

and C_{4v} as well as C_{6v} . The theory is in qualitative agreement with experiment with regard to the optical dichroism for poled BaTiO₃ in the tetragonal phase.¹³

¹³ R. C. Casella and S. P. Keller (to be published).

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Exciton States in Ionic Crystals*

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Exciton states in ionic crystals are analyzed according to configurations allowed by cubic point symmetry. The "excitation" and "electron transfer" models of the exciton structure are reintroduced as two slightly different aspects of the same general group-theoretical problem. Predictions of these models concerning multiplicity of absorption peaks are shown to be essentially identical. A theory of the "halogen atom doublet" appearing in the experimental absorption spectra of certain alkali halide crystals is given and is used in a preliminary interpretation of the electronic structure of low-lying exciton states in these solids.

I. INTRODUCTION

THE ultraviolet absorption spectra of alkali halide crystals were studied at an early date.¹ Hilsch and Pohl and their collaborators measured the spectra up to energies corresponding to 1600 Å in the vacuum uv region, and, somewhat later, Schneider and O'Bryan extended the measurements to 1100 Å. More recently, the alkali iodides have been studied extensively,^{2,3} since the first peak of their fundamental absorption lies in the vicinity of 2000 Å, a region of the spectrum which can be reached with conventional uv apparatus. The recent work has, among other things, confirmed that free electrons are not produced when light is absorbed in the region of the first peak of the fundamental absorption, so it is very likely that this process results in the creation of excitons.

The first attempts to interpret the structure of the exciton in alkali halide crystals were made by Hilsch and Pohl¹ and by Mott,⁴ who pointed out that most of the spectra of the iodides and bromides exhibit a strong doublet structure, at least in the first absorption peak. The separation of this doublet is about equal to the

separation of the ground-state doublet of the free halogen atom, which is 0.942 eV in iodine and 0.457 eV in bromine. The interpretation of the doublet structure followed the interpretation of spectra of alkali halide vapors: when a photon is absorbed, an electron is ejected from the halogen ion and a neutral atom is left behind. In a crystal, the electron is not set free, but remains associated with the neutral halogen atom, or alternatively speaking, with the p^5 hole present in the halogen ion. If the direct interaction of the electron and hole is small compared to the spin-orbit interaction of the hole, one may have conditions somewhat similar to jj coupling in an atom, i.e., there exist two neighboring states which differ essentially only in the j -value assigned to the hole ($\frac{1}{2}$ or $\frac{3}{2}$). As in the atom, both of these states may be reached by optical transitions from the p^6 ground state, provided the electron is in an s -like state ($j = \frac{1}{2}$).

Recently, attempts have been made to describe the alkali halide exciton on a more quantitative basis. The calculations have centered mainly around two electronic models. In one, which is analogous to the Frenkel exciton model, the unit excitation of the exciton wave is sufficiently localized in a unit cell that it is somewhat characteristic of an excited state of a free atom. This model, which has been studied by Dexter^{5,6} and by Muto and co-workers,⁷ will be referred to as the "excitation" model. In the other,¹ which was developed by von Hippel,⁸ the unit excitation involves the transfer of an electron from a halogen ion to the nearest neighboring positive ion. This model, which has been

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¹ R. Hilsch and R. W. Pohl, *Z. Physik* **57**, 145 (1929); **59**, 812 (1930); H. Fesefeldt, *Z. Physik* **64**, 623 (1930); E. G. Schneider and H. M. O'Bryan, *Phys. Rev.* **51**, 293 (1937).

² W. Martienssen, *Nachr. Akad. Wiss. Göttingen* **2a**, No. 11, 257 (1955); *J. Phys. Chem. Solids* **2**, 257 (1957); E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957); K. J. Teegarden, *Phys. Rev.* **105**, 1222 (1957); *Phys. Rev.* **108**, 660 (1957).

³ K. J. Teegarden, U. S. Air Force technical note AFOSR TN-59-303, April 10, 1959 (unpublished).

⁴ N. F. Mott, *Proc. Roy. Soc. (London)* **A167**, 384 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), second edition, pp. 95-100.

⁵ D. L. Dexter, *Phys. Rev.* **83**, 435 (1951).

⁶ D. L. Dexter, *Phys. Rev.* **108**, 707 (1957).

⁷ Muto, Oyama, and Okuno, *Progr. Theoret. Phys.* **20**, 804 (1958).

⁸ A. von Hippel, *Z. Physik* **101**, 680 (1936).

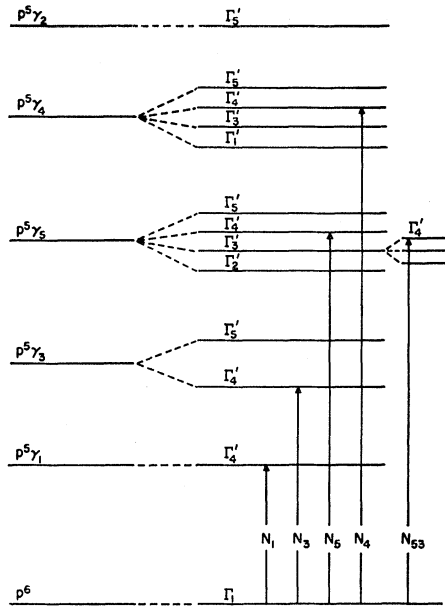


FIG. 1. Parentage of all types of singlet exciton states involving a p^6 hole in a cubic lattice. Transitions to the various levels of Γ'_4 symmetry are labelled N_α (α denoting the symmetry of the electron wave function from which the level is derived). The transition N_{53} is included as an illustration of the additional structure when spin-orbit interaction is present.

used recently by Overhauser⁹ and others,¹⁰ will be referred to as the "transfer" model. It should be noted that both models describe the unit excitation as fairly well localized in a unit cell, as contrasted to the case of the Wannier exciton, in which the unit excitation spreads over many cells, and for which the well-known hydrogenic model seems to be an adequate approximation.

Since both the excitation and transfer models seem plausible, one might hope that their predictions about the general features of alkali halide absorption spectra would be similar. It is one purpose of this note to point out a fundamental correspondence between the two models. For example, it was mentioned above that the p^5s configuration of the exciton can lead to two absorption lines. If, in the excitation model, one considers the configuration p^5d , additional absorption lines result. The cubic field of the crystal splits the states of the d electron into two groups, d_γ and d_e , and the p^5d_γ and p^5d_e configurations lead respectively to three and four new absorption lines. These lines correspond to lines that Overhauser obtains using the transfer model.

In Sec. II, a unified group-theoretical background for the excitation and transfer models is developed, and the relationship between the various optical transitions they predict is given. In Sec. III, the low-lying levels of the models are discussed in an attempt to clarify the concept of the "halogen doublet in the solid" and to

interpret the presently available alkali halide absorption data. A brief summary (Sec. IV) and an appendix containing certain relevant calculations are included.

II. THEORY

Exciton states of interest in the optical absorption of cubic ionic crystals are derived from localized functions of Γ'_4 symmetry.¹¹ Although these localized functions are threefold degenerate, an essential splitting into transverse and longitudinal exciton states is introduced by the translation symmetry of the lattice.¹² The arguments of this note are not affected by the existence of this splitting, as long as transverse states in the vicinity of $\mathbf{k}=0$ (\mathbf{k} =exciton momentum) are considered. Our principal concern is to search for various Γ'_4 states from which to construct exciton states. The formalism will apply equally well to trapped excitons as long as the point symmetry of the excited center remains cubic.

The states of a cubic ionic crystal considered are those produced when a photon knocks a valence electron away from the outer closed (p^6) shell of a particular negative ion. The electron can remain tightly bound to the resulting hole, in which case the state formed is a localized Frenkel exciton; or it may go into a large positronium-like orbit, forming a localized Wannier exciton. The wave function of the electron must, in any event, have symmetry properties appropriate to the cubic symmetry of the Hamiltonian. As in previous work,⁶⁻¹⁰ electron-lattice interactions will not be treated.

(a) Singlet States

Consideration of spin is at first postponed and the space states of the hole are coupled to any of the several possible space states of the electron. The threefold-degenerate hole functions transform¹³ according to the representation γ'_4 , while the electron function or functions may transform according to any of the ten irreducible representations of the full cubic group. Only electron functions of even parity are of major importance, since the hole has odd parity and the coupled states of optical interest must be odd. The five possible uncoupled configurations from which optically important states may be constructed are thus denoted schematically¹⁴ by $p^5\gamma_1$, $p^5\gamma_2$, $p^5\gamma_3$, $p^5\gamma_4$, and $p^5\gamma_5$. Any state based on a p^5 hole plus an even-parity electron must arise from one of these configurations. While there

¹¹ For representation notation, see H. A. Bethe, Ann. Physik **3**, 133 (1929); and Overhauser, reference 9.

¹² See, e.g., R. S. Knox, J. Phys. Chem. Solids **9**, 238 (1959).

¹³ Lower case γ 's are used to identify the symmetry types of the individual wave functions of the hole and electron. Upper case Γ 's are used to identify the symmetry types of the total (coupled) wave functions. This conforms with the usage of Bethe, reference 11.

¹⁴ In strict conformity with Bethe's notation, one should write $\gamma'_4\gamma_1$, $\gamma'_4\gamma_2$, etc. However, it is useful in view of the general agreement about the nature of the hole states to retain a semi-atomic but adequate notation.

⁹ A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

¹⁰ F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957); B. Goodman and O. S. Oen, J. Phys. Chem. Solids **8**, 291 (1959).

may be many $p^5\gamma_4$ configurations, for example, they all lead to similar optical transitions from the ground state and can differ only in the "principal quantum number" of the γ_4 electron.

In Fig. 1 these five configurations, and the states which arise when the hole and electron are coupled, are illustrated. There are four ways in which Γ_4' states can arise, depending on their parentage. Transitions may take place between the ground state and any Γ_4' level, and each such transition is denoted by N_α , where α indicates that the parentage of the particular Γ_4' level involved is $p^5\gamma_\alpha$. The states shown in Fig. 1 comprise the entire set of types of singlet states possible in the crystal, since a singlet spin function has symmetry Γ_1 and appears as a simple factor in each complete state function.⁹ We now show how both models discussed in the introduction fit into this unified picture.

Excitation Model⁵⁻⁷

Here the electron wave function is considered to remain explicitly centered at the site of the hole, its angular distribution being roughly described by atomic (s , p , d , etc.) quantum numbers. Since an s function transforms as γ_1 , the p^5s configuration of the excitation model leads to an N_1 transition. This is the only excitation-model singlet transition discussed in reference 9. If a p^5d configuration is introduced, transitions of types N_3 and N_5 are obtained, since d functions in the crystal decompose into $\gamma_3 + \gamma_5$. Thus, in adding a simple and plausible configuration, two new absorption lines are introduced without recourse to spin-orbit interaction, electron-lattice interactions, or explicit transfer of the electron. Transitions of type N_4 do not become available until a p^5g configuration is included. It is to be emphasized that all of these transitions can be strong and are fully symmetry-allowed.

Transfer Model⁹

One constructs electron states of γ_1 , γ_3 , and γ_4' symmetry by placing spherical charge distributions on nearest-neighbor sites in the NaCl lattice, thus obtaining two transitions (types N_1 and N_3). (The configuration $p^5\gamma_4'$ is of even parity and affords no transitions. It corresponds to the configuration p^5p of the excitation model.) In the CsCl lattice one again obtains two transitions, this time N_1 and N_5 , because the electron states constructed are of symmetries γ_1 , γ_2' , γ_4' , and γ_5 . More transitions are readily obtained on this model by including transfer to other-than nearest alkali neighbors or by allowing the transferred electron to go into less symmetric (say, p) orbitals at the alkali ion. For example, including both nearest and next-nearest neighbors in the NaCl lattice, the standard transfer model is able to predict one N_3 , one N_5 , and two N_1 transitions. Again, no spin-orbit or phonon interactions are necessary.

TABLE I. Enumeration of certain allowed transitions in cubic ionic crystals (see text for notation). Only nearest-neighbor configurations are considered in the transfer model here; however, the "CsCl" transitions are actually the same as those which can be obtained by using second-nearest alkali neighbors in the NaCl lattice.

		Singlet	Triplet
Excitation model	p^5s	N_1	N_{14}
	p^5d_γ	N_3	N_{34}, N_{35}
	p^5d_ϵ	N_5	N_{53}, N_{54}, N_{55}
Transfer model	NaCl lattice	N_1, N_3	N_{14}, N_{34}, N_{35}
	CsCl lattice	N_1, N_5	$N_{14}, N_{53}, N_{54}, N_{55}$

A detailed correspondence between the models, which is mainly of heuristic value, can be outlined; excitation-model configurations are on the left, and transfer-model configurations (NaCl lattice) are on the right:

$$p^5s \leftarrow p^5\gamma_1 \rightarrow p^5 \text{ (} s \text{: nearest neighbors),}$$

$$p^5p \leftarrow p^5\gamma_4' \rightarrow p^5 \text{ (} p, q, r \text{: nearest neighbors),}$$

$$p^5d_\gamma \leftarrow p^5\gamma_3 \rightarrow p^5 \text{ (} u, v \text{: nearest neighbors),}$$

$$p^5d_\epsilon \leftarrow p^5\gamma_5 \rightarrow p^5 \text{ (} U, V, W \text{: next nearest neighbors).}$$

The detailed form of the functions s , p , q , etc. are given in reference 9. Of this correspondence it may be said that the nearest-neighbor transfer states seem to "fill an s and p shell" and "partially fill a d shell" of the excitation states. To "complete the d shell" one goes to more distant transfer sites. This correspondence was first given qualitatively by Seitz.¹⁵ While these two specific models are thus ultimately equivalent in their predictions of multiplicities, it must be borne in mind that in one typical solid (NaCl) it appears that the excitation model provides a more tractable and accurate description of the lowest $p^5\gamma_1$ configuration.⁶

(b) Triplet States and Other Coupling Schemes

In the presence of spin-orbit interaction, transitions to triplet states of Γ_4' symmetry are allowed. To obtain a list of all possible transitions of this type, the direct product representation $\gamma_4' \times \gamma_\alpha \times \Gamma_4$ must be reduced (as in reference 9). Whereas only four singlet Γ_4' levels of different parentage exist (Fig. 1), eleven types of triplet levels can be distinguished according to parentage. The resulting allowed transitions will be denoted by $N_{\alpha\beta}$, indicating derivation from $(p^5\gamma_\alpha)\Gamma_\beta' \times \Gamma_4$. Thus, for example, N_{53} is a transition to the Γ_4' level obtained from $(p^5\gamma_5)\Gamma_3$. The analysis of the two models and of their coalescence is similar to that of the singlet case, and we summarize the results in Table I. It is clear that an arbitrary number of transitions can be located on either model by adding "higher" configurations.

It will be recognized that in treating the excitation model the Bethe "strong crystal field" case has been assumed, i.e., electron wave functions have been

¹⁵ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 411-412.

decomposed according to the crystal symmetry before being coupled to the hole. The less realistic weak-field case, in which atomic LS - or jj -coupled states are constructed at the outset, and are then split by the field, must lead to exactly the same number of allowed transitions. For example, the N_3 and N_5 transitions of p^5d may be associated, although not necessarily uniquely, with Γ_4' states derived from $p^5d(^1P_1)$ and $p^5d(^1F_3)$. The most cumbersome way to enumerate the transitions is to work in the strong-field limit with jj coupling, which requires recourse to the full double-valued cubic group. The total number of transitions is always 2 (for p^5s), 7 (for p^5d).

(c) Connection with the Wannier Model¹⁶

One can regard tightly bound excitons as limiting cases of Wannier excitons, as follows. If Bloch functions for the halide valence bands and for the various conduction bands are available, localized (Wannier) functions may be constructed for a hole and an electron. The two particles thus localized are bound to each other electrostatically, their relative position vector being denoted here by β . The "excitation model" $p^5\gamma_i$ exciton corresponds roughly to a Wannier exciton with $\beta=0$ constructed from a p^5 halide valence band and a γ_i -like halide conduction band. The nearest-neighbor transfer model using alkali s functions corresponds roughly to the case $\beta=a$ (nearest neighbor distance), using a p^5 halide valence band and an s -like alkali conduction band.

The Wannier model is based on the effective mass approximation and therefore cannot really apply to stationary exciton states of extremely small radii, since here the details of the cubic field are dominant in determining the motion of the hole about the electron. A crude estimate of the "radius" of the alkali halide exciton can be obtained from κa_0 (a result of the effective mass formalism), where κ is an effective dielectric constant and a_0 is the Bohr radius. Using $\kappa \sim 3$ or 4 we find a radius of the order of magnitude of an interatomic distance, which very roughly justifies the use of the Frenkel model at the outset. The Frenkel states can be given the above Wannier-like connotation, but they do not follow naturally from the Wannier effective mass model. In the case of small exciton "radii," the most important physical considerations are the point symmetry of the lattice and the details of the potential seen by the hole and electron. Considerably higher energy exciton states, having large radii, can be built from both the alkali and halide conduction bands and may be best described by effective mass terminology. The states considered explicitly in this paper, however, are those expected to be of lowest energy and of greatest experimental interest in alkali halides and related solids at the present.

¹⁶ See Y. Takeuti, *Progr. Theoret. Phys.* **18**, 421 (1957) for a very interesting semiquantitative account of the transition between the Frenkel and Wannier excitons.

III. COMPARISON WITH EXPERIMENT

(a) The Halogen Doublet

Although the determination of relative positions of exciton levels is a matter for detailed computation, it is suggested in Fig. 1 that a $p^5\gamma_1$ configuration contributes low-lying levels. That this is probably the case may be argued on the basis of the high symmetry of the γ_1 electron function¹⁵; there are fewest "nodes" in the $p^5\gamma_1$ functions. For this reason, and since there are only two strong absorption peaks associated with $p^5\gamma_1$, one is led to attempt a closer analysis of this configuration. The atomic analogs of the transitions involved are $^1S_0 \rightarrow ^1P_1$ and $^1S_0 \rightarrow ^3P_1$ (LS coupling) and $^1S_0 \rightarrow (\frac{3}{2}, \frac{1}{2}, J=1)$ and $^1S_0 \rightarrow (\frac{1}{2}, \frac{1}{2}, J=1)$ (jj coupling). The corresponding transitions in the solid form the "halogen doublet" discussed in the introduction. A brief quantitative analysis of the two relevant energy levels is given in the Appendix, where it is shown that the splitting $W-W'$ of the exciton doublet has a lower limit

$$W - W' \geq (8/9)^{1/2} \lambda = \begin{array}{l} 0.047 \text{ ev (fluorides)} \\ 0.103 \text{ ev (chlorides)} \\ 0.432 \text{ ev (bromides)} \\ 0.889 \text{ ev (iodides)}, \end{array} \quad (1)$$

where λ is the halogen atom ground-state doublet splitting. This inequality, reminiscent of a jj -coupling limit, replaces a precise predicted " jj -coupling" value of the doublet splitting because the two states involved are in all generality *intermediate*-coupled. "Pure jj coupling" is an expression used in atomic spectra to describe a situation in which an electrostatic interaction is known to be small compared with the spin-orbit interaction. Here, the corresponding "electrostatic interaction" is considerably more difficult to compute than the spin-orbit energy (see Appendix), but regardless of its value in a given halide, the computed splitting $W-W'$ has a lower limit given by Eq. (1).

If two particular exciton absorption peaks in an alkali halide are to be related to a halogen doublet, the energies of the peaks must obey the minimum splitting condition (1). If they do not, the assignment is still possible but with any of several qualifications: (i) There are strongly perturbing Γ_4' states in the vicinity of the $p^5\gamma_1$ configuration, in which case a simple description of the peaks is difficult. (ii) The excited electron contributes to the spin orbit energy ζ (see Appendix), causing some cancellation and effectively lowering λ . Such a contribution is not considered in the derivation of (1). This will not be the case in an "excitation" p^5s configuration or in a "transfer" $p^5\gamma_1$ configuration built from s functions, since the electrons involved have no orbital momentum. (iii) The excited electron is so localized that the p^5 core functions do not resemble halogen atom functions, in which case λ must be computed rather than obtained from atomic data. The problem of choosing among these three possibilities, particularly (i) and (iii), has been discussed at length

by one of the authors elsewhere.¹⁷ When configuration interaction, alternative (i), causes the minimum splitting criterion to break down, the interacting states may possibly be identified by their associated absorption peaks, which will lie close to the $p^5\gamma_1$ doublet under consideration. With these observations in mind, let us turn to the experimental situation in several halides.

Fluorides¹

Single absorption peaks are found in the region of 9–11 eV, well separated from peaks of higher energy, at room temperature. It is possible that these peaks are actually doublets which will be resolved at low temperatures; if the transitions involved may be assigned to a $p^5\gamma_1$ configuration, the doublet splitting should be governed by Eq. (1) and might even be as great as 0.07 eV. A $p^5\gamma_1$ assignment is still valid even if the peak remains single, since *LS* coupling might be applicable (see Appendix).

Chlorides^{1,18–20}

At room temperature single absorption peaks lie at about 7.6 eV in NaCl, KCl, RbCl, and CsCl, well separated from peaks of higher energy. Recent experiments^{18,19} at low temperatures have shown these peaks to be resolved in NaCl and KCl into a doublet of 0.13-eV separation. Thus a $p^5\gamma_1$ configuration appears sufficient to account for these low-energy peaks. In AgCl the first absorption peak shows similar doublet structure at sufficiently low temperatures.²⁰

Dexter⁶ computed the total oscillator strength to all states in the $p^5\gamma_1$ and $p^5\gamma_3$ nearest-neighbor transfer configurations in NaCl, with the result $f_{tot} = 1.59$. It is easily deduced from his calculation that 85% of this strength is associated with $p^5\gamma_1$ states (N_1 and N_{14} transitions) and only 15% with $p^5\gamma_3$ (N_3, N_{34}, N_{35}). Hence the $p^5\gamma_3$ transfer states appear to cause much weaker absorption than the $p^5\gamma_1$ transfer states, in addition to probably lying higher in energy. Dexter further showed that the total oscillator strength of the low-lying N_1 and N_{14} transitions as computed on the excitation model is in better agreement with the best available experimental value ($f \sim 0.5$).

Bromides^{1,19,20}

Distinct “doublets”, well separated from higher energy absorption peaks, and all obeying the minimum splitting condition, are found in NaBr, KBr, RbBr, and AgBr (e.g., in KBr, at 6.63 and 7.17 eV at room temperature). It thus appears reasonable to assign these

pairs of transitions to a $p^5\gamma_1$ configuration. In CsBr, a similar doublet may be distinguished, but many absorption peaks are present¹⁹ and considerable configuration interaction may exist (see below).

Iodides^{1,2,19}

The two lowest lying prominent peaks in NaI, KI, and RbI obey the minimum splitting condition, but since higher states seem to lie very close, a pure $p^5\gamma_1$ assignment seems unrealistic. In CsI, it is difficult to find any pair of adjacent peaks to assign to $p^5\gamma_1$, and it is probable that strong configuration interaction is present, as in CsBr.

(b) Other Absorption Peaks

It is possible to give a tentative interpretation of some of the multiple absorption peaks¹⁹ other than the halogen doublet. Assume that either a $p^5\gamma_3$ or $p^5\gamma_5$ configuration lies next above the $p^5\gamma_1$ of the halogen doublet and is well separated from higher configurations. In the former case, a triplet of lines (N_3, N_{34}, N_{35}) is expected and in the latter a quartet ($N_5, N_{53}, N_{54}, N_{55}$), regardless of the zero-order model chosen. The transfer model is heuristically useful at this point. Its lowest energy states most probably involve nearest-neighbor transfer, so in the NaCl lattice $p^5\gamma_3$ is suggested as the lower configuration, while $p^5\gamma_5$ is suggested as the lower one in the CsCl lattice. Eby, Teegarden, and Dutton¹⁹ discuss the possible appearance of triplets in their low-temperature data on NaCl-type alkali halides; the situation is rather complex in the CsCl-type salts, as discussed above. A further interesting test of this interpretation will be a low-temperature investigation of the 9.1-eV peak in CsF, which should accordingly turn out to be a triplet if resolved. CsF is the only cesium halide of NaCl-type structure.

As in the case of the doublet, these assignments are subject to important qualifications, e.g., one must consider the possibility that an observed triplet or quartet is just a superposition of, say, two higher $p^5\gamma_1$ configurations. There may be any number of configurations of a given type, as mentioned in Sec. II (a).

Finally, mention should be made of the existence of “shoulders” in many of the absorption spectra. Taft and Apker²¹ have found that in some iodides, light absorbed in the region of these shoulders causes photoemission and Teegarden³ has identified photoconductivity in this region in RbI and KI. It is probable therefore that light absorbed in “exciton” peaks of energy higher than the shoulder energy will lead to photoemission and photoconductivity. This is similar to the case of photoconductivity in the β -absorption band which has been more thoroughly investigated.^{21–23}

¹⁷ R. S. Knox, Phys. Rev. **115**, 1095 (1959).

¹⁸ P. L. Hartman, Phys. Rev. **105**, 123 (1957).

¹⁹ Eby, Teegarden, and Dutton, following paper [Phys. Rev. **116**, 1099 (1959)].

²⁰ Y. Okamoto, Nachr. Akad. Wiss. Göttingen **2a**, No. 14, 275 (1956); see also F. C. Brown and F. Seitz, in: *Photographic Sensitivity*, edited by S. Fujisawa (Maruzen Company, Ltd., Tokyo, 1957), Vol. 2, p. 11, Paper A2.

²¹ E. Taft and L. Apker, Phys. Rev. **82**, 814 (1951); **83**, 479 (1951).

²² N. Inchauspé, Phys. Rev. **106**, 898 (1957).

²³ R. Fuchs, Phys. Rev. **111**, 387 (1958).

This well-defined peak lies at an energy several volts higher than the energy necessary to free an electron from an F -center. The analysis of Fuchs²³ indicates that the autoionization probability is sufficiently small ($\sim 10^{13}$ sec⁻¹) that it does not broaden the β -band exceptionally. Similar considerations may apply in the case of exciton peaks lying above the ionization shoulder. In the two silver halides mentioned earlier, even the first "exciton" peaks lie in a photoconductive region.²⁰

IV. SUMMARY

It has been pointed out that the "excitation" and "transfer" models of the internal structure of the exciton in simple ionic crystals are equivalent, with regard to predictions of *multiplicity* of exciton absorption bands. (It is not meant to imply that they are otherwise equivalent, such as regarding predictions of positions and strengths of absorption peaks.) The doublet structure of a particular configuration which occurs in either model has been analyzed, and a criterion for assigning this configuration to observed energy levels is given. The well-known alkali halide absorption peaks seem to fit into the general theoretical framework, although certain crystals such as CsBr appear to exhibit strong configuration interaction among their low-lying excited states.

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APPENDIX

The total electronic Hamiltonian of the crystal is written

$$H = H_E + H_S, \quad (\text{A1})$$

where H_E is the total kinetic and electrostatic potential energy of the electrons and H_S is the total spin-dependent energy (in which the spin-orbit energy is assumed to be dominant). The LS representation is used for convenience, and ${}^1\Phi_k$ and ${}^3\Phi_k$ denote pure transverse singlet and triplet exciton states constructed from a $p^5\gamma_1$ configuration (see text). The energies of the two resulting (intermediate-coupled) states are the eigenvalues of the 2×2 matrix

$$\langle {}^\mu\Phi_k | H | {}^\nu\Phi_k \rangle \equiv H_{\mu\nu} \quad (\mu, \nu = 1, 3), \quad (\text{A2})$$

and are given by

$$W, W' = \frac{1}{2}(H_{11} + H_{33}) \pm \left[\frac{1}{4}(H_{11} - H_{33})^2 + |H_{13}|^2 \right]^{1/2}. \quad (\text{A3})$$

Their difference is

$$W - W' = 2 \left[\frac{1}{4}(H_{11} - H_{33})^2 + |H_{13}|^2 \right]^{1/2}. \quad (\text{A4})$$

A method of computing the matrix elements $H_{\mu\nu}$ is given in detail in reference 12, but only certain essentials are of interest here. First, because of the spin-independent nature of H_E , there are only two independent electrostatic matrix elements:

$$\langle {}^\mu\Phi_k | H_E | {}^\nu\Phi_k \rangle = \delta_{\mu\nu} E_{\mu k} \quad (\mu, \nu = 1, 3). \quad (\text{A5})$$

Next, since H_S does not couple singlet states, there are only two nonzero spin-orbit matrix elements, which will be written

$$\langle {}^3\Phi_k | H_S | {}^3\Phi_k \rangle \equiv \frac{1}{2}\zeta, \quad (\text{A6})$$

and²⁴

$$\langle {}^1\Phi_k | H_S | {}^3\Phi_k \rangle \equiv -2^{-1/2}\zeta' \approx -2^{-1/2}\zeta. \quad (\text{A7})$$

It follows that Eq. (A4) has the form

$$W - W' = 2 \left[\frac{1}{4}(\Delta_k - \frac{1}{2}\zeta)^2 + \frac{1}{2}\zeta'^2 \right]^{1/2} \geq 2^{1/2}|\zeta| \quad (\text{A8})$$

where $\Delta_k = E_{1k} - E_{3k}$. This is the quantitative statement of a "minimum splitting condition" for $p^5\gamma_1$ excitons and is analogous to a similar criterion derived by one of the authors¹⁷ in connection with alkali halide phosphors. The utility of (A8) lies in the fact that ζ may be assigned a fairly reliable value, whereas Δ_k is extremely difficult to compute and may be regarded as an adjustable parameter.

A good approximation to ζ is its value in the halogen atom, since the "excited halogen ion" in a crystal has essentially lost an electron, as far as the spin-orbit interaction is concerned. Suppose the lattice constant of the crystal is allowed to become infinite. Then Eq. (A8) gives the energy difference between the intermediate-coupled 1P_1 and 3P_1 terms of a single "excited halide ion" in a p^5s configuration. The parameter Δ_k approaches a constant value Δ which may be identified with the exchange interaction between the p^5 hole and the s electron.²⁵ In the traditional jj coupling limit ($\Delta \ll \zeta$), $W - W'$ approaches $\frac{2}{3}\zeta$. This is precisely the expression for the halogen atom ground-state doublet separation λ , provided ζ is evaluated with the proper wave functions. Assuming, then, that ζ in Eq. (A8) is given by $\frac{2}{3}\lambda$, we obtain

$$W - W' \geq (2\sqrt{2}/3)\lambda = (8/9)\lambda. \quad (\text{A9})$$

It is clear that ζ , computed with crystal wave functions, will not be precisely equal to $\frac{2}{3}\lambda$, for at least two reasons. The excited halide p functions will not be exactly the same as halogen p functions and will moreover be renormalized by overlap effects. For the various reasons given in reference 17, however, the inequality is felt to be quite reliable. For example, in the case of phosphors, renormalization effects strengthen the inequality and will probably do so here as well.

The atomic counterpart Δ of Δ_k is generally positive (Hund's first rule states that singlets lie above triplets),

²⁴ The quantities ζ and ζ' are different only if the radial function of the halide p electron is different in the singlet and the triplet states. It will henceforth be assumed for simplicity that $\zeta = \zeta'$.

²⁵ R. S. Knox, Phys. Rev. **110**, 375 (1958).

but $\Delta_{\mathbf{k}}$ itself may be negative. It includes, along with the electron-hole exchange interaction and other lattice interactions, a term approximately equal to twice the Heller-Marcus term for transverse excitons (at $\mathbf{k} \approx 0$)²⁶

$$-2\left(\frac{4}{3}\pi n_0 |\mathbf{u}|^2\right),$$

where n_0 is the atomic density and \mathbf{u} is the dipole moment of the optical transition involved. This term, which is present in singlet exciton states only, may

²⁶ W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

easily cause $E_{1\mathbf{k}}$ to lie below $E_{3\mathbf{k}}$ in the vicinity of $\mathbf{k}=0$.

If $\Delta_{\mathbf{k}}$ is large compared to ζ , the "LS coupling" limit is reached and very little of ${}^1\Phi_{\mathbf{k}}$ is mixed into ${}^3\Phi_{\mathbf{k}}$ by the spin-orbit interaction. In this case only one absorption line (N_1) will be strong.

The formalism of this appendix is rigorous only in the case of a "pure" $p^6\gamma_1$ configuration, i.e., one which is unperturbed by nearby configurations, and in which the electron contributes nothing to the spin-orbit matrix element. These restrictions are discussed briefly in Sec. III(a) of the text.

Ultraviolet Absorption of Alkali Halides*

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The absorption spectra of evaporated films of the alkali halides, with the exception of LiF, have been measured at room temperature and 80°K in the region from 1100 Å to 2500 Å. The spectra are rather complex at low temperature, but agree fairly well with current theory concerning the multiplicity and grouping of the exciton peaks. In addition, a shoulder has been found in many of the spectra, similar to the ones previously seen and associated with the band-to-band transition in the alkali iodides.

INTRODUCTION

THE optical absorption spectra of the alkali halides in the vacuum ultraviolet region have been investigated by several authors.^{1,2} As a necessary experimental background for proposed work on the low-temperature luminescence of these materials and in view of recent interest in exciton absorption,³⁻⁵ some of these measurements have been repeated and extended to liquid nitrogen temperature, using an instrument capable of rather high wavelength resolution. The results show a complexity of structure in the absorption spectra which had not been indicated by the earlier work.

EXPERIMENTAL APPARATUS

The monochromator used was very similar to that described by Tousey and Johnson.⁶ Its useful range for

this experiment was from 1100 Å to 2500 Å, and band widths of from 0.5 to 5.0 Å were employed. The light source was a modified Hanovia hydrogen arc lamp with one end window removed, operated on direct current. This source was very stable after being allowed to warm up, and provided a continuum down to about 1650 Å, with a line spectrum from there on to the 1100 Å limit imposed by the lithium fluoride substrates upon which the thin films were deposited. The detection system employed a sodium salicylate phosphor,⁷ the luminescence of which was detected by a 6199 end-on photomultiplier. The output of this photomultiplier was recorded on a Brown recording potentiometer.

The samples were mounted in a metal cryostat of double Dewar construction, provided with a rotating seal which allowed either of two symmetrical substrate holders to be placed in the beam of radiation from the monochromator. This cryostat also contained a small electric oven which was used to evaporate the samples. A lithium fluoride window was placed at the exit slit of the monochromator to exclude hydrogen from the cryostat, and thus the cryostat formed a separate vacuum system.

Initially this system was evacuated by a small oil diffusion pump, but it was found that in spite of the baffling provided by the outer Dewar of the cryostat, deposition on the sample of condensable vapors from the pumps interfered seriously with the low-temperature absorption measurements. Quite satisfactory results

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

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⁶ Tousey, Johnson, Richardson, and Toran, J. Opt. Soc. Am. **41**, 696 (1951).

⁷ K. Watanabe and E. Inn, J. Opt. Soc. Am. **43**, 32 (1953).