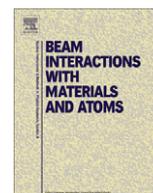




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## Nuclear Instruments and Methods in Physics Research B

journal homepage: [www.elsevier.com/locate/nimb](http://www.elsevier.com/locate/nimb)Basic properties of the *F*-type centers in halides, oxides and perovskitesA.I. Popov<sup>a,b,c,\*</sup>, E.A. Kotomin<sup>a,b</sup>, J. Maier<sup>a</sup><sup>a</sup>Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany<sup>b</sup>Institute for Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV-1063, Latvia<sup>c</sup>Institute Laue Langevin, 6 rue Jule Horowitz, 38042 Grenoble, France

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## ABSTRACT

We present a short survey of the optical properties of primary radiation-induced point defects in alkali halides, simple oxides and some  $ABO_3$  perovskites. We discuss in details the optical properties of single electron *F* and  $F^+$  centers in rock-salt (f.c.c.) alkali halides and oxides and show that the Mollwo–Ivey law well-known for the *F*-type centers in alkali halides may be extended for other rock-salt structure insulators. We also discuss the major differences in point defect production mechanisms in halides and oxides. We show that the Rabin–Klick diagram may be generalized for a whole family of alkali halides. The *F*-type center migration and aggregation into metal colloids in alkali halides and oxides is also discussed.

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## 1. Introduction

In the last 50 years much attention has been paid to the radiation-induced formation of lattice defects in alkali- and alkaline-earth halides. Several review papers and books have been published [1]. The defects in these materials are traditionally called color centers and were classified in a few large groups among them the electron centers, the hole centers and the interstitials are very prominent primary radiation point defects. As to the electron centers, the *F*-centers are among the most intensively investigated point defects therein. The ordinary the *F*-center consists of a single electron trapped at a halogen vacancy.

Now it is firmly established that the *F*-centers in alkali halides arise through a non-radiative recombination of electron–hole pairs via intermediate creation of the self-trapped excitons (STE). Such the non-radiative exciton decay is accompanied also by a simultaneous creation of interstitial halide atoms (or so called *H* centers). Both neutral *F* and *H* centers form the so-called neutral Frenkel defect pair.

At low-temperature irradiation, the *F*–*H* pairs are spatially well correlated within the so-called geminate pairs. Because of the electron tunnelling between electron and hole components of such close Frenkel pairs, secondary charged Frenkel defects, the so-

called  $\alpha$ - and *I* centers, arise also. The main portion of *F* and *H* centers created in alkali halides are destroyed by the mutual recombination almost immediately even at 2 K after the pulsed electron irradiation [2]. Processes of the correlated recombination of *F*–*H* and  $\alpha$ –*I* defect pairs with the detailed analysis of experiments have been reported [3]. Their annealing is caused by *I* and *H* center motion, as the temperature increases typically above 10–50 K, since the electron partners ( $\alpha$  and *F* centers) become mobile at much higher temperatures, close to (or higher than) RT. The stabilization of the *H* centers by “foreign” ions of alkali metals with the formation of the so-called  $H_A$  centers has been observed [4].

Note that all these color centers can be studied by means of the optical spectroscopy, and for most alkali halides their appropriate absorption bands are firmly established. The appropriate data for optical absorption of the *F* centers in alkali halides are summarized in Table 1 together with the corresponding data for the band gap energies and lattice constant parameters.

The *F* centers have been observed in incredibly large range of inorganic materials, including oxygen containing compounds, like MgO, CaO, BaO [5,6], BeO [7], ZnO [8],  $Al_2O_3$  [9,10],  $Li_2O$  [11–13], yttria-stabilized zirconia YSZ (or  $ZrO_2:Y$ ), [14,15],  $YAlO_3$  [16] and  $Y_3Al_5O_{12}$  [17], as well as in some less-studied compounds are  $ZrO_2$  [18],  $TiO_2$  [19], ternary oxide  $LiAlO_2$  [20], aluminium oxy-nitride  $Al_{23}O_{27}N_5$  [21], oxyorthosilicates  $Ln_2SiO_5$  [22,23], tetraborates [24,25] and a lot of other materials. It is important to note that main interest in these studies is connected with the extensive search for better scintillator and storage phosphor materials. In

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**Table 1**

Optical absorption peak energies of the  $F$  center in alkali halides or  $F^+$  center absorption in some oxides and sulfides with NaCl-structure. Lattice constants for alkali halides are taken from Ref. [37], for oxides and sulfides [38]. The  $F$  center absorption energy for alkali halides from Ref. [39], for oxides are from Ref. [40], for CaS, SrS and BaS [41] and references therein.

Crystal	Lattice constant	$F$ center absorption in alkali halides or $F^+$ center absorption in other (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
BaO	5.52	2.0
MgO	4.207	4.9
CaO	4.80	3.7
SrO	5.13	3.0
BaS	6.36	1.94
MgS	5.19	
CaS	5.68	2.6
SrS	5.87	2.3

particular, the  $F$  centers play a very important role in the performance of photostimulated X-ray storage phosphors (BaFBr, CsBr, RbBr, RbI, KBr [26–29], etc.) for radiation imaging and dosimetry. Tunable, solid state, so-called “color center lasers” and some passive Q-switchers are also based on the  $F$ -centers [30]. However, in many cases the  $F$ -centers and their large conglomerates are often undesirable additions, limiting the performance of the luminescent screens, scintillators, and windows [31–34]. The  $F$  centers are also a very important topic in classical surface science and recent nanomaterial research, when surface and near-surface structural defects play an important role in the functionality of nanophosphors, nanotubes, etc. [35,36].

There are many interesting and fundamental questions regarding the  $F$ -centers in these materials. For example, what energy is needed to form the  $F$  center? What fraction of the  $F$ -center electron density is concentrated in the vacancy site and how much of it is delocalized over the surrounding atoms? Where does the  $F$ -center electron reside energetically, i.e., where in the band gap its energy level lie? In other words, are the  $F$  centers deep or shallow donors? The purpose of the paper is a brief survey of the main characteristics for only one subgroup of basic radiation color centers, namely, the electron  $F$  centers in a series of insulating materials: alkali halides, binary oxides and some  $ABO_3$  perovskites. Second limitation is that mainly the optical absorption properties and the defect production mechanisms will be sketched and discussed.

## 2. The $F$ center optical absorption in alkali halides and Mollwo–Ivey law

The  $F$ -center in alkali halides consists of an anion vacancy and a trapped electron, so that it can be viewed as a hydrogen-like atom in solids. Its ground state is the  $1s$  state, and the first excited state is composed of the  $2s$  and  $2p$  states. The absorption and emission spectra of the  $F$ -centers exhibit the large Stokes shift (1–2 eV) and quite broad bandwidths (0.2–0.3 eV). These features indicate strong electron–phonon coupling. The  $F$  center absorption as well

as band gap energies for alkali halides with NaCl (f.c.c)-structure are listed in Table 1.

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 ( $\text{Me}-\text{X}$  distance =  $1/2 a$ ).

It was found that similar relations hold for other  $F$ -type centers, including dimers and trimers,  $F_2^-$  and  $F_3^-$ -type centers in alkali halides [45]. Optical properties of these defects in oxides are discussed in more detail in a review article [40].

The  $F$  center in halides is electrically neutral. However, it may lose its electron by thermal or optical excitation thus transforming into a positively charged empty vacancy (the  $\alpha$  center) or gain another electron forming a negatively charged defect (the  $F^-$  center). The  $F^-$  centers are stable only at low temperatures (100–200 K). They have a broad absorption bands in a visible spectral range, while the  $\alpha$  centers give rise to an optical absorption in the UV-VUV region, close to the first exciton peak.

## 3. The $F$ centers in alkali-earth oxides and sulfides and extension of the Mollwo–Ivey law

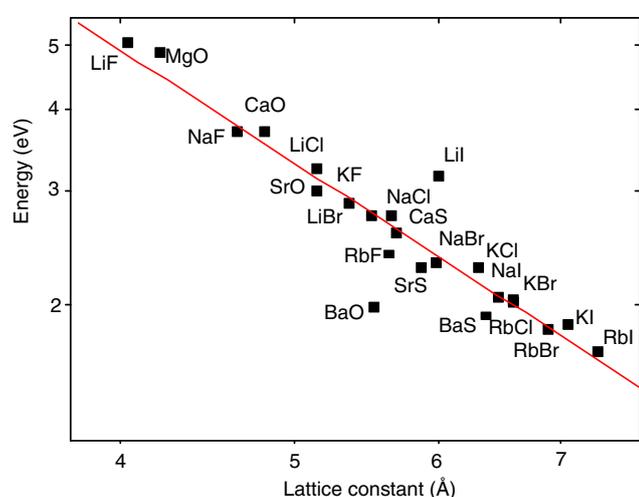
In contrast to alkali halides, oxygen vacancy in ionic oxides can have two charge states: the one-electron  $F^+$  center and the two-electron  $F$  center. The  $F^+$  center closely resembles the  $F$  center in alkali halides, while the two-electron defect ( $F^0$ ) as noted in Ref. [46] “occasionally misleadingly written as  $F$  center” corresponds better to the  $F^-$  center in halides. The hypothetical  $F^-$  center (O vacancy with three electrons) was simulated in  $\text{Al}_2\text{O}_3$  [47]; it was found that its ground state level lies about 1 eV below the bottom of the conduction band. The existence of this defect was discussed also in review article [40]. Recently, the existence of the  $F^-$  center was suggested in  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , it could be connected with the absorption bands at 360, 480, and 830 nm, which differ from the  $F$  and  $F^+$  bands in this material [17]. Multi-charged states of oxygen vacancy  $\text{HfO}_2$  have been discussed theoretically in Ref. [48].

The absorption bands of the  $F^+$  and  $F$  centers in most oxides occur at different energies, as demonstrated in Table 2, but in MgO they almost coincide, with energy of 4.9–5.0 eV. Interesting to note that in MgO, CaO and SrO irradiated with energetic particles, the preferred charge state of oxygen vacancy is the  $F^+$  center. The  $F^+$  centers have been also identified in some rock-salt sulfides (CaS, SrS and BaS) ([41,50] and references therein), while for additively-colored single crystals of BaS the  $F$  center absorption bands at 1.77, 2.33 and 2.75 eV were identified [51].

As was mentioned in previous paragraph, for alkali halides having NaCl-structure the position of the peaks of the  $F$  band follows the Mollwo–Ivey rule. It is easy to see (Table 1) that, for example, the  $F$  center absorption maximum (3.702 eV) in NaF almost coincides with the  $F^+$  center position in CaO (3.7 eV) while these materials have quite close lattice parameters (4.634 and 4.80 Å, respectively). Similar situation is valid for LiF and MgO. This one may conclude that the Mollwo–Ivey rule probably works for a

**Table 2**  
Optical properties for single-vacancy centers in oxides, energies are in eV. The  $F$  center absorption, except where otherwise noted, are taken from Ref. [40] and references therein.

Material	$F$ center		$F^+$ center		Reference
	Absorption	Luminescence	Absorption	Luminescence	
MgO	5.0	2.3	4.9	3.1	
CaO	3.1	2.1	3.7	3.3	
SrO	2.49		3.0	2.42	
BaO	2.3		2.0		
BeO	6.3, 6.6	4.9, 3.4	5.35	3.92	[7]
ZnO			2.95	2.38	[49]
Al <sub>2</sub> O <sub>3</sub>	6.0	3.0	6.3, 5.4, 4.8	3.8	
Li <sub>2</sub> O		3.65	4.00	3.26	
LiAlO <sub>2</sub>		4.43	5.25	3.26	
MgAl <sub>2</sub> O <sub>4</sub>	5.3		4.8		
Al <sub>23</sub> O <sub>27</sub> N <sub>5</sub>	5.46		5.00		
YAlO <sub>3</sub>	5.84, 5.15	2.95	6.5, 5.63, 4.3	3.49	[16]
Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>	6.35, 5.16	2.7	5.27, 3.35	3.1	[17]



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

larger family of crystals with NaCl-structure; the relevant plot based on data from Table 1 is shown in Fig. 1.

With two exceptions (LiI and BaO), all other data for the  $F$  and  $F^+$  centers quite well fit the straight line, thus confirming the simple model of  $F$  center as an electron localized by the net positive charge of a missing anion. On the other hand, it is clear that this is not a general rule and does not predict directly position of the  $F$  centers in all materials having NaCl structure. Some of them, like UN, are just simply metals, while in some others like AgCl or AgBr the  $F$  centers were not found yet and most probably do not exist at all. Theoretically, the absorption transition energy depends entirely on the lattice parameter only if the potential in which the  $F$ -center electrons move scales with the lattice parameter. The only simple model of this sort is the point-ion potential. Detailed quantitative analysis of corrections to the point ion model was made by Bartram et al. [52]. It was shown that in some cases the deviations from Mollwo–Ivey rule took place because the detailed structure of the ions cannot be ignored, particularly when the cations are large, like in CsF and BaF<sub>2</sub>. In such cases the potential is not a function just of lattice parameter [52,53]. This is probably true also for LiI and BaO.

#### 4. Photo-stimulated electron center conversion in MgO and Al<sub>2</sub>O<sub>3</sub>

The photoexcitation of charged one-electron  $F^+$  centers in oxides shows an interesting puzzle, namely their optical pumping in

corundum and MgO crystals leads to the formation of the two-electron  $F$  centers [54]. This process of color center *photoconversion* is accompanied by the formation of *hole* centers [55,56]. The latter excludes the simple explanation that thermal ionization of the excited  $F^{*+}$  centers is followed by a further electron trapping by another  $F^+$  center. A relevant theoretical model was firstly developed for Al<sub>2</sub>O<sub>3</sub> [57]. The main idea is that the positively charged  $F^+$  centers perturb surrounding atoms which results in the formation of several quasi-local energy levels in the upper part of the oxygen valence band. Under optical excitation with electron transition from these quasi-local levels to the *ground* state level of the  $F^+$  center, overlapping with the optical excitation energy of  $F/F^+$  centers, the defect transforms into the  $F$  center. Simultaneously, a *hole* is produced at one of the quasi-local levels and then a hole escapes to the valence band and either becomes self-trapped, or trapped by a cation vacancy or an impurity (see more in Ref. [40]).

Due to expectations that thermochemically reduced oxides are promising materials for development continuous-wave tunable lasers, the detailed comparative study of the  $F$ -type center photoconversion in neutron and thermochemical reduced MgO was performed [58,59]. In neutron-irradiated MgO crystals, experiments and theory demonstrate that photon excitation of the positively charged  $F^+$  centers at 5.0 eV releases holes that are subsequently firmly trapped at  $V$ -type centers, which are cation vacancies charge-compensated by impurities, such as Al<sup>3+</sup>, F, and OH ions. The quantum chemical simulations of the  $F^+$  centers confirmed the appearance of two induced quasi-local states, at 1.2 and 2.0 eV below the top of the valence band. A photoconversion mechanism is similar to Al<sub>2</sub>O<sub>3</sub>. In contrast to neutron-irradiated samples, in thermochemically reduced crystals with high concentrations of both hydride ions and  $F$  centers ( $10^{18}$  cm<sup>-3</sup>), the electrons from the  $F$  to  $F^+$  photoconversion are trapped mainly at the hydride ions to form  $H^{2-}$  ions, which are metastable at room temperature. In the latter case  $H^-$  ions [60] strongly affect the optical and photoconversion properties of anion vacancies in MgO as well as the kinetics of their luminescence.

#### 5. Differences in the $F$ center diffusion in alkali halides and MgO

The behaviour of point defects on oxides differs in many respects from that in alkali halides. It is important to remind that oxides generally have very high melting point (e.g. 2850 °C in MgO) so that intrinsic point defect concentrations at temperatures below 1000 °C are usually negligibly small here while the melting points of all alkali halides are lower than 1000 °C (e.g. 770 °C in KCl). This clearly means that the activation energy for diffusion of defects and relevant temperatures should also differ considerably. The summary of experimental and theoretical diffusion energies (in eV) for cation and anion vacancies and the  $F$ -centers in KCl crystals ([61] and references therein) and similar defects in MgO [62,63] is presented in Table 3. The quantum chemical simulations of the defect diffusion energy in MgO suggested a monotonic increase in the following series: a cation vacancy – anion vacancy –  $F^+$  center –  $F$  center (2.43, 2.50, 2.72 and 3.13 eV, respectively), much higher than the energy of 1.64 eV in KCl. This conclusion is important for the quantitative analysis of the possible secondary reactions in irradiated MgO, including metal colloid formation due to aggregation of mobile  $F$  centers, and the radiation-induced degradation effects observed in ceramics. Recently, it was confirmed that indeed the metal colloid formation in form of nanocavities via intrinsic diffusion of the  $F$  centers occurs in MgO only at very high temperatures (1400–1600 K) and high defect concentrations ( $>10^{18}$  cm<sup>-3</sup>) [64,65]. The relevant activation energy for the  $F$  center diffusion was found to be 3.4 eV [65], close to theoretically predicted. Note that the  $F$  center diffusion and colloid formation in

**Table 3**  
Comparative summary of the activation energies for vacancy-type defect diffusion in KCl and MgO.

Crystal	Defect	Experimental	Theoretical	Reference
KCl	Cation vacancy	0.67–0.76	1.19	[61] and references therein
	Anion vacancy	0.83–1.19	1.44	
	F center	1.35–1.65	1.64	
MgO	Cation vacancy	1.56–2.76	2.43	[62] and references therein, [63]
	Anion vacancy	1.90–2.71	2.50	
	F <sup>•</sup> center		2.72	
	F center	3.4 [65]	3.13	

alkali and alkaline-earth halides occurs at much lower temperatures (<600 K) [66,67].

### 6. Defect creation in alkali halides and oxides

It is well established nowadays that electronic excitations could create point defects in a regular lattice in some insulators, such as alkali, alkaline-earth and silver halides, rare gas solids, but in most insulators and semiconductors such photolytic reactions do not occur [1].

#### 6.1. Radiolysis of halides

The radiolysis process is well understood in alkali and some related halides where primary defects arise due to non-radiative recombination of the self-trapped excitons (STE) [1]. In alkali halides, the F–H pairs can be created by UV photons with energy, corresponding to free exciton absorption, but the apparent production energy of stable F centers is quite high, approximately 10<sup>4</sup> eV. According to Hirai et al. [2], most of transient defects are unstable and recombine.

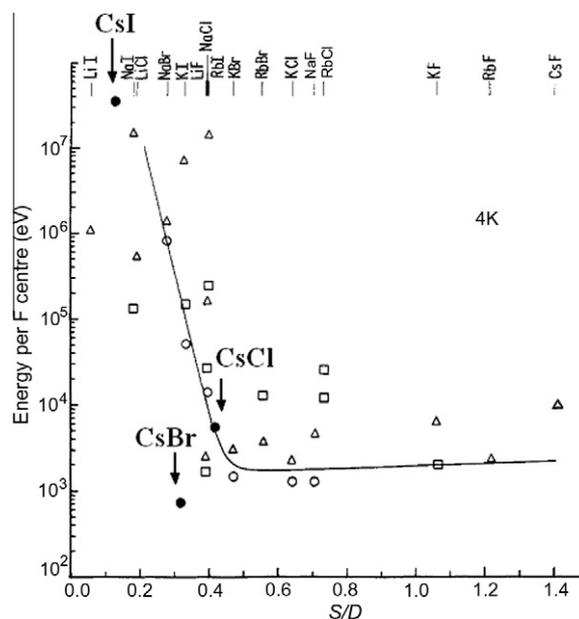
In 1960 Rabin and Klick [68] have found that the efficiency of the X-ray production of the stable immobile F centers at liquid helium temperature is clearly dependent on the lattice parameters of alkali halides. Since the production of F centers occurs as a result of the creation of halide ion vacancies by the ejection of halide ions from their normal lattice sites into interstitial positions, they proposed an “available space” explanation. They found that the absorbed energy to produce the F–H pair varied inversely with the space available to accept an interstitial ion. It can be characterized by S/D, the ratio of the separation between halogen ions in the [109] direction and the diameter of the halogen ion D. Low temperature defect production occurs much more efficient in the materials where S/D > 0.45, where there is enough space to accommodate an interstitial. As it was summarized by P. Townsend [69], this relationship holds for nearly all alkali halides with NaCl (f.c.c.) structure, except LiBr for which there is still no data. In alkali halides with close-packed (1 1 0) CsCl (b.c.c.) structure, the stable F center production efficiency was earlier determined for CsCl and CsBr [70] and recently for CsI [71]. The appropriate values of the production efficiency with corresponding S/D parameters determined for CsCl structure are given in Table 4.

A high value obtained for CsI confirms its high radiation stability as a well-known scintillator, while a low value reported for CsBr is in agreement with its application in imaging plate development.

Data in Table 4 allows us to draw a new Rabin–Klick diagram (Fig. 2). However, a few comments are needed here. The S/D value is an important quantity for several aspects of defect formation. Rabin and Klick [68] first suggested that the value of S/D indicates

**Table 4**  
The F center production efficiency (eV/center) vs. S/D parameter for cesium halides.

Material	S/D parameter	Production efficiency (eV/center)	Reference
CsCl	0.43	6–15 × 10 <sup>2</sup>	[70]
CsBr	0.32	8.1 × 10 <sup>2</sup>	[70]
CsI	0.17	2.5 × 10 <sup>7</sup>	[71]



**Fig. 2.** A new plot of the Rabin and Klick diagram for a whole family of alkali halides.

the available space for an ion or an atom to be incorporated at an interstitial position. Later, Townsend [69] suggested a somewhat different justification of the Rabin–Klick rule: as the distance S between the ‘hard-sphere’ anions decreases, these ions on the close-packed row act more as a bonded unity of large effective mass; hence only a little momentum could be transferred from the moving halogen atom to propagate a collision sequence. Another, theoretical explanation [72] was suggested in terms of off-center self-trapped-exciton displacement which looks the most suitable, especially for Cs-halides. This model allows to consider all alkali halides as one family, where STE structure varies according to the relevant S/D parameter.

It is necessary to notice that energy yield for CsBr is considerably smaller than expected value. The most probably this is due to some impurities which commonly increase the F center accumulation under irradiation and thus decrease the appropriate value “energy per F center”

#### 6.2. Displacement damage in oxides

The excitonic mechanism of defect creation cannot occur in simple oxides (MgO, Al<sub>2</sub>O<sub>3</sub>, etc.) and ABO<sub>3</sub> perovskites, because the displacement energies for both anion and cation species are significantly larger than the band gap or free exciton energy [96]. Direct displacement of lattice ions can arise here only above an incident electron energy threshold of 0.33–0.35 MeV, which corresponds to the displacement energy of about 60 eV for oxygen [40].

An accurate knowledge of the displacement energies is very important for modeling radiation damage effects. Various experimental techniques have been used to monitor defect production. These include: the detection of dislocation loops by transmission

electron microscopy (TEM), optical absorption, time-resolved cathodoluminescence spectroscopy.

For relativistic particles such as electrons, the maximum energy  $E_d$  (in eV) transferable from an incident electron of energy  $E$  (in MeV) to a lattice ion of mass number  $A$  is given by relation:

$$E_d = 2147.7E(E + 1.022)/A$$

Experimentally determined displacement energies are given in Table 5. For the most compounds, the displacement energy for oxygen is between 40 and 60 eV. If one assumes the displaced ions are other than oxygen, this equation yields  $E_d$  values that are unrealistically low compared to experimental and calculated cation displacement energies in other oxides.

### 7. F centers in perovskites

The characteristic feature of the  $F$ -type center in most alkali and alkaline-earth halides and oxides is a strong localization of electron(s) inside a vacancy, at least in its ground state. This is also true for fluoroperovskites (e.g. LiBaF<sub>3</sub>, KMgF<sub>3</sub>, RbMgF<sub>3</sub>, etc.), where the  $F$  centers were studied and their optical properties are well documented [97–103] and listed in Table 6.

On the other hand, it should be mentioned here that in some oxides (SiO<sub>2</sub>, GeO<sub>2</sub>, TeO<sub>2</sub>, TiO<sub>2</sub>, BaTiO<sub>3</sub>) it is very questionable whether the term  $F$  center is applicable to the observed defects because in partly-covalent solids an electron trapped by the  $V_0$  is likely to sit mainly on a ‘dangling’ bond [104]. Analogs of the  $F$  centers in covalent oxides, such as SiO<sub>2</sub> and TeO<sub>2</sub>, are called  $E'_1$  and  $V_0$  centers, respectively [105,106].

**Table 5**  
Experimental displacement energies for some oxygen compounds.

Material	Displacement energy (eV)		Reference
	Metal	Oxygen	
Al <sub>2</sub> O <sub>3</sub>	18	75	[73]
		70	[74]
		90	[75]
	24	79	[76]
		41–53	[77]
		53	[78]
MgO		60	[79]
	64		[80]
	60	53	[81]
		49	[82]
	37	55	[83]
		30	[84]
CaO		58	[83]
		50	[85]
CaO-Mg MgAl <sub>2</sub> O <sub>4</sub>	65	33	[85]
		59 (77 K)	[86]
		130 (300 K)	[86]
ZnO	57	57	[8]
BSO (Bi <sub>12</sub> SiO <sub>20</sub> )		49	[87]
LiNbO <sub>3</sub>		53	[88]
KNbO <sub>3</sub>		64	[89]
BaTiO <sub>3</sub>		60	[90]
CaTiO <sub>3</sub>		45	[91]
SrTiO <sub>3</sub>		45	[91]
BaTiO <sub>3</sub>		45	[91]
CaZrO <sub>3</sub>		53	[92]
Y <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>		47	[92]
La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>		47	[92]
CaZrTi <sub>2</sub> O <sub>7</sub>		45	[92,93]
TiO <sub>2</sub>		39	[93]
Li <sub>2</sub> O		43	[94]
BeO		76	[95]
UO <sub>2</sub>	40	20	[95]

**Table 6**  
Optical absorption peak energies of  $F$ -type centers in some fluoroperovskites.

	$F$ center nm/eV	$F_2$ center nm/eV	$F_3$ center nm/eV	Reference
NaMgF <sub>3</sub>	290/4.28	405/3.06		[97,98]
CaRbF <sub>3</sub>	320/3.86	570/2.17		[97]
BaLiF <sub>3</sub>	260/4.80	420/2.95	386/3.21	[99]
KZnF <sub>3</sub>	230/5.39			[45]
KMgF <sub>3</sub>	270/4.59	282/4.40	250/4.96	[100]
		445/2.79	395/3.14	
RbCdF <sub>3</sub>	315/3.93			[101]
RbMgF <sub>3</sub>	295 /4.20	255/4.86	300/4.13	[102,103]
		285/4.35		
	325/3.82	387/3.20		

Recent first principles DFT calculations of the neutral oxygen vacancy in ABO<sub>3</sub> perovskites [107] confirmed this pattern also for the titanates (SrTiO<sub>3</sub>, PbTiO<sub>3</sub>); unlike being deep defects like in MgO here oxygen vacancies are quite shallow defects with the energy level located 0.5–1 eV below the conduction band bottom. Although there are some indications that Mollwo–Ivey law is applicable fluoroperovskites [98], no optical absorption was observed for oxygen vacancies in ABO<sub>3</sub> perovskites. The single-electron center in SrTiO<sub>3</sub> is a deeper defect compared to neutral vacancy, and reveals also a larger segregation energy towards the surface [108].

On perovskite surfaces oxygen vacancies become even more shallow defects [103]. However, calculations [109] show that in zirconates (e.g. PbZrO<sub>3</sub>) this defect is a considerably more deep defect, both in the bulk and on the surface. This demonstrates that chemical composition of perovskite affects considerably properties of defects therein. Calculations demonstrate also that the migration energy in the SrTiO<sub>3</sub> bulk is quite small (0.5 eV); on the surface it is even smaller [110,111]. This means that these defects are unstable at room temperature.

### 8. Conclusions

In this short review article we updated recent information on properties of the basic radiation defects in ionic solids – the  $F$  centers – and suggested generalization of the well-known Mollwo–Ivey relation for a wide class of solids including alkaline-earth oxides and sulfides. The generalization of the Rabin–Klick diagram (energy necessary for production stable  $F$  centers vs. space available for an interstitial atom insertion) for b.c.c. crystals (Cs halides) has been also presented.

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