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Transformation of Cd$^+$ centers containing an anion vacancy and their thermal stability

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In this work, we studied the temperature stability of Cd$^+$ centers having different nearest environments, mainly on calcium fluoride crystals. The results of various optical and thermal transformations of these centers are also presented. It is shown that the attachment of an anionic vacancy to a Cd$^+$ ion increases its thermal stability in a crystal.

1. Introduction

A number of defects in solids may have more than one charge state. The simplest example is provided by anion-vacancy centers in alkali metal halides. These centers are observed in three states: α-center (anion vacancy), F-center (anion vacancy that has captured an electron), and F′-center (anion vacancy that has captured two electrons) [1]. The useful properties of crystals are often governed by the introduced impurity and its charge state. Different charge states of impurities either are associated with the conditions of crystal formation or arise under the influence of ionizing radiation or additive coloring of crystals. Certain charge states in different matrices may have zero stable states. This instability has the following causes [2]:

(1) instability associated with electron loss (i.e., the ground state of the impurity is localized either close to the conduction band or in the conduction band);

(2) instability caused by the loss of a hole (i.e., capture of an electron from the valence band);

(3) instability associated with the so-called centers with negative correlation energy, which may exist in three charge states. Notably, the intermediate charge state is unstable and decays into the remaining two [3]. Although this type of instability is rare in ionic crystals (it normally emerges under strong covalent interactions), it is still taken into account in certain cases in the examination of such crystals [4].

A number of theoretical estimates of the position of levels in the band diagram indicate that monovalent transition metal ions should be unstable in numerous materials (see, e.g., [2,5]) due to localization of the ground state close to the conduction band. At the same time, the results of numerous experimental studies indicate that such a valence state is nevertheless realized in a certain way (examples were provided in [2,4]). Our research is focused, among other things, on finding possible answers to this contradiction.

Radiation coloring leads to the formation of impurity centers containing an anion vacancy in crystals of alkaline earth fluorides. Mechanisms inducing the formation of such centers may vary greatly depending on the impurity type. Several options for this formation process were discussed in [6].

In the present study, the temperature stability of a number of centers associated with the monovalent state of cadmium ions (primarily in calcium fluoride crystals) is examined. We have demonstrated earlier [7,8] that radiation coloring in crystals of alkaline earth fluorides activated by divalent cadmium or zinc ions leads to the formation of Zn$^+$ and Cd$^+$ centers with different nearest-neighbor environments and different kinds of temperature stability. Some of these centers have an anion vacancy in their nearest-neighbor environment.

2. Experimental procedure

Crystals of alkaline earth fluorides doped with Cd^{2+} ions were grown from melt by the Bridgman−Stockbarger method in a graphite crucible in an inert atmosphere. Since cadmium fluoride is usually added in the process of growth of fluoride crystals to prevent the formation of oxygen impurities and escapes during growth, our experiment had to be carried out under a seal from own melt to prevent the cadmium impurity from evaporating.

Radiation coloring of crystals was performed using an X-ray tube with a Pd anode at 30 mA, 40 kV, and an irradiation time no greater than 60 min.

Absorption spectra were recorded with a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer. A Janis Research (CCS-100/204) closed-cycle helium optical cryostat was used for measurements at low temperatures (6−330 K).
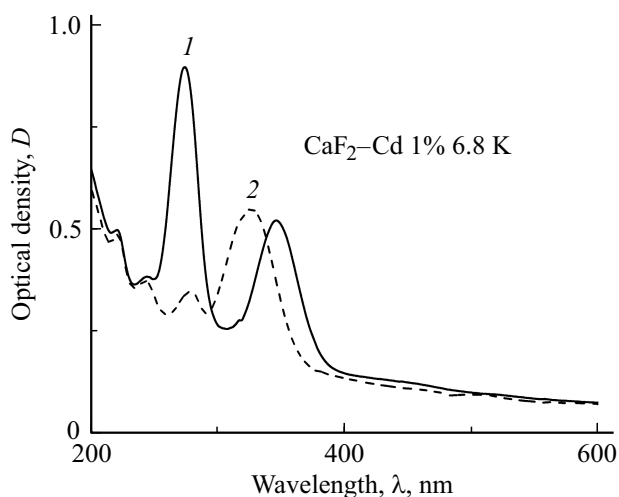
Figure 1. Spectra of absorption at 6.8 K of CaF_2-1% Cd crystals subjected to X-ray irradiation at room temperature (*1*) followed by bleaching (254 nm) with a low-pressure mercury lamp at 6.8 K (*2*).

Luminescence and excitation spectra in the $200-900$ nm spectral range were recorded with an LS-55 luminescence spectrometer (Perkin Elmer) with an R928 photomultiplier.

3. Experimental results

3.1. Optical transformation of centers at 7 K

In the process of growth of crystals of alkaline earth fluorides activated by cadmium impurities, cadmium ions are incorporated into the lattice of these crystals in the form of divalent ions. $Cd^+(C_{3v})$-centers (Cd^+ ions near an anion vacancy) [7,8] usually form following coloring of CaF_2-Cd crystals with X-ray radiation at room temperature. The same studies [7,8] were also the first to use the above notation for centers containing Cd^+. In certain rare cases, Cd^+-centers in a cubic environment ($Cd^+(O_h)$-centers [9]) are produced under X-ray irradiation at room temperature. However, irradiation at 77 K results in the formation of Cd^+-centers in a cubic environment; when heated, they transform into $Cd^+(C_{3v})$-centers [10]. Curve *1* in Fig. 1 corresponds to the spectrum of absorption at 6.8 K of $Cd^+(C_{3v})$-centers having two absorption bands with peaks at 347 nm (3.57 eV) and 274 nm (4.52 eV); the approximate ratio of these bands is 1 : 2. The positions of absorption bands of all types of Cd^+-centers do not change as the temperature drops from room temperature to 7 K. Bleaching with a low-pressure mercury lamp, which has an intense 254 nm line, leads to the formation of $Cd^+(O_h)$ with an absorption band maximum at 326 nm. Optical bleaching is fairly efficient, and an almost complete conversion of $Cd^+(C_{3v})$-centers into $Cd^+(O_h)$-centers (estimated by the absorption areas of these centers) may be achieved within a short interval of time. Longer-term bleaching results in destruction of $Cd^+(O_h)$-centers. The production of centers in a cubic environment in the

process of bleaching is confirmed by electron paramagnetic resonance (EPR) spectra.

The formation of $Cd^+(O_h)$-centers during the optical destruction of $Cd^+(C_{3v})$ in the high-energy absorption band at 7 K is quite unexpected. One is forced to assume that the bleaching of $Cd^+(C_{3v})$-centers stimulates somehow the motion of fluorine ions, which end up in an anionic vacancy; the vacancy moves to a certain distance, and, upon subsequent heating, $Cd^+(C_{3v})$ are restored (Fig. 2). The restoration of $Cd^+(C_{3v})$-centers involves at least two stages: above 100 K (100−150 K) and above 250 K (250−300 K). Similar stages are observed in the formation of centers with an anion vacancy attached [10,11], although the temperature ranges of formation may differ slightly. It is not entirely clear why two intervals are generally observed in the temperature curve of formation of centers upon the attachment of an anion vacancy.

It should be noted that bleaching of $Cd^+(C_{3v})$-centers at 7 K occurs only under illumination into the high-energy 274 nm absorption band (4.52 eV). The absorption bands remain unchanged under illumination into the low-energy 347 nm absorption band (3.57 eV). It is fair to assume that an electron is released into the conduction band under illumination into the high-energy absorption band.

This effect is also observed in SrF_2−Cd crystals (Fig. 3), although with a lower efficiency.

3.2. Optical transformation of centers at 300 K

Optical bleaching of $Cd^+(C_{3v})$-centers at 77 K with the formation of Cd^+ centers in a cubic environment also occurs only under illumination into the high-energy 274 nm absorption band (4.52 eV); when illuminated into the low-energy 347 nm absorption band (3.57 eV), the absorption bands remain unchanged. At room temperature, this optical destruction of $Cd^+(C_{3v})$-centers is accompanied by the formation of $Cd^+(C_{2v})$-centers [7,8] instead of centers
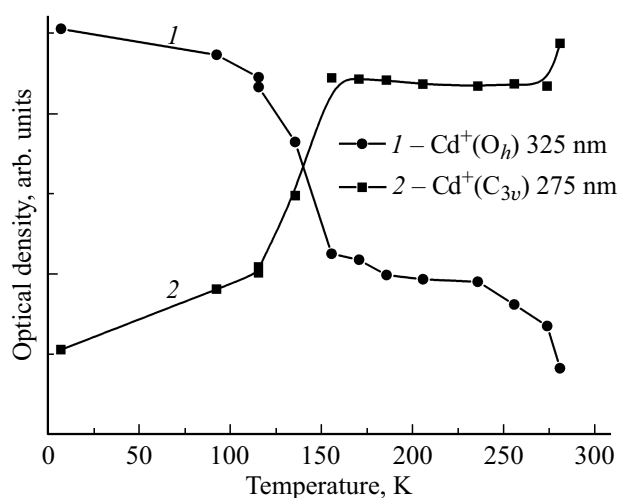

Figure 2. Temperature dependences of the thermal transformation of $Cd^+(O_h)$-centers (in the 325 nm absorption band) (*1*) into $Cd^+(C_{3v})$-centers (in the 275 nm absorption band) (*2*).
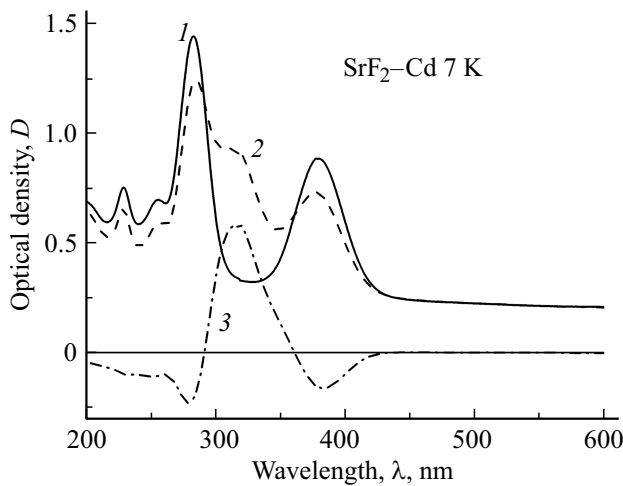
Figure 3. Spectra of absorption at 7 K of SrF$_2$-Cd crystals subjected to X-ray irradiation at room temperature (*1*) followed by bleaching (254 nm) with a low-pressure mercury lamp at 7 K (*2*). Difference curve (*3*).
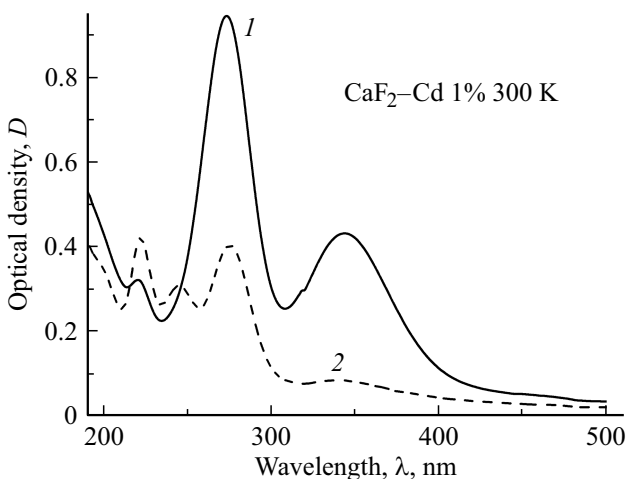

Figure 4. Spectra of absorption at 300 K of CaF$_2$-Cd crystals subjected to X-ray irradiation at room temperature and annealed for 5 min at 370°C (*1*) and 520°C (*2*).

in a cubic environment. It can be assumed that, just as at 7 K, an anion vacancy under bleaching at 300 K gets displaced and attached to Cd$^+(C_{3v})$, forming Cd$^+$-centers containing two anion vacancies (Cd$^+(C_{2v})$-centers). The remaining Cd$^+(O_h)$ in a cubic environment are more unstable (compared to destruction at 7 K) and vanish quickly.

4. Thermal transformation of centers

Having examined the optical transformation of Cd$^+(C_{3v})$ into Cd$^+(C_{2v})$-centers, we concluded that an anion vacancy in this process shifts away from one Cd$^+(C_{3v})$-center and gets attached to another Cd$^+(C_{3v})$-center. However, the same transformation may also be achieved by thermal

annealing; it can be assumed that the displacement and attachment of an anion vacancy also occur in this case. Figure 4 shows the results of thermal annealing of CaF$_2$−Cd crystals irradiated with X-rays at room temperature. Heating to 370°C is accompanied by a slight increase in the number of Cd$^+(C_{3v})$-centers; with further heating, they are destroyed and transformed into Cd$^+(C_{2v})$-centers that have three absorption bands (Fig. 4, curve *2*), although (judging by the integral absorption areas) with a low efficiency.

Photoexcitation of Cd$^+$ centers with a symmetry lower than cubic induces luminescence in the infrared region for Cd$^+(C_{3v})$-centers and in the green region for Cd$^+(C_{2v})$-centers [7,8,12]. Therefore, it is convenient to monitor the thermal transformation of centers using luminescence spectra. Figure 5 illustrates the thermal transformation of centers determined from the luminescence spectra of these centers.

The transformation of Cd$^+(C_{3v})$-centers into Cd$^+(C_{2v})$-centers proceeds in a wide temperature range, while the destruction of both centers is confined to in a narrow temperature interval (i.e., the thermal stabilities of these centers are close). We have already observed a similar (not quite ordinary) thermal transformation and destruction of photochromic centers containing an anion vacancy in CaF$_2$ and SrF$_2$ crystals activated by certain rare earth ions [13]. It is fair to assume that similar processes occur in both cases.

5. Discussion and conclusion

Room-temperature radiation coloring of CaF$_2$, SrF$_2$, and BaF$_2$ crystals activated by divalent cadmium ions leads to the formation of Cd$^+(O_h)$-centers in a cubic environment, but these centers remain stable against destruction at room temperature only in BaF$_2$ crystals. In CaF$_2$ and SrF$_2$ crystals, a fraction of cubic Cd$^+(O_h)$-centers is transformed

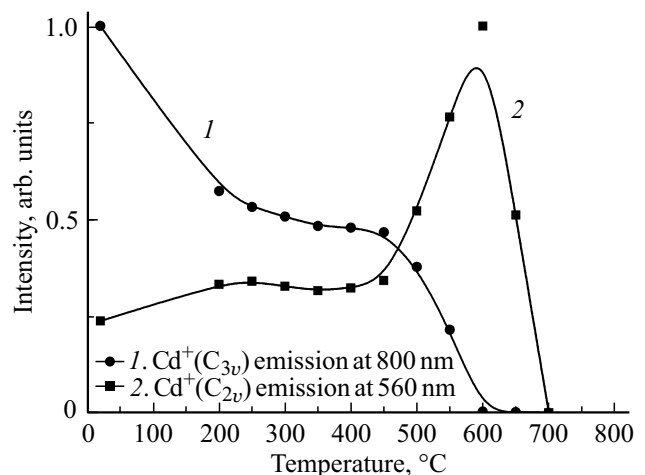**Figure 5.** Dependence of the emission intensity of Cd$^+C_{2v}$-centers (560 nm) and Cd$^+(C_{3v})$-centers (800 nm) on the temperature of annealing of CaF$_2$-Cd crystals subjected to X-ray irradiation at room temperature. Luminescence measurements were performed at 300 K.

quickly (within minutes) into Cd$^+$(C_{3v})-centers via anion vacancy attachment, and a significant fraction of cubic Cd$^+$(O_h)-centers is simply destroyed with restoration of the lattice within 24 hours. This was immediately apparent from the first results of EPR measurements: in CaF$_2$ and SrF$_2$ crystals, Cd$^+$(O_h)-centers were obtained only under radiation coloring at liquid nitrogen temperature, while measurements for BaF$_2$ crystals could also be performed at room temperature [14]. It should be noted that EPR in CaF$_2$ and SrF$_2$ crystals was obtained only for Cd$^+$(O_h)-centers [7,8,14], while EPR spectra in BaF$_2$ crystals were recorded for both Cd$^+$(O_h)-centers and Cd$^+$(C_{3v}) (the lack of one fluorine ion in the environment was noted for these centers) at 300 and 77 K [10,15,16].

Radiation coloring at low temperatures produces Cd$^+$(O_h) in a cubic environment and anion vacancies, which are apparently located nearby, but not in the nearest-neighbor environment (since F-centers do not form from these anion vacancies), in crystals of alkaline earth fluorides activated by divalent cadmium ions. No anion vacancies are produced in pure crystals. When heated, anion vacancies attach to Cd$^+$ ions, forming Cd$^+$(C_{3v})-centers [10]. It was assumed in [7,8] that the formation of anion vacancies is attributable to a more efficient separation of intrinsic pairs in electric fields produced by an excess charge of the impurity. Thus, the processes of radiation-induced formation of Cd$^+$(O_h)-ions in a cubic environment and anion vacancies are correlated. Apparently, the formation of Cd$^+$(O_h)-centers in the course of photobleaching of Cd$^+$(C_{3v})-centers at a temperature of 7 K (Fig. 1) is also associated with the correlation between Cd$^+$ defects and anion vacancies.

The stability of Cd$^+$(O_h)-centers at low temperatures and their thermal destruction at room temperature in CaF$_2$ and SrF$_2$ crystals indicate that the ground state of the center is located close to the conduction band, while this state in BaF$_2$ crystals is positioned significantly lower. The energy needed to transfer an electron from a monovalent cadmium ion to the conduction band may be determined using a cycle similar to the one used in the exciton charge transfer model [17,18]: a metal ion is removed from a cation site, ionized, and returned back to the cation site. A similar method was used to estimate the ionization thresholds of divalent rare earth ions in alkaline earth fluorides [19–22]. The energy position of the ground state of Cd$^+$ ions is determined by the following expression (negative energy corresponds to a stable state):

$$E_{pi} = -I(\text{Cd}^+) + E_M(M^{++}) - E_p(M^{++})$$
$$- E_\chi + \Delta_M(M^{++}) = \sum E + \Delta E_M(M^{++})$$

where $a(M^{++})$ is the distance between cations (face-centered lattice of alkaline earth metal ions), $a(M^{++} - X^-)$ is the cation–anion distance, $\Delta E_M(M^{++})$ is the Madelung energy per electron for a cation site [24,25], $\Delta E_p(M^{++})$ is the Madelung energy correction for an impurity cation site, and is the polarization energy for a cation site [26,27].

Table 1. Energy position of the Cd$^+$ ion in fluorite lattices

Parameters	Crystal			Reference
	CaF$_2$	SrF$_2$	BaF$_2$	
$a(M^{++})$ Å	3.865	4.1012	4.3842	[23]
$a(M^{++} - X)$, Å	2.3668	2.5114	2.6847	[23]
$E_M(M^{++})$, eV	19.94	18.78	17.59	[24,25]
$I(\text{Cd}^+)$, eV	16.908	16.908	16.908	[29]
$E_p(M^{++})$, eV	1.73	2.01	2.02	[26,27]
E_χ, eV	0.312	0.652	1.2	[28]
$\sum E$, eV	0.99	−0.79	−2.538	

The electron affinity for these E_χ crystals is not precisely known, but is commonly assumed to be lower than 1 eV. The E_χ values given in the table were obtained using the formula from [28], and the value for BaF$_2$ crystals appears to be implausibly large. $\sum E$ is the provisional sum separating the $\Delta E_M(M^{++})$ term from the principal sum, which will be discussed separately. All data pertaining to the formula are presented in the table. The provisional sum $\sum E$ data demonstrate that it characterizes the experimental data correctly: Cd$^+$(O_h)-centers in CaF$_2$ and SrF$_2$ crystals are less stable than in BaF$_2$ crystals. The last $\Delta E_M(M^{++})$ correction is related to the difference in ionic radii between alkaline earth fluoride ions and impurity ions. This correction introduces a rather substantial arbitrariness in energy due, on the one hand, to a strong dependence of energy on the ionic radius (a 0.01 Å change in ionic radius translates into a 0.2 eV change in energy) and, on the other hand, to uncertainty in the values of ionic radii (in particular, the radius of Cd$^+$). Notably, the change in environment around the impurity is usually less significant than the difference in ionic radii (the estimate given in [21] is 0.7). Although no experimental values of the ionic radius of Cd$^+$ have been reported, it was estimated theoretically in [30]: $r(C_d^+) = 1.14$ Å. This value is greater than the ionic radius of Ca^{2+}, close to the ionic radius of Sr^{2+}, and smaller than the ionic radius of Ba^{2+}. Therefore, the $\Delta E_M(M^{++})$ correction will shift the Cd$^+$ level below the conduction band in CaF$_2$ crystals, will not change the position of the level in SrF$_2$ crystals, and will raise the ground state of Cd$^+$ closer to the conduction band in BaF$_2$ crystals. Although the effects of this correction are qualitatively clear, there is a significant quantitative uncertainty and spread in energy. However, these results still allow one to state that the ground state of Cd$^+$ ions in a cubic environment is located close to the edge of the conduction band in all fluorite-type crystals, while the same state in BaF$_2$ crystals is localized lower than in CaF$_2$ and SrF$_2$ and is thermally stable.

Cadmium ions in the monovalent state in CaF$_2$ and SrF$_2$ crystals acquire a considerable temperature stability upon the attachment of an anion vacancy (Fig. 5). An anion vacancy lowers the ground state of Cd$^+$ ions significantly relative to the conduction band (this estimate was made in [22] for rare earth divalent ions). Apparently, the

attachment of an anion vacancy is a common method of thermal stabilization of an unstable impurity state (not only for Cd^+ and Zn^+ ions, but also for unstable divalent rare earth ions [22,31]).

Similar data on the stability of Cd^+ ions were obtained in Rb_2ZnCl_4 crystals [31]. At low temperatures, $Cd^+(I)$ ions are stable and substitute zinc ions isomorphically. At temperatures above 190 K, they are transformed into $Cd^+(II)$-centers, which have an anion vacancy in the nearest-neighbor environment; the latter are stable even at room temperature. However, it follows from the thermal transformation curves of centers that only a fraction of $Cd^+(I)$-centers is transformed into $Cd^+(II)$-centers; the majority of them are destroyed without forming stable states of Cd^+ ions.

It was demonstrated in [22] that the formation of photochromic PC^+-centers, which contain an impurity ion and an anion vacancy, is associated with the configurational instability of the ground $d1$ state of a divalent rare earth ion, since its ground state is localized in the conduction band. Thus, the chemical instability of divalent compounds for these ions (La, Ce, Gd, Tb, Lu, and Y) leads to the formation of PC^+-centers, which may be represented as a divalent ion near an anion vacancy in alkaline earth fluorides.

If we assume that the transformation of $Cd^+(C_{3v})$-centers into $Cd^+(C_{2v})$-centers is associated with the attachment of another anion vacancy, an increase in the number of vacancies does not exert a significant effect on the thermal stability of the center. In the general case, other types of distortion of the nearest-neighbor environment leading to thermal stabilization of an unstable impurity ion should apparently be present. It is possible that the shift of Ni^+ ions to an off-center position in alkaline earth fluorides is also associated with the thermal instability of this ion (and not only with its small size [5,32,33]). In semiconductors, rearrangement of the nearest-neighbor environment around an impurity ion results in the formation of so-called DX centers (see, e.g., [13]).

As was noted above, an anion vacancy lowers the ground state of Cd^+ ions relative to the conduction band; however, a simple estimate reveals that the ground state of Cd^{2+} ions is localized even lower relative to the conduction band (and closer to the valence band). Therefore, the difference between the ionization energies of an Cd^{2+} ion and a $Cd^+(C_{3v})$-center (correlation energy) is positive, and, consequently, the examined ion instability is not associated with a negative correlation energy [3] and is related only to the positioning of the ground state close to the conduction band.

Attention should also be paid to one more experimental fact: thermal instability of Cd^+ and Zn^+ ions in a cubic environment in CaF_2 and SrF_2 crystals ($Cd^+(O_h)$ and $Zn^+(O_h)$ centers) is accompanied by the formation of anion vacancies, which do not form in the same crystals without impurities, during radiation coloring. In BaF_2 crystals, $Cd^+(O_h)$ centers are stable at room temperature, and anion vacancies are not formed in these crystals. In other words, it is fairly difficult to produce $Cd^+(C_{3v})$)-centers (i.e., impurity centers containing an anion vacancy) in these crystals. In certain cases, the formation of such centers is attributed either to the presence of an additional alkali metal impurity [15,16] complementing cadmium and acting as a source of anion vacancies or to a nonuniform distribution of impurity cadmium throughout the crystal in large boules [10]. A natural question arises: are the thermal instability and anion vacancy formation processes related or is this just a chance coincidence? A qualitative explanation for the relationship between the formation of an anion vacancy and the stability of Cd^+ ions in the CaF_2, SrF_2, BaF_2 series may be devised. The formation of anion vacancies is apparently associated with a more efficient separation of intrinsic $\alpha - I$ pairs in electric fields produced by an excess charge of the Cd^+ impurity in CaF_2 and SrF_2 due to the smallness of the lattice constant of these crystals (compared to BaF_2). Large dimensions of the BaF_2 lattice contribute to a reduction of the Madelung energy and lowering of the ground state of Cd^+ ions relative to the conduction band, thus stabilizing Cd^+ ions, while the higher Madelung energy in CaF_2 and SrF_2 with smaller lattice dimensions raises the ground state of Cd^+ ions to the conduction band.

Thus, one may conclude that thermal stabilization of unstable states of monovalent ions (specifically, those that are unstable due to localization of the ground state in the conduction band) is achieved in certain cases via rearrangement of the nearest-neighbor environment (in particular, the attachment of an anion vacancy to a monovalent ion).

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Conflict of interest

The authors declare that they have no conflict of interest.

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