

Multiplet Structure of Excitons in Ionic Crystals*

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The excited states of crystals arising from the configuration in which an electron is transferred from a negative ion to a nearest neighbor positive ion are analyzed. It is concluded that 72 overlapping exciton bands result for crystals having the NaCl structure. Optical transitions from the ground state are allowed to only 5 of the 30 energy levels into which the 72 bands collapse at the center of the Brillouin zone. For crystals having the CsCl structure, 96 bands occur which collapse into 40 energy levels at $k=0$, 6 of which can be reached from the ground state by allowed optical dipole transitions. In the absence of spin-orbit interaction, only two transitions are allowed for both structures. It is concluded that the lifetime of exciton states, as limited by interaction with optical phonons, is sufficiently short to account for the width and temperature dependence of fundamental absorption lines. Approximate wave functions describing the exciton states are constructed and a procedure for calculating energy levels and relative intensities of absorption components is formulated.

I. INTRODUCTION AND CONCLUSION

THE first peak in the fundamental optical absorption of alkali halide crystals is generally interpreted¹ as the result of an electronic transition from the ground state to an exciton state² of the crystal. These absorption peaks³ are generally a few tenths of an ev in width, and their position and width are sensitive to temperature. For the bromides and iodides there is a second absorption maximum at a slightly higher energy, the separation from the first being about equal to the spin-orbit splitting of the ground-state configuration of Br and I, respectively. Therefore this structure has been attributed to the spin-orbit coupling of the hole left on the Br⁻ or I⁻ ion during the formation of an exciton.

Recent studies of the optical absorption of several alkali halides and BaO at low temperatures using high-resolution techniques have revealed considerably more structure in the exciton region than has been indicated previously. Zollweg⁴ has measured the optical absorption of evaporated BaO films at low temperatures and has found four components, two large and two small, in the first half-volt of the fundamental absorption. His results are shown in Fig. 1. The two small components, which lie on the low-energy side of the larger ones, appeared at low temperatures for all of a large

number of films and are well established. They cannot be attributed to absorption processes analogous to the α and β bands⁵ observed in alkali halides because they were not altered when the BaO films were heated either in barium vapor or oxygen gas, and, furthermore, their peak absorption constant is several orders of magnitude larger than that of typical α and β bands. Hartman and Nelson⁶ have measured the optical absorption of evaporated films of NaCl and KCl and the reflectivity of single crystals of the same materials in the fundamental region. At low temperatures the "first" peak in both materials is well resolved, having two strong components. For NaCl there appears one and perhaps two smaller components on the low-energy side of the larger peaks, similar to Zollweg's observations for BaO.

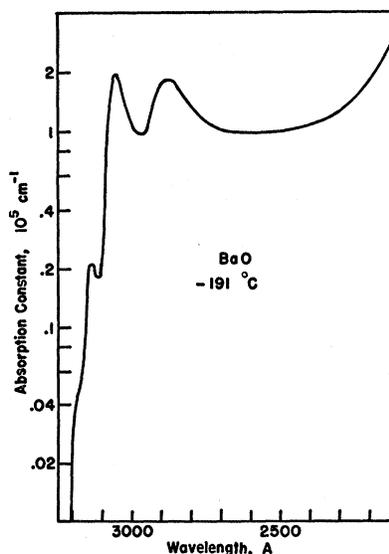


FIG. 1. Optical absorption of BaO, after Zollweg.

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¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 12; Revs. Modern Phys. **26**, 27 (1954); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), Chap. 3.

² J. Frenkel, Phys. Rev. **37**, 17 (1931); **37**, 1276 (1931); Physik. Z. Sowjetunion **9**, 158 (1936); R. Peierls, Ann. Physik **13**, 905 (1932); J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936); G. H. Wannier, Phys. Rev. **52**, 191 (1937); W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

³ R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930); H. Fesefeldt, Z. Physik **64**, 623 (1930); E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937); for a complete survey see H. Pick, Landolt-Bornstein Tables (Springer-Verlag, Berlin, 1955), Vol. I, Part IV, p. 869.

⁴ R. J. Zollweg, Phys. Rev. **97**, 288 (1955); thesis, Cornell University, 1955 (unpublished).

⁵ Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952); for a summary see F. Seitz, Revs. Modern Phys. **26**, 53 (1954).

⁶ Nelson, Siegfried, and Hartman, Phys. Rev. **99**, 658 (1955); P. L. Hartman and J. R. Nelson (to be published).

The discovery of the additional structure mentioned above indicates the necessity for carrying out such experiments at low temperatures and with single crystalline materials whenever possible, or at least with carefully prepared and well annealed films. A complete study of the effect of substrate temperature and annealing treatment on the fundamental absorption of KI evaporated films has been made by Fischer.⁷

In his work on the temperature dependence of the absorption peaks in KI, Fesefeldt⁸ resolved quite clearly (at liquid nitrogen and liquid hydrogen temperatures) a moderately strong peak lying between the first two peaks apparent at room temperature. As the data of Hilsch and Pohl⁸ for KI show a third peak a fraction of an electron volt higher in energy than the two just mentioned, it is possible that the exciton absorption of KI has at least four components. It is the purpose of the present paper to explain the origin of a complex absorption structure associated with exciton creation. In fact we shall conclude that the primary exciton multiplet for ionic crystals having the NaCl lattice should consist of five components and that the exciton multiplet for crystals with the CsCl structure should have six components.

The traditional view regarding the nature of an exciton in an ionic crystal is as follows. (Throughout the remainder of the discussion we shall refer to NaCl only, regarding it as a prototype for the other salts.) The electronic configuration of the Na⁺ ion consists of closed shells up to and including the 2*p* shell. The lowest energy state available on the ion is the 3*s* state ordinarily occupied by the valence electron. The Cl⁻ ion consists of closed shells up to and including the 3*p* shell. The electronic transition associated with exciton formation has usually been ascribed to the removal of one electron from a Cl⁻ 3*p* state and its reassignment to a 3*s* state of a nearest neighbor Na⁺ ion. Since such a state of excitation in one unit cell of the crystal is energetically equivalent to that in any other unit cell (as a result of the translational symmetry of the lattice), the excitation will readily propagate through the crystal. Experimental evidence regarding the mobility of the excitation has been provided by the work of Apker and Taft.⁸

Theoretical calculations⁹ of the energy of the first excitation state relative to the ground state have been based upon the assumption that the excited electron is on a nearest neighbor alkali ion relative to the hole on the halogen ion. Agreement with the experimental

values is quite satisfactory for most of the alkali halides, provided electronic polarization effects (Klemm⁹) and overlap effects of the neutralized ions with their surroundings (von Hippel⁹) have been taken into account. In calculating the absorption cross section associated with exciton creation, Dexter¹⁰ used a wave function for the exciton state in which the excited electron was concentrated primarily on the same Cl atom as its associated hole and which had the character of a Cl 4*s* state. There is no doubt that the wave function of the excited electron overlaps the Cl atom considerably, otherwise the transition probability would not be so large as it is. Furthermore, within the framework of a variational calculation one may expect that a Cl 4*s*-type state will be admixed in so far as it is energetically favorable. Nevertheless, it seems legitimate to ask whether the best "zeroth-order" description of an exciton in NaCl would require the electron to be primarily in a Cl 4*s* state or in a Na 3*s* state. The agreement with observation of the calculated exciton energies mentioned above supports the latter alternative. As shown below, the occurrence of many components in the exciton absorption can be understood also only if the latter alternative is the correct one.

Let us consider the electronic configuration (3*p*)⁵4*s* associated with the former alternative. The total orbital angular momentum is $L=1$. The total spin S is either 0 or 1. There is one resulting energy level with total angular momentum $J=0$ and one with $J=2$. There are two energy levels with $J=1$. Since the total angular momentum of the ground state is 0, optical dipole transitions are strictly forbidden to the states $J=0, 2$. The only allowed transitions are to the two states with $J=1$. If the spin-orbit coupling is negligibly small, only one of these states ($S=0$) can be reached by an allowed transition. If the spin-orbit interaction is weak, there will be one strong and one weak transition. The case of BaO cited above illustrates the inadequacy of the model under consideration. Four lines are observed instead of two. The two observed weak lines cannot be attributed to transitions to the forbidden levels, $J=0, 2$ made possible by phonon interactions because the lines would then be considerably broadened, whereas in fact they are quite narrow. Furthermore, the two strong components are of comparable magnitude, whereas the spin-orbit splitting of the O⁻ ion is small (~ 0.03 eV) compared to the splitting (0.24 eV) of the large components. For the alkali halides the model is also inadequate in those cases where more than two components have been resolved. The foregoing argument is not altered in essence if the cubic structure of the lattice is taken into consideration.

We shall now enumerate the various exciton states that arise according to the traditional configuration. Consider a hole to be located on a particular Cl⁻ ion. Since the 3*p* state is triply degenerate, and since there

⁷ F. Fischer, *Z. Physik* **139**, 328 (1954).

⁸ L. Apker and E. Taft, *Phys. Rev.* **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951); *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), Chap. 9; M. H. Hebb, *Phys. Rev.* **81**, 702 (1951); D. L. Dexter and W. R. Heller, *Phys. Rev.* **84**, 377 (1951).

⁹ K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1928), Vol. 20, p. 632; M. Born, *Z. Physik* **79**, 62 (1932); W. Klemm, *Z. Physik* **82**, 529 (1933); A. von Hippel, *Z. Physik* **101**, 680 (1936); T. Neugebauer, *Z. Physik* **104**, 207 (1937).

¹⁰ D. L. Dexter, *Phys. Rev.* **83**, 435 (1951).

are six nearest neighbor Na^+ ions, there will be a total of $3 \times 6 \times 4 = 72$ excited states. The extra factor of 4 is due to the four possible spin states of the electron-hole pair. Since the hole can be located on any of the N chlorine ions of the crystal, each of the 72 states will be N -fold degenerate in the zeroth approximation. When appropriate interactions are taken into account,² each N -fold degenerate level will spread into a band of states, each state being associated with one of the N allowed wave vectors \mathbf{k} of the fundamental Brillouin zone. The exciton configuration gives rise, therefore, to 72 complete energy bands, all of which are nondegenerate for a general point in k space. One would expect the energy width of each exciton band to be the same order of magnitude (several ev) as that of electronic conduction bands, a feature which is born out by detailed calculations (Heller and Marcus²). The 72 exciton bands will be mutually overlapping. The wave function of a specific exciton state can be represented approximately as a linear combination of the $72N$ wave functions associated with the localized excitation states considered originally.

If we are concerned only with those exciton states that can be excited as a result of an optical transition from the ground state of the crystal, our study is greatly simplified as a result of the wave vector selection rule.² The wave vector of an absorbed photon must equal the wave vector of the created exciton. Because typical optical wave lengths are very large compared to a lattice constant we can assume for all practical purposes that $k=0$. The problem of classifying energy levels lying at the center ($k=0$) of the fundamental Brillouin zone is determined to a large extent by the symmetry properties of the lattice.¹¹ There are many degeneracies imposed by the symmetry alone. The classification of the 72 states at $k=0$ into energy levels and symmetry types is carried out in Sec. II. A result is that the 72 states fall into 30 energy levels, each belonging to one of the 10 symmetry types possible for a cubic structure.

Since the ground-state wave function of the crystal is invariant under all of the cubic symmetry operations, it follows from the general principles of group theory¹² that the only energy levels which can be reached by an allowed electric dipole transition are those which belong to the same symmetry type as the perturbing Hamiltonian responsible for the transition. Only 5 of the 30 energy levels have this appropriate symmetry. Consequently, there will be in general 5 lines in the exciton multiplet. If the spin-orbit interaction of the electrons can be neglected, the total spin is a good quantum number and must be conserved during the transition. It follows from the analysis in Sec. II that for this

circumstance only two exciton levels can be reached by an allowed transition. If the spin-orbit interaction is weak, but not zero, there will be two strong and three weak transitions. If the spin-orbit interaction is comparable to other interactions involved, all five components will be of similar magnitude. These are the major conclusions of the present work.

For ionic crystals with the CsCl structure the number of components is changed. Since there are 8 nearest neighbor metal ions to a given negative ion, there will be $3 \times 8 \times 4 = 96$ exciton bands. At $k=0$ the exciton states collapse into 40 energy levels, 6 of which can be reached by allowed transitions. In the case of weak spin-orbit interaction, there will be 2 strong and 4 weak components. Compared to the NaCl lattice there is one extra component.

If one examines the data of Hilsch and Pohl¹³ for the sequence of salts NaI, KI, RbI, and CsI, an obvious correspondence between three peaks in each of the four materials is observed (Fig. 2). CsI, the only one having the CsCl structure, has one extra and relatively strong peak lying between what otherwise would have been the first and second peak. Since the spin-orbit splitting of the iodides is very large, the appearance of an extra absorption peak of fair magnitude seems to be well accounted for by the present analysis. However, until further low-temperature and high-resolution studies are performed on the bromides and iodides, it would be best to regard such apparent confirmation as tentative.

It is of interest to consider the interaction of excitons with lattice phonons. The writer is not aware of any theoretical study of this subject. It is to be expected that the primary interaction will be with the optical modes of the lattice vibration spectrum, as is the case for electrons¹³ in the conduction band. At first sight one may expect the interaction of excitons to be weaker than that of electrons because the exciton is a neutral unit and will not feel the electric field arising from the polarization (longitudinal, optical) waves. This consideration does not apply, however, to transitions between many of the 72 exciton bands because the "internal state" of the exciton can be changed in a way analogous to the change effected by an electric dipole transition in an atom. Consequently the lifetime of an individual exciton state is very likely as short as

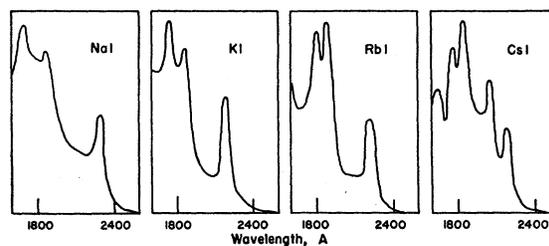


FIG. 2. Optical absorption of NaI, KI, RbI, and CsI, after Hilsch and Pohl.

¹¹ Bouckaert, Smoluchowski, and Wigner, *Phys. Rev.* **50**, 58 (1936); C. Herring, *J. Franklin Inst.* **233**, 525 (1952).

¹² E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik* (Vieweg und Sohn, Braunschweig, 1931); B. L. van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik* (Verlag Julius Springer, Berlin, 1932).

¹³ H. Frohlich, *Proc. Roy. Soc. (London)* **A160**, 230 (1937); for a review see H. Frohlich, *Advances in Phys.* **3**, 325 (1954).

that of a conduction electron state. It is relatively easy to observe that such is the case. Consider the electrostatic potential V arising from a polarization wave with wave number q . The direct interaction of an electron with the potential produces a perturbation energy eV . An exciton will have associated with it an electric dipole moment of magnitude ea (where a is the lattice constant) and will interact with the electric field, $\nabla V = iqV$, so that the matrix element of a transition will be of magnitude $eVqa$. Since $qa \sim 1$ for most phonons, it follows that the transition probabilities will be of similar magnitude.

The lifetime of a conduction electron state can be estimated from the observed mobilities¹⁴ of electrons in typical ionic crystals, and is of the order of 10^{-16} to 10^{-14} sec at room temperature. According to the uncertainty principle, therefore, the energy width of an exciton state may be a few tenths of an eV, a magnitude which agrees with the width of observed fundamental absorption peaks at room temperature.

Since the lifetime determined by phonon interactions will increase with decreasing temperature, the narrowing of the fundamental absorption lines at low temperatures, observed by Zollweg⁴ and others, is to be expected. For temperatures considerably below the Debye temperature of the lattice only a temperature independent, spontaneous emission of optical phonons can occur, because the optical modes undergo only their zero-point oscillations at such temperatures. This fact may account for the observations of Fischer⁷ and Zollweg,⁴ who find that the exciton lines do not continue to narrow below liquid nitrogen temperature. Since emission of optical phonons by an exciton is possible energetically only if there are exciton states or bands lying lower in energy, one may expect a general trend (not without exception) for exciton absorption lines of lower energy (in the same material and *measured at low temperatures*) to be narrower than those of higher energy, for the simple reason that a low-energy exciton will have fewer exciton bands lying below it. Such a trend is apparent in the data of Fischer on KI and that of Zollweg on BaO.

In the preceding paragraphs we have been speaking of the lifetime of an individual exciton state and not of the ultimate life of the electronic excitation as such, which we shall consider now. To avoid ambiguity we shall refer to this process in terms of its *decay* time. There are many conceivable mechanisms by which excitons can decay: direct luminescence of a free exciton, transfer of the excitation to or capture at a foreign atom with subsequent luminescence or non-radiative (multiple phonon) decay, capture at a dislocation with subsequent production of lattice vacancies,¹⁵

capture at a negative ion vacancy to produce an F center and a free hole (Dexter and Heller⁸), capture at an F center to produce a vacancy and a free electron,⁸ etc. All but the first of the processes just mentioned require lattice imperfections, and these processes will probably predominate in even the best crystals available.

It is of interest, nevertheless, to consider the characteristics to be associated with the direct luminescence of a free exciton. A newly created exciton will have a decay time of about 10^{-8} sec with respect to re-emission of a photon. However, as has been discussed above, the exciton will probably undergo phonon-induced (nonradiative) transitions to other exciton states in about 10^{-14} sec. These latter states will almost invariably fail to satisfy the wave-number selection rule or the other selection rules (Sec. II) governing allowed optical transitions. Consequently, in a perfect lattice direct optical decay must be accompanied by the simultaneous emission or absorption of one or more phonons. Since interaction with optical phonons is strong, it is possible that the decay time associated with such higher order processes is not many orders of magnitude longer than 10^{-8} sec.

The energy of the direct luminescence may be considerably lower than the energy of the first fundamental absorption peak, since the excitation will be degraded by phonon interactions to within kT of the lowest exciton state prior to radiative decay. The long-wavelength tail observed in the fundamental absorption of many crystals may possibly be attributed to low-lying exciton bands which can be reached via optical transitions only with the simultaneous emission or absorption of phonons. If, however, the lowest exciton band has its minimum at the center of the Brillouin zone and can be reached from the ground state by an allowed optical transition, the direct luminescence will lie near the edge of the fundamental absorption, and a long-wavelength tail in the absorption may not occur. Other mechanisms that might produce a tail in the fundamental absorption have been discussed by Seitz¹⁶ with regard to the silver halides.

It is very unlikely that the strong luminescence observed in unactivated NaI by Van Sciver and Hofstadter¹⁷ arises from the decay of free excitons since the energy of the radiation was about 1.5 eV lower than that of the fundamental absorption edge whereas the decay time was only 10^{-8} sec. If an emission process characteristic of a pure crystal could occur so rapidly, a corresponding strong-absorption process having about the same energy would occur in the fundamental absorption. For the case of CdS it is also very unlikely that the edge luminescence observed by Klick¹⁸ and others is caused by free exciton decay, an interpretation

¹⁴ E. M. Pell, Phys. Rev. **87**, 457 (1952); A. G. Redfield, Phys. Rev. **94**, 537 (1954); J. R. Macdonald and J. E. Robinson, Phys. Rev. **95**, 44 (1954).

¹⁵ F. Seitz, Revs. Modern Phys. **26**, 7 (1954), p. 80; for a quantitative study of such processes see H. Ruchardt, Z. Physik **140**, 547 (1955).

¹⁶ F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

¹⁷ W. Van Sciver and R. Hofstadter, Phys. Rev. **97**, 1181 (1955).

¹⁸ C. C. Klick, Phys. Rev. **89**, 274 (1953); L. R. Furlong, Phys. Rev. **95**, 1086 (1954).

which has been suggested by Kröger and Meyer.¹⁹ The observed uniform sharpness and spacing of all the vibrational components of the emission could not occur if the structure were produced by multiple phonon induced radiative decay of excitons, since phonons having all frequencies of the vibration spectrum would participate. The interpretation of the data proposed by Furlong¹⁸ in terms of localized luminescence centers is probably correct. It seems likely that crystals having a concentration of one part in 10^{10} or less of active impurities or other imperfections are necessary if luminescent decay of free excitons is to compete favorably with other processes.

We have described how the first, or primary, exciton configuration gives rise to 72 exciton bands. Wannier² has shown (in his paper establishing effective mass theory) that an electron and hole in a rigid lattice can be associated with one another in a way analogous to a hydrogen atom, or better to positronium. An entire spectrum of exciton levels results, extending in energy to a series or "ionization" limit beyond which a free electron and free hole description is appropriate. The theory is accurate only for states in which the mean separation of the electron and hole is large compared to a lattice constant. Consequently the states described by the theory will be higher than those of the primary configuration and will be relatively closely spaced. When interaction with phonons is considered, these levels may be expected to be largely obscured by the broadening resulting from their short lifetime. The mean free path of the electron or hole may be small or comparable to their separation. Under such circumstances it is difficult to anticipate the manner and extent of the manifestation of these levels in optical absorption spectra. Sharp absorption lines in the fundamental region of Cu_2O have been attributed to such levels.²⁰

In the following section we shall analyze and classify the exciton bands arising from the primary configuration. In Sec. III we shall construct wave functions for the states of the primary exciton multiplet, and in Sec. IV we shall discuss the Hamiltonian matrix relevant to this multiplet and the relative intensities of the absorption components.

II. GROUP THEORETIC CLASSIFICATION OF STATES

There are five irreducible representations Γ_j , $j=1$ to 5, of the cubic group containing 24 proper rotations. Following the notation of Bethe,²¹ Γ_1 is the completely symmetric representation, Γ_2 is the other one-dimensional representation, Γ_3 is the two-dimensional representation, Γ_4 is the three-dimensional representation having the transformation properties (under proper

rotations) of the functions x , y , z , and Γ_5 is the remaining three-dimensional representation. The decomposition of the product representations is as follows:

$$\begin{aligned}\Gamma_1 \times \Gamma_j &= \Gamma_j, \\ \Gamma_2 \times \Gamma_2 &= \Gamma_1, \\ \Gamma_2 \times \Gamma_3 &= \Gamma_3, \\ \Gamma_2 \times \Gamma_4 &= \Gamma_5, \\ \Gamma_2 \times \Gamma_5 &= \Gamma_4, \\ \Gamma_3 \times \Gamma_3 &= \Gamma_1 + \Gamma_2 + \Gamma_3, \\ \Gamma_3 \times \Gamma_4 &= \Gamma_4 + \Gamma_5, \\ \Gamma_3 \times \Gamma_5 &= \Gamma_4 + \Gamma_5, \\ \Gamma_4 \times \Gamma_4 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5, \\ \Gamma_4 \times \Gamma_5 &= \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5, \\ \Gamma_5 \times \Gamma_5 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5.\end{aligned}\tag{1}$$

The full cubic group (48 elements) contains 24 additional symmetry operations (which are the same proper rotations followed by an inversion) and has ten irreducible representations Γ_j , Γ'_j , $j=1$ to 5. The unprimed representations have even parity and the primed representations have odd parity. As a result of the fact that the inversion operation commutes with proper rotations, the above multiplication rules (1) still apply and the parity can be considered separately as follows:

$$\begin{aligned}\text{unprimed} \times \text{unprimed} &= \text{unprimed}, \\ \text{primed} \times \text{primed} &= \text{unprimed}, \\ \text{primed} \times \text{unprimed} &= \text{primed}.\end{aligned}\tag{2}$$

The spherical harmonics decompose into cubic irreducible representations as follows²¹: s : Γ_1 , p : Γ_4' , d : $\Gamma_3 + \Gamma_5$, f : $\Gamma_2' + \Gamma_4' + \Gamma_5'$, etc.

In order to classify the states that will occur in the primary exciton configuration, consider a hole to be localized on one Cl^- ion. The hole states (neglecting spin) will belong to Γ_4' since they are p states. The excited electron can be in any of the six nearest neighbor Na^+ $3s$ states, which we can represent by the symbols x , x' , y , y' , z , z' , where x and x' are on opposite sides of the Cl^- ion, etc. These six states will form a reducible representation of the cubic group which can be reduced by inspection. The appropriate basis functions, formed from linear combinations of the foregoing six states are as follows:

$$\begin{aligned}\Gamma_1: s &= (x+x'+y+y'+z+z')/\sqrt{6}, \\ \Gamma_3: u &= [z+z' - \frac{1}{2}(x+x'+y+y')] / \sqrt{3}, \\ &v = [x+x' - (y+y')] / 2, \\ \Gamma_4': p &= (x-x')/\sqrt{2}, \\ &q = (y-y')/\sqrt{2}, \\ &r = (z-z')/\sqrt{2}.\end{aligned}\tag{3}$$

If we wish to find the irreducible representations that

¹⁹ F. A. Kröger and H. J. G. Meyer, *Physica* **20**, 1149 (1954).

²⁰ M. Hayashi and K. Katsuki, *J. Phys. Soc. Japan* **7**, 599 (1952); Gross, Zakharchenya, and Reinov, *Doklady Akad. Nauk SSSR* **90**, 745 (1953); **92**, 265 (1953).

²¹ H. A. Bethe, *Ann. Physik* **3**, 133 (1929).

will occur for the total wave functions, formed by products of the hole state functions and the electron functions (3) (continuing the neglect of spin), we need only evaluate the following product using (1) and (2):

$$\Gamma_4' \times (\Gamma_1 + \Gamma_3 + \Gamma_4') = 2\Gamma_4' + \Gamma_5' + \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5. \quad (4)$$

Seven energy levels and six symmetry types occur.

If we consider spin and neglect any spin-orbit interaction, the spin of the hole and electron will couple to form either a singlet ($S=0$) or triplet ($S=1$) state. Space wave functions of the symmetry types in (4) may then be combined with a singlet spin function, which has Γ_1 symmetry. The resulting symmetries are given by

$$\begin{aligned} \Gamma_4' \times (\Gamma_1 + \Gamma_3 + \Gamma_4') \times \Gamma_1 \\ = 2\Gamma_4' + \Gamma_5' + \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5. \end{aligned} \quad (5)$$

If the space wave functions are combined with triplet spin functions, which have Γ_4 symmetry, the resulting representations are given by

$$\begin{aligned} \Gamma_4' \times (\Gamma_1 + \Gamma_3 + \Gamma_4') \times \Gamma_4 = 2\Gamma_1' + \Gamma_2' + 3\Gamma_3' + 3\Gamma_4' \\ + 3\Gamma_5' + \Gamma_1 + \Gamma_2 + 2\Gamma_3 + 4\Gamma_4 + 3\Gamma_5. \end{aligned} \quad (6)$$

There are a total of 23 triplet energy levels. A spin-orbit interaction will mix the singlet and triplet energy levels having the same symmetry. The sum of (5) and (6) gives a total of 30 energy levels into which the 72 exciton states must collapse as a result of cubic symmetry:

$$\begin{aligned} 2\Gamma_1' + \Gamma_2' + 3\Gamma_3' + 5\Gamma_4' + 4\Gamma_5' \\ + 2\Gamma_1 + \Gamma_2 + 3\Gamma_3 + 5\Gamma_4 + 4\Gamma_5. \end{aligned} \quad (7)$$

This classification will apply to the exciton states at the center of the Brillouin zone.¹¹ Although the wave functions will be nonlocalized (see Sec. III), they will have the same transformation properties under cubic symmetry operations as the localized functions described above.

As a result of the orthogonality of functions belonging to different irreducible representations of a symmetry group,¹² it is easy to derive selection rules governing optical transitions. The integrand of the matrix element for such a transition contains the ground-state wave function (Γ_1 symmetry), the momentum operator (Γ_4' symmetry), and the final state wave function. Since $\Gamma_1 \times \Gamma_4' = \Gamma_4'$, only a final state having Γ_4' symmetry will yield a nonzero matrix element. Only 5 of the 30 energy levels in (7) have this symmetry, so that there will be just 5 allowed transitions to the excited configuration. If there is no spin-orbit interaction, total spin will be conserved during a transition. For this case, only the singlet energy levels having Γ_4' symmetry can be excited. There are two such levels in (5).

The Cl^- ion in the CsCl lattice has eight nearest neighbor metal ions located in (1,1,1) type directions. We shall denote the s -type valence electron wave

functions of the metal ions in each of the eight directions by the following symbols: (1,1,1): a , (-1, -1, -1): a' , (-1, 1, -1): b , (1, -1, 1): b' , (-1, -1, 1): c , (1, 1, -1): c' , (1, -1, -1): d , (-1, 1, 1): d' . These eight states are the basis functions of a reducible representation of the cubic group. The appropriate linear combinations which form the bases of the reduced representation are as follows:

$$\begin{aligned} \Gamma_1: S &= (a+a'+b+b'+c+c'+d+d')/\sqrt{8}, \\ \Gamma_2': T &= (a-a'+b-b'+c-c'+d-d')/\sqrt{8}, \\ \Gamma_4': P &= (a+d+b'+c'-b-c-a'-d')/\sqrt{8}, \\ Q &= (a+b+c'+d'-c-d-a'-b')/\sqrt{8}, \\ R &= (a+c+b'+d'-b-d-a'-c')/\sqrt{8}, \\ \Gamma_5: U &= (a+d+a'+d'-b-c-b'-c')/\sqrt{8}, \\ V &= (a+b+a'+b'-c-d-c'-d')/\sqrt{8}, \\ W &= (a+c+a'+c'-b-d-b'-d')/\sqrt{8}. \end{aligned} \quad (8)$$

Following the procedure used above for the NaCl structure, the symmetries that the space part of the exciton wave function can have are

$$\begin{aligned} \Gamma_4' \times (\Gamma_1 + \Gamma_2' + \Gamma_4' + \Gamma_5) \\ = \Gamma_2' + \Gamma_3' + 2\Gamma_4' + \Gamma_5' + \Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5. \end{aligned} \quad (9)$$

Combining this set of irreducible representations with a singlet spin function yields the same set. For a triplet spin function, one obtains

$$\begin{aligned} \Gamma_4' \times (\Gamma_1 + \Gamma_2' + \Gamma_4' + \Gamma_5) \times \Gamma_4 = 2\Gamma_1' + \Gamma_2' + 3\Gamma_3' \\ + 4\Gamma_4' + 5\Gamma_5' + \Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 5\Gamma_4 + 4\Gamma_5. \end{aligned} \quad (10)$$

With spin-orbit coupling, the levels in (9) and (10) which belong to the same representation will be mixed. Our total list of levels is

$$\begin{aligned} 2\Gamma_1' + 2\Gamma_2' + 4\Gamma_3' + 6\Gamma_4' + 6\Gamma_5' \\ + 2\Gamma_1 + 2\Gamma_2 + 4\Gamma_3 + 6\Gamma_4 + 6\Gamma_5. \end{aligned} \quad (11)$$

We observe that the 96 possible exciton states collapse into 40 energy levels. The number of times Γ_4' appears in (11) is six, so there will be six allowed transitions from the ground state. Since Γ_4' appears twice in (9), there will be only two allowed transitions in the absence of spin-orbit interaction.

III. CONSTRUCTION OF WAVE FUNCTIONS

In this section we shall construct the zeroth-order exciton wave functions having wave number $k=0$ and belonging to the Γ_4' representation of the cubic group. In order to carry out this construction we must know how to find a wave function $\psi_{i\lambda}$ belonging to Γ_i if it is formed from product functions $\phi_{j\mu}$ and $\phi_{k\nu}$ belonging to Γ_j and Γ_k , respectively. The appropriate relationship is

$$\psi_{i\lambda} = \sum_{\mu\nu} a_{i\lambda j\mu k\nu} \phi_{j\mu} \phi_{k\nu}. \quad (12)$$

The coefficients $a_{i\lambda j\mu k\nu}$ are the cubic symmetry analogs

of the Clebsch-Gordan coefficients¹² associated with the irreducible representations of the rotation group. For the cubic group, tables of these coefficients can be constructed most easily by trial and error, especially if one has Bethe's table of Kubic Harmonics²² as a guide. These coefficients have been determined for all of the products (1) and yield the following basis functions of the product representations:

$$\Gamma_1 \times \Gamma_i:$$

$$\psi_{i\lambda} = \phi_1 \phi_{i\lambda}'; \quad (13a)$$

$$\Gamma_2 \times \Gamma_2:$$

$$\psi_1 = \phi_2 \phi_2'; \quad (13b)$$

$$\Gamma_2 \times \Gamma_3:$$

$$\psi_{3u} = \phi_2 \phi_{3u}', \quad (13c)$$

$$\psi_{3v} = \phi_2 \phi_{3v}';$$

$$\Gamma_2 \times \Gamma_4:$$

$$\psi_{5x} = \phi_2 \phi_{4x}', \quad (13d)$$

$$\psi_{5y} = \phi_2 \phi_{4y}',$$

$$\psi_{5z} = \phi_2 \phi_{4z}';$$

$$\Gamma_2 \times \Gamma_5:$$

$$\psi_{4x} = \phi_2 \phi_{5x}', \quad (13e)$$

$$\psi_{4y} = \phi_2 \phi_{5y}',$$

$$\psi_{4z} = \phi_2 \phi_{5z}';$$

$$\Gamma_3 \times \Gamma_3:$$

$$\psi_1 = (\phi_{3u} \phi_{3u}' + \phi_{3v} \phi_{3v}')/\sqrt{2}, \quad (13f)$$

$$\psi_2 = (-\phi_{3u} \phi_{3v}' + \phi_{3v} \phi_{3u}')/\sqrt{2},$$

$$\psi_{3u} = (\phi_{3u} \phi_{3u}' - \phi_{3v} \phi_{3v}')/\sqrt{2},$$

$$\psi_{3v} = (-\phi_{3u} \phi_{3v}' - \phi_{3v} \phi_{3u}')/\sqrt{2};$$

$$\Gamma_3 \times \Gamma_4:$$

$$\psi_{4x} = (-\phi_{3u} \phi_{4x}' + \sqrt{3} \phi_{3v} \phi_{4x}')/2, \quad (13g)$$

$$\psi_{4y} = (-\phi_{3u} \phi_{4y}' - \sqrt{3} \phi_{3v} \phi_{4y}')/2,$$

$$\psi_{4z} = \phi_{3u} \phi_{4z}',$$

$$\psi_{5x} = (-\sqrt{3} \phi_{3u} \phi_{4x}' - \phi_{3v} \phi_{4x}')/2,$$

$$\psi_{5y} = (\sqrt{3} \phi_{3u} \phi_{4y}' - \phi_{3v} \phi_{4y}')/2,$$

$$\psi_{5z} = \phi_{3v} \phi_{4z}';$$

$$\Gamma_3 \times \Gamma_5:$$

$$\psi_{4x} = (-\sqrt{3} \phi_{3u} \phi_{5x}' - \phi_{3v} \phi_{5x}')/2, \quad (13h)$$

$$\psi_{4y} = (\sqrt{3} \phi_{3u} \phi_{5y}' - \phi_{3v} \phi_{5y}')/2,$$

$$\psi_{4z} = \phi_{3v} \phi_{5z},$$

$$\psi_{5x} = (-\phi_{3u} \phi_{5x}' + \sqrt{3} \phi_{3v} \phi_{5x}')/2,$$

$$\psi_{5y} = (-\phi_{3u} \phi_{5y}' - \sqrt{3} \phi_{3v} \phi_{5y}')/2,$$

$$\psi_{5z} = \phi_{3u} \phi_{5z}';$$

$$\Gamma_4 \times \Gamma_4:$$

$$\begin{aligned} \psi_1 &= (\phi_{4x} \phi_{4x}' + \phi_{4y} \phi_{4y}' + \phi_{4z} \phi_{4z}')/\sqrt{3}, \\ \psi_{3u} &= (-\phi_{4x} \phi_{4x}' - \phi_{4y} \phi_{4y}' + 2\phi_{4z} \phi_{4z}')/\sqrt{6}, \\ \psi_{3v} &= (\phi_{4x} \phi_{4x}' - \phi_{4y} \phi_{4y}')/\sqrt{2}, \\ \psi_{4x} &= (-\phi_{4y} \phi_{4x}' + \phi_{4z} \phi_{4y}')/\sqrt{2}, \\ \psi_{4y} &= (\phi_{4x} \phi_{4x}' - \phi_{4z} \phi_{4z}')/\sqrt{2}, \\ \psi_{4z} &= (-\phi_{4x} \phi_{4y}' + \phi_{4y} \phi_{4x}')/\sqrt{2}, \\ \psi_{5x} &= (\phi_{4y} \phi_{4z}' + \phi_{4z} \phi_{4y}')/\sqrt{2}, \\ \psi_{5y} &= (\phi_{4x} \phi_{4z}' + \phi_{4z} \phi_{4x}')/\sqrt{2}, \\ \psi_{5z} &= (\phi_{4x} \phi_{4y}' + \phi_{4y} \phi_{4x}')/\sqrt{2}; \end{aligned} \quad (13i)$$

$$\Gamma_4 \times \Gamma_5:$$

$$\begin{aligned} \psi_2 &= (\phi_{4x} \phi_{5x}' + \phi_{4y} \phi_{5y}' + \phi_{4z} \phi_{5z}')/\sqrt{3}, \\ \psi_{3u} &= (\phi_{4x} \phi_{5x}' - \phi_{4y} \phi_{5y}')/\sqrt{2}, \\ \psi_{3v} &= (\phi_{4x} \phi_{5x}' + \phi_{4y} \phi_{5y}' - 2\phi_{4z} \phi_{5z}')/\sqrt{6}, \\ \psi_{4x} &= (\phi_{4y} \phi_{5z}' + \phi_{4z} \phi_{5y}')/\sqrt{2}, \\ \psi_{4y} &= (\phi_{4x} \phi_{5z}' + \phi_{4z} \phi_{5x}')/\sqrt{2}, \\ \psi_{4z} &= (\phi_{4x} \phi_{5y}' + \phi_{4y} \phi_{5x}')/\sqrt{2}, \\ \psi_{5x} &= (\phi_{4y} \phi_{5z}' - \phi_{4z} \phi_{5y}')/\sqrt{2}, \\ \psi_{5y} &= (-\phi_{4x} \phi_{5z}' + \phi_{4z} \phi_{5x}')/\sqrt{2}, \\ \psi_{5z} &= (\phi_{4x} \phi_{5y}' - \phi_{4y} \phi_{5x}')/\sqrt{2}; \end{aligned} \quad (13j)$$

$$\Gamma_5 \times \Gamma_5:$$

$$\begin{aligned} \psi_1 &= (\phi_{5x} \phi_{5x}' + \phi_{5y} \phi_{5y}' + \phi_{5z} \phi_{5z}')/\sqrt{3}, \\ \psi_{3u} &= (-\phi_{5x} \phi_{5x}' - \phi_{5y} \phi_{5y}' + 2\phi_{5z} \phi_{5z}')/\sqrt{6}, \\ \psi_{3v} &= (\phi_{5x} \phi_{5x}' - \phi_{5y} \phi_{5y}')/\sqrt{2}, \\ \psi_{4x} &= (-\phi_{5y} \phi_{5z}' + \phi_{5z} \phi_{5y}')/\sqrt{2}, \\ \psi_{4y} &= (\phi_{5x} \phi_{5z}' - \phi_{5z} \phi_{5x}')/\sqrt{2}, \\ \psi_{4z} &= (-\phi_{5x} \phi_{5y}' + \phi_{5y} \phi_{5x}')/\sqrt{2}, \\ \psi_{5x} &= (\phi_{5y} \phi_{5z}' + \phi_{5z} \phi_{5y}')/\sqrt{2}, \\ \psi_{5y} &= (\phi_{5x} \phi_{5z}' + \phi_{5z} \phi_{5x}')/\sqrt{2}, \\ \psi_{5z} &= (\phi_{5x} \phi_{5y}' + \phi_{5y} \phi_{5x}')/\sqrt{2}. \end{aligned} \quad (13k)$$

We will also need to know how spin functions are to be combined with space functions so as to yield wave functions belonging to irreducible representations of the cubic group. Since our crystal contains an even number of electrons, it is not necessary to consider the double valued representations²¹ of the cubic group. It is sufficient to know the linear combinations of spin functions for a two electron system which are basis functions of (single valued) representations of the cubic group. Let $\alpha(j)$ and $\beta(j)$ be the usual spin-up and spin-down functions, respectively, associated with electron j . For a pair of electrons one can construct spin functions for which $S=0$ or 1. They are as follows:

$$\begin{aligned} S=0, \Gamma_1: \sigma &= [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}, \\ S=1, \Gamma_4: \chi &= [-\alpha(1)\alpha(2) + \beta(1)\beta(2)]/\sqrt{2}, \\ &\eta = i[\alpha(1)\alpha(2) + \beta(1)\beta(2)]/\sqrt{2}, \\ &\zeta = [\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}. \end{aligned} \quad (14)$$

σ belongs to Γ_1 . It is readily verified that χ, η, ζ transform like x, y, z under proper rotations and belong therefore to Γ_4 . To observe this fact, one must make use of the transformation properties of spin functions under rotation operations.¹² It should be evident now that wave functions of the type (14) can be combined with space functions according to the rules presented in (13).

We are now prepared to construct approximate exciton wave functions. It is emphasized that this construction should be considered in the spirit of the Heitler-London and molecular orbital approximations familiar in molecular problems. The resulting functions can be expected to represent the energy levels only somewhat crudely. They will, however, provide a starting point for further refinement.

Let us represent the p -type functions associated with the outermost shell of the halogen ions by $\Phi_x, \Phi_y,$ and Φ_z . We shall indicate the particular lattice cell under consideration by adding a subscript L , and shall indicate the spin state by the superscript $+$ or $-$ for spin-up and spin-down, respectively. The wave function representing the state for which an electron is missing from the state Φ_{xL^-} , for example, can be written

$$X_{L^+}' = [(6N-1)!]^{-\frac{1}{2}} \mathcal{A} X_{L^+},$$

where X_{L^+} is the simple product function,

$$X_{L^+} = \Phi_{xL^+}(2)\Phi_{yL^+}(3)\Phi_{zL^+}(4) \times \Phi_{zL^+}(5)\Phi_{zL^+}(6) \prod_{L' \neq L} \mathcal{S}_{L'}, \quad (15)$$

$\mathcal{S}_{L'}$ being the product function for a closed-shell configuration on the halogen ion in lattice cell L' . \mathcal{A} is the antisymmetrization operator. It should be observed that X_{L^+}' belongs to Γ_4' and is an eigenfunction of the spin operator,

$$\mathbf{S} = \sum_{i=2}^{6N} \mathbf{s}(i),$$

with total spin $\frac{1}{2}$ and $S_z = \frac{1}{2}$. Recalling the definitions, (3) of the excited electron configurations and extending the notation as above to include spin state and lattice location, it follows from (13a) and (14) that the function,

$$[s_{L^+}(1)X_{L^-}' - s_{L^-}(1)X_{L^+}']/\sqrt{2},$$

has total spin 0 and belongs to Γ_4' . If we antisymmetrize this function and take a linear combination of such states for all N lattice cells so as to generate a running wave solution with $k=0$, we obtain,

$$\Psi_x = [(6N)!]^{-\frac{1}{2}} N^{-\frac{1}{2}} \mathcal{A} \sum_L (s_{L^+} X_{L^-}' - s_{L^-} X_{L^+}')/\sqrt{2}. \quad (16)$$

We have dropped the prime from the X_{L^-} , etc., since it is sufficient to antisymmetrize only once. The wave function (16) is that of an exciton with $k=0$ and which belongs to the x component of Γ_4' .

In a similar manner we can construct all 72 of the exciton wave functions for $k=0$. We shall present only

the five functions belonging to the y component of Γ_4' which occur for the NaCl lattice. The corresponding $x, y,$ and z components will be degenerate, of course, and only one of them is needed for calculating energies and matrix elements. We have chosen to present the y components for the trivial reason that they turn out to be real, whereas the x and z components are sometimes complex. Each of the five functions is labeled by its parentage, the meaning of which should be clear from the discussion of Sec. II. Letting $\mathcal{B} = (6N)!^{-\frac{1}{2}} N^{-\frac{1}{2}} \mathcal{A}$, the functions are as follows:

$$(\Gamma_4' \times \Gamma_1 \rightarrow \Gamma_4') \times \Gamma_1 \rightarrow \Gamma_4': \\ \Psi_y = \mathcal{B} \sum_L (s_{L^+} Y_{L^-} - s_{L^-} Y_{L^+})/\sqrt{2}; \quad (17a)$$

$$(\Gamma_4' \times \Gamma_3 \rightarrow \Gamma_4') \times \Gamma_1 \rightarrow \Gamma_4': \\ \Psi_y = \mathcal{B} \sum_L (-u_{L^+} Y_{L^-} - \sqrt{3} v_{L^+} Y_{L^-} + u_{L^-} Y_{L^+} \\ + \sqrt{3} v_{L^-} Y_{L^+})/2\sqrt{2}; \quad (17b)$$

$$(\Gamma_4' \times \Gamma_1 \rightarrow \Gamma_4') \times \Gamma_4 \rightarrow \Gamma_4': \\ \Psi_y = \mathcal{B} \sum_L (s_{L^+} X_{L^-} + s_{L^-} X_{L^+} \\ + s_{L^+} Z_{L^+} - s_{L^-} Z_{L^-})/2; \quad (17c)$$

$$(\Gamma_4' \times \Gamma_3 \rightarrow \Gamma_4') \times \Gamma_4 \rightarrow \Gamma_4': \\ \Psi_y = \mathcal{B} \sum_L (-u_{L^+} X_{L^-} + \sqrt{3} v_{L^+} X_{L^-} - u_{L^-} X_{L^+} \\ + \sqrt{3} v_{L^-} X_{L^+} + 2u_{L^+} Z_{L^+} - 2u_{L^-} Z_{L^-})/4; \quad (17d)$$

$$(\Gamma_4' \times \Gamma_3 \rightarrow \Gamma_5') \times \Gamma_4 \rightarrow \Gamma_4': \\ \Psi_y = \mathcal{B} \sum_L (-\sqrt{3} u_{L^+} X_{L^-} - v_{L^+} X_{L^-} - \sqrt{3} u_{L^-} X_{L^+} \\ - v_{L^-} X_{L^+} - 2v_{L^+} Z_{L^+} + 2v_{L^-} Z_{L^-})/4. \quad (17e)$$

These functions are mutually orthogonal and normalized if and only if the atomic p functions on the Cl^- ions and the atomic s functions on the Na^+ ions are all mutually orthogonal. Such orthogonality would never obtain. It may be a fair approximation to consider the various Na^+ $3s$ functions to be mutually orthogonal and the various Cl^- $3p$ functions also, but there is certainly considerable overlap between Na^+ $3s$ functions and nearest neighbor Cl^- $3p$ functions. Only one overlap integral of this type occurs, namely that between, say, a Φ_{xL^+} Cl^- function and the $3s$ function on the nearest neighbor Na^+ ion in the positive x direction. If we call this overlap integral γ , then a straightforward calculation (but one involving considerable mental exercise) yields the following matrix related to the functions (17):

$$\rho_{ij} = (\Psi_{yi}, \Psi_{yj}) \\ = \begin{pmatrix} 1-7\gamma^2 & -\sqrt{2}\gamma^2 & 0 & 0 & 0 \\ -\sqrt{2}\gamma^2 & 1-8\gamma^2 & 0 & 0 & 0 \\ 0 & 0 & 1-17\gamma^2/3 & \gamma^2/\sqrt{2} & 0 \\ 0 & 0 & \gamma^2/\sqrt{2} & 1-16\gamma^2/3 & 0 \\ 0 & 0 & 0 & 0 & 1-6\gamma^2 \end{pmatrix}. \quad (18)$$

The off-diagonal elements can occur between (17a) and (17b) because they have the same space symmetry and spin symmetry, and similarly for (17c) and (17d). All

other off-diagonal matrix elements are necessarily zero, as can be shown from the orthogonality theorem.¹²

The correct zeroth-order exciton functions will be linear combinations of the five functions (17). The proper linear combination is determined by a five by five matrix equation and will be discussed briefly in the following section.

For the sake of completeness we shall present also the six wave functions associated with the y component of Γ_4' for the CsCl structure. Using the definitions, (8) and (15), and the rules for construction, (13) and (14), the functions are found to be as follows:

$$(\Gamma_4' \times \Gamma_1 \rightarrow \Gamma_4') \times \Gamma_1 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (S_L^+ Y_L^- - S_L^- Y_L^+) / \sqrt{2}; \quad (19a)$$

$$(\Gamma_4' \times \Gamma_6 \rightarrow \Gamma_4') \times \Gamma_1 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (U_L^+ Z_L^- - U_L^- Z_L^+ + W_L^+ X_L^- - W_L^- X_L^+) / 2; \quad (19b)$$

$$(\Gamma_4' \times \Gamma_1 \rightarrow \Gamma_4') \times \Gamma_4 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (S_L^+ X_L^- + S_L^- X_L^+ + S_L^+ Z_L^- - S_L^- Z_L^+) / 2; \quad (19c)$$

$$(\Gamma_4' \times \Gamma_6 \rightarrow \Gamma_4') \times \Gamma_4 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (V_L^+ Z_L^- + W_L^+ Y_L^- + V_L^- Z_L^+ + W_L^- Y_L^+ + U_L^+ Y_L^+ + V_L^+ X_L^+ - U_L^- Y_L^- - V_L^- X_L^-) / 2\sqrt{2}; \quad (19d)$$

$$(\Gamma_4' \times \Gamma_6 \rightarrow \Gamma_3') \times \Gamma_4 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (U_L^+ X_L^- - W_L^+ Z_L^+ + U_L^- X_L^- - W_L^- Z_L^-) / 2i; \quad (19e)$$

$$(\Gamma_4' \times \Gamma_6 \rightarrow \Gamma_6') \times \Gamma_4 \rightarrow \Gamma_4':$$

$$\Psi_y = \mathfrak{B} \sum_L (V_L^+ Z_L^- - W_L^+ Y_L^- + V_L^- Z_L^+ - W_L^- Y_L^+ - U_L^+ Y_L^+ + V_L^+ X_L^+ + U_L^- Y_L^- - V_L^- X_L^-) / 2\sqrt{2}. \quad (19f)$$

If the matrix analogous to (18) is computed for these functions, the only nonzero off-diagonal elements will be between (19a) and (19b) and between (19c) and (19d).

In the foregoing development it appears that we have failed to treat the excited electron and hole on an equivalent basis, since prior to Eq. (16) the hole was localized on a particular ion whereas the electron was regarded as "revolving" about the hole on the nearest neighbor ions. We could have proceeded by constructing wave functions corresponding to the excited electron being localized on a particular ion and the hole revolving about it on its nearest neighbor ions. The two procedures are equivalent, however. The only difference is that the alternative method would yield exciton wave functions that are linear combinations of (17). Since the linear combinations corresponding to stationary states of the system must be determined in either case

by the solution of an eigenvalue equation, there is no reason to prefer a particular set of basis functions.

IV. THE HAMILTONIAN MATRIX

A primary objective of the theory is the determination from first principles of the relative positions and intensities of the absorption lines. Needless to say such a task is quite difficult and has not yet been accomplished. We shall limit ourselves here to a qualitative discussion and formulation of the problem.

The zeroth-order wave functions for exciton states having symmetry corresponding to the y component of Γ_4' will be linear combinations of the functions (17):

$$\phi = \Psi_j a_j. \quad (20)$$

The index j is summed from 1 to 5. If \mathfrak{H} is the Hamiltonian operator of the system, then

$$\mathfrak{H}\phi = \mathfrak{H}\Psi_j a_j \approx E\Psi_j a_j, \quad (21)$$

where E is the energy of the state whose wave function is ϕ . The last equality is only an approximation as a consequence of the crudeness of our starting wave functions. The approximation results from the neglect of other electronic configurations. If one forms the inner product of Eq. (21) with Ψ_i , the equation becomes,

$$(\mathfrak{H}_{ij} - E\rho_{ij})a_j = 0, \quad (22)$$

where \mathfrak{H}_{ij} are the matrix elements of \mathfrak{H} in the space defined by the functions (17) and ρ_{ij} is the matrix (18). This is a secular equation of order five, and it will have five energy eigenvalues E^n and five corresponding eigenvectors a_j^n . The wave functions (20) determined by these solutions are presumably the best representations of the exciton states neglecting configuration interaction.

The major problem is the determination of the matrix elements \mathfrak{H}_{ij} . There are a number of contributions to \mathfrak{H} which must be considered, some of which will affect only the energy location of the entire multiplet and others which will contribute also to the fine structure of the multiplet. We shall consider a number of them briefly:

(a) Our wave functions have been constructed as linear combinations of atomic orbitals. Consequently a contribution to the energy difference between the ground state and exciton configuration will arise from the change that would occur if the electron were transferred from a free Cl^- ion to a remote Na^+ ion. This energy is the electron affinity of a Cl atom minus the ionization potential of a Na atom. It should be appreciated that if overlap between $3p$ functions on adjacent Cl^- ions is neglected and also between $3s$ functions on adjacent Na^+ ions, this term includes the entire energy difference arising from the kinetic energy operator of the system. This term also takes into account the potential interaction with the Cl core and the other five $3p$ electrons when the electron is on the Cl^- ion, and it includes the potential interaction with

the Na core when the electron is on the Na⁺ ion. This energy difference has a magnitude of one or two eV, and does not contribute to the fine structure of the multiplet.

(b) The potential energy of an electron at the center of a Na⁺ ion arising from all of the other ions is the Madelung potential, M . The corresponding potential at the center of a Cl⁻ ion is $-M$. That part of the energy of an exciton arising from the ionic potential is at first sight $2M$. One must consider the fact that the electronic states involved are not localized at the center of the ions concerned and that the ionic potential is a rapidly varying function of position. The ionic potential near a Cl⁻ ion arising from all other ions can be expanded in a series,

$$V(r, \theta, \phi) = \sum_{l, m} a_{lm} Y_{lm}(\theta, \phi) r^l, \quad (23)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics. This expression is valid only at points in space where the ionic charge density is zero, since it is a solution of Laplace's equation. The Madelung potential is

$$M = ea_{00} Y_{00}.$$

Since the charge density $\rho(\mathbf{r})$ associated with a $3p$ state of a Cl⁻ ion does not overlap the nearest neighbor Na⁺ nucleus, the potential energy of the charge distribution is,

$$\int \rho(\mathbf{r}) V(r, \theta, \phi) d^3r. \quad (24)$$

(The ionic charge of a positive ion is a point charge located at the nucleus.) An harmonic expansion of the charge density associated with a p function contains only harmonics of order 0 and 2. Furthermore, since the potential (23) has cubic symmetry, the terms of the series for which $l=1, 2, 3$ are all zero.²² Consequently the only nonzero contribution to (24) will be from the $l=0$ term of (23). We find the following:

$$\int \rho(\mathbf{r}) V(r, \theta, \phi) d^3r = \int \rho(\mathbf{r}) a_{00} Y_{00} d^3r = -M.$$

If one makes the same analysis for the interaction of a Na⁺ $3s$ state with the ionic potential, one can obtain a value M only by neglecting the overlap of the $3s$ function with the ionic charge on the six nearest neighbor atoms. This overlap is appreciable, however, and will give rise to a significant correction. Therefore the contribution of the ionic field to the exciton energy is not $2M$, but $2M - \delta$, where

$$\delta = (6e^2/R) - \int \rho_p(r_1) \rho_s(r_2) d^3r_1 d^3r_2 / r_{12}. \quad (25)$$

In this expression ρ_p is the charge density associated with six $3p$ electrons on a Cl⁻ ion and ρ_s is the charge

density associated with one $3s$ electron on a nearest neighbor Na⁺ ion, the distance of separation being R .

(c) The atomic orbitals will overlap the nearest neighbor ion cores to some extent. The interaction of Cl⁻ $3p$ functions with the outer-shell electrons of Na⁺ ions provides, for example, the repulsive forces which prevent the lattice from collapsing. If g is the repulsive energy of the crystal per molecule, an additional amount of energy $-g/6$ is required to remove one Cl⁻ $3p$ electron from its state. Similarly, an electron in a Na⁺ $3s$ state will experience the overlap potential with nearest neighbor ion cores. This term will include the Coulomb interaction with the five $3p$ electrons on each of the six neighboring Cl atoms. [The Coulomb interaction with the sixth electron has already been considered in (b) above. All exchange interactions associated with the excited electron will be included in (e) below.]

(d) Formation of an exciton causes a separation of electric charge relative to the perfect crystal which will induce electronic polarization of the surrounding medium. This polarization energy has been calculated by Klemm⁹ for the state in which the electron and hole are localized. Since electronic response is very rapid, the calculation is probably still valid even if exciton motion is taken into account. On the other hand, the response of ionic polarization is sufficiently slow compared to the motion of an excitation wave that it probably does not play an important role. The extent to which this latter assumption is not valid is an interesting theoretical question somewhat analogous to the polaron problem.

The four interactions mentioned so far will contribute a constant energy E_0 to the multiplet and will not split the levels of the multiplet at $k=0$. The matrix \mathcal{H}_{ij} associated with these terms will be $E_0 \rho_{ij}$. The two remaining contributions will determine the fine structure of the multiplet.

(e) With the Coulomb and exchange interaction of the electron and hole we shall include all other terms of Coulombic origin which we have not already mentioned. The only safe way to evaluate these interactions is to determine the matrix elements of the function,

$$\frac{1}{2} \sum_{k, l=1}^{6N} e^2 / r_{kl}, \quad (26)$$

between the exciton states (17) and to subtract from them the expectation value of (26) for the ground state multiplied by ρ_{ij} . The physical origin of all terms must be identified so that those already included in (a), (b), (c) can be discarded. In addition those Coulomb integrals which will be canceled by interactions of the electrons with the nuclear charge, $5e$, on the Cl⁻ ions must be discarded. Since (26) is invariant under cubic symmetry operations and does not depend on spin coordinates, it follows that the only nonzero off-diagonal elements will be between the states (17a) and (17b) and between (17c) and (17d).

²² F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

(f) Finally, we must consider the effect of spin-orbit interaction on the structure of the multiplet. As a consequence of the approximations we have made, the only contribution from the spin-orbit coupling will be associated with the hole in a $\text{Cl}^- 3p$ state, and will be related to the spin-orbit splitting of the Cl atom ground-state configuration. If \mathbf{L} and $\boldsymbol{\sigma}$ are the orbital and spin angular momentum operators, respectively, for a single electron, the matrix of the total spin-orbit interaction can be easily evaluated with the help of the following relations applicable to atomic p states:

$$\begin{aligned}\boldsymbol{\sigma} \cdot \mathbf{L} \Phi_x^+ &= \Phi_z^- + i\Phi_y^+, \\ \boldsymbol{\sigma} \cdot \mathbf{L} \Phi_y^+ &= i\Phi_z^- - i\Phi_x^+, \\ \boldsymbol{\sigma} \cdot \mathbf{L} \Phi_z^+ &= -i\Phi_y^- - \Phi_x^-, \\ \boldsymbol{\sigma} \cdot \mathbf{L} \Phi_x^- &= -\Phi_z^+ - i\Phi_y^-, \\ \boldsymbol{\sigma} \cdot \mathbf{L} \Phi_y^- &= i\Phi_z^+ + i\Phi_x^-, \\ \boldsymbol{\sigma} \cdot \mathbf{L} \Phi_z^- &= -i\Phi_y^+ + \Phi_x^+.\end{aligned}\quad (27)$$

If \mathcal{H}' is the total spin-orbit interaction operator, one obtains the following for the NaCl structure:

$$\mathcal{H}'_{ij} = \sum_{\mu=1}^5 \rho_{i\mu} h_{\mu j}, \quad (28)$$

where the matrix h is

$$h = - \begin{pmatrix} \lambda \\ - \\ 6 \end{pmatrix} \begin{pmatrix} 0 & 0 & -2\sqrt{2}i & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}i & -\sqrt{6}i \\ 2\sqrt{2}i & 0 & -2 & 0 & 0 \\ 0 & -\sqrt{2}i & 0 & 1 & \sqrt{3} \\ 0 & \sqrt{6}i & 0 & \sqrt{3} & -1 \end{pmatrix}. \quad (29)$$

The constant λ is here the magnitude of the spin-orbit splitting of the halogen atom ground state. If the spin-orbit coupling is large compared to the splitting arising from Coulomb and exchange interactions, then (28) can be used as an approximation for \mathcal{H}'_{ij} in (22), and the solution of the resulting secular equation is equivalent to the diagonalization of (29). This matrix has double root, $2\lambda/3$, corresponding to a $j=1/2$ hole state and a triple root, $-\lambda/3$, corresponding to a $j=3/2$ hole state.

The energy levels of the other exciton states at $k=0$ having different symmetry can be derived according

to the same procedures described here for Γ_4' symmetry. The only difference will be that the order of the secular equation will equal the number of times the symmetry type under consideration appears in (7). For exciton states having a wave vector that is not a symmetry point of the Brillouin zone one will obtain a 72 by 72 secular equation, since such states have no symmetry properties whatsoever.

The relative intensities of the exciton absorption components can be computed very easily once the eigenvectors of (22) are known. The absorption constant of a cubic crystal is independent of crystal orientation and the direction of polarization of the light. Consider, then, light which is incident in the z direction and which has electric polarization in the y direction. The matrix element for the transition depends on the overlap between $\text{Cl}^- 3p$ functions, Φ_y and $\text{Na}^+ 3s$ functions, (y) , and is proportional to an integral of the type,

$$\int (y) p_y \Phi_y d\tau,$$

where p_y is a momentum operator. Evaluating the matrix element of the perturbing Hamiltonian (associated with the incident light) between the ground state of the crystal and the exciton states (17), one readily finds that the five matrix elements are proportional to,

$$1:\sqrt{2}:0:0:0.$$

Consequently the relative intensity of an absorption line will be given by

$$I = |a_1 + \sqrt{2}a_2|^2, \quad (30)$$

where a_1 and a_2 are the first two coefficients in (20).

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