

Role of Crystal Structure in the F -Center Spectrum of Cesium Halides*

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Spectral positions of the F centers of cesium halides (body-centered cubic structure) are computed by applying a purely geometry-dependent theory, the point-ion-lattice approximation of Gourary and Adrian. Results are compared with those previously obtained in alkali halides with NaCl structure (two superimposed face-centered cubic lattices). Although theoretical results coincide well with the Mollwo-Ivey relation regardless of type of crystal structure, experiments show large deviations from this relation in certain cases. Since the point-ion-lattice approximation does not predict these deviations, it is concluded that within this approximation difference of geometry alone has insignificant effect on spectral positions of F centers in the alkali halides, and that the point-ion-lattice method is not sufficient for their computation.

INTRODUCTION

RECENT studies of color centers in cesium halide single crystals^{1,2} showed that the F -band wavelengths closely follow a Mollwo-Ivey-type^{3,4} relation: $\lambda_{\max} = (\text{const})a_0^n$, where a_0 is the nearest neighbor distance (half-body diagonal). The exponent n is found to be *circa* 2.5 (although, of course, it varies somewhat with temperature). In the case of the F band in alkali halides with the NaCl structure, Ivey⁴ obtained an average value of $n=1.84$ from experimental data.

Attaching great physical significance to this average value can prove quite misleading. However, an examination of the plot of $\log(\lambda_{\max})$ vs $\log(a_0)$ (Fig. 1) indicates that among the NaCl-structure crystals⁵ considerable variation from the Mollwo-Ivey relation occurs from substance to substance. There is some grouping of certain crystals that obey the Mollwo-Ivey relation much more closely (where, for example, NaF, NaCl, KCl, NaI is one group, KF, NaBr, KI another, etc.). Within these groups the exponent lies between 1.65 and 1.70 at room temperature; the constant, of course, varies from group to group. Crystals with constant cations and varied anions tend to form a single such group, but with notable exceptions: e.g., between KF and KCl $n \approx 1.2$; between KCl and KBr $n \approx 2.5$; and between NaCl and NaBr $n \approx 2.45$.

It has previously been a natural first assumption to associate differences in the Mollwo-Ivey exponent with differences in crystal structure⁶ and thereby explain the apparent deviation in the Mollwo-Ivey law between the body-centered cubic cesium halides and the NaCl-structure alkali halides. However, as has been shown,

there is considerable deviation from the Mollwo-Ivey law among the NaCl-structure crystals. Thus, we must re-examine the question of the physical significance of the exponent.

POINT-ION-LATTICE METHOD

There exists a relatively simple theoretical method that lends itself well to examination of the role played by crystal structure alone in the spectral position of the F centers: the point-ion-lattice approximation of Gourary and Adrian.⁷ By applying this method to F

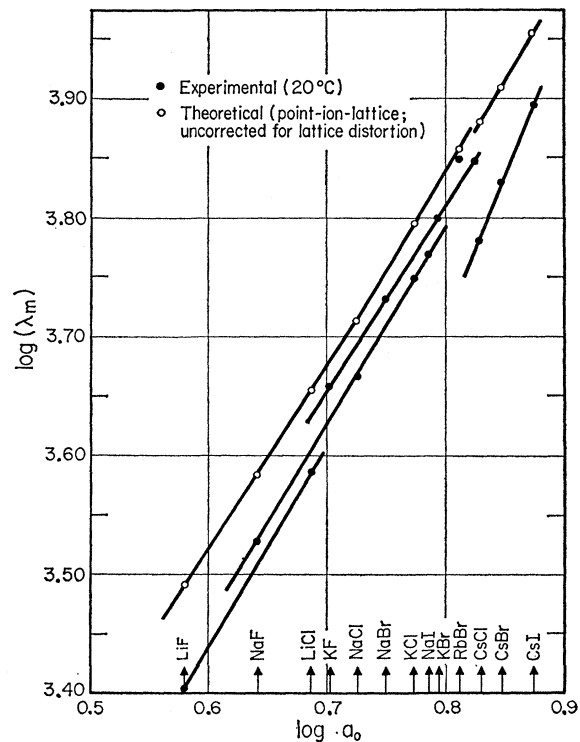


FIG. 1. Comparison of experimental and theoretical data for F centers in face- and body-centered alkali halides. a_0 is the nearest neighbor distance.

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¹ P. Avakian and A. Smakula, *Phys. Rev.* **120**, 2007 (1960).

² A. Smakula, in *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovak Academy of Science, Prague, 1961), p. 729.

³ E. Mollwo, *Nachr. Ges. Wiss. Göttingen, II. Math. Physik Kl.* **97** (1931).

⁴ H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

⁵ Experimental data, all taken at room temperature, taken from J. P. Molnar, Ph.D. thesis, Massachusetts Institute of Technology, 1940 (unpublished); R. Ottmer, *Z. Physik* **46**, 798 (1928); E. Mollwo, *ibid.* **85**, 56 (1933).

⁶ K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press Inc., New York, 1956), p. 22.

⁷ B. S. Gourary and F. J. Adrian, *Phys. Rev.* **105**, 1180 (1957).

centers in the NaCl-structure alkali halides they obtained results that agreed with averaged experimental data to within 15%. Corrections due to lattice-distortion effects improved this agreement somewhat. In our calculations we have essentially followed this method; the major differences are due to the varying geometry of the body-centered cesium halides. The notation of Gourary and Adrian, and Hartree atomic units are used throughout.

A simplified Hartree-Fock method was applied. The binding energy of the F -center electron (E_F^{SH}) is determined by minimizing the functional

$$E_F^{\text{SH}} = \int \psi_n(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V_L(\mathbf{r}) \right] \psi_n(\mathbf{r}) d\mathbf{v}$$

subject to normalization

$$\int [\psi_n(\mathbf{r})]^2 d\mathbf{v} = 1,$$

where $V_L(\mathbf{r})$ is the potential of the trapped electron in the field of a point-ion lattice, assumed perfect for this part of the calculation.

Considering the cesium halide lattice we see that

$$V_L(\mathbf{r}) = \sum'_{x_i, y_i, z_i = -\infty}^{\infty} [(x - sx_i)^2 + (y - sy_i)^2 + (z - sz_i)^2]^{-1/2} \\ - \sum_{x_i, y_i, z_i = -\infty}^{\infty} [(x + \frac{1}{2}s - sx_i)^2 + (y + \frac{1}{2}s - sy_i)^2 + (z + \frac{1}{2}s - sz_i)^2]^{-1/2},$$

where s is the distance between ions of like sign $s = (2/\sqrt{3})a_0$. The primed summation sign signifies that the point $(0,0,0)$ is omitted. Combining these equations,

$$V_L(\mathbf{r}) = \sum''_{x_i, y_i, z_i = -\infty}^{\infty} \frac{(-1)^{x_i + y_i + z_i}}{[(x - \frac{1}{2}sx_i)^2 + (y - \frac{1}{2}sy_i)^2 + (z - \frac{1}{2}sz_i)^2]^{1/2}},$$

where the double prime of the summation sign means the point $(0,0,0)$ is again omitted and x_i, y_i, z_i are either all even or all odd (0 considered even). The only difference in $V_L(\mathbf{r})$ between the body-centered and NaCl-structure crystals is the definition of the summation sign. The resulting expansion of the energy should, thus, also have the same form in both cases, differing only in the set of (x_i, y_i, z_i) over which the sum is taken. Clearly this model ignores all considerations except those of interionic distance and geometry; hence, its applicability to our problem.

V_L is expanded about the center of the vacancy in terms of cubic harmonics (linear combinations of spherical harmonics, which belong to the various irreducible representations of the cubic group). An s function for the ground state and a p function for the excited state to which optical transitions can occur are chosen. In the notation of Gourary and Adrian,

$$\psi_F(\text{ground}) = (1/4\pi)^{1/2} R(\Gamma_1^e, 0, 0 | r), \\ \psi_F(\text{excited}) = (3/4\pi)^{1/2} R(\Gamma_4^e, 1, 0 | r) \cos\theta,$$

where R is the radial function. Using these, only the spherically symmetric term in the expansion of V_L (called V_∞) makes a nonvanishing contribution. After expanding V_L term by term in a series of spherical harmonics, it is found that $V_\infty(r)$ is constant for $0 \leq r \leq a_0$, then undergoes a sharp, Coulomb-like rise for a short distance, whereupon it undergoes violent oscillations. These characteristics of V_∞ are used in choosing the trial functions R .

Two types of trial functions were used (called type II and type III in Gourary and Adrian's notation). Type II

is for a potential constant for $0 \leq r \leq a_0$ and hydrogenic for $r > a_0$. Type III is for a constant negative potential $0 \leq r \leq a_0$, and a large positive constant potential for $r > a_0$. The functions are

III ground

$$R(\Gamma_1^e, 0, 0 | r) = \begin{cases} A j_0(\xi r/a_0) k_0(\eta), & r < a_0 \\ A j_0(\xi) k_0(\eta r/a_0), & r > a_0 \end{cases}$$

where $\eta = -\xi \cot \xi$, and $k_0(x) = e^{-x}/x$;

III excited

$$R(\Gamma_4^e, 1, 0 | r) = \begin{cases} A' j_1(\xi' r/a_0) k_1(\eta'), & r < a_0 \\ A' j_1(\xi') k_1(\eta' r/a_0), & r > a_0 \end{cases}$$

where

$$\eta' = \frac{1}{2} \xi'^2 (\xi' \cot \xi' - 1)^{-1} + \left[\frac{1}{2} \xi'^2 (\xi' \cot \xi' - 1)^{-1} \right]^2 \\ + 2 \left[\frac{1}{2} \xi'^2 (\xi' \cot \xi' - 1)^{-1} \right]$$

and

$$k_1(x) = (1/x + 1/x^2) e^{-x};$$

II ground

$$R(\Gamma_1^e, 0, 0 | r) = \begin{cases} A j_0(\xi r/a_0) e^{-\eta}, & r < a_0 \\ A j_0(\xi) e^{-\eta r/a_0}, & r > a_0 \end{cases}$$

II excited

$$R(\Gamma_4^e, 1, 0 | r) = \begin{cases} A' j_1(\xi r/a_0) e^{-\eta}, & r < a_0 \\ A' j_1(\xi) (r/a_0) e^{-\eta r/a_0}, & r > a_0 \end{cases}$$

$$\eta = 3 - \frac{\xi^2}{1 - \xi \cot \xi}$$

$[j_n(x)$ is the spherical Bessel function of order n].

TABLE I. Minimized energies in cesium halides.

	a_0	E_F^{SH} ground	E_F^{SH} excited	ξ ground	ξ excited	ΔE_F^{SH}
CsCl	6.74	0.200	0.140	2.43	3.41	0.060
CsBr	7.01	0.194	0.138	2.44	3.41	0.056
CsI	7.47	0.185	0.135	2.44	3.42	0.050

It was found (as Gourary and Adrian found for the face-centered alkali halides) that type III gives consistently lower energies for the ground state, and type II for the excited state. Therefore, these are the functions used below.

After performing the integrations (using V_∞ in place of V_L) we find that

III ground

$$E_F^{\text{SH}} = \frac{1}{2a_0^2} \xi^2 (1+\eta)^{-1} - \frac{1}{a_0} \left\{ \alpha_M - \frac{2\xi\eta^2}{(1+\eta)(\xi^2+\eta^2)} \right. \\ \times \sum_{z_i \geq y_i \geq x_i \geq 0}'' h_i (-1)^{x_i+y_i+z_i+1} \\ \times \left[\frac{e^{-2\eta(\rho_i-1)}}{2\eta\rho_i} + e^{2\eta} \text{Ei}(-2\eta\rho_i) \right] \Bigg\}, \\ h_i = \frac{3!}{n_i!} 2^{3-o_i}, \\ \rho_i = \frac{(x_i^2 + y_i^2 + z_i^2)^{1/2}}{\sqrt{3}},$$

where n_i is the number of times any given number occurs in the triplet (x_i, y_i, z_i) ; o_i is the number of times that zero occurs in the triplet; and $\alpha_M = 1.76$ is the Madelung constant for the CsCl lattice (\sum'' has the above-mentioned meaning).

II excited

$$E_F^{\text{SH}} = \frac{1}{2a_0} \left\{ \xi^2 - G(\xi) \left[\frac{2(\xi^2 + \eta^2)}{(2\eta)^5} \right. \right. \\ \times [(2\eta)^4 + 4(2\eta)^3 + 12(2\eta)^2 + 24(2\eta) + 24] \\ \left. \left. - \frac{4}{(2\eta)^3} [(2\eta)^3 + 3(2\eta)^2 + 6(2\eta) + 6] \right] \right\} \\ - \frac{1}{a_0} \left\{ \alpha_M - \frac{G(\xi)}{(2\eta)^5} \sum_{z_i \geq y_i \geq x_i \geq 0}'' h_i (-1)^{x_i+y_i+z_i} \right. \\ \times \frac{e^{-2\eta(\rho_i-1)}}{\rho_i} \left[3 + \frac{9(\eta\rho_i)}{2} + 3(\eta\rho_i)^2 + (\eta\rho_i)^3 \right] \Bigg\},$$

where

$$\frac{1}{G(\xi)} = 1 - \frac{j_0(\xi)j_2(\xi)}{[j_1(\xi)]^2} + \frac{2}{(2\eta)^5} \\ \times [(2\eta)^4 + 4(2\eta)^3 + 12(2\eta)^2 + 24(2\eta) + 24].$$

The minimized energies are given in Table I.

Corrections due to polarization and lattice distortion effects were also treated by approximation, analogous to the Gourary and Adrian method. The largest errors involved in ignoring polarization effects (in the first excited state) are of the order of 3% or less. A great oversimplification is made in the treatment of lattice distortion by allowing only the eight ions nearest the vacancy to move radially, again resulting in insignificantly small corrections. The values of the final corrected wavelengths are given in Table II.

TABLE II. Values of wavelengths (in Å).

	$\lambda_m(\text{exp})$	$\lambda_m(\text{point-ion})$
CsCl	6030	7337
CsBr	6730	7802
CsI	7840	8696

CONCLUSIONS

We see from Fig. 1 that comparison of the results of the point-ion-lattice approximation to body-centered and NaCl-structure alkali halides leads to the conclusion that the differing geometry *per se* of the two structures is not a significant factor in the deviation from the Mollwo-Ivey relation for F centers. Indeed, this comparison indicates the fruitlessness of attaching great physical significance to the Mollwo-Ivey relation. Clearly, the point-ion method can be regarded as no more than a zero-order approximation. Even though comparison with the averaged experimental Mollwo-Ivey relation might lead to the assumption that theory and experiment agree quite well (for the NaCl structure), the assumptions underlying the point-ion model, the ignoring of the effects of exchange, overlap, and finite ion size and structure generally, *a priori* prevent the approximation from predicting the observed irregular deviations from Mollwo-Ivey behavior if these deviations are not dependent on geometry. Since, however, they seem to be geometry-independent and since the deviations are quite significant (especially in the body-centered case), we must conclude the necessity for a theoretical method incorporating the above-mentioned effects.

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