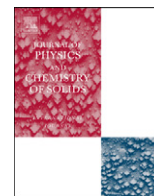




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Configurational instability at the excited impurity ions in alkaline earth fluorites

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ABSTRACT

The formation of intrinsic defects by ionizing radiation in some ionic crystals in the anion sublattice is only associated with the instability of the self-trapped exciton up to now. In this paper, on the basis of an analysis of experimental evidence already in the literature, we want to show that there are phenomena in the ionic crystals doped with some cations, which cannot be explained on the basis of existing models of the formation of radiation defects. A new mechanism for the formation of the defects in the anion sublattice associated with the Jahn–Teller instability occurring near the cation impurities in the excited state is proposed. The instability occurs when the degenerate excited state of the impurity ion is localized in the conduction band. We believe that the configuration interaction between the discrete impurity level and host continuum (effect Fano) plays an important role in this process.

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1. Introduction

Frenkel pairs comprising a vacancy and an interstitial in the anion sublattice are generated by ionizing radiation in some insulators in which electron–lattice coupling is strong. The mechanism of generation of Frenkel pairs in several solids, typically in alkali halides has been studied extensively and it has been generally accepted that they are generated as a result of the adiabatic instability of self-trapped excitons [1–5]. These processes have been studied well enough in alkali halide crystals. These crystals are easily colored by ionizing radiation and defects responsible for this coloration were called color centers.

It has been found that alkaline earth fluoride crystals which have not been deliberately doped with impurities are much less susceptible to coloration at room temperature by x irradiation than most alkali halides. Several review articles and books have deal with this subject, but the situation is still not clearly understood and no direct analogy appears to exist with the more widely studied alkali halides [3,4,6]. The behavior of x-irradiated alkaline earth fluorides doped with some cation impurities differs markedly from that of the pure crystals. The crystals can be easily colored by ionizing radiation. The defects formed are not only associated with changes in the valence state of the impurities, but also with the intrinsic damages in the anion sublattice [7,8].

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The photochromic centers are produced either by x-irradiation or by additive coloration (by heating the crystals in a calcium atmosphere) of CaF₂ crystals doped with certain rare earths ions (La, Ce, Gd, Tb and Lu) or yttrium. On the basis of optical and electron paramagnetic resonance (EPR) work, as well as theoretical investigations, it has been suggested that the ionized and thermally stable photochromic centers in CaF₂ crystals consist of one and two electrons bound at an anion vacancy adjacent to a trivalent impurity cation [9–11] and they were called as PC⁺ (Fig. 1) and PC, respectively. It has been found that photochromic centers can be formed by the shallower trivalent traps, e.g. by Y, La, Ce, Gd, Tb and Lu where low third ionization potentials are expected; the deeper traps with the higher ionization potentials will form divalent ions.

In the review by Hayes and Staebler at 1974 [6], it was concluded that “the formation mechanism of the PC centre is not yet understood, and little known of the mechanism by which the centre is optically ionized. There is clearly a need for further exploration of these interesting systems”. So far, little has changed. In this paper we want to show that the formation of the anionic intrinsic defects (the photochromic centres) is not associated with the decay of self-trapped excitons in a regular lattice and is due to the instability at the excited cationic impurities.

2. Photochromic centers

Two experimental results obtained recently could help us to understand the processes which occurs under radiation excitation in the crystals [12]:

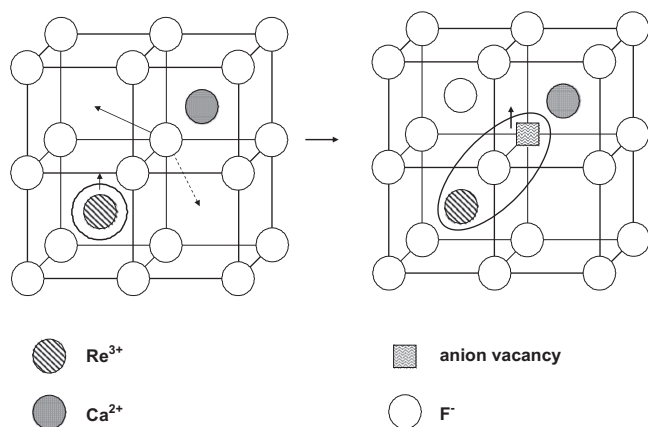


Fig. 1. Formation of the PC^+ centres. (a) Electron capture by the trivalent rare earth ion having O_h symmetry leads to the formation of the divalent rare earth ion in an excited degenerate state. This state is unstable to a Jahn–Teller distortion. The distortion leading to PC^+ formation involves a replacement of one of the nearest-neighbor F^- ion into an interstitial position and the relaxation of the electron from the excited state into the anion vacancy. (b) The result is a PC^+ center perturbed by interstitial fluorine ion, which prevents the subsequent capture of an additional electron by this complex.

- x-irradiation at 77 K of the CaF_2 and SrF_2 crystals doped with the impurities which can form the photochromic centers, results in creation PC^+ and V_k centers (self-trapped hole which have the structure of molecular ion – F_2^-).
- efficiency of the formation of the photochromic centers decreases from CaF_2 to SrF_2 and in BaF_2 crystals the centers are not created under x-irradiation.

Anion vacancy (α -centre) which is part of the PC^+ center is an intrinsic radiation defect usually arising from radiationless decay of self-trapped excitons. Creation of anion vacancy at nearest-neighbor of trivalent rare earth ions at 77 K is unexpected process and as far as we know it is the unique case (at least of the most reliable results). The defects having an anion vacancy at the nearest-neighbor position are created at the temperatures higher than the onset of the motion of anion vacancies. Thus F_A centers are fully converted to $(F_2^+)_A$ centers in CaF_2 –Na crystals according to thermal conversion process $F_A + \alpha \rightarrow (F_2^+)_A$ [13] or in SrF_2 and CaF_2 crystal doped with Cd the reduction of symmetry of the Cd^+ center is due to the attachment of anion vacancy in the nearest neighbor site [7,8]. Onset of the motion of an anion vacancy in CaF_2 crystal is at about 200 K [13].

This fact indicates that the instability which leading to the formation of anion vacancy at nearest-neighbor of trivalent rare earth ion is not associated with the decay of self-trapped excitons in a regular lattice because they are immobile at this temperature. Ionizing radiation produces in a crystal free electrons and holes. The holes are self-trapped at 77 K with the formation of a quasimolecule F_2^- and the electrons can be trapped by the impurity ions. It is reasonable to assume that the instability occurs when trivalent rare earth ion captures electrons to form a divalent ion in an excited state. Catlow [14] first suggested the possibility of such instability at the excited cation ion after an electron capture.

Most of the previous studies of the photochromic centers were carried out on additively colored crystals. However, there are a number of works on coloration of these crystals by x-irradiation at low temperatures [15–17]. It was noted [6,15] that the absorption caused by ultraviolet excitation of PC centres at 78 K in additively colored CaF_2 –Y is similar to that produced by x-irradiation of CaF_2 –Y at 78 K. The results show unequivocally that x-irradiation at 78 K creates PC^+ centers in CaF_2 –Y, but this

conclusion is why it has not been made. The situation is very much complicated by the strong overlapping of the PC^+ centers and the divalent ions absorption. The optical absorption spectra of divalent rare earths in CaF_2 after x-irradiation at 77 K have been given by Merz and Pershan [16]. Only a small part of trivalent ion converted to divalent by x-ray irradiation. Therefore, the divalent ions have a relatively weak absorption. However, the absorption spectra for La, Ce, Gd and Tb (Lu has not been studied) is somewhat different from the rest. The “divalent bands” at wavelengths longer than 400 nm for La, Ce, Gd, and Tb are much stronger than the absorption bands in this region of the spectrum for the other ions. The existence of these anomalous bands, as well as the hole absorption at 310 nm (V_k -centres), casts some doubt on the blanket assertion that the radiation-induced absorption curves are due solely to the divalent rare earths. Comparison between these results and those obtained later [10] indicates that these absorption spectra are associated with PC^+ centers.

From the above considerations it is clear that, despite the experimental results indicating the formation of PC^+ centers at low temperatures by x-irradiation, it was assumed that the formation of the PC centers arises from thermally activated motion of anion vacancies [6].

Since the instability, leading to the formation of anion vacancies, is associated with the distortion of the nearest anion environment at the excited impurity divalent ion, it is reasonable to assume that this distortion is conditioned by the Jahn–Teller effect. The Re^{2+} impurity occupies a substitutional site of metal in the fluorite-type structure crystal. The site symmetry is cubic (point group O_h) with eightfold coordination. At 77 K Re^{2+} ion producing electron capture of Re^{3+} after x-irradiation may be perturbed by interstitial F^- ion locating in nearest-neighbour (nn) positions, thus leaving this dipolar (Re^{3+} – F^-) complex with tetragonal (C_{4v}) symmetry. There is evidence that, at least at low temperatures, only those lanthanide ions with non-local compensator (cubic sites) can be reduced to the divalent state. Thus the spectra of the thermoluminescence corresponds to the fluorescence of the trivalent ion in sites of cubic symmetry for the low-temperature glow peaks, and tetragonal symmetry above room temperature [16].

For free ions the ground configuration of La^{2+} , Gd^{2+} and Y^{2+} is $5d^1$, for Ce^{2+} , Tb^{2+} , Lu^{2+} is f^7 but $f^{n-1}5d$ and f^n states are close to each other. For crystals with the fluorite-type structure, the crystal field acting at the Re^{2+} ion possesses cubic symmetry with eightfold coordination which splits the fivefold orbital degeneracy of the d-energy level into doubly degenerate (2E_g) and threefold degenerate (${}^2T_{2g}$) energy levels with the 2E_g level lowest. The spin–orbit coupling splits the ${}^2T_{2g}$ energy level into the two states [18] and particular quenches the Jahn–Teller distortion. In cubic symmetry the spin–orbit coupling does not split the 2E_g state.

Experimental and theoretical evaluations of the location of the energy levels of rare earth ions in CaF_2 , SrF_2 , and BaF_2 relative to the conduction band states of the host crystal show that threefold degenerate (${}^2T_{2g}$) energy levels of the divalent rare earth ions are in conduction band of the crystals [19,20]. For example, the energy levels of Ce^{2+} and Ce^{3+} in cubic F^- coordination relative to the conduction band in CaF_2 are shown in Fig. 2. Since the ${}^2T_{2g}$ orbital of the 5d electron is orbitally degenerate, it will interact with e – or t – symmetry vibrational modes of the eight neighboring fluorine ions and this interaction leads to the Jahn–Teller effect in its many forms. Jahn–Teller distortion arises when trivalent rare earth captures electron forming divalent rare earth ion in excited ${}^2T_{2g}$ state. The distortion leading to PC^+ formation involves a motion of the nearest-neighbor F^- ion into an interstitial position and the relaxation of the electron from the excited state into the anion vacancy. The PC^+ center is disturbed by interstitial fluoride ion (Fig. 1), which prevents the subsequent

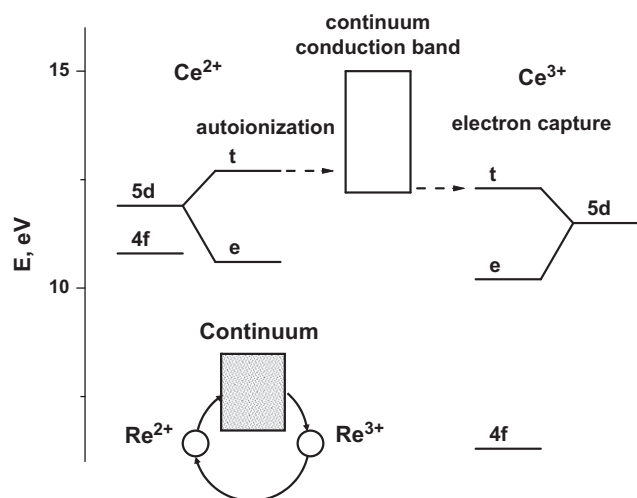


Fig. 2. Energy levels of Ce^{2+} and Ce^{3+} in cubic F^- coordination (schematic) relative to the conduction band in CaF_2 . Spin-orbit coupling is neglected. The inset shows the cycle associated with the valence fluctuation of the rare earth ion.

capture of an additional electron by this complex. At about room temperature the interstitial fluoride ion can be removed from the neighborhood of the PC^+ center and capture of an additional electron by the PC^+ center can occur. As a result, x-irradiation at room temperature leads to the formation of PC center having two electrons.

The PC^+ center is a lower-energy equilibrium complex than the divalent state for the rare earth ions with low third ionization potentials. Consequently, the formation of an anion vacancy lowers the energy of the system and symmetry reduces from O_h to C_{3v} . It should be noted that none of these rare earth metals exhibits a stable $+2$ state in any of its compounds and consideration of factors such as their ionization energies suggests they are unlikely to form stable compounds in this state [21].

For some divalent rare earth ions having the $d^1(^2E_g)$ configuration (La^{2+} , Gd^{2+} and Y^{2+}) in the ground state the Jahn–Teller effect has been observed by EPR [22–27], but this distortion does not leads to the formation anion vacancy. Essential requirement for the Jahn–Teller distortion leading to the PC^+ formation is the localization of $^2T_{2g}$ state of the divalent rare earth ion in conduction band. The excited state $^2T_{2g}$ of Re^{2+} embedded in the continuum energy state which can autoionize can also decay to a lower-lying state forming the divalent ion in the ground state or can distort by Jahn–Teller effect with the formation of the PC^+ center. The formation of the divalent ions has a low efficiency, regardless of the efficiency of formation of the photochromic centers in different crystals. The independence of the formation of the divalent ions and the photochromic centers provided via autoionization. PC and PC^+ centers can be efficiently created in CaF_2 by x-irradiation, can be inefficiently created in SrF_2 and cannot be created in BaF_2 crystals [12]. This fact may be explained by decrease of the covalent interaction between Re^{2+} and eight F^- neighbors with increase of the lattice parameter from CaF_2 to BaF_2 .

3. “Anomalous” emission

Let us consider another case that as we believe is close to the former. For the divalent lanthanides (Re^{2+}) in alkaline earth fluorides, under photoexcitation $d \rightarrow f$ emission has been only observed for Eu^{2+} and Yb^{2+} ions. In the other divalent lanthanides, again relaxation to lower-lying $4f^n$ levels quenches the $d \rightarrow f$ emission [28]. For Yb^{2+} in CaF_2 , SrF_2 and Eu^{2+} in BaF_2 have been observed the broadband emissions with large Stokes shift which

is due to strong distortion of the environment and these emissions were called as “anomalous” emission. At first the anomaly of this emission was explained as arising from the Jahn–Teller distortion [29]. It was shown subsequently that the emission is observed when doubly-degenerate $d(^2E_g)$ level from which electron delay to ground state via emitted photon must be localized in conduction band [30,31,28]. It is now accepted that the location of the 5d levels relative to conduction band state and the presence of the “anomalous” emission are related to each other.

It has been suggested that the “anomalous” luminescence results from the radiative decay of the so called impurity trapped exciton [30,31,28]. The structure of the impurity trapped exciton is of the hole localized on the luminescent ion and the electron delocalized over the surrounding cations. The impurity trapped exciton in $\text{SrF}_2:\text{Yb}^{2+}$, for example, consists of a Yb^{3+} core with the electron delocalized over the 12 nearest neighbors Sr^{2+} ions [30].

The large Stokes shift observed has been explained on the basis of the distortion induced in the excited state with respect to the ground state geometry of the impurity trapped exciton. This effect is a consequence of the different radii between Re^{3+} and Re^{2+} . After creation of the impurity trapped exciton, F^- ligands collapse towards Re^{3+} . The model of the impurity trapped exciton is based on the important, however, only single experimental result associated with localization of the excited state in conduction band and ignores the facts received early.

In this model the distortion has the cubic symmetry. However, the data obtained by Kaplyanskiy [29] from polarized luminescence and uniaxial stress studies have been shown that the distortion has the symmetry lower than cubic. From the polarization measurements of the luminescence the authors [32] of the model of the impurity trapped exciton concluded also that the luminescence center has C_4 orientation.

The “anomalous” emission due to the ionization process is not confined to the Eu^{2+} and Yb^{2+} ions and the $d \rightarrow f$ transitions (let via autoionization) but has been observed in the luminescence of ions such as Tm^{2+} [30], Ce^{3+} [33], Bi^{3+} [34] ($p \rightarrow s$ transition) and Cu^+ [35] ($^3E_g(d^9s) \rightarrow ^1A_{1g}(d^{10})$ transition).

However, unlike the $\text{BaF}_2:\text{Eu}^{2+}$ system, the luminescence of $\text{BaF}_2:\text{Sm}^{2+}$ appears to be “normal”; it is dominated by the sharp $f^6(^5D_0) \rightarrow f^6(^7F_1)$ transition as for the luminescence in $\text{SrF}_2:\text{Sm}^{2+}$, in spite of the $f^6(^5D_0)$ state is located in the conduction band [36]. The 5D_0 state in $\text{BaF}_2:\text{Sm}^{2+}$ is just 1000 cm^{-1} below the lowest $f^5d(e_g)$ state.

The shielding character of the 4f orbitals by the filled $5s^2$ and $5p^6$ orbitals determines the weak interaction with the neighbouring ions. This explains the small influence of the host lattice and the sharp lines observed in spectra based on f–f transitions and the quench the Jahn–Teller effect if electron occupies the f-orbital. We thought that the processes of the formation of the photochromic centers and the “anomalous” luminescence are similar to each other. In both cases it is needed the localization of excited d state in conduction band leading to the distortion of the environment. The distinction is that the formation of PC^+ centers is energetically favorable for the shallow traps (Y^{2+} , La^{2+} , Ce^{2+} , Gd^{2+} , Tb^{2+} , Lu^{2+}), whereas for the deep traps (Eu^{2+} , Yb^{2+}) the divalent state is energetically more favorable.

4. Discussion

The fact that coloration of alkaline earth fluorides at room temperature by ionizing radiation are strongly affected by some cations was known many years ago [6]. Much effort both in experimental and in theoretical investigations has been devoted to determining the spatial and electronic structures of the radiation impurity defects. It has been found that in some cases the

composition of the radiation defects includes anion vacancies that in general it is unusual, as in the undoped crystals, they are not created with such efficiency. The cation impurities in this case are rather diverse – these are trivalent rare-earth ions (the photochromic centers [6]), divalent transition metal ions [37] and monovalent ions of alkali metals (formation of F_{2A}^+ centers [13]). Nevertheless, the question of how the cation impurity promotes the formation of radiation defects in the anion sublattice is not considered. Some propositions on the matter were made by us in the previous papers [7,8]. The formation of the defects is associated with the temperature movement of anion vacancies. However, the formation of the photochromic centers at low temperatures, which we discussed above, does not fit the known schemes of the formation of radiation defects. The displacement of anions depending on the electronic state of the impurity cation involves the Jahn–Teller effect. However, in some cases, this is a relatively small distortion [22–27]. Some thoughts on a significant Jahn–Teller distortion will be discussed below. Before that, let us remark that recent experimental evidences and theoretical results showing that a huge off-center displacement of some impurity ions is due to pseudo Jahn–Teller vibronic coupling mechanism [38]. Prior to this, it was widely held that off-center instabilities are only related to the substitution of a lattice ion by smaller impurity.

The fact that the “anomalous” emission and the formation of the photochromic centers occur from the d-degenerate states of the divalent rare earth ion embedded in the continuum energy state indicate that the configuration interaction between the discrete level and continuum plays an important role in these processes. Fano investigated the stationary states with configuration mixing under conditions of autoionization and he pointed out the basic physics of the quantum interference phenomenon between a discrete level and a continuum [39]. The lifetimes of these excited states due to allowed autoionization (maybe via phonon – vibrational autoionization) (typically 10^{-15} – 10^{-13} s) are shorter by many orders of magnitude than the lifetimes due to allowed emission transitions (typically 10^{-9} s). In the case of $BaF_2:Eu^{2+}$, the spectrum of the group of f^6d excited states from 3 to 4 eV is broadened by some radiationless process suggested to be autoionization. The lifetime was found to be 25 fs for the f^6d excited states and 70 fs for the $f^7({}^6P_7/2)$ excited state which has comparable energy and is observed via two photon spectroscopy [40]. After the autoionization the electron can be then recaptured due to coulomb interaction with the excess charge of the trivalent rare earth ion. This means that the valence of the rare earth ion (Re) will fluctuate between the states Re^{2+} and Re^{3+} . It is possible that this valence fluctuation creates the resonant electron–phonon interaction that leads to the enhancement the Jahn–Teller distortion. However, there is the need of a theoretical exploration of this effect (maybe by using Barry phase cycle [41], Fig. 2). The Fano type interference can occur between two channels of the autoionizations either by the direct hopping or via phonon.

It is noteworthy to mention that in the rare-earth compound such as SmB_6 which belongs to the class of intermediate-valence systems maybe the similar effect has been found. Jahn–Teller effect on Er^{3+} , Sm^{3+} , Gd^{3+} ions was observed only in a compound with fluctuating valence SmB_6 but neither in an isomorphous compound LaB_6 where La has a constant valence nor in the semiconductors BaB_6 , YbB_6 , CaB_6 , etc. [42,43]. Authors concluded that strong electron–phonon interaction which is essential for observation of the Jahn–Teller effect plays a significant role in the nature of fluctuating valence.

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