property of preserving the sharp line fluorescence of rare-earth ions (typically <1 cm^{-1} wide at 77°K), the transfer agent may be incorporated in high concentration. For example, it was found that emission from 1% Tm^{3+} ions in the aluminum garnet $(Er_{0.5}Y_{0.5})_3Al_5O_{12}$ is 100 times stronger than in $Y_3Al_5O_{12}$. Similarly, Ho^{3+} (1%) emission is 40 times stronger in the erbium substituted compound. However, the full merit of these systems as optical masers can only be realized when larger crystals are available.

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Excited States of Cesium Halide Crystals

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A model of the conduction band structure of cesium halide crystals is suggested. It combines the features of two earlier electron-transfer models by Fischer and Hilsch and by Klick and Kabler into one which, in the language of effective mass theory, amounts to requiring several, but at least three, separate conduction bands having a splitting of the order of 0.1 eV. On the basis of this model, both the fine structure of the cesium halide *F* bands and the unusually high multiplicity of cesium halide exciton bands can be consistently understood. Further implications of the model are discussed.

I. INTRODUCTION

In contrast with most alkali halides, the cesium halides show marked structure in absorption bands attributed to *F* centers.[1,2] As is well known, the *F* center is composed of an electron bound to a negative ion vacancy, a model well verified in the noncesium alkali halides and one which seems most reasonable to associate with the *F* bands seen in the cesium halides. Except for CsF, the cesium halides possess simple cubic Bravais lattices, so it appeared possible,[1] at least, that the *F*-band splitting in CsCl and CsBr was a consequence of the different local structure of the *F* center. The discovery of similar structure in CsF, a face-centered cubic crystal, eliminated this possibility,[2] while experiments on simple cubic phases of normally fcc alkali halides also failed to reveal structure-induced splitting in rubidium halide *F* centers.[3] Consequently, the blame seemed to fall on cesium itself, and Suffczynski[4] computed the spin-orbit splitting expected in a certain localized effective mass state in a cesium halide. His results indicated that the splitting should be negligible, again opening the entire issue to speculation.

It is our belief that spin-orbit effects do produce at least part of the *F*-band splitting, but in a more indirect way than that considered by Suffczynski. We propose that there are three conduction-band branches in the cesium halide crystal which display a splitting appropriate to that seen in the *F* band. This contention is supported by the existence of a similar unusual structure in the exciton bands of the cesium halides, which are, therefore, also to be understood on a many-branch conduction-band model.

II. THEORY

In Fig. 1 we present three hypothetical band structures of alkali halides. It is Fig. 1 (a) which we suggest represents the band structure of alkali halides not containing cesium, and Fig. 1 (b) which we suggest represents that of the cesium halides. Figure 1 (c) shows an

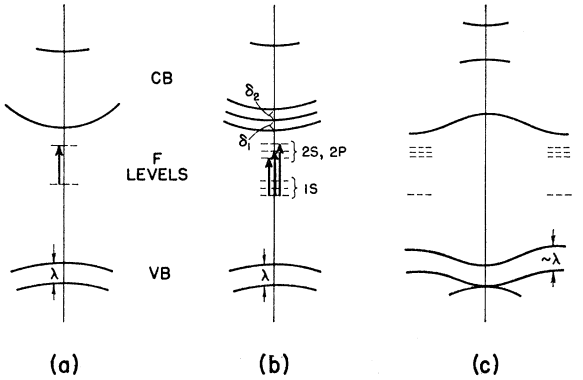

FIG. 1. Schematic band structures for alkali halide crystals. (a) Bands for crystals not containing cesium. (b) Proposed bands in cesium halides. (c) Possible bands in the cesium halides (see text). In all cases, λ is the spin-orbit splitting of the valence band.

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[1] H. Rabin and J. H. Schulman, Phys. Rev. Letters **4**, 280 (1961); Phys. Rev. **125**, 1584 (1962) (for CsCl, CsBr).

[2] F. Hughes and H. Rabin, J. Phys. Chem. Solids **24**, 586 (1963) (for CsF).

[3] D. Fitchen, Thesis, University of Illinois, 1962 (unpublished).

[4] M. Suffczynski, J. Chem. Phys. **38**, 1558 (1963).

alternative model in which the usual direct exciton and band-to-band transitions take place at an edge of the Brillouin zone. Here, impurity levels constructed from the conduction band could have a valley-valley splitting. For reasons discussed below, this structure is only a possibility, not a likelihood.

With a sufficiently large perturbation (such as that provided by a negative ion vacancy), localized impurity levels can drop out of one band and "through" another.[5] Thus, the localized levels shown in Fig. 1 (b) are taken to correspond to states built primarily from any of the three lowest conduction bands. For example, the middle "1*S*" state and the middle states marked "2*S*, 2*P*" both come from the middle conduction band. It is likely that only the lowest "1*S*" state will be populated at ordinary temperatures, since the "1*S*" splittings will be of order $\gtrsim 0.07$ eV, the proposed conduction-band splittings. Thus, the three observed *F*-band transitions are taken to correspond to the three transitions marked in Fig. 1 (b).

Although it is very difficult to make our discussion more quantitative, we will assume for definiteness that the three conduction band branches have symmetries Γ_6^+, Γ_6^-, and Γ_8^-, in increasing order of energy.[6] These symmetries would result from one *s*-like band and a spin-orbit split *p* band.

The over-all symmetry of an impurity state will correspond to one of the irreducible representations contained in

$$\Gamma_e \times \Gamma_c ,$$

where Γ_e and Γ_c are the irreducible representations to which the envelope function F_{nl} and conduction electron state belong, respectively.[7] On the other hand, the over-all symmetry of an exciton state[8,9] constructed from Bloch states near the center of the zone is given by any of the irreducible representations contained in the direct product

$$\Gamma_v \times \Gamma_e \times \Gamma_c , \tag{2}$$

where Γ_v is the valence band electron symmetry.[7]

Since it is quite clear that the ground state of the *F* center will have 1*S* symmetry (Γ_6^+) we can conclude that allowed dipole transitions can occur to excited states having Γ_6^- and Γ_8^- symmetry:

$$\Gamma_6^+(\text{ground state}) \times \Gamma_{15}(\text{light}) = \Gamma_6^- + \Gamma_8^- . \tag{3}$$

Thus, using Eq. (1), we see that allowed transitions may be made to 2*S*-like *F*-center states built from the upper two conduction bands and a 2*P*-like state built from the lower one.[10] Here *S* and *P* refer to envelope symmetries. [An illustration of states such as these may be seen in Figs. 10 (b) and 10 (c) of Ref. 9.] Since 2*S* and 2*P* states will not necessarily have identical energies in a non-Coulombic potential, and since different electron masses and, therefore, binding energies will be associated with each conduction band, it is clear that the spacings seen between *F*-center peaks will not precisely reflect the conduction band spacings at $\mathbf{k}=0$.

TABLE I. Possible Γ_{15} excitons for the valence and conduction bands and envelope symmetries shown. The "approximate energy" is highly schematic; *G*, the exciton Rydberg, is different for each different pair of valence and conduction bands, and central-cell and non-Coulombic corrections are *not* included in the 1*S* and 2*S* states, respectively. See text regarding "degeneracy." The energies λ, δ_1, and δ_2 are the splittings shown in Fig. 1 (b).

Level no.	Envelope	Valence electron	Cond. electron	Degeneracy	Approx. energy
1	1*S*	$\Gamma_8^-(p\frac{3}{2})$	$\Gamma_6^+(s\frac{1}{2})$	1	E_G-G
2	2*S*	$\Gamma_8^-(p\frac{3}{2})$	$\Gamma_6^+(s\frac{1}{2})$	1	$E_G-\frac{1}{4}G$
3	2*P*	$\Gamma_8^-(p\frac{3}{2})$	$\Gamma_6^-(p\frac{1}{2})$	3	$E_G-\frac{1}{4}G+\delta_1$
4	2*P*	$\Gamma_8^-(p\frac{3}{2})$	$\Gamma_8^-(p\frac{3}{2})$	6	$E_G-\frac{1}{4}G+\delta_1+\delta_2$
1′	1*S*	$\Gamma_6^-(p\frac{1}{2})$	$\Gamma_6^+(s\frac{1}{2})$	1	$E_G-G+\lambda$
2′	2*S*	$\Gamma_6^-(p\frac{1}{2})$	$\Gamma_6^+(s\frac{1}{2})$	1	$E_G-\frac{1}{4}G+\lambda$
3′	2*P*	$\Gamma_6^-(p\frac{1}{2})$	$\Gamma_6^-(p\frac{1}{2})$	2	$E_G-\frac{1}{4}G+\delta_1+\lambda$
4′	2*P*	$\Gamma_6^-(p\frac{1}{2})$	$\Gamma_8^-(p\frac{3}{2})$	2	$E_G-\frac{1}{4}G+\delta_1+\delta_2+\lambda$

In the foregoing we have neglected all envelope symmetries in the excited states except 2*S* and 2*P*, for simplicity. For the case of the exciton, we must include 1*S* states (the lowest excited bound pairs in the crystal) as well. Thus, a rather large collection of effective-mass exciton states which have Γ_{15} symmetry (those states which can be reached by dipole-allowed transitions) is made available. They are listed in Table I, along with a rough indication of their energies. The "degeneracy" noted there is in addition to the usual threefold degeneracy of Γ_{15} states. It is lifted only when electron-hole exchange effects are accounted for. It should be further noted that the "2*P*" states are prepared in transitions which Elliott calls forbidden.[11] This does not prevent their oscillator strengths from

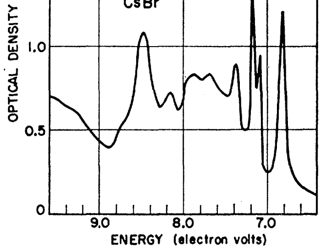

FIG. 2. Absorption spectrum of a CsBr film at 80°K (after Eby *et al.*, Ref. 12).

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[5] P. G. Dawber (private communication).

[6] Our cubic group representation notation follows that of L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, Phys. Rev. **50**, 58(1936), and R. J. Elliott, Phys. Rev. **96**, 130 (1954).

[7] Here, Γ_i is the symmetry of the Bloch state in band *i* at $\mathbf{k}=0$, or that of a localized state constructed from Bloch states. We restrict our discussion to band edges at $\mathbf{k}=0$.

[8] J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).

[9] R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

[10] It is the spin-orbit splitting of the latter (2*P*) state which Suffczynski (Ref. 4) has computed and found to be small.

[11] R. J. Elliott, Phys. Rev. **108**, 1384 (1957); see also footnote 209 of Ref. 9.

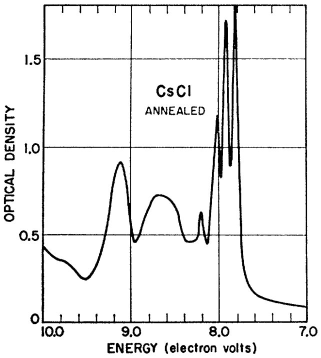

Fig. 3. Absorption spectrum of an annealed film of CsCl at 80°K (after Eby *et al.*, Ref. 12).

being comparable with the "allowed" transitions in our case, because exciton radii in alkali halides are formally of the order of magnitude of the lattice constant. We discuss the applicability of this effective mass theory in the next section.

From the complexity of the available exciton levels, it is evident that one can proceed only qualitatively at this point. We will discuss the three cesium halides involved individually, with the main goal of rendering the case for multiple conduction bands plausible.

Cesium Bromide

The valence splitting is $\lambda \sim 0.6$ eV and the two peaks at 6.8 and 7.4 eV (Fig. 2)[12] are usually attributed to states which we are calling 1 and 1′ (see Table I).

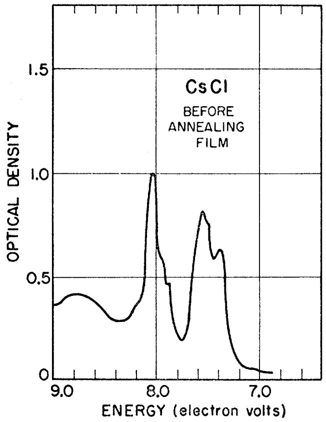

Fig. 4. Absorption spectrum of a CsCl film at 80°K before annealing (after Eby *et al.*, Ref. 12).

Attention is directed to the two sharp lines at 7.2 eV. They may be assigned to levels 3 and 4 of Table I, and have a splitting of about 0.1 eV, which compares favorably with that of a cesium atomic $6p$ function (0.07 eV). These considerations are not new; they were first suggested by Fischer and Hilsch in the terminology of the electron-transfer model.[13] Now in the CsBr F center, there exist three components of over–all splitting 0.2 eV, and it does not seem out of the question that there be a one-to-one correspondence between these and the first three exciton peaks, in the context of the foregoing theory.

Cesium Chloride

Figure 3 indicates clearly that a complicated electronic structure exists in CsCl, as contrasted to all other chlorides.[12] The valence band splitting λ is expected to be 0.1 eV, so any attempt to sort out structure due to conduction-band splittings appears hopeless. There will be strong mixing of all the states listed in Table I, which has the unfortunate consequence that the oscillator strengths of the principal peaks should bear no specific relations to each other. One might venture to say that the smaller peak at 8.2 eV appears to be a $2S$ state. A discussion of the CsCl F center proceeds exactly as in the case of the CsBr F center.

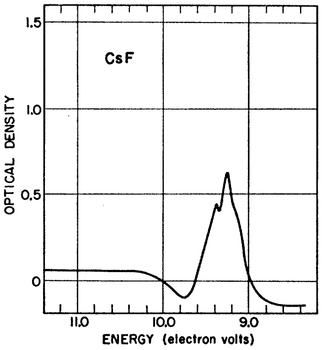

Fig. 5. Absorption spectrum of a CsF film at 80°K (after Eby *et al.*, Ref. 12).

Eby, Teegarden, and Dutton[12] found two phases of CsCl in their experiment, and conjectured that the first or preannealing phase, which showed "normal" halide doublet structure, corresponded to the fcc modification of the crystal (see Fig. 4). It was not verified, however, that this structure really obtained, and one view consistent with the present theory would be that their preannealing phase was merely a disordered sc crystal. [When the annealed-phase absorption spectrum is measured at high (room) temperatures, the structure of Fig. 3, which is 80°K data, washes out and moves toward lower energies.] Another view consistent with the present theory is that the preannealed phase, is, in fact, face-centered cubic, and that there is unresolved structure in the peak at 7.6 eV which again results from a complex conduction-band structure. This peak is abnormally broad.

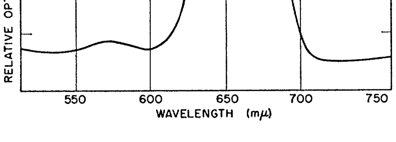

Fig. 6. Absorption spectrum attributed to the F center in CsF at 18°K (after Hughes and Rabin, Ref. 2).

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[12] The data on exciton absorption is that of J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[13] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Gottingen, II. Math. Physik. Kl. **8**, 241 (1959).

Cesium Fluoride

The fluoride doublet splitting is expected to be of the order of 0.05 eV, and has not been observed in any of the fluorides[12] unless we accept the splitting of 0.15 eV seen in CsF (Fig. 5). A splitting of this size is not inconsistent with an intermediate-coupled fluoride doublet,[14] but it is unlikely that both components of the doublet will maintain enough oscillator strength to be readily observable under these conditions.[15] Hence, we take the obvious structure in Fig. 5, along with the apparent weak shoulder at 9.2 eV, as indication that even CsF, a face-centered cubic crystal, enjoys a complex conduction band structure and the striking F-band splitting (Fig. 6) is thereby explained.

III. DISCUSSION

There seems to be no way at present to argue convincingly on purely theoretical grounds that cesium salts have complex conduction bands. The excitation energy of the lowest p level in cesium is the smallest of those of all the alkalis, but is not extraordinarily small (1.38 eV compared with 1.61 eV in K, for example). Other characteristics of cesium are its high polarizability as an ion (Cs^+) and its weak diamagnetism as an atom. The Madelung potential may have a particularly strong effect on a $6p$-like state simply because of its relatively large number of nodes. Only a detailed band calculation can answer such a question, and we must rely on the indirect information supplied by exciton and F-band spectra.

A further word about Fig. 1 (c) is in order. We suggest, there, a simple conduction band but one having minima at the edges of the zone. While this model might explain the F-band splitting as a valley-valley splitting, it would be necessary to bend the valence band upward to provide *direct* excitons, which appear at present to be the lowest excited state of the perfect solid. Such an upward bending in ionic crystals is known at present only in the silver halides, where it occurs as a result of p-d mixing.[16] Although cesium has filled d shells, they are not close enough to the halide p band to cause a large effect, as they are in AgCl. Furthermore, rubidium halides also have filled d bands and we would not care to be forced to propose Fig. 1 (c) for those solids.

Our arguments have been made in the language of Wannier exciton theory merely for convenience. Nearly all models of exciton structure in alkali halides which have been proposed are equivalent in principle,[9,14] and we could as easily have used the language of the electron-transfer model. In that case, we would have been extending Overhauser's exciton calculation[17] by including transfer of electrons from the halide to p-like alkali states as well as s-like alkali states. As remarked above, this has been proposed already by Fischer and Hilsch for CsBr and CsI. Moreover, we are in fact extending a recent F-center model proposed by Klick and Kabler,[18] in which the L bands[19] are attributed to transitions to p-like alkali states in the noncesium alkali halides. In a sense, then, the cesium halide F-band structure is an "F,L complex" in which L bands happen to lie close to the F band and have not lost their strength to conduction states with which they might have been in partial resonance.

Certain experiments will be of interest in checking the F-center model proposed here. One is, of course, the measurement of the F-center absorption in CsI, which has proved difficult to color up to the present. Another is the high temperature spectrum of the other cesium salts' F centers: if the "ground states" built from the upper two conduction bands become appreciably populated, as they may if their energies are only about 0.1 eV above the normally populated ground state, new absorption bands should appear on the long-wavelength side of the presently observed bands.

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[14] R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[15] It should be recalled that a splitting much larger than the minimum (Ref. 14) carries with it the implication that one state is mostly singlet and the other mostly triplet.

[16] R. S. Knox, F. Bassani, and W. B. Fowler, in *Symposium on Photographic Sensitivity* (Maruzen and Co., Ltd., Tokyo, 1963), Vol. 3, p. 11.

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

[18] C. C. Klick and M. N. Kabler, Phys. Rev. **131**, 1075 (1963).

[19] F. Luty, Z. Physik **160**, 1 (1960).