Color-center Absorption Bands for Cesium Halide Crystals

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I. Introduction

Since the F-type and V-type color-center absorption bands were proposed by the experimenters, there have been a number of theoretical analyses of these absorption bands. [1]-[4] Up to now, these theoretical calculations have been confined mainly to the NaCl-type alkali halide crystals.

Recently, P. Avakian and A. Smakula extended the experimental work in this field further to the CsCl-type crystals, and found many abosrption bands. [5] The wave lengths of these absorption band-maxima, are given in Table I.

Table I The spectral position of color-center absorption band-maxima for CsCl-type crystals, in mμ, measured at $-78°C$

	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8	λ_9	λ_{10}
CsCl:	229		270	~370	~430	590	735	780	860	990
CsBr:	244	~280	~315	390	~490	662		850	~930	1065
CsI:	273	333		430	540	768			1065	1200

The CsCl-type crystals and the NaCl-type crystals are both alkali halides, but they are widely different from each other in crystal structure. In view of this, we would expect the absorption bands of CsCl-type to be different from those of the NaCl-type crystals. According to the experiment, the absorption band λ_6 which is given in Table I behaves similarly to the F-band in the NaCl-type crystals. If we want to discuss this point further, a theoretical calculation is necessary. This paper is a theoretical calculation of this problem under the continuum model.

II. Calculations

If the absorption band λ_6 in Table I is the F-band of CsCl-type crystals, this absorption must be produced by F-centers in that cyrstal. An F-center consists of an electron trapped at in the vicinity of a negative ion vacancy. The Hamiltonian of this trapped electron is, therefore, in atomic units,

$$H=-\frac{\triangle}{2}+V \qquad \text{(II-1)}$$

Then, the Schroedinger equation is

$$(-\frac{\triangle}{2}+V)\psi=E\psi \qquad (II\text{-}2)$$

where V is the potential energy. When this electron is at a distance from the negative ion vacancy, if we deal the crystal as a continuous dielectrics, the potential energy of this electron is, in atomic units, $-1/\varepsilon_0 r$. Where r is the distance of this electron from the centre of the negative ion vacancy, ε_0 is the optical dielectric constant. But at the centre of the vacancy, the potential energy is a constant, now, let this potential energy be V_0, the value of V_0 is, in atomic units,

$$V_0=-\frac{A}{a}+\frac{1}{R}(1-\frac{1}{\varepsilon_0}) \qquad (II\text{-}3)$$

The quantity A is known as the Madelung constant and is a property of the crystal structure. a is the distance of the nearest neighbor ions. Thus, the first term is the interaction energy between the electron which is at the center of the ion vacancy and the neighbor ions. The second term of (II-3) is the energy gained from the polarization of the vacancy's surrounding medium when the electron is removed. R is the radius of the vacancy, which for alkali halide cyrstals is

$$R\simeq 0.9a$$

The energy states of this trapped electron can determine by the variation method, thus, we must first calculate the energy E

$$E=\int\psi^*H\psi d\tau \qquad (II\text{-}4)$$

and then minimize the energy value E by varying the parameter. Here ψ is the normalized wavefunction. In this case, we can write this E as

$$E=\int\psi^*(-\frac{\triangle}{2}\psi)d\tau+\int\psi^*V_0\psi d\tau+\int\psi^*(-\frac{1}{\varepsilon_0 r})\psi d\tau \qquad (II\text{-}5)$$

In order to determined the energy level of this trapped electron for the ground state, we must find the wavefunction corresponding to this state. As the F-center is just like the hydrogen atom, the wavefunction of this state must be of the form of

$$\psi_1=(\frac{\alpha^3}{\pi})^{\frac{1}{2}}\exp(-\alpha r) \qquad (II\text{-}6)$$

The α is a parameter. Here, when ψ in (II-5) isreplaced by ψ_1, let E be denoted by E_1. Then, the E_1 may be written

$$E_1=\int_0^\infty\int_0^\pi\int_0^{2\pi}\psi_1^*(-\frac{\triangle}{2}\psi_1)r^2\sin\theta dr d\theta d\varphi+\int_0^R\int_0^\pi\int_0^{2\pi}\psi_1^*V_0\psi_1 r^2\sin\theta dr d\theta d\varphi$$
$$+\int_R^\infty\int_0^\pi\int_0^{2\pi}\psi_1^*(-\frac{1}{\varepsilon_0 r})\psi_1^* r^2\sin\theta dr d\theta d\varphi \qquad (II\text{-}7)$$

Substituting (II-6) in (II-7) and integrating, we obtain

$$E_1=\frac{\alpha^2}{2}-\exp(-2\alpha R)[2V_0(\alpha R)^2+(1+2\alpha R)(V_0+\frac{\alpha}{\varepsilon_0})]+V_0 \qquad (II\text{-}8)$$

Then minimize the energy E_1 by varying the parameter α, thus, we have

$$\alpha+\exp(-2\alpha R)[4V_0\alpha^2R^3+\frac{1}{\varepsilon_0}(4\alpha^2R^2-2\alpha R-1)]=0$$

Now let α_0 denote the α which satisfies the above equation. Substituting this α_0 in (II-8), we get as the energy E_{1s} for its ground state

$$E_{1s}=\frac{\alpha_0^2}{2}-\exp(-2\alpha_0 R)[2V_0(\alpha_0 R)^2+(1+2\alpha_0 R)(V_0+\frac{\alpha_0}{\varepsilon_0})]+V_0 \qquad (II\text{-}9)$$

The values for a, R, V_0 and ε_0 for the CsCl-type crystals are given in Table II, a, R and V_0 are all in atomic units. The Madelung constant of this type crystal is about 1.763. Substituting these values in (II-9), the value of the energy level for the ground state may be gotten. The value of E_{1s} for CsCl-type crystals is given in Table III.

Table II

substance	a	R	ε_0	V_0
CsCl	6.70	6.00	2.60	−0.160
CsBr	7.00	6.30	2.78	−0.150
CsI	7.45	6.70	3.03	−0.137

Since the F absorption correspond to the ls-2p transition of an F-center, we must calculate the energy level for the 2p state. The wavefunction corresponding to this state, may be approximated as

$$\psi_{2}=(\frac{\beta^3}{\pi})^{\frac{1}{2}}\beta r\exp(-\beta r)\cos\theta \qquad (II\text{-}10)$$

the form of this function is like that of hydrogen atom. Substituting this ψ_2 in (II-5) and integrating, we may get the energy E_2

$$E_2=\frac{\beta^2}{2}-\frac{1}{3}V_0\exp(-2\beta R)\{2(\beta R)^4+4(\beta R)^3+6(\beta R)^2+6\beta R+3\}$$
$$+V_0-\frac{\beta}{3\varepsilon_0}\exp(-2\beta R)\{2(\beta R)^3+3(\beta R)^2+3\beta R+\frac{3}{2}\} \qquad (II\text{-}11)$$

Where β is also a parameter. Then minimize the E_2 by varying this parameter β. Accordingly, we have

$$\beta+\frac{4}{3}V_0\exp(-2\beta R)\beta^4R^5+\frac{1}{3\varepsilon_0}\exp(-2\beta R)[4(\beta R)^4-2(\beta R)^3-3(\beta R)^2-3\beta R-\frac{3}{2}]=0$$

Let the β be denoted by β_0 which satisfies the above equation. The numerical value of this β_0 can be calculated. When we put it into equation (II-11), we can

get the energy level E_{2p} for its 2p state

$$E_{2p}=\frac{\beta_0^2}{2}-\frac{1}{3}V_0\exp(-2\beta_0R)\{2(\beta_0R)^4+4(\beta_0R)^3+6(\beta_0R)^2+6\beta_0R+3\}$$
$$+V_0-\frac{\beta_0}{3\varepsilon_0}\exp(-2\beta_0R)\{2(\beta_0R)^3+3(\beta_0R)^2+3\beta_0R+\frac{3}{2}\} \qquad \text{(II-12)}$$

The values of E_{2p} for CsCl-type crystals are given in Table III.

The position of the F absorption band may be deduced, as the energy difference between E_{2p} and E_{1s}, from the next equation

$$h\nu=E_{2p}-E_{1s}$$

These values for CsCl-type cyrstals also are given in Table III.

Table III. The value of E_{1s}, E_{2p} and $h\nu$ in electron volts.

substance	E_{1s}	E_{2p}	$h\nu$ (theoretical value)	$h\nu$(observed value for λ_6)
CsCl	−2.222	−0.845	1.377	2.102
CsBr	−2.087	−0.797	1.290	1.873
CsI	−1.913	−0.740	1.173	1.615

III. Discussion

Following Table III, the theoretical results are about 70% of the experimental results. In the many body problem, this degree of agreement is good. Accordingly, the λ_6 values in Table I must be the wavelengths of F absorption band-maxima, produced by the F-centers.

In this calculation of the potential energy of the trapped electron only two terms in equation (II-2) were used. If we included the other terms which were neglected, even better agreement might be expected.

References

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銫鹵化物結晶之吸收帶

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氯化鈉型結晶之 F 型及 V 型吸收帶經實驗家提出後，即有很多人從事其理論的計算。近幾年來，對於此方面特具興趣的實驗家，又從事銫鹵化物結晶之吸收帶的量度，而於最近，始由 P. Avakian 和 A. Smakula 提出。其實驗結果，如表 I 所示，該表中諸 λ 分示各該結晶之諸吸收帶最大值之位置。

氯化銫型結晶雖亦屬鹼鹵化物結晶，但其結晶構造異於氯化鈉型結晶，於是其吸收帶將與氯化鈉型者不同。從實驗上觀之，表 I 中之 λ_6 吸收帶好像是 F 吸收帶。若想進一步求證此點，吾人須從理論上計算之。本文即是此問題之理論計算，此計算結果可與實驗結果相比，於是吾人可以斷言表 I 中之 λ_6 吸收帶爲 F 吸收帶，而爲該結晶中之 F 中心所引起者。