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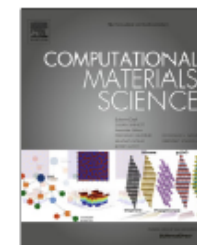


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### *Ab initio* study of F-centers in alkali halides

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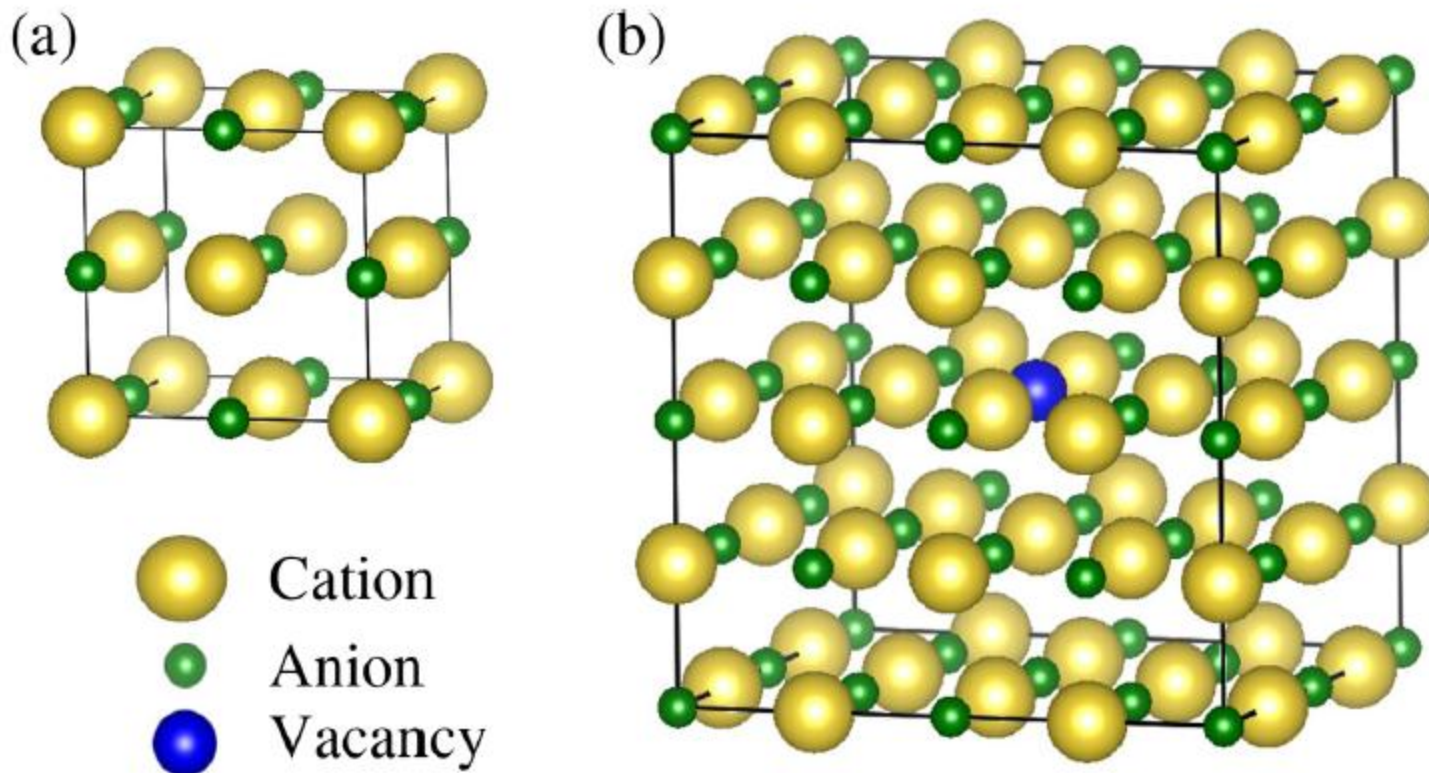
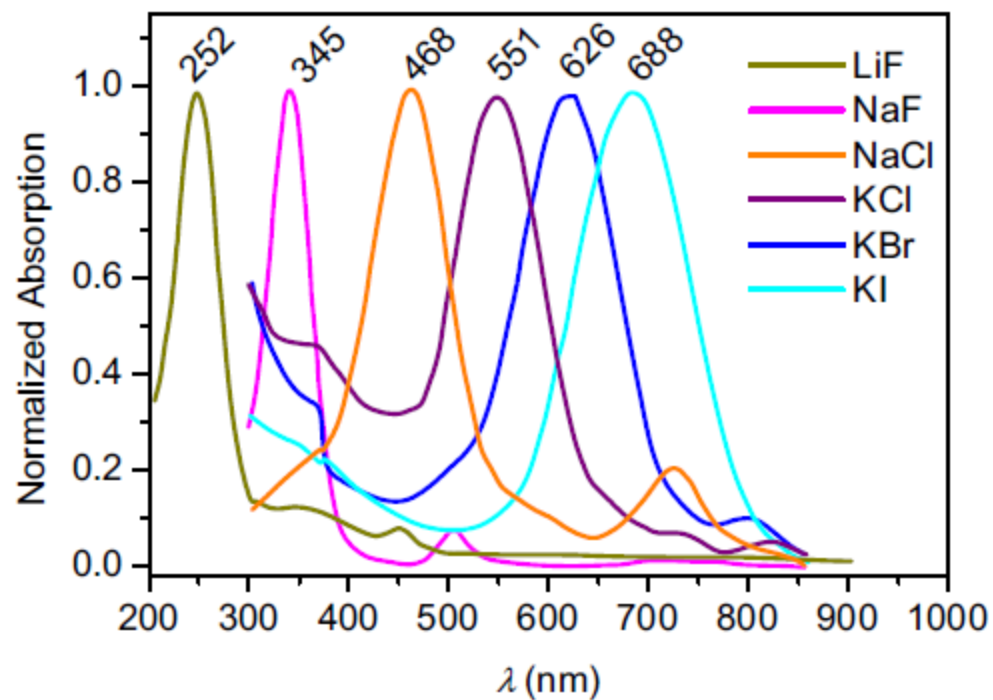
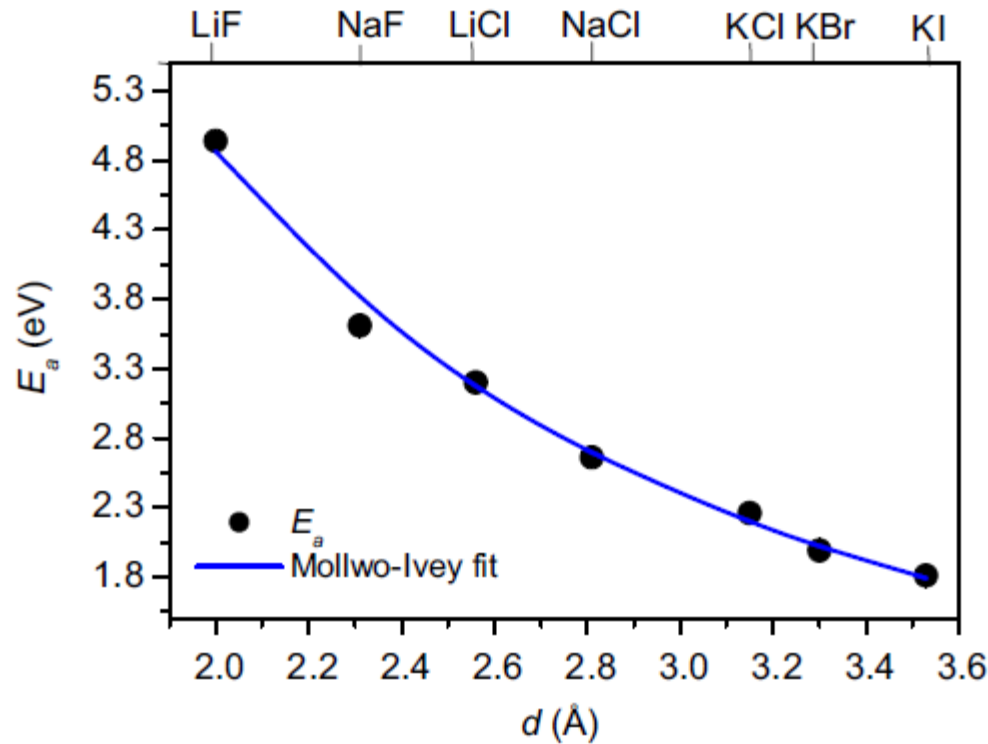


Fig. 3. Cubic NaCl unit cell (a) and  $2 \times 2 \times 2$  supercell with an anion vacancy (b).

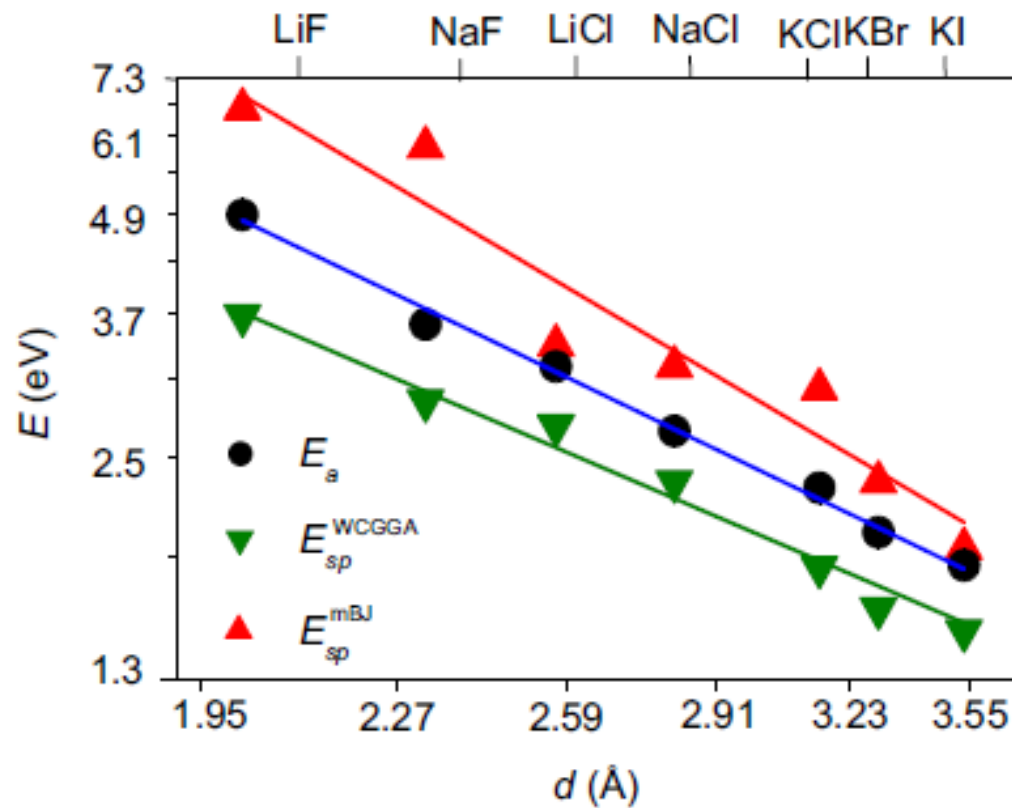


**Fig. 1.** Normalized absorption spectra for the studied compounds. The peak maxima are indicated in nm.



**Fig. 2.** Experimental absorption energy  $E_a$  as a function of the interionic distance  $d$  (the respective system names are indicated on the top). The blue solid line stands for best least-squares fit of the Mollwo-Ivey relation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

# Centros F en Haluros Alcalinos



**Fig. 8.** Experimental absorption energy  $E_a$  and calculated  $E_{sp}$  energies as a function of the interionic distance  $d$  (the respective system names are indicated on the top). Solid lines are best least-squares fits of the Mollwo-Ivey relation for each data set (see text).

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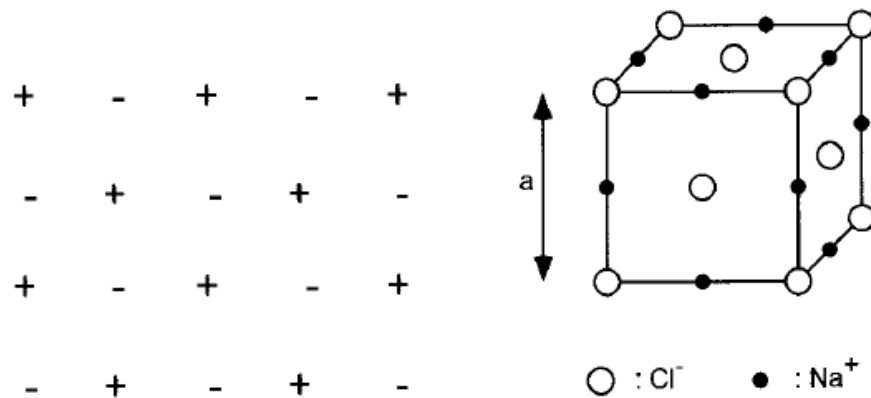
1.	<b>Colored Centers in Ionic Crystals</b> .....	1
1.1	The Mollwo–Ivey Law .....	2
1.2	The Jahn–Teller Effect .....	3
1.3	The Stokes Shift .....	4
1.4	Solutions .....	5
	Further Comments on F-Centers .....	10

**1. Colored Centers in Ionic Crystals**

When a vacancy is created in a crystal, an electron may be trapped at this location. This bound electron can absorb light at well defined frequencies, thus changing the color of the crystal.

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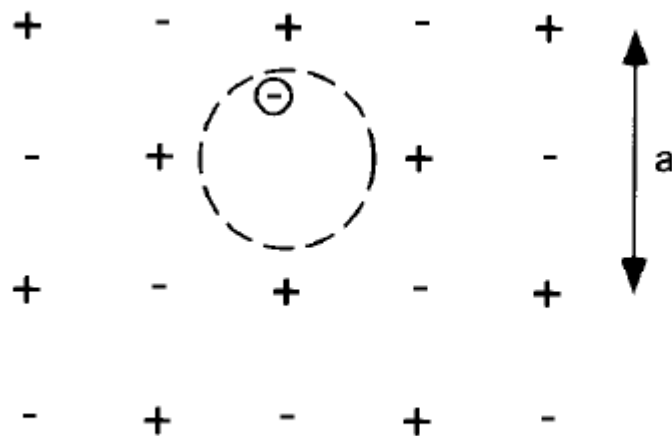
Consider the diatomic crystal NaCl. It is called an ionic crystal because, when the crystal forms, the outer electron of a sodium atom is transferred to a chlorine atom. Hence, in the crystal, the electronic configuration is ( $\text{Na}^+$ ,  $\text{Cl}^-$ ), and the electrostatic interaction between the  $\text{Na}^+$  and  $\text{Cl}^-$  ions is responsible for the binding of the structure. The crystal is face centered cubic for both ions. Schematically, the crystal, as seen parallel to one face of the cube can be represented as in Fig. 1.1. Such a structure, called the NaCl structure, is very frequently encountered. It is, in particular, the structure of all alkali halides.



**Fig. 1.1.** Structure of the ionic crystal  $\text{Na}^+ \text{Cl}^-$ .

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These crystals are transparent if they are sufficiently pure. However, if they are irradiated by energetic photons ( $X$  or  $\gamma$  rays), alkali halides become colored. The reason for this is the following. A photon can eject an anion from its site, creating an unoccupied site called a vacancy. This anion vacancy, surrounded by positively charged ions, can trap an electron and restore the local electrical neutrality of the crystal. The trapped electron has a series of energy levels. It can absorb light and jump from the ground state to an excited state. This process is responsible for the color of the crystal. The electron trapped in the vacancy is called a colored centre, or F-center (from the German Farbenzentrum). The structure of an F-center is shown on Fig. 1.2.

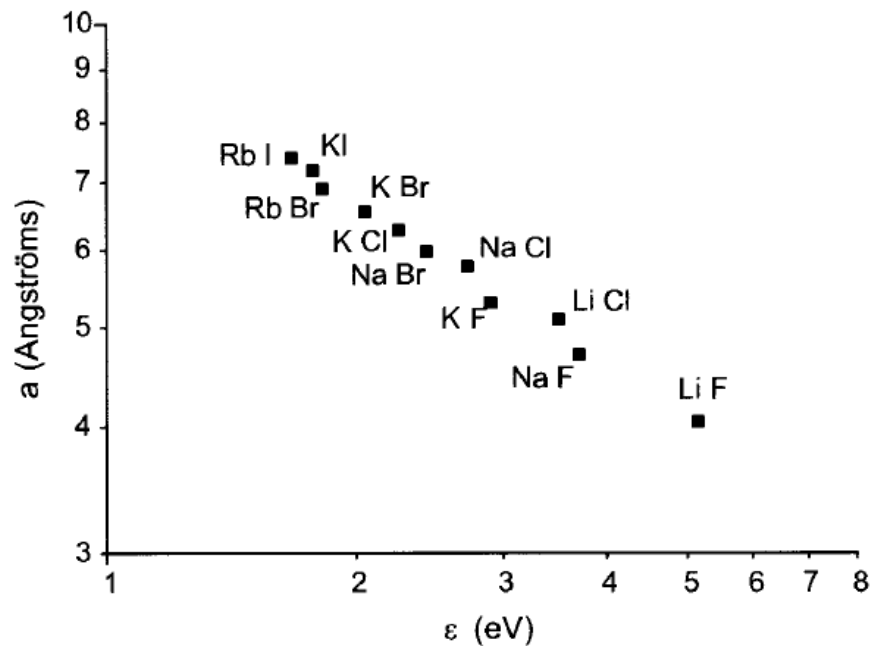


**Fig. 1.2.** Structure of an F-center in a NaCl crystal.



## 1.1 The Mollwo–Ivey Law

Let  $a$  be the lattice spacing, i.e. the distance between two neighboring  $\text{Na}^+$  ions. Measurements of the wavelengths  $\lambda$  or energies  $\varepsilon$  of absorption lines on various alkali halides have been performed by Mollwo and Ivey. The results are displayed in Fig. 1.3. They show that the variations of the absorption energy with the lattice spacing  $a$  follow a simple law.



**Fig. 1.3.** Energy of the absorption peaks of various alkali halides, versus the lattice spacing  $a$ .

**1.1.1.** Express the empirical law that emerges from these measurements as

$$\varepsilon = K a^n, \quad (1.1)$$

where  $\varepsilon$  is in eV and  $a$  is in Å. This is called the Mollwo-Ivey law.

Since, in good approximation, the absorption energy  $\varepsilon$  depends only on the lattice spacing  $a$  and not on its particular nature, one may assume that the shapes of F-centers are the same for all of these crystals and that they only differ by their sizes.

The simplest model one can build consists in assuming that the  $Z$  positive ions nearest neighbors to the F-center form a cubic square well potential inside which the electron is trapped. In first approximation, we shall assume that it is an infinitely deep potential well:

$$\begin{aligned} V &= 0 && \text{for} && 0 < x, y, z < a \\ V &= \infty && \text{otherwise.} \end{aligned}$$

**1.1.2.** What is the number  $Z$  of positive ions directly neighboring to an F-center?

**1.1.3.** Give the energy levels  $E_1$  and  $E_2$  of the ground state and of the first excited state in the potential well, and the corresponding wave functions. What is the degeneracy of each level?

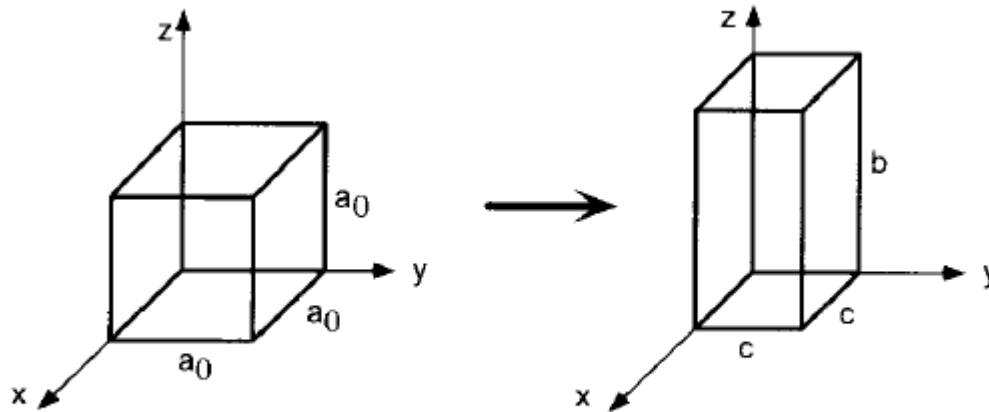
**1.1.4.** Assuming that the absorption of light is due to the transition of the electrons from  $E_1$  to  $E_2$ , express the absorption energy in terms of the lattice spacing  $a$ . Since this model leads to an expression of the form (1.1), compare the experimental and the theoretical values of the exponent  $n$  and of the constant  $K$ .

**1.1.5.** Clearly, the previous simple model accounts quite successfully for the exponent  $n$  but not for the constant  $K$ . In order to cure this defect, we remark that the size of the square well is rather arbitrary. By introducing an *effective* size  $a_0 = \alpha a$ , choose  $\alpha$  in order to fit the experimental data. Give a brief physical comment on the effective size  $a_0$  of the well. Plot the theoretical curve of Fig. 1.3.

## 1.2 The Jahn–Teller Effect

When a state of a nonlinear molecule is degenerate, one can show that a distortion of the molecule lifts the degeneracy and stabilizes the molecule. This general effect is called the Jahn-Teller effect<sup>1</sup>. In the present case, the F-center and the surrounding ions can be considered as a pseudomolecule which can undergo a Jahn-Teller distortion.

<sup>1</sup> H.A. Jahn and E. Teller, Proc. Royal Soc. A **161**, 220 (1937).



**Fig. 1.4.** Distortion of an F-center.

**1.2.1.** Let us distort the potential well of the vacancy into a parallelepiped as shown in Fig. 1.4. The lengths along the  $x$  and  $y$  axes are equal and denoted  $c$  in the following. The length along the  $z$  axis is  $b$ . It is reasonable to assume that, owing to the rigidity of the crystal, this distortion occurs at constant volume, i.e.  $a_0^3 = bc^2$ . The distortion is characterized by the parameter  $\eta = b/c$ .

Show that this distortion lifts the degeneracy of the excited level  $E_2$ .

Calculate the dependence of the corresponding excited sublevels on the parameter  $\eta$ . Show that for each excited state, the energy is minimum for a certain value of  $\eta$ . We denote by  $E_2^0$  the smallest energy, corresponding to a value  $\eta_0$  of the distortion. Is the F-center stretched along the  $z$  axis or flattened in the  $(x, y)$  plane?

**1.2.2.** Calculate the variations with respect to  $\eta$  of the ground state energy  $E_1$ . Calculate the value  $E_1^0 = E_1(\eta_0)$ .

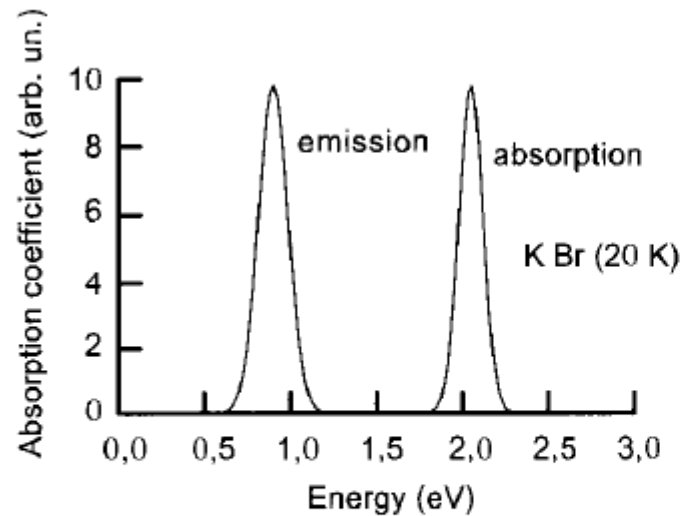
**1.2.3.** Plot the variations of  $E_1$  and  $E_2$  as a function of  $\eta$ .

## 1.3 The Stokes Shift

We can now give a simple account of the absorption and emission of light by an F-center. In Sect. 1.1, we have described the absorption of light by an F-center. After a time of the order of  $10^{-6}$  s, the electron makes a transition to the ground state and emits radiation, called “luminescence”.

Experiment shows that the emission lines are systematically shifted towards longer wavelengths – or equivalently smaller energies – than the corresponding absorption lines. This shift, an example of which is shown in Fig. 1.5 is called the Stokes shift.

**1.3.1.** Let us first assume that most lines are shifted to the infrared part of the spectrum, which is not visible. Under this assumption, by what *simple* mechanism do the F-centers color a crystal when the crystal is placed in visible light?



**Fig. 1.5.** Absorption and emission spectra of an F-center in KBr at low temperature. The maxima of the two lines are respectively at 2.06 and 0.92 eV. Data are taken from W. Gebbart and A. Kuhnert, *Physica Status Solidi*, **14**, p.157 (1966).

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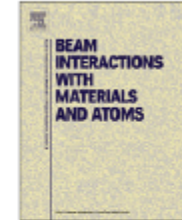


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## Basic properties of the *F*-type centers in halides, oxides and perovskites

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**Table 1**Optical absorption peak energies of the *F* center in alkali halides

[39] R.K. Dowson, D. Poole, Phys. Status Solidi 35 (1969) 95.

Crystal	Lattice constant	<i>F</i> center absorption energy (eV)
LiF	4.028	5.083
LiCl	5.14	3.256
LiBr	5.502	2.767
LiI	6.00	3.176
NaF	4.634	3.702
NaCl	5.64	2.746
NaBr	5.978	2.345
NaI	6.474	2.063
KF	5.348	2.873
KCl	6.294	2.295
KBr	6.596	2.059
KI	7.066	1.874
RbF	5.63	2.409
RbCl	6.582	2.036
RbBr	6.89	1.851
RbI	7.342	1.705

It has been observed that the *F*-band absorption energies  $E_F$  are approximately proportional to the inverse square of the lattice parameter  $a$ , which is called the Mollwo-Ivey law:

$$E_F = 17.7a^{-1.84} \quad (1)$$

where  $a$  is in Angstroms and  $E_F$  in electron volts. This relation has been first derived by Mollwo in 1931 [42] and later modified by Ivey in 1947 [43].

This relation has its origin in the simple picture of an electron in a potential well [44]:

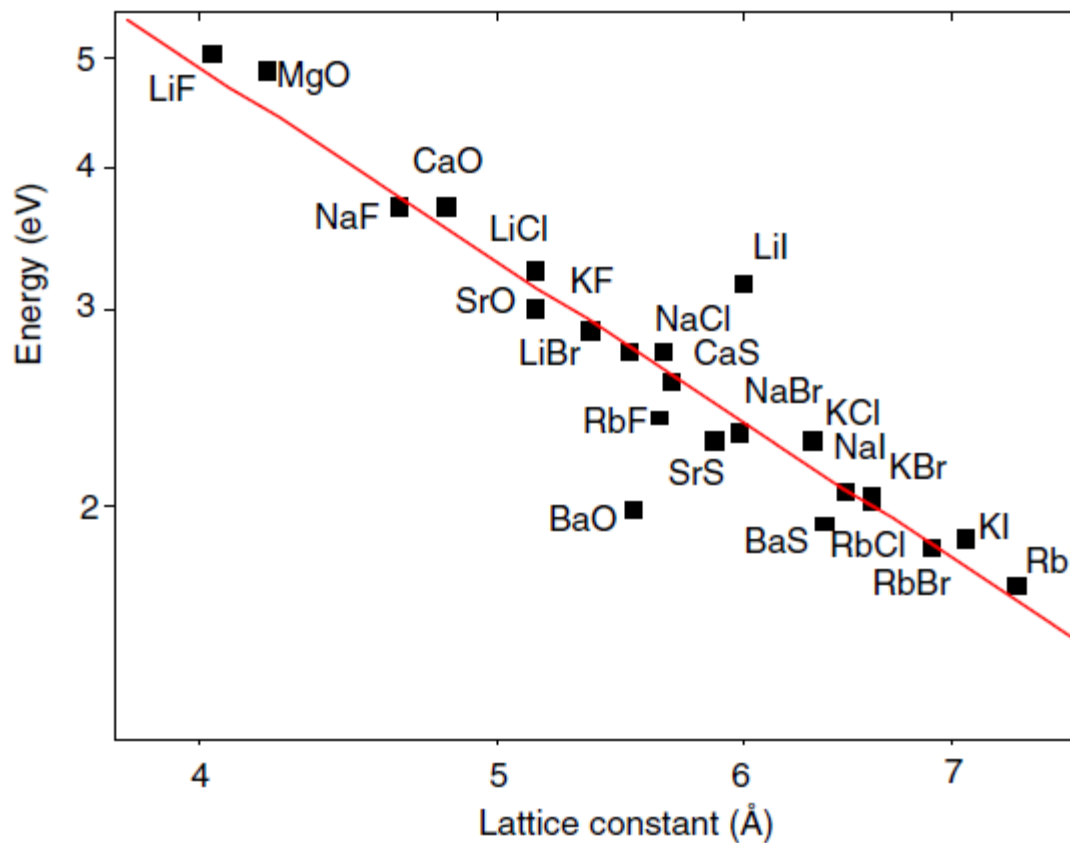
$$\Delta E = E_{2p} - E_{1s} = 3\pi^2\hbar^2/8md^2 \quad (2)$$

where  $E_{1s}$  and  $E_{2p}$  represent the energy in the ground state and the excited state, respectively.  $m$  is the effective electron mass and  $d$  the width of the potential well (Me-X distance =  $1/2 a$ ).

[42] E. Mollwo, Nachr. Ges. Wiss. Göttingen II Math. Physik. Kl. (1931) 97.

[43] H.F. Ivey, Phys. Rev. 72 (1947) 341.

[44] W.B. Fowler, Physics of Color Centers, Academic Press, 1968, p. 57.



**Fig. 1.** The generalized plot of Mollwo-Ivey relation for the  $F$  band in alkali halides, oxides and sulfides with f.c.c. structure.