case of a free exciton where it has been estimated by De Boer and Mott to be of the order of 2 ev. In the framework of the present model, it is possible to see that

$$h\nu(\text{free exciton}) > h\nu(\beta\text{-exciton}) > h\nu(\alpha\text{-exciton}).$$

The inequality follows from Eqs. (1), (2), and (3) and the fact that intuitively the energy ${}^1W_- + {}^1W_+^{[-]}$ required to obtain two vacancies in the perfect lattice is expected to be greater than the energy required to obtain two vacancies near the F center, which in turn should be greater than the energy required to obtain two vacancies near a negative ion vacancy.

It is generally true in lattice energy calculations that, though some of the quantities involved are affected by considerable error, the difference between two quantities evaluated in the same way is quite reliable. For this reason the model is particularly suited for calculating the positions of the α and β bands relative to the position of the first fundamental absorption.

II. POSITION OF THE β BAND

The quantity to be evaluated is obtained by subtracting formula (2) from formula (1). The result is

$$h\nu(\text{free exc.}) - h\nu(\beta\text{ exc.}) = {}^1W_- + {}^1W_+^{[-]} - {}^2W_- - {}^2W_+^{[-]}. \quad (4)$$

The assumption that Ω_1 is equal to Ω_2 has been used.

The energy required to extract an ion from a lattice point to infinity is the average of the potential energy at the lattice point before the ion has been removed and of the potential energy of the same point after the ion has been removed. During this removal no displacement of the ions from their equilibrium positions is considered because the ideal cycle must be completed in the short time during which the optical absorption occurs.

The potential energy at a lattice point consists of three parts: (a) the electrostatic energy due to the Coulomb interaction of the charges in the lattice; (b) the repulsive energy between closed shells of electrons; (c) the polarization energy due to the dipole moments induced on the ions by the charges present in the lattice.

The first part gives no final contribution to the expression of formula (4) because the electrostatic energies involved in the extraction of the positive and the negative ion are the same in the case of the free exciton as in the case of the β exciton.

For the repulsive energy the Mott and Littleton approximation can be used.[4] This includes only the interaction between nearest neighbors. The formula for the repulsive energy between a positive and a negative ion at a distance r is

$$W(r) = \frac{\alpha_M}{6}\frac{\rho}{r_0}\frac{e^2}{r_0}\exp[(r_0 - r)/\rho],$$

where r_0 is the lattice distance, α_M the Madelung constant, e the electronic charge, and ρ is a constant which can be determined from the values of the elastic constants of the crystal and is equal to about 0.32 A for all alkali halides.[5] The contribution to formula (4) arises from the lack of interaction between the ions 2 and 3 in Fig. 2; it is equal to $-W(r_0)$.

The main contribution to the difference in energy is due to the different polarization energies of the F center and of the negative ion. If the F center and the negative ion are considered to be localized in a very small region around the lattice position, the Mott and Littleton zero-order approximation can be employed to evaluate the energy which they contribute. In this approximation the dipole moment induced on a negative ion at a distance r from a charge e is given by

$$M_- r_0^3 e/r_2,$$

with

$$M_- = \frac{2\alpha_-}{\alpha_+ + \alpha_-}\frac{1}{4\pi}\left(1 - \frac{1}{k_0}\right),$$

where the α's are the ionic polarizabilities and k_0 is the high-frequency dielectric constant. The assumption is

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[4] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[5] P. Brauer, Z. Naturforsch. **6a**, 255 (1951).

made that the effective polarizing field is the same at all lattice points of the crystal. If one also assumes that the average polarization is unchanged by the presence of the F center, the dipole moment created on an F center by a charge e at a distance r can be expressed as:

$$\mu_F = M_F e r_0^3/r^2,$$

with

$$M_F = \frac{2\alpha_F}{\alpha_- + \alpha_+}\frac{1}{4\pi}\left(1 - \frac{1}{k_0}\right). \tag{5}$$

The polarizability of the F center, α_F, can be evaluated easily because the center has only one electron and there is one optical transition preferred with an oscillator strength close to 1. Under these conditions the polarizability can be obtained from the formula:

$$\alpha_F = e^2/(4\pi m \nu_F^2),$$

where m is the electronic mass and ν_F is the frequency corresponding to the observed position of the maximum of the F band. The contribution to the difference in energy due to the polarization term can be obtained by inspection of Fig. 2 and Fig. 1. The result is:

$$\left[\frac{1}{r_{13}^4} + \frac{1}{r_{23}^4} - \frac{2\cos(r_{13}, r_{23})}{r_{13}^2 r_{23}^2}\right](M_F - M_-)\frac{e^2}{2r_0},$$

where r_{ij} measures the distance from ion i to ion j in units of r_0.

Finally, the formula which gives the position of the β band relative to the first absorption peak is:

$$h\nu(\text{free exc.}) - h\nu(\beta\text{ exc.}) = \frac{2.5 - \sqrt{2}}{2}(M_F - M_-)\frac{e^2}{2r_0} - \frac{\alpha_M}{6}\frac{\rho}{r_0}\frac{e^2}{r_0}. \tag{6}$$

The results for some ionic crystals are given in Table I.[1,6,7] For comparison the experimental data available are presented in parentheses in Column 4.

TABLE I. Position in energy of the β band relative to the first absorption peak (ev).[a]

Crystal	$-\frac{\alpha_M}{6}\frac{\rho}{r_0}\frac{e^2}{r_0}$	$\left(\frac{2.5-\sqrt{2}}{2}\right) \times (M_F - M_-)\frac{e^2}{2r_0}$	$h\nu$(free exc.) $-h\nu$(β exc.)
NaCl	−0.169	0.355	0.19
KCl	−0.136	0.416	0.28
KBr	−0.124	0.418	0.29 (0.30)
KI	−0.108	0.341	0.23 (0.32)

[a] In obtaining M_- and M_F, the Pauling theoretical values of the ionic polarizability and the positions of the F band given by Mollwo[6] have been used. The experimental results have been derived from Martienssen's measurements of the α and β bands[1] and from the positions of the first absorption band measured at liquid nitrogen temperature in KI,[7] and extrapolated to liquid nitrogen temperature in the case of KBr.

TABLE II. Position of the α band relative to the first absorption peak (ev).[a]

Crystal	$\left(1-\frac{1}{\sqrt{2}}\right)\frac{e^2}{r_0}$	$-\frac{\alpha_M}{6}\frac{\rho}{r_0}\frac{e^2}{r_0}$	$-[0.2714M_- + 0.7015M_+' + 1.2320M_-']\frac{e^2}{r_0}$	$h\nu$(free exc.) $-h\nu$(α exc.)
NaCl	1.498	−0.169	−0.829	0.50
KCl	1.343	−0.136	−0.678	0.53
KBr	1.282	−0.124	−0.669	0.49 (0.59)
KI	1.195	−0.108	−0.652	0.44 (0.59)

[a] The values in parentheses represent the experimental data after Martienssen.[1] As in Table I, the Pauling values of the ionic polarizabilities have been used in evaluating the polarization term. These and the other constants are found in Mott and Gurney's book.[1]

III. POSITION OF THE α BAND

When the exciton is created in the vicinity of a negative-ion vacancy, as is indicated in Fig. 3, the calculation of the energy involved should take into account the relaxation of the lattice in the immediate vicinity of the vacancy. However, as a crude approximation, it is assumed that the ions 1 and 2 are in their regular lattice positions when the exciton is created. The other ions of the lattice have a permanent dipole due to the presence of the vacancy. This dipole can be estimated by the Mott and Littleton zero-order approximation and, on a positive ion at a distance r from the negative-ion vacancy, can be written as

$$M_+' e r_0^3/r^2,$$

with

$$M_+' = \frac{\alpha + \alpha_+}{\alpha + \frac{1}{2}(\alpha_+ + \alpha_-)}\frac{1}{4\pi}\left(1 - \frac{1}{K}\right).$$

An analogous formula holds for the negative ions. The quantity K represents the dielectric constant for static fields. The quantity α is the polarizability due to the displacement of the ions and has been derived by Mott and Littleton[4] from the repulsive forces. From their work, one obtains the expression

$$\alpha = 3r_0^3\rho/[2\alpha_M(r_0 - 2\rho)],$$

where α_M is the Madelung constant, and ρ the constant appearing in the expression for the repulsive energy.

The energies of the cycle considered in the creation of the excitons can then be calculated in the same way as in Sec. I. Assuming that $\Omega_1 = \Omega_3$,

$$h\nu(\text{free exc.}) - h\nu(\alpha\text{ exc.}) = {}^1W_- + {}^1W_+^{[-]} - {}^3W_- - {}^3W_+^{[-]}. \tag{7}$$

It is not obvious in this case that the assumption $\Omega_1 = \Omega_3$ is justified; to support it there is only a calculation of Mott[2] in which he evaluated the energy of the lowest state of the conduction band under the assumption that the presence of a nearest positive charge does not change the energy obtained by bringing a metal atom into a lattice position. The agreement of this with other calculations and with experiments seems to indicate that the assumption is not incorrect.

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[6] E. Mollwo, Z. Physik **85**, 56 (1933).

[7] H. Fesenfeld, Z. Physik **64**, 623 (1930).

The contribution to the energy in formula (7) due to Coulombic forces is $(1-1/\sqrt{2})(e^2/r_0)$.

The contribution due to the repulsive forces is the same as in the case of Sec. II, i.e., $-W(r_0)$.

The contribution of the polarization of the ions consists of two parts: one due to the absence of the negative ion in position 3 of Fig. 3 and the other due to the effect of the permanent dipoles induced on the ions of the lattice by the charge present in position 3 of Fig. 3. It can be written as

$$-\left(\frac{2.5-\sqrt{2}}{2}\right)M_-\frac{e^2}{2r_0}$$

$$-\left[\sum_{\text{pos. ions}}{}_i''\frac{\cos(r_{2i},r_{3i})}{r_{2i}^2r_{3i}^2}-\sum_{\text{pos. ions}}{}_i''\frac{\cos(r_{1i},r_{3i})}{r_{1i}^2r_{3i}^2}\right]M_+'\frac{e^2}{r_0}$$

$$-\left[\sum_{\text{neg. ions}}{}_i''\frac{\cos(r_{2i},r_{3i})}{r_{2i}^2r_{3i}^2}-\sum_{\text{neg. ions}}{}_i''\frac{\cos(r_{1i},r_{3i})}{r_{1i}^2r_{3i}^2}\right]M_-'\frac{e^2}{r_0}.$$

The relations used to indicate lattice summations refer to Fig. 3, the distances are measured in units of r_0, and the double prime indicates that the ions 1, 2, and 3 are excluded.

Finally, the shift in energy of the α band relative to the fundamental band is

$$h\nu(\text{free exc.})-h\nu(\alpha\text{ exc.})$$

$$=\left(1-\frac{1}{\sqrt{2}}\right)\frac{e^2}{r_0}-\frac{\alpha_M}{6}\frac{e^2}{r_0}\frac{\rho}{r_0}-0.2714M_-\frac{e^2}{r_0}$$

$$-S_+M_+'\frac{e^2}{r_0}-S_-M_-'\frac{e^2}{r_0},\qquad(8)$$

with

$$S_+=\sum_{\text{pos. ions}}{}_i''\frac{\cos(r_{2i}r_{3i})}{r_{2i}^2r_{3i}^2}-\sum_{\text{pos. ions}}{}_i''\frac{\cos(r_{1i}r_{3i})}{r_{1i}^2r_{3i}^2},$$

$$S_-=\sum_{\text{neg. ions}}{}_i''\frac{\cos(r_{2i}r_{3i})}{r_{2i}^2r_{3i}^2}-\sum_{\text{neg. ions}}{}_i''\frac{\cos(r_{1i}r_{3i})}{r_{1i}^2r_{3i}^2}.$$

The values of the above summations on the positive and negative ions can be obtained from the calculations of similar lattice summations made by Rittner and others,[8] Jones and Ingham,[9] Reitz and Gammel.[10] From the work of reference 8,

$$\sum{}_i'\left[\frac{1}{r_{2i}^4}+\frac{1}{r_{3i}^4}-\frac{2\cos(r_{2i}r_{3i})}{r_{2i}^2r_{3i}^2}\right]=2C,$$

where $C=2.0285$. The summation has the same value for positive ions as for negative ions. The prime indicates that ions 2 and 3 must be excluded from the summation. From Jones and Ingham,[9]

$$\sum{}_i'\left[\frac{1}{r_{2i}^4}+\frac{1}{r_{3i}^4}\right]=15.5323,$$

so that

$$\sum_{\text{pos. ions}}{}_i''\frac{\cos(r_{2i},r_{3i})}{r_{2i}^2r_{3i}^2}=5.7375.$$

The corresponding summation over the negative ion has the same value, except for the fact that the term arising from ion 1 must be excluded. The summations of the type

$$\sum{}_i''\frac{\cos(r_{1i}r_{3i})}{r_{1i}^2r_{3i}^2}$$

over positive and negative ions have been calculated by Reitz and Gammel[10] in connection with a different problem. They obtained for the summations over positive and negative ions the values 5.036 and 4.152, respectively. The final results are $S_+=0.7015$, $S_-=1.232$.

The numerical results for some alkali-halides crystals are presented in Table II and are compared with the experimental data in the cases of KI and KBr.

IV. CONCLUSIONS

The agreement between the available experimental results and the values calculated in the preceding sections is good, as is shown in Tables I and II. This can be considered as a further argument in support of the current theory on the α and β bands. It is however possible that the agreement is partially due to a compension of the errors arising from the approximations made.

It may be of some interest to note that the present model can be used to calculate the positions of the absorption bands due to excitons trapped at other defects of the lattice, such as divalent impurities, positive-ion vacancies, or dislocations.

ACKNOWLEDGMENTS

The authors are pleased to express their gratitude to Professor R. Maurer and Professor F. Seitz for their interest and constant encouragement. They are also indebted to Professor F. Fumi and Dr. C. Klick for stimulating correspondence.

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[8] Rittner, Hunter and DuPre, J. Chem. Phys. **17**, 198, 204 (1949).

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

[10] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).