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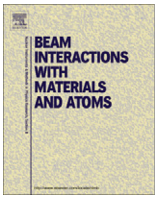

Basic properties of the *F*-type centers in halides, oxides and perovskites

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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.

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 intermidiate creation of the self-trapped excitons (STE). Such the non-radiative exciton decay is accompanied also by a simulataneous 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 α- 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 α–*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 (α 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 establised. 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 ZrO2: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 constansts 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

partucular, 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 1*s* state, and the first excited state is composed of the 2*s* and 2*p* 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:

$$E_F = 17.7a^{-1.84} \tag{1}$$

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]:

$$\Delta E = E_{2p} - E_{1s} = 3\pi^2 h^2 / 8md^2 \tag{2}$$

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*).

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 loose its electron by thermal or optical excitation thus transforming into a positively charged empty vacancy (the α 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 α 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 contract 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 Al_2O_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 $Y_3Al_5O_{12}$, 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 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 refrences 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 coinsides with the F^+ center position in CaO (3.7 eV) while these materials have quite close lattice parameters (4.634 and 4.80 A, respectively). Similar situation is valid for LiF and MgO. This one may conclude that the Mollwo–Ivey rule probably works for a