

Calculation of *F*-Band Peak Energy in CsF†

WILLIAM A. SMITH, JR.

Edgerton, Germeshausen and Grier, Inc., Santa Barbara Division, Goleta, California

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A calculation of the *F*-band peak energy in CsF has been made using a quantum-mechanical self-consistent-field method of the variation type. This calculation gave a value of 1.71 eV for the CsF absorption-band peak. This result is only 2.3% lower than the 1.75-eV peak of the triplet absorption measured by Hughes and Rabin in x-ray colored CsF crystals. Similar calculations have been made for *F*-band peaks in LiF, NaF, KF, and RbF and numerical results are presented. Comparison of existing experimental data on the alkali fluorides and the present theoretical results lends credence to the suggestion made by Hughes and Rabin that the triplet absorption at 1.95, 1.86, and 1.75 eV in CsF is due to the *F* center. The absorption peak observed at 2.18 eV in CsF could not be considered as a candidate for the *F*-band, since it is 21.5% higher than the calculated value.

THE optical absorption bands in x-ray irradiated and additively colored CsF investigated by Hughes and Rabin¹ have been found to contain a principal absorption band which displays fine structure. At room temperature the absorption structure consists of a principal triplet with peaks at 1.95, 1.86, and 1.75 eV and a weak component at approximately 2.18 eV. Since the triplet absorption band was found to have many of the properties normally associated with the *F* band in other alkali halides, Hughes and Rabin concluded that this triplet in CsF should probably be assigned as the *F* band. Many speculations have been advanced to explain the *F*-band splitting observed in CsBr, CsCl, and now in CsF. These speculations have been summarized by Knox² in a paper which proposes a model for understanding the fine structure of the cesium halide *F* bands as well as the unusually high multiplicity of cesium halide exciton bands.

The purpose of this paper is to report the results of a theoretical calculation of the *F*-band peak energy in CsF using a method due to Simpson.³ The validity of this method has been discussed elsewhere^{4,5} and will not be commented upon here. Since the Simpson method was used previously to predict with good accuracy,⁶ the *F*-band location in the halides of Li, Na, K, and Rb, its application to the CsF problem seemed worthwhile.

Briefly, the problem is reduced to one of determining the wave function of an electron bound to a positive point charge (a negative ion vacancy) by a Coulomb force acting in a polarizable medium. A quantum-mechanical self-consistent field method of the varia-

tion type has been used. Hydrogen-like electron wave functions containing one variable parameter were chosen for the ground state for which $\Psi_{1s} = (\lambda^3/7\pi)^{1/2} \times (1 + \lambda r) \exp(-\lambda r)$, and for the first excited state for which $\Psi_{2p} = (\beta^5/\pi)^{1/2} r \exp(-\beta r) \cos\theta$. Further, it was assumed that the principal absorption peak arises from an optical transition between these states.

Since the equations to be solved for best values of the variable parameters were rather cumbersome from a computational standpoint, the entire problem was coded for solution on a Recomp-II computer. The input data included values of the interionic spacing a_0 , the ionic polarizabilities⁷ α_1 (negative ion) and α_2 (positive ion), and the dielectric constants K and K_0 . Values for the input constants of CsF were available in the literature⁸ with the exception of a value for the dielectric constant K . An estimate for K was obtained by plotting values of the polaron theory constant C , defined by $C = (1/K_0) - (1/K)$, versus values of the interionic spacing for LiF, NaF, KF, and RbF and extrapolating the smooth curve drawn through these points to give a value of C for CsF. The value of C thus determined was 0.314. Using this extrapolated value for C and the experimental value of 2.19 for K_0 , one obtains a value of 7.02 for the dielectric constant of CsF.

The computer-calculated best values for the variable parameters λ and β were 0.446 and 0.075 Hartree atomic unit, respectively. Using these parameters in the energy equations gave 1.777 eV for the ground-state energy E_{1s} and 0.067 eV for the excited-state energy E_{2p} . The transition energy ΔE_{1s-2p} was found by difference to be 1.71 eV (a peak wavelength of 7250 Å). This value is only 2.3% lower than the 1.75-eV peak of the triplet absorption reported by Hughes and Rabin. It is to be noted that this result is in sharp contrast to the poor agreement obtained when using the empirical Ivey equation⁹ which predicts a peak energy of 2.33 eV for the *F* band in CsF—a deviation

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⁶ W. A. Smith, Jr. and A. B. Scott, *Phys. Rev.* **91**, 219 (1953). Details of the calculations are given in an AEC Research and Development Report KAPL-1720, April 1957 (unpublished).

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⁸ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), 2nd ed., p. 12.

⁹ H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

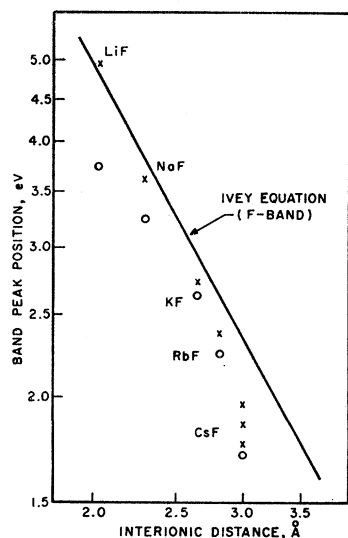


Fig. 1. The circles are the calculated F -band positions at room temperature for the alkali fluorides, and the crosses are experimentally determined positions. A compilation by Gourary and Adrian (Ref. 5) was used for the LiF, NaF, and KF experimental points. The data of Hughes and Rabin (Ref. 1) were used for RbF and CsF. The three experimental points for CsF are the 1.75-, 1.86-, and 1.95-eV components of the triplet absorption. The solid line is that obtained from the empirical relation of Ivey (Ref. 9).

of 33% from the 1.75-eV triplet peak and 19% from the 1.95-eV triplet peak. Table I summarizes the numerical results.¹⁰

Since the extrapolation method used to obtain a value of the dielectric constant K for CsF could introduce an unknown error into the calculation of the F -band peak energy, it was pertinent to evaluate the dependence of the calculated peak energy upon K . Values of K ranging from 6.5 to 12.0 were used as input constants, and the computed peak energy ranged from 1.70–1.74 eV—a variation of only 2% for a two-fold difference in the dielectric constant. Thus, we see that even a gross error in the input value chosen for K would have a negligible effect on the calculated F -band peak energy in CsF.

In Fig. 1 we have displayed experimental data for

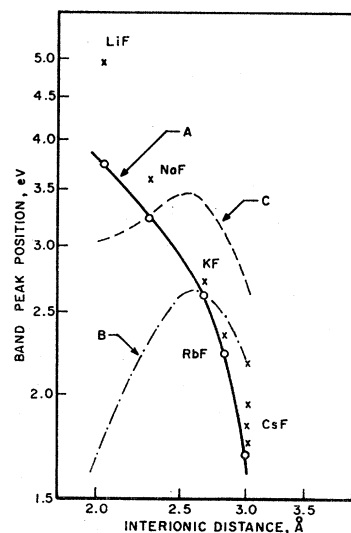


Fig. 2. Curve A shows the results of the present theoretical calculation of F -band peak energies in the alkali fluorides. The crosses are experimentally determined peak energies. Curve B was obtained by using the ionic radii ratios of Pauling as correction factors to adjust the data of curve A. Curve C was obtained by adjusting curve A with ionic radii ratios from experimentally determined electron density distribution maps of the alkali fluorides (Ref. 5).

¹⁰ The values of β and E_{2p} for LiF, NaF, KF, and RbF in Table I differ slightly from the values given in KAPL-1720 (Ref. 6). A minor error was found in the computer program used in the previous work.

F -band peaks in the alkali fluorides together with the F -band peak energies calculated by the method described above. The Ivey equation is plotted for reference, and it is obvious that much better agreement between calculated and experimental results is obtained with the present work than with the empirical Ivey relationship. The notable exception, of course, is LiF.

Attempts were made to adjust the calculated peak energies by using the positive ion to negative ion radius ratio as a correction factor. These attempts were not particularly illuminating since the LiF points were all low by a factor of about 2. In Fig. 2 we have plotted the results of the present calculation (curve A) and two adjusted curves. Curve B was obtained by using the ionic radii data of Pauling, and curve C was obtained by using ionic radii derived from experimental electron density distribution maps of the alkali halides.⁵ Two observations are pertinent: First, the Pauling data bring the theoretical CsF point into exact coincidence with the 2.18-eV experimental point of

TABLE I. Calculated values of the F -band peak energy ΔE_{1s-2p} in the alkali fluorides. The variable parameters determined for the ground state and the first excited state are listed under λ and β , respectively. Experimental F -band peak energy ΔE_{obs} is given for comparison.

Crystal ^a	Variable parameters ^b		Calculated energies ^c			F -band ΔE_{obs}	Error %
	λ	β	E_{1s}	E_{2p}	ΔE_{1s-2p}		
LiF	0.655	0.493	4.31	0.56	3.75	4.96	-24.4
NaF	0.600	0.460	3.91	0.67	3.24	3.64	11.0
KF	0.529	0.369	2.80	0.18	2.62	2.73	4.0
RbF	0.492	0.099	2.34	0.10	2.24	2.36	-5.1
CsF	0.446	0.075	1.78	0.07	1.71	1.75 ^d	-2.3
						1.86	-8.1
						1.95	-12.3

^a Room temperature values of the crystal properties were used.

^b Variable parameters are given in Hartree atomic units where λ is defined by $\Psi_{1s} = (\lambda^3/7\pi)^{1/2}(1 + \lambda r) \exp(-\lambda r)$ and β is defined by $\Psi_{2p} = (\beta^5/\pi)^{1/2} \exp(-\beta r) \cos\theta$.

^c Energies are given in electron volts.

^d Hughes and Rabin triplet (Ref. 1).

Hughes and Rabin; and second, use of the ionic radii from electron density maps gives an adjusted curve which shows very large deviations from the experimental curve for KF, RbF, and CsF. The two adjusted curves are displaced from each other, as shown, because of the different normalizing factors involved. The Pauling ionic radii ratio for KF is 0.978 and is used as the normalizing factor for curve B, whereas the NaF ratio of 1.01 is used for curve C. Substantially, the same result was obtained with the ionic radii data of Goldschmidt⁵ as with the Pauling data.

We interpret the results of the present theoretical calculation of F -band peak energy in CsF as lending credence to the suggestion made by Hughes and Rabin¹ that their triplet absorption is due to the F center. The absorption peak observed at 2.18 eV in CsF could not be considered as a candidate for the F band, since it is 21.5% above the theoretical curve in sharp contrast to the good agreement observed for NaF, KF, RbF, and any one of the three peaks of the CsF triplet absorption.