

Theoretical study of self-trapped hole diffusion in CaF₂, SrF₂, BaF₂ crystals

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ABSTRACT

In this paper we present the results of *ab initio* molecular dynamics (MD) study of the V_k-center in CaF₂, SrF₂, BaF₂ crystals. The calculations have been carried using density functional theory in DFT + U approximation. The MD simulation showed three possible diffusion channels of V_k-center: (i) 0°-degree jump, (ii) jump with 90° reorientation, and (iii) jump through an intermediate state in BaF₂ and SrF₂ crystals. The intermediate state appears when one of the fluorine ions composing V_k-center is displaced into the nearest interstitial position and may be considered as the pair of nearest anion vacancy and H-center. This state cannot be considered as standalone V_k-center configuration but is rather metastable and briefly relaxes into ground state of V_k-center. The existence of this state in SrF₂ and BaF₂ crystals distinguish them from CaF₂ crystal where it has not been observed.

1. Introduction

One of the most common electronic excitations in alkaline-earth halides is self-trapped hole (STH or V_k-center). The self-trapping of holes in CaF₂, SrF₂, BaF₂ crystals has long been studied by EPR and optical methods (Emin D., 1993; Castner T. G. et al., 1957; Suzuki T. et al., 1993; Postawa Z. et al., 1995). The self-trapped hole comprises a hole localized on two adjacent fluorine ions thereby bound to each other in an F₂⁻ molecular configuration (Williams et al., 1976; K.S. Song et al., 1993; A.M. Stoneham et al., 2007; A.M. Stoneham, 1979).

V_k-center is formed in alkaline-earth halides as a result of exposure to various types of radiation: UV radiation, X-ray, gamma radiation, etc. The diffusion of self-trapped hole through the crystal determines the interaction of the electron and hole components of the defect and, as a result, has a strong influence on the properties of the material, for example, radiation sensitivity (Popov A.I. et al., 2017). Therefore, the mechanism of V_k-center motion through a crystal and its influence on the properties of the materials, especially on the properties of scintillator crystals, attracts considerable attention.

The purpose of this work is to investigate possible diffusion mechanisms of self-trapped hole in XF₂ (X = Ca, Sr, Ba) crystals. All the crystals belong to *Fm3m* space group symmetry.

2. Calculation details

The method of molecular dynamics is used to model and predict

structures, to study the transport and spectroscopic properties of solids, to simulate diffusion, to develop models of nucleation and growth of crystals. This method is often used with the density functional theory in the LDA or GGA approximation in combination with a periodic cell model.

However, the application of this method to fluoride crystals meets some difficulties in the description of the self-trapped state. This is due to the fact that density functional theory in the LDA or GGA approximations (Sun J. et al., 2011; Zhao Y et al., 2006; Gavartin J. et al., 2003) overestimates the degree of electronic states delocalization and therefore gives greatly underestimated value of the band gap and can not predict the phenomenon of self-trapping. The use of hybrid functionals that take into account the Hartree-Fock exchange provides a correct description of the self-trapped state (Loftager S. et al., 2016), but this method is more computationally expensive and is not compatible with molecular dynamics.

Another approach suitable for correct description of self-trapping in ionic crystals is embedded cluster model (Shluger A. L. et al., 1991), although it is also incompatible with molecular dynamics. One of the most recent applications to halides concerns NaI crystal (Prange M. P. et al., 2013) and was performed at hybrid DFT level in embedded quantum cluster with frozen border. There were many more earlier works on V_k-centers in halide crystals, for example, one of the first *ab initio* calculations of V_k-center in LiF crystal (R. Pandey, A.B. Kunz, 1988). As early as in 1990 the importance of lattice polarization and deformation for the description of self-trapping had been already

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recognized (J. Meng et al., 1990). We have obtained similar results in our previous work (A. Mysovsky et al., 2006) where it was shown that the frozen border of embedded quantum cluster strongly affects the localization energy of V_k -center in CaF_2 crystal and, for small clusters, even prevents self-trapping.

The simplest solution we have found is to use the DFT + U (Cococcioni M. et al., 2005; Anisimov, V. I. et al., 1997) approximation in Liechtenstein's formulation (Liechtenstein et al., 1995) to correct the degree of hole states localization on the 2p-orbitals of the fluorine ion. Similar approach was previously shown to describe correctly hole self-trapping in various oxide systems (Droghetti A. et al., 2010; Nolan M. et al., 2006; Slipukhina I. et al., 2011). Recently developed polaron self-interaction corrected density functional (pSIC-DFT) could be another choice (Sadigh B. et al., 2015) and probably will be used in our future works. However, it was shown (Lindman A. et al., 2016) that pSIC-GGA, GGA + U and hybrid functional HSE06 give largely the same results for hole polaron in BaZrO_3 crystal.

For the study of STH localization and mobility in fluoride materials we used the DFT + U with PBESol (Perdew J. P. et al., 2008) exchange-correlation functional because it has shown very good agreement with experimental lattice parameters and elastic properties in other solids. For fluorides with a cubic lattice the values of the parameters $U = 11$ and $J = 3$ for the 2p orbitals of fluorine ions were chosen. This choice was made on the basis of preliminary calculations of V_k -center localization in those crystals and of isolated F_2^- molecular ion. With $U = 0$ and $J = 0$ (no U correction) the self-trapped state of the hole cannot be reproduced in all considered crystals with both PBE and PBESol functional. With $U > 6$ and J ranging from 1 to 4 the self-trapped state becomes stable and the fluorine-fluorine distance in V_k -center appears to be about 2 Å. However, for $U > 13$ this distance starts to rapidly increase with the growth of the U parameter. Those calculations allow one to conclude that required parameters values must reside in the range $6 \leq U \leq 13$ and $1 \leq J \leq 4$.

Then the isolated F_2^- molecular ion was calculated with PBE and PBESol functionals for U and J values covering this region. The energy dependence on the internuclear distance is shown on Fig. 1. Without U correction for both PBE and PBESol the calculated energy term have unphysical maximum at the distance about 3 Å. The U correction with $U < 6$ does not greatly improve the situation, but the values $U = 11$ and $J = 3$ do the trick best. The same values turned out to be the best choice for V_k -center localization leading to the hole migration energies in good agreement with experimental ones (this is discussed in the next section).

PBESol exchange-correlation functional itself tends to underestimate the bulk lattice constants (Table 1). Addition of U-correction term makes the situation slightly worse, especially for SrF_2 crystal where the deviation from experimental lattice constant reaches 3.8%. For CaF_2 and BaF_2 crystals this deviation does not exceed 3%. The comparison of band structures calculated with and without U-

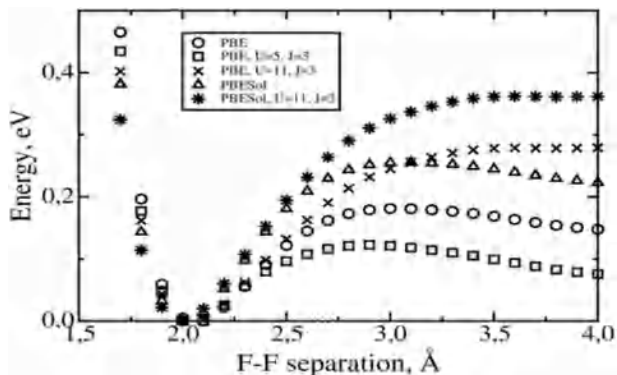


Fig. 1. F_2^- molecular ion energy terms calculated with PBE and PBESol functionals for different U and J parameters.

Table 1
The calculated values of the bulk lattice constants (Å).

crystal	GGA	GGA + U (U = 11, J = 3)	Experimental
CaF_2	5.4	5.32	5.45
SrF_2	5.63	5.57	5.79
BaF_2	6.08	6	6.19

correction (Fig. 2) shows no qualitative difference. However, the band gap value becomes larger by about 1 eV for DFT + U.

To apply a method of molecular dynamics, the VASP (Kresse and Furthmüller, 1993; Kresse and Furthmüller, 1996) software package is used. The calculations are performed using the NVE ensemble (the constant value of the particles number, volume and energy) and with the step of integrating the MD motion equation of 10 fs. The total duration of the simulation was 200 ps. Molecular dynamics is carried out with temperature linearly increasing from 70 to 600 K. We continue to use the DFT + U with PBESol exchange-correlation functional for the calculations of the energy barriers associated the polaron hops which were determined using the nudged elastic band (NEB) method in which the minimum-energy paths were calculated (Henkelman, G. et al., 2000). Because of the size of the supercell, generated by a $2 \times 2 \times 2$ repetition of a cubic unit cell, used in the NEB calculations, it was sufficient to consider only the Γ -point.

The formation of a hole polaron was studied with charge +1 and a system total spin $\frac{1}{2}$ assigned to the supercell, keeping its neutrality by adding a uniform negative compensation charge. However, when a structure containing a positive charge excess was relaxed, no localization of the hole was observed (i.e. the hole was completely delocalized). This delocalization, which occurs when the perfect structure of the host lattice is used as initial guess, has been observed in computational studies of polaron (Loftager S. et al., 2016; Ong, S. P. et al., 2012). The standard procedure to avoid this is to break the host symmetry manually and then run a relaxation of the geometry. Thus, before starting the geometry optimization, we shifted two neighbouring fluorine ions from the nodes to each other to make distance between them equal to 1.9–2.0.

3. Results and discussion

3.1. Intermediate state

During molecular dynamics simulation for SrF_2 and BaF_2 crystals we observed such event as a transition to an intermediate state, but this was not observed in CaF_2 crystal. The intermediate state is formed when one of the fluorine ions composing V_k -center jumps into the nearest interstitial position (Fig. 4 c). The intermediate state also may be considered as the pair of H-center and nearest anion vacancy. Fig. 3 shows two configurations of self-trapped hole: both “stable” and “metastable”. This intermediate state is thermodynamically unstable and disintegrates shortly either by returning to an initial V_k -center or by the bond switching with subsequent V_k -center reorientation. With the increase in the temperature the number of events with the transition to an intermediate state increases linearly.

The presence of the V_k -center in the crystal gives a hole level, which manifests itself in various luminescence and absorption spectra. We determined the position of the hole level (ϵ_h) in the band gap relative to the top of valence band both for the ground and intermediate state. We observed a shift in the position of the hole level during the transition to the intermediate state. In SrF_2 crystal the position of the hole level in intermediate state is shifted by 0.6 eV relative to such for V_k -center in the ground state, while in BaF_2 crystal this shift is of 0.5 eV. The reason for the shift of the hole level is the presumably transformation of the V_k -center to the H-center and an anion vacancy (Table 2).

For the crystals ranging from CaF_2 to BaF_2 with increasing value of

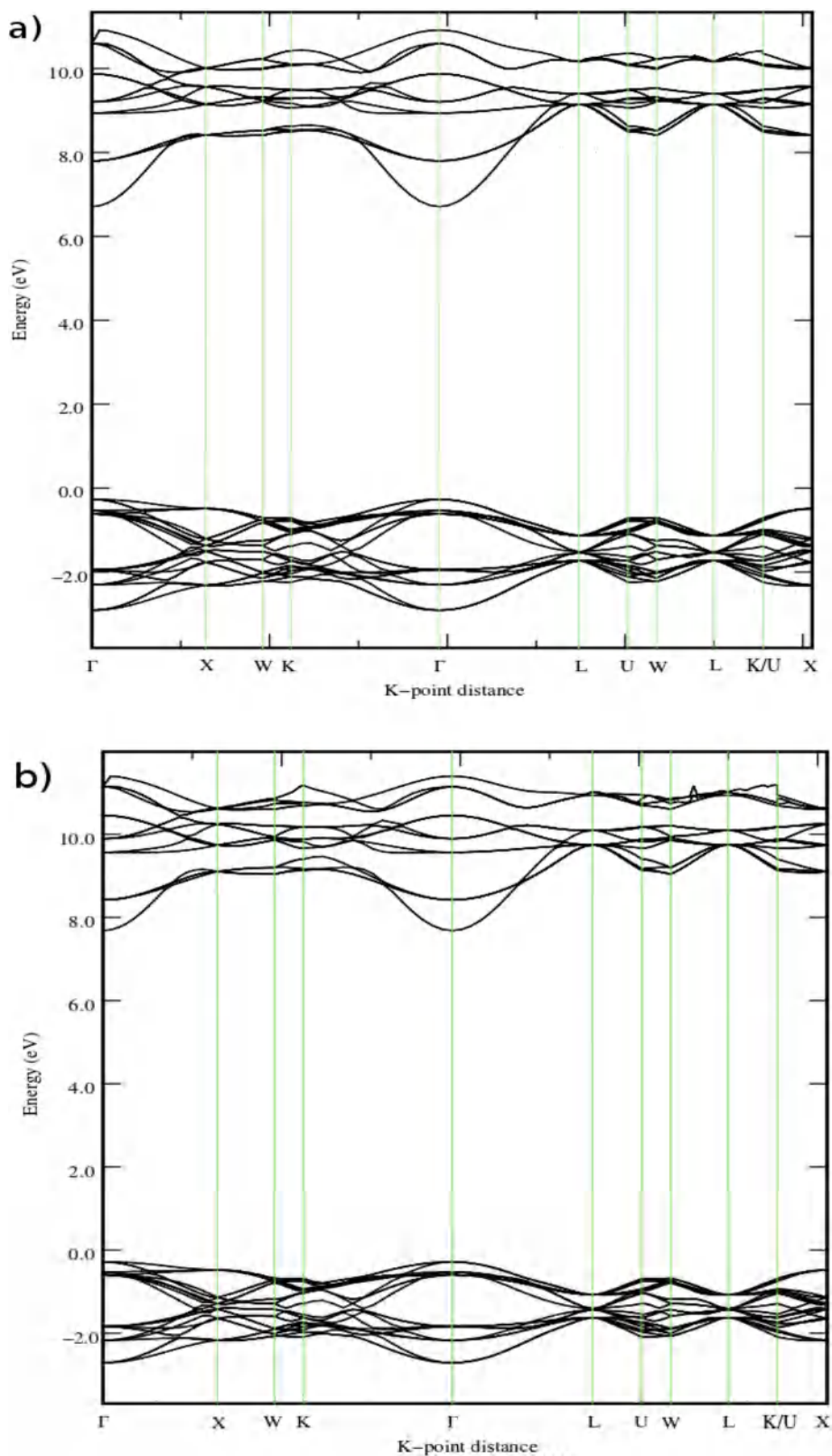


Fig. 2. Calculated band structure of CaF₂ crystal a) without and b) with the U correction for U = 11, J = 3.

lattice constant the hole level position for V_k-center in the ground state systematically increases by a constant value of 0.2 eV. Also with the growing value of lattice constant the value of localization energy (E_{loc}) increases. By the localization energy (also presented in Table 2) we mean the energy gain for the hole self-trapping, in other words, the

energy difference between the hole delocalized over entire supercell and its localized configuration. From Table 2 one can see that in SrF₂ crystal the difference between localization energies for the ground and intermediate states is larger than in BaF₂ crystal resulting in lower probability of intermediate state formation in SrF₂ crystal. This is

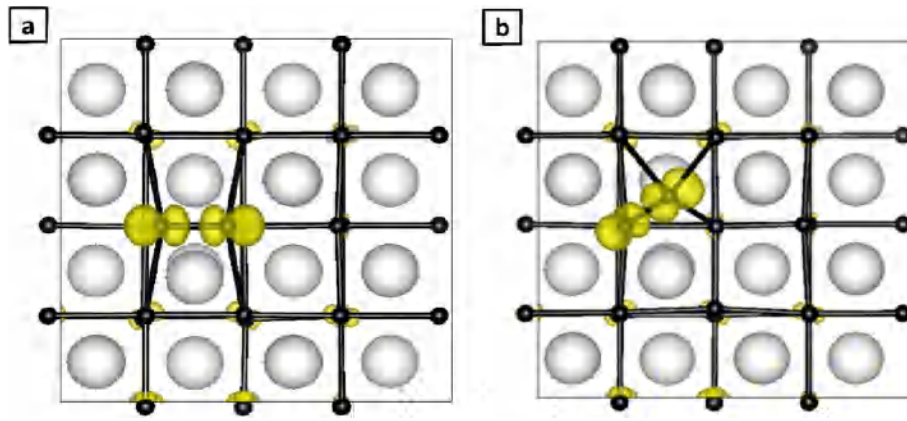


Fig. 3. The localized state of STH: a-stable state; b-intermediate state.

consistent with what we observe in the molecular dynamics simulation.

3.2. Diffusion mechanism of V_k -center

In all three considered crystals there are two common channels of V_k -center diffusion, namely the 0° jump (Fig. 4a) and reorientation (Fig. 4b). Additionally, in SrF_2 and BaF_2 crystals, unlike CaF_2 , the existence of the intermediate state gives rise to third diffusion channel schematically shown on Fig. 4d and named “diffusion through the intermediate state”. Diffusion through the intermediate state is a two-stage process, unlike two other diffusion mechanisms.

Values of the activation energy (E_a) are directly related to the temperatures of the defect diffusion (T_{migr}) in the crystal. The higher the value of the energy barrier is the higher the temperature of corresponding process becomes (Table 2). However, this rule seems to be violated for the diffusion through the intermediate state. In fact, this diffusion channel has two stages. As shown in Fig. 5c for BaF_2 crystal at the first stage the transition to intermediate state must happen with the activation energy of 0.18 eV, and then, at the second stage the bond switching must occur with the corresponding activation energy of 0.19 eV. Two-staged character of third diffusion mechanism makes its probability lower and corresponding temperature higher than for two other mechanisms.

The values of migration temperatures calculated in this work cannot be directly compared to experimental values. We simulate the molecular dynamics at very high temperature growth rate to be able to observe the “rare events” (such as diffusion) at computationally feasible timescale. This is why the calculated diffusion temperatures are much higher than experimental ones.

As can be seen from Table 3 the transition into intermediate state becomes energetically favorable with increasing halogen-halogen distance, so the life time spent in intermediate state also increases.

Table 2

The position of the hole level (ϵ_h) of V_k -center in CaF_2 , SrF_2 and BaF_2 crystals relative to the top of the valence band and the values of localization energy (E_{loc}).

crystal	Stable V_k -center configuration		Intermediate state	
	ϵ_h , eV	E_{loc} , eV	ϵ_h , eV	E_{loc} , eV
CaF_2	1.2	0.3	×	×
SrF_2	1.4	0.43	2.2	0.18
BaF_2	1.6	1.02	2.3	0.94

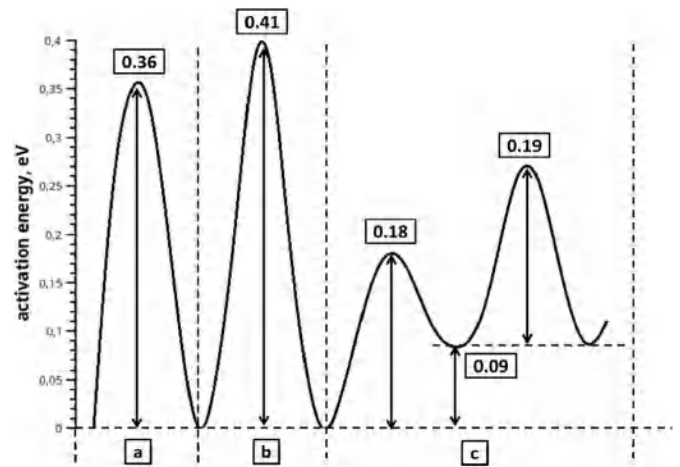


Fig. 5. Energy landscape representation of STH migration pathways for BaF_2 crystal: a- 0° degree jump; b - jump with reorientation; c - jump through an intermediate state.

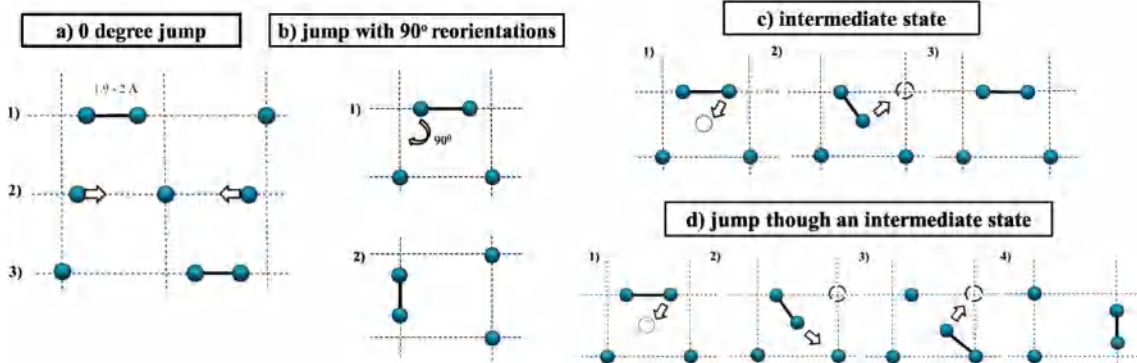


Fig. 4. The scheme of STH: a- 0° degree jump; b-jump with reorientations; c-intermediate state; d-jump through an intermediate state.

Table 3

The values of activation energy and the reorientation temperature of V_k -center in CaF_2 , SrF_2 and BaF_2 crystals, experimental values from Ref. W. Hayes (W. Hayes, 1974) are shown in parentheses.

crystal	CaF_2		SrF_2		BaF_2	
	E_a , eV	T_{migr} , K	E_a , eV	T_{migr} , K	E_a , eV	T_{migr} , K
0° jump	0.2 (0.19)	77	0.25 (0.21)	354	0.36 (0.3)	395
jump with reorientations	0.33 (0.31)	490	0.36 (0.3)	439	0.41 (0.38)	496
intermediate state	×	×	0.25	453	0.18	279
jump through intermediate state	×	×	0.16	454	0.19	530

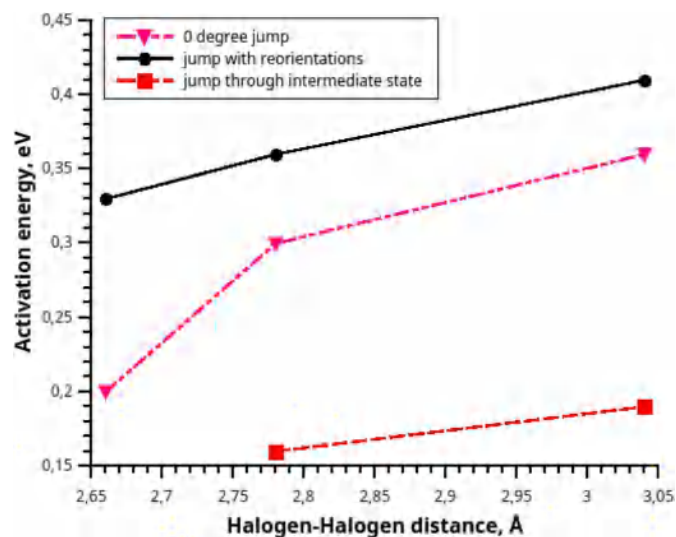


Fig. 6. Dependence of activation energy for various diffusion channels on halogen-halogen distance in CaF_2 , BaF_2 and SrF_2 crystals.

However, as the barrier for this type transition is relatively low the defect appears in both configurations. Increasing halogen-halogen distance leads to higher value of activation energy for various diffusion channels (Fig. 6), with exception for “jump through the intermediate state”. This observation clearly demonstrates that in this case the main factor determining the activation energy is the lattice constant.

4. Conclusion

The first principles molecular dynamics simulation of SrF_2 and BaF_2 crystals with V_k -center unveiled one unexpected and previously unknown result, namely, the existence of intermediate state in these two crystals, which is, however, is not observed in CaF_2 crystal. The intermediate state is formed when one of the fluorine ions composing V_k -center jumps into nearest interstitial position. This state also may be considered as the pair of H-center and nearest anion vacancy. The accuracy of present calculations does not allow to determine whether the intermediate state is a shallow local minimum of total energy or it is a saddle point surrounded by a region with a very gentle slope of potential energy surface. In both cases the intermediate state must be thermodynamically unstable. However, it still can significantly influence the behavior of V_k -center, appearing for short periods of time and thus implementing additional channel for diffusion and transformation of V_k -center. This is consistent with what has been seen in MD simulations where the intermediate state lives only for short period of time (about 100 fs)

There are three are possible diffusion channels of V_k -center in BaF_2 and SrF_2 crystals, including the jump through an intermediate state.

Two other channels, namely the 0° jump and the 90° reorientation are common for all three considered crystals. The existence of additional channel for V_k -center diffusion and transformations in SrF_2 and BaF_2 crystals compared to CaF_2 can possibly explain certain qualitative difference in radiative defect formation between these crystals (Catlow C R A, 1979).

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