

Defect aggregation in anion-excess fluorites. Dopant monomers and dimers

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This paper is concerned with a theoretical examination of the stability of small clusters of substitutional trivalent cation impurities and interstitial fluoride ions in the three fluorites CaF_2 , SrF_2 , and BaF_2 . The energies of a variety of clusters have been calculated and the stability of the clusters examined; of particular interest is their ability to trap or lose interstitials and their ability to change their orientation. We find that in CaF_2 the nearest-neighbor (NN) C_{4v} complex $M_s^{3+}F_i^-$ (s denotes substitutional, i denotes interstitial) is more stable, whereas in BaF_2 it is the next-NN (NNN) C_{3v} complex that is more stable; in SrF_2 the NN and NNN complexes have comparable stability. The stabilization of NN dimer clusters containing two M_s^{3+} and two F_i^- by the relaxation in opposite $\langle 111 \rangle$ directions of NN lattice F^- ions is confirmed. Dimers in which the F_i^- ions are in NNN rather than NN positions have comparable stability to the NN dimers and so are presumably formed when it is the NNN monomer that is favored. Like the monomers, the dimers can lose F_i^- by dissociation and so may contribute to charge-transport processes. The NN dimer can trap free F^- interstitials with remarkable facility; in CaF_2 this is so even when these interstitials must come from the dimers themselves. In both CaF_2 and SrF_2 the NN dimers can take F_i^- from NN monomers. Wherever possible our theoretical results have been compared with experimental data. Our results on the stability of clusters are in general qualitative agreement with experiment in every case where data are available. It is perhaps surprising, therefore, that the calculated activation energies for dipolar orientation are generally too high by about 0.2 eV and we have been unable to find the origin of this discrepancy; it seems, however, not to lie with the $M_s^{3+}F_i^-$ potentials.

I. INTRODUCTION

Anion excess fluorites provide an ideal system for studying detailed structural properties of defective solid solutions. In the first place, they exhibit an exceptionally wide range of solubilities for substitutional trivalent cations of which yttrium and the rare-earth cations are the most commonly used. Secondly, a variety of experimental techniques can be brought to bear on such systems: These include diffraction techniques, EPR, NMR, optical spectroscopy, dielectric loss, transport measurements, and computer simulations. Nevertheless, the complexity of these systems is such that there remain several problems concerning detailed structural

properties of the defects; in some cases these relate to the fundamental nature of the solid solution.

This paper is concerned with the first of these problems, namely, the structural properties of small discrete aggregates (containing not more than two dopant ions): The validity of the description of dilute solutions, containing less than 1 mol %, in these terms is well established. In a future paper, which will be involved with the more heavily doped solutions, we plan to discuss the fundamental problem as to whether, under appropriate conditions, discrete cluster models can provide an adequate description of the structural properties of these solutions.

We use computer-simulation methods, the relia-

bility of which are well proved and which have recently been applied successfully to analogous problems in other systems.¹ The calculations reported in this paper allow us to distinguish between the relative stabilities of various possible configurations of small defect clusters and the variation of the stability of these clusters with the size of the dopant ion. We also comment on the mechanisms for dipolar reorientation of some of these species and on the possibility of further stabilization by the capture of additional interstitial ions. The next section discusses the available experimental data on these systems after which the techniques and lattice potentials which we use are described in greater detail. We then present the results of the calculations and discuss their relationship to experiment.

II. EXPERIMENTAL EVIDENCE ON SMALL CLUSTERS

The formation of discrete clusters containing a trivalent dopant ion and a charge-compensating interstitial fluoride ion was first conclusively shown by EPR studies.² Thus the electron-nuclear double resonance (ENDOR) study of Baker *et al.*³ on $\text{CaF}_2:\text{Yb}^{3+}$ identified the tetragonal pair cluster shown in Fig. 1(a). Indeed it is now clear⁴ that

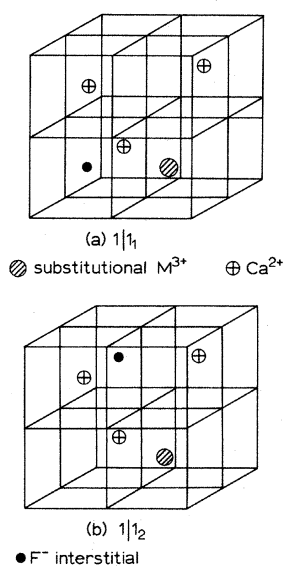


FIG. 1. (a) Nearest-neighbor and (b) next-nearest-neighbor clusters containing one trivalent M^{3+} ion and one F^- interstitial. In the new notation introduced in this paper these are called $1|_1$ and $1|_{1/2}$, respectively.

such nearest-neighbor (NN) clusters are the dominant pair cluster in CaF_2 doped with any trivalent ion. However, for other halides the formation of the alternative pair cluster in which the interstitial fluoride occupies the second-neighbor (NNN) site, Fig. 1(b), has been reported.⁵ The ratio of tetragonal to trigonal defects is evidently sensitive to the lattice parameter of the host crystal. By analogy with divalent dopants in alkali halides¹ one would suspect this ratio would also depend on the size of the trivalent substitutional ion.

Despite the simplicity of the structural properties of these complexes their reorientation processes are surprisingly complex. Relaxation experiments (including the measurement of dielectric loss and thermal depolarization spectra) have yielded a large number of different reorientation energies.⁶⁻¹⁴ The mechanisms may involve the transfer of interstitials of the type $\text{NN} \rightarrow \text{NN}$, $\text{NN} \rightarrow \text{NNN}$, $\text{NNN} \rightarrow \text{NN}$, and $\text{NNN} \rightarrow \text{NNN}$ although the details of these processes and their assignment in the observed spectra are not always clear. Some of the complexity of the observed data may, however, be due to the presence of clusters containing higher dopant aggregates. Evidence for the formation of dopant dimers and trimers is found in the laser spectroscopy of $\text{CaF}_2:\text{Er}^{3+}$.¹⁵ Earlier theoretical work¹⁶ favored a complex structure for the dopant dimer shown in Fig. 2(a), which rationalized the neutron diffraction data of Cheetham *et al.*¹⁷ on more heavily doped $\text{CaF}_2:\text{Y}^{3+}$.

We believe that the time has come to develop a more rational notation for clusters in fluorite crystals based on that introduced recently.¹⁸ The original description¹⁷ of the dimer cluster, for example, as 2:2:2, i.e., a cluster comprised of two vacancies, two $\langle 110 \rangle$ interstitials, and two $\langle 111 \rangle$ interstitials, though perhaps a rational one at the time, is now seen to be somewhat misleading. This cluster does not contain any vacancies, nor are there $\langle 111 \rangle$ interstitials. Rather, the two lattice ions above and below the plane containing the impurity ions have undergone a relaxation in $\langle 111 \rangle$ directions. The new notation which we find useful is

$i|v|q_r s_t \dots$, in which i is the number of impurity ions, q the number of interstitials which are in NN sites ($r=1$) to an impurity ion, and s is the number of interstitials that are in NNN sites ($t=2$) relative to an impurity ion: v is the number of vacancies and $|v$ is omitted if there are no vacancies in the cluster. Thus clusters containing one M^{3+} ion and one interstitial in a NN site are called $1|_1$ while a similar cluster with the interstitial in

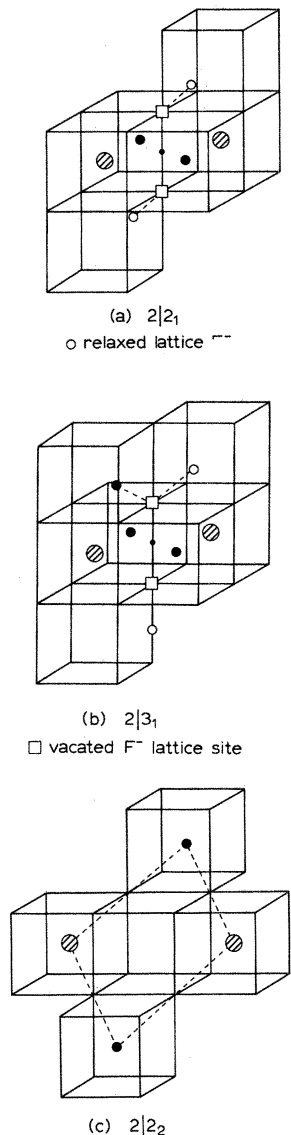


FIG. 2. Dimer clusters in fluorite crystals. (a) The $2|2_1$ cluster. (b) The $2|2_1$ cluster which has trapped an extra interstitial, making it a $2|3_1$ cluster. The trapped interstitial relaxes away from the normal cube-center interstitial site towards the site which is occupied in the perfect crystal by one of the lattice ions that undergoes a $\langle 111 \rangle$ relaxation in $2|2_1$. (c) The $2|2_2$ cluster. --- indicates $\langle 111 \rangle$ directions; the small filled circles show the origin of the coordinate system.)

a NNN site would be called $1|1_2$. The previously called 2:2:2 cluster we now term $2|2_1$.

Our own neutron diffraction study on 5-mol % $\text{CaF}_2:\text{La}^{3+}$ strongly suggests the formation of a dimer in which the aggregate has captured an extra interstitial [Fig. 2(b)]. The formation of this type of cluster is supported indirectly by the observation

of a dipolar relaxation in dielectric loss and thermal depolarization studies of the same crystal¹⁹ and by the detailed analysis of conductivity data on more lightly doped samples.⁹ Since it turns out that NNN complexes $1|1_2$ are favored in the BaF_2 we have also examined the stability of the dimer shown in Fig. 2(c) in which the F^- interstitials occupy NNN positions with respect to the substitutional M^{3+} ions. Thus the problems posed by the experimental results are the following: (i) the factors that determine the relative stabilities of NN and NNN pairs, (ii) the structures and energetics of aggregates containing two dopant ions, and (iii) the reorientation mechanisms of dipolar complexes. These unresolved problems are examined by the methods described in the next section.

III. METHODS

A. Computer simulation methods

We used standard defect simulation procedures, based on the Mott-Littleton method, which are programmed in the HADES code. Several calculations using this code have been reported, and their reliability for the study of defect aggregation has been established recently in divalently doped alkali halides.¹ The sizes of the explicitly simulated regions in all calculations were carefully matched and contained approximately 115 ions. Previous calculations have shown that the reliability of the results depend crucially on the interionic potentials which are discussed in the next section. In view of the complexity of the calculations and the large amounts of both core and computer time required, we have limited our approach to the harmonic approximation. It is not expected that any of our conclusions would be seriously affected by this limitation.

B. Potentials

The host-lattice potentials are those of Catlow *et al.*,²⁰ who used the shell-model treatment of ionic polarization and central-force pair potentials to represent the short-range interactions. Unlike previous theoretical studies of doped alkaline-earth fluorides the present study includes an explicit representation of ion size effects. These were calculated using electron-gas methods developed by Wedepohl²¹ and Gordon and Kim.²² The numerical potentials calculated by these methods were fit-

ted to a Born-Mayer form of potential and the resulting parameters are reported in Table I. The effect of varying the polarizability of the impurity ions was investigated and found to be negligible. In the results reported the shell parameters of the impurities were set equal to those of the host cation. The inclusion of M^{3+} - M^{3+} interactions, when the defects contained more than one impurity ion, was also found to have negligible effects (Table II).

IV. RESULTS AND DISCUSSION

A. Relative stabilities of $1|1_1$, $1|1_2$, and $1|1_3$ clusters

We present in Table III the calculated association energies for the formation the three types of dopant interstitial pairs for a number of M^{3+} ions in the three host lattices. Also listed is the difference $\Delta u(1-2)$ between the association energies of the $1|1_1$ [$\Delta u(1)$] and $1|1_2$ [$\Delta u(2)$] complexes. The following trends are evident. (i) For nearest- and next-nearest-neighbor complexes the dominant factor is the lattice constant of the host. The binding energy of $1|1_1$ complexes decreases as the lattice spacing increases, while that of the $1|1_2$ complexes increases correspondingly. (ii) The binding energy of third-neighbor complexes is close to the Coulomb value and consequently has rather similar values for CaF_2 , SrF_2 , and BaF_2 . (iii) In any one host there is a trend for the binding energy of the $1|1_1$ complex $-\Delta u(1)$ to increase with the radius R of the trivalent ion, while $-\Delta u(2)$ decreases slightly with R . This dependence of the type of complex formed on the radius of the trivalent ion was first studied systematically by Brown *et al.*²³ using EPR spectroscopy. That the dependence of

TABLE I. Interionic potentials: These are all of the form $\phi(r)=A \exp(-r/\rho)$ for M^{3+} - F^- interactions.

	A (eV)	ρ (Å)
Y^{3+}	1635.61	0.3023
Lu^{3+}	2281.96	0.2983
Yb^{3+}	3320.90	0.2808
Er^{3+}	2654.49	0.2920
Tb^{3+}	1951.01	0.3064
Gd^{3+}	2080.43	0.3032
Eu^{3+}	2596.24	0.2950
La^{3+}	2537.52	0.2980

$\Delta u(1-2)$ on R is a trend rather than a quantitative relationship is shown by Fig. 3 in which $\Delta u(1-2)$ is plotted against R . The effects of electron configuration are clearly evident. La^{3+} and Y^{3+} have closed shells while the remaining six dopants have an incomplete f shell. The $1|1_1$ clusters formed by these six ions are more stable (particularly in CaF_2 and SrF_2) and the $1|1_2$ clusters are correspondingly less stable than those formed by Y^{3+} . The general conclusion is that $1|1_1$ clusters are favored, primarily, by small lattice constants and, secondarily, by large ion radii with the exception already noted for Y^{3+} , for which the $1|1_2$ cluster is anomalously stable, compared to those of dopant ions of comparable radii but with incomplete f shells. This effect is particularly evident for CaF_2 and SrF_2 (Fig. 3).

Thus we find that in CaF_2 the $1|1_1$ cluster is predicted to be the dominant species for all the dopant ions studied except Y^{3+} , whereas for BaF_2 the $1|1_2$ clusters are calculated to be more stable. Strontium fluoride shows intermediate behavior with $1|1_1$ and $1|1_2$ clusters having comparable

TABLE II. Interionic potentials. These are all of the form $\phi(r)=A \exp(-r/\rho)$ for M^{2+} - M^{3+} interactions.

Impurity	Host	CaF_2		SrF_2		BaF_2	
		A (eV)	ρ (Å)	A (eV)	ρ (Å)	A (eV)	ρ (Å)
Y^{3+}		26 181.3	0.1983	16 622.5	0.2232	16 316.1	0.2419
Lu^{3+}		27 805.3	0.2000	39 160.0	0.2066	27 186.0	0.2334
Yb^{3+}		17 318.6	0.2127	20 907.6	0.2231	26 555.7	0.2346
Er^{3+}		28 857.9	0.2009	34 150.7	0.2115	28 004.3	0.2336
Tb^{3+}		24 246.6	0.2073	29 266.9	0.2172	28 470.3	0.2353
Gd^{3+}		35 733.9	0.1997	27 602.0	0.2194	26 896.2	0.2374
Eu^{3+}		21 191.1	0.2124	25 897.1	0.2218	25 274.3	0.2397
La^{3+}		25 549.6	0.2152	14 687.2	0.2431	16 050.9	0.2575

TABLE III. Energy changes in eV on substituting an M^{3+} ion for the host cation, on forming a $1|1_1$ NN complex from an isolated $1|0$ substitutional M^{3+} ion and a $0|1$ F_i^- [$\Delta u(1)$], on forming a $1|1_2$ NNN complex from an isolated $1|0$ M^{3+} ion and $0|1$ F_i^- [$\Delta u(2)$], on forming a $1|1_3$ third-NN complex from isolated $1|0$ and $0|1$ [$\Delta u(3)$], and the energy difference $\Delta u(1-2)$ between the formation energy of $1|1_1$ and $1|1_2$ clusters [$\Delta u(1) - \Delta u(2)$].

System	M_s^{3+}	$\Delta u(1)$	$\Delta u(2)$	$\Delta u(3)$	$\Delta u(1-2)$
CaF ₂ :Y ³⁺	-21.905	-0.502	-0.484	-0.390	-0.018
CaF ₂ :Lu ³⁺	-20.066	-0.710	-0.413		-0.297
CaF ₂ :Yb ³⁺	-20.895	-0.706	-0.419	-0.379	-0.287
CaF ₂ :Er ³⁺	-20.191	-0.730	-0.409		-0.321
CaF ₂ :Tb ³⁺	-19.663	-0.708	-0.408	-0.379	-0.300
CaF ₂ :Gd ³⁺	-19.794	-0.713	-0.411	-0.381	-0.302
CaF ₂ :Eu ³⁺	-19.716	-0.765	-0.395		-0.370
CaF ₂ :La ³⁺	-19.244	-0.799	-0.384	-0.377	-0.415
SrF ₂ :Y ³⁺	-23.568	-0.401	-0.592	-0.390	+0.191
SrF ₂ :Lu ³⁺	-21.905	-0.524	-0.537		+0.013
SrF ₂ :Yb ³⁺	-22.694	-0.509	-0.543	-0.379	+0.034
SrF ₂ :Er ³⁺	-22.032	-0.535	-0.534		-0.001
SrF ₂ :Tb ³⁺	-21.522	-0.527	-0.532	-0.384	+0.005
SrF ₂ :Gd ³⁺	-21.647	-0.529	-0.535	-0.386	+0.006
SrF ₂ :Eu ³⁺	-21.598	-0.563	-0.523		-0.040
SrF ₂ :La ³⁺	-21.163	-0.592	-0.515	-0.384	-0.077
BaF ₂ :Y ³⁺	-24.690	-0.376	-0.626	-0.344	+0.250
BaF ₂ :Lu ³⁺	-23.184	-0.369	-0.567		+0.198
BaF ₂ :Yb ³⁺	-23.937	-0.344	-0.572	-0.327	+0.228
BaF ₂ :Er ³⁺	-23.313	-0.372	-0.565		+0.193
BaF ₂ :Tb ³⁺	-22.822	-0.380	-0.565	-0.334	+0.185
BaF ₂ :Gd ³⁺	-22.491	-0.379	-0.568	-0.336	+0.189
BaF ₂ :Eu ³⁺	-22.916	-0.397	-0.555		+0.158
BaF ₂ :La ³⁺	-22.521	-0.423	-0.546	-0.332	+0.123

stability, especially for trivalent ions of small R , with the $1|1_1$ cluster being favored slightly at large R . Again Y^{3+} clusters form an exceptional case and in SrF₂ the $1|1_2$ cluster of Y^{3+} is predicted to be more stable than the $1|1_1$ cluster. We should note that these predictions rely entirely on calculated energies and could be modified by entropy effects in those cases where $\Delta u(1-2)$ is calculated to be small. However, they are in striking agreement with the recent systematic investigation of dielectric relaxation in CaF₂, SrF₂, and BaF₂ doped with trivalent cations.⁴ The relaxation results for $\epsilon''(T)$ show only $1|1_1$ clusters in CaF₂ (no data for Y^{3+} are presented); in SrF₂ $1|1_1$ clusters predominate for large R and $1|1_2$ clusters for small R , while in BaF₂ $1|1_2$ clusters appear exclusively except for La³⁺ and Ce³⁺. In a preliminary theoretical study¹⁶ similar conclusions were drawn with respect to the relative stabilities of $1|1_1$ and $1|1_2$ clusters. The same study also discussed the reasons for the variation in the values of

Δu with the radius of the dopant ion and the host-crystal lattice parameter. The essential factor appears to be the relaxations of the *lattice* ions surrounding the dopant. An outward movement, which would be most pronounced for the largest dopant ion, assists in the relaxation of the interstitial ion towards the dopant ion in the $1|1_1$ cluster and thus stabilizes the cluster. On the other hand, an inward relaxation of the lattice ions, which would be favored by a low ratio of dopant-ion radius to lattice parameter, assists the stabilization of the $1|1_2$ cluster relative to the $1|1_1$ cluster.

While the qualitative trends exhibited in Table III are certainly reliable, numerical accuracy to the third decimal place should not be presumed. $\Delta u(1)$ and $\Delta u(2)$ both arise from taking the difference of two much larger quantities of the order of 20 eV. Thus an accuracy of 0.1% in the energies of a $1|1_1$ or $1|1_2$ complex and also in the sum of the energies of $1|0$ and $0|1$, would result in uncertainties of ± 0.02 eV in $\Delta u(1)$ and $\Delta u(2)$ and

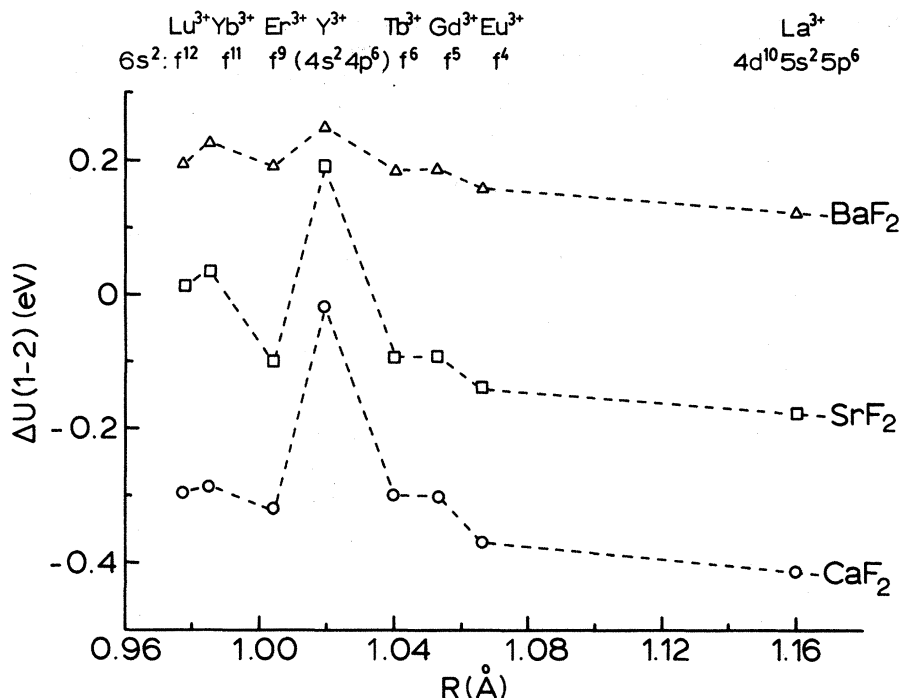


FIG. 3. Variation of the difference in the formation energy of $1|1_1$ and $1|1_2$ clusters $\Delta u(1-2)$ with the radius R of the M^{3+} substitutional impurity ion. The dashed lines are intended as an aid to the eye and do not imply that interpolation will necessarily yield a result of comparable accuracy, since the electron configuration evidently has some effect, this being particularly pronounced for Y^{3+} .

therefore of ± 0.04 eV in $\Delta u(1-2)$. A comparison of our calculated value of 0.006 eV for $\Delta u(1-2)$ for $\text{SrF}_2:\text{Gd}^{3+}$ with that of -0.046 eV which was derived by Matthews and Crawford²⁴ from quenching experiments in the temperature range 185–215 K, suggests that the above-mentioned uncertainties may be realistic.

B. Addition of fluoride interstitials to $1|1_1$ and $1|1_2$ clusters

It has been suggested by several authors²⁵⁻³⁰ that neutral clusters in doped fluorites might capture additional interstitials. Some possible configurations of the resulting clusters are shown in Fig. 4. We have investigated the energetics of this process for $1|1_1$ clusters and also, though in less detail, for $1|1_2$ clusters. The results of these calculations are summarized in Table IV, which gives the association energies of the additional interstitial with the dopant-interstitial complex in two possible configurations of each kind of cluster $1|2_1$ or $1|2_2$ and for a number of systems.

A clear trend that is apparent in the $1|2_1$ clus-

ters is the greater stability of the nonlinear relative to the linear complex. This result would not be predicted on the basis of a simple point-charge model for calculation of cluster energies, and may be attributed to the extra lattice polarization energy associated with the dipolar L complex. Indeed for CaF_2 we predict that additional free interstitials will be trapped by NN $1|1_1$ complexes to form stable nonlinear $1|2_1$ clusters. For the other systems investigated no trapping of fluoride interstitials by NN complexes is predicted, except in $\text{SrF}_2:\text{Y}^{3+}$. We have also investigated linear and bent complexes formed by the addition of a free fluoride interstitial to a $1|1_2$ cluster and found the resulting linear cluster to be stable in BaF_2 and in SrF_2 and marginally stable in $\text{CaF}_2:\text{Y}^{3+}$. The "bent" NNN cluster $1|2_2(b)$ in which the two F_i^- ions lie along a $\langle 110 \rangle$ direction [Fig. 4(d)] is also stable in SrF_2 , in BaF_2 , and in $\text{CaF}_2:\text{Y}^{3+}$, although uniformly less so than the NNN cluster in a linear configuration, presumably because of the greater $\text{F}_i^- - \text{F}_i^-$ Coulomb repulsion in the bent configuration. The sources of the additional interstitial ions required to form the clusters described here will be discussed in Sec. IV D.

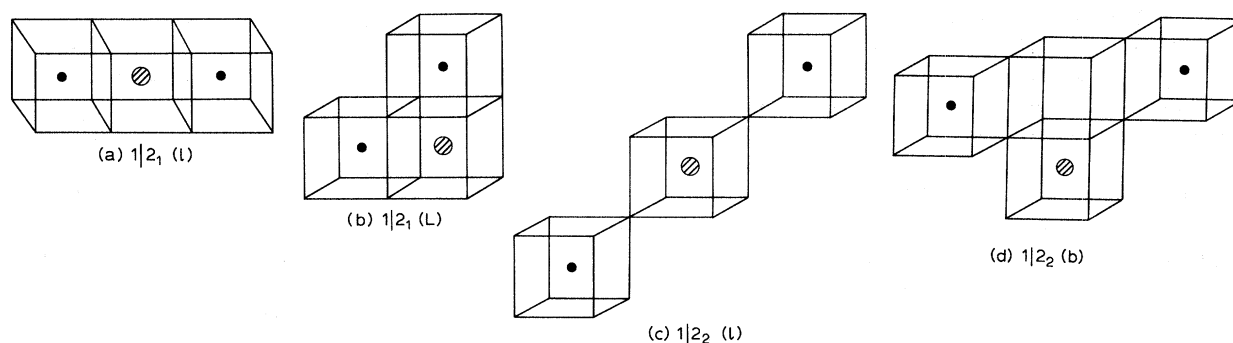


FIG. 4. Clusters containing one trivalent impurity ion and two interstitial fluoride ions. (a) linear $1|2_1(l)$; (b) L-shaped $1|2_1(L)$; (c) linear $1|2_2(l)$; (d) bent $1|2_2(b)$.

C. Dimerization

The existence of dimer clusters formed by the aggregation of two $1|1_1$ monomers was suggested by Cheetham, Fender, and Cooper¹⁷ to explain the early neutron diffraction results on heavily doped $\text{CaF}_2:\text{Y}^{3+}$. As discussed earlier, these $2|2_1$ dimers are stabilized^{16,17} by the relaxation in opposite $\langle 111 \rangle$ directions of the NN lattice F^- ions immediately above and below the center of the complex [Fig. 2(a)]. Figure 2(c) shows an alternative configuration $2|2_2$ for the dimer, one that one might have expected to occur when $1|1_2$ complexes are favored rather than the $1|1_1$ monomer.

We have also investigated the possibility of the $2|2_1$ clusters losing interstitials, a process analogous to the dissociation of monomers to yield isolated M_s^{3+} ions and free F^- interstitials, and therefore of possible importance in ionic transport in doped fluorites containing dimers.¹⁴ A preliminary study showed that the energy required to ionize off a free interstitial F^- ion from a $2|2_1$ complex was lower for one of the interstitials in the plane of the two M_s^{3+} ions than for one of the $\langle 111 \rangle$ relaxed-lattice F^- ions, and so the ionization energies in Table V refer to the processes



TABLE IV. Energy changes (in eV) on adding a free interstitial fluoride ion $0|1$ to a NN complex $1|1_1$ to form either a linear $1|2_1(l)$ or an L-shaped $1|2_1(L)$ cluster, or to a NNN complex $1|1_2$, along $\langle 111 \rangle$ directions, to form either a linear $1|2_2(l)$ or a bent $1|2_2(b)$ cluster.

System	$\Delta u(1l)$	$\Delta u(1L)$	$\Delta u(2l)$	$\Delta u(2b)$
$\text{CaF}_2:\text{Y}^{3+}$	0.270	-0.536	-0.159	-0.136
$\text{CaF}_2:\text{Yb}^{3+}$	0.117	-0.483	-0.079	-0.071
$\text{CaF}_2:\text{Tb}^{3+}$	0.079	-0.389	-0.073	-0.061
$\text{CaF}_2:\text{Gd}^{3+}$	0.081	-0.399	-0.071	-0.063
$\text{CaF}_2:\text{La}^{3+}$	0.004	-0.367	-0.042	-0.034
$\text{SrF}_2:\text{Y}^{3+}$	0.257	-0.241	-0.298	-0.223
$\text{SrF}_2:\text{Yb}^{3+}$	0.144	0.005	-0.243	-0.182
$\text{SrF}_2:\text{Tb}^{3+}$	0.119	-0.004	-0.235	-0.173
$\text{SrF}_2:\text{Gd}^{3+}$	0.121	-0.004	-0.235	-0.174
$\text{SrF}_2:\text{La}^{3+}$	0.074	-0.050	-0.213	-0.157
$\text{BaF}_2:\text{Y}^{3+}$	0.431	0.048	-0.302	-0.235
$\text{BaF}_2:\text{Yb}^{3+}$	0.159	0.083	-0.279	-0.208
$\text{BaF}_2:\text{Tb}^{3+}$	0.154	0.083	-0.257	-0.197
$\text{BaF}_2:\text{Gd}^{3+}$	0.153	0.071	-0.260	-0.198
$\text{BaF}_2:\text{La}^{3+}$	0.130	0.054	-0.244	-0.183

TABLE V. Energy changes (in eV) on forming a $2|2_1$ cluster from two $1|1_1$ complexes, on forming a $2|2_2$ cluster from two $1|1_2$ complexes, on ionizing off successive interstitials from $2|2_1$ clusters to form $2|1_1$ and $2|0$ clusters, and on trapping free F^- interstitials $0|1$ by $2|2_1$ clusters to form $2|3_1$ clusters. ED indicates that minimum-energy configuration could not be found due to excessive displacement of lattice-fluoride ions.

System	Dimerization		Ionization		Trapping $2 3_1$
	$2 2_1$	$2 2_2$	$2 1_1$	$2 0$	
CaF ₂ :Y ³⁺	-0.595	-0.392	1.196	0.958	-1.288
CaF ₂ :Lu ³⁺	-0.346	-0.306			
CaF ₂ :Yb ³⁺	-0.423		0.944	1.395	-1.482
CaF ₂ :Er ³⁺	-0.351	-0.301			
CaF ₂ :Tb ³⁺	-0.318		0.950	1.396	-1.405
CaF ₂ :Gd ³⁺	-0.327	-0.304	0.960	1.402	-1.416
CaF ₂ :Eu ³⁺	-0.307	-0.294			
CaF ₂ :La ³⁺	-0.419	-0.288	1.066	1.578	-1.283
SrF ₂ :Y ³⁺	-0.400	-0.538	1.028	0.707	-0.709
SrF ₂ :Lu ³⁺	-0.251	-0.397			
SrF ₂ :Yb ³⁺	-0.317		0.935	0.995	-0.838
SrF ₂ :Er ³⁺	-0.261	-0.394			
SrF ₂ :Tb ³⁺	-0.228		0.844	1.021	-0.721
SrF ₂ :Gd ³⁺	-0.237	-0.395	0.853	1.023	-0.832
SrF ₂ :Eu ³⁺	-0.227	-0.381			
SrF ₂ :La ³⁺	-0.197	-0.369	0.812	1.159	-0.910
BaF ₂ :Y ³⁺	ED	-0.462			ED
BaF ₂ :Lu ³⁺	-0.478	-0.419			
BaF ₂ :Yb ³⁺	-0.471		1.103	0.615	-0.545
BaF ₂ :Er ³⁺	-0.456	-0.420			
BaF ₂ :Tb ³⁺	-0.483		1.105	0.649	-0.551
BaF ₂ :Gd ³⁺	-0.478	-0.413	1.100	0.649	-0.553
BaF ₂ :Eu ³⁺	-0.422	-0.407			
BaF ₂ :La ³⁺	-0.282	-0.394	0.885	0.763	-0.704



We have also investigated the stability of the $2|3_1$ complexes that have been suggested as being formed by the trapping of $0|1$ by $2|2_1$ complexes^{4,15,27} and as possible sources of interstitials contributing to the ionic conductivity of CaF₂:Y³⁺,⁹ and the existence of which has recently been confirmed by neutron scattering experiments on heavily doped CaF₂:La³⁺.¹⁸ The relaxed positions of certain ions in the $2|2_1$ and $2|3_1$ clusters are given in Tables VI and VII.

The results of our calculations on $2|2_1$ clusters in Table V show that this dimer is stable with respect to two $1|1_1$ monomers in all the systems investigated. Similarly, the $2|2_2$ dimer [Fig. 2(b)] is stable with respect to two $1|1_2$ monomers. In CaF₂ $1|1_1$ complexes predominate and dimerization of these leads to $2|2_1$ clusters. In SrF₂ the $1|1_1$ and $1|1_2$ complexes have comparable stability. Dimerization favors the $2|2_2$ complex slightly,

except for SrF₂:Eu³⁺, where the difference in stability is very small, and for SrF₂:La³⁺, where the overall energy decrease Δ , on forming the dimer from two isolated $1|0 M^{3+}$ ions and two $0|1$ interstitials, is practically the same for the $2|2_1$ and $2|2_2$ dimers. In BaF₂ the $1|1_2$ complexes are more stable and Δ is lower for the $2|2_2$ dimers, showing that these are the favored form. Thus, both in CaF₂ and BaF₂, the dimer that forms depends on the type of monomer present. In SrF₂ the possibility of a switch from a NN to a NNN configuration on dimerization must be entertained. Of course these generalizations are subject to the same qualifications with respect to the influence of entropy effects and the size of the particular trivalent substituent ion, as were made in Sec. IV A.

Our calculations on the successive removal of the $\langle 110 \rangle$ interstitials from $2|2_1$ clusters show that the $2|1_1$ cluster and $0|1$ free interstitial are less stable than the $2|2_1$ cluster by 0.8–1.2 eV.

TABLE VI. Ion positions in the minimum energy configuration of the $2|2_1$ clusters. The ion coordinates refer to the origin shown in Fig. 2(a). Only the coordinates of one of the pair of ions related by symmetry are given, but those of the other member of the pair may be obtained from the information given and the coordinates of the corresponding unrelaxed ion.

System	Impurity ions relaxed from $\pm 0.5, \pm 0.5, 0$	F ⁻ interstitials relaxed from $\pm 0.5, \mp 0.5, 0$	F ⁻ lattice ions relaxed from the sites $0, 0, \pm 0.5$
CaF ₂ :Y ³⁺	0.491,0.491,0.040	0.339,-0.339,0.000	0.246,0.246,0.773
CaF ₂ :Lu ³⁺	0.494,0.494,0.029	0.358,-0.358,0.000	0.198,0.198,0.766
CaF ₂ :Yb ³⁺	0.495,0.495,0.029	0.353,-0.353,0.000	0.208,0.208,0.768
CaF ₂ :Er ³⁺	0.494,0.494,0.028	0.359,-0.359,0.000	0.196,0.196,0.764
CaF ₂ :Tb ³⁺	0.494,0.494,0.029	0.361,-0.361,0.000	0.193,0.193,0.764
CaF ₂ :Gd ³⁺	0.494,0.494,0.029	0.360,-0.360,0.000	0.194,0.194,0.764
CaF ₂ :Eu ³⁺	0.492,0.492,0.025	0.370,-0.370,0.000	0.171,0.171,0.754
CaF ₂ :La ³⁺	0.471,0.471,0.000	0.447,-0.447,0.000	0.000,0.000,0.657
SrF ₂ :Y ³⁺	0.463,0.463,0.052	0.318,-0.318,0.000	0.261,0.261,0.739
SrF ₂ :Lu ³⁺	0.480,0.480,0.038	0.326,-0.326,0.000	0.242,0.242,0.747
SrF ₂ :Yb ³⁺	0.480,0.480,0.036	0.324,-0.324,0.000	0.246,0.246,0.747
SrF ₂ :Er ³⁺	0.480,0.480,0.036	0.326,-0.326,0.000	0.241,0.241,0.748
SrF ₂ :Tb ³⁺	0.480,0.480,0.038	0.328,-0.328,0.000	0.240,0.240,0.748
SrF ₂ :Gd ³⁺	0.480,0.480,0.038	0.327,-0.327,0.000	0.240,0.240,0.748
SrF ₂ :Eu ³⁺	0.482,0.482,0.035	0.329,-0.329,0.000	0.235,0.235,0.748
SrF ₂ :La ³⁺	0.483,0.483,0.033	0.332,-0.332,0.000	0.229,0.229,0.748
BaF ₂ :Y ³⁺ ^a			
BaF ₂ :Lu ³⁺	0.461,0.461,0.070	0.297,-0.297,0.000	0.242,0.242,0.687
BaF ₂ :Yb ³⁺	0.461,0.461,0.065	0.295,-0.295,0.000	0.240,0.240,0.689
BaF ₂ :Er ³⁺	0.463,0.463,0.065	0.297,-0.297,0.000	0.239,0.239,0.689
BaF ₂ :Tb ³⁺	0.462,0.462,0.072	0.298,-0.298,0.000	0.243,0.243,0.685
BaF ₂ :Gd ³⁺	0.462,0.462,0.071	0.298,-0.298,0.000	0.242,0.242,0.687
BaF ₂ :Eu ³⁺	0.465,0.465,0.061	0.299,-0.299,0.000	0.236,0.236,0.691
BaF ₂ :La ³⁺	0.468,0.468,0.066	0.298,-0.298,0.000	0.239,0.239,0.711

^aNo minimum energy configuration found. Excessive displacements of lattice anions originally occurred at, e.g., 0, -1, -0.5.

Similarly, the $2|0$ cluster and free interstitial are less stable than the $2|1_1$ cluster by 0.6–1.4 eV. Thus, although the $2|2_1$ cluster is the stable form at low temperatures, these dimers are possible sources of interstitials in highly doped crystals at high temperatures just as the monomers are at lower temperatures and lower doping levels. Finally, we note that the $2|2_1$ clusters form deep traps for any free interstitials that might otherwise be present. The resulting $2|3_1$ cluster is most stable in CaF₂, less so in SrF₂, and least stable in BaF₂.

The coordinates of the defect ions in their fully relaxed positions in the minimum energy configurations are given in Tables VI and VII for the $2|2_1$ and $2|3_1$ clusters, respectively. These tables show that the impurity ions relax from their lattice sites along $\langle 110 \rangle$ directions towards the interstitials situated on these axes; the F⁻ interstitials similarly relax from cube-center positions along $\langle 110 \rangle$ to-

wards the impurity ions to a much greater extent. As already pointed out¹⁶ the key to the stability of these $2|2_1$ complexes is the relaxation of the F⁻ lattice ions at $0, 0, \pm 0.5$ approximately towards cube-center positions. The extent of this relaxation is typically about halfway towards the cube-center positions at $\pm 0.5, \pm 0.5, \pm 1.0$. In $2|3_1$ clusters the impurity ions occupy nearly the same positions as in $2|2_1$ clusters, but the two F⁻ interstitials that are in the (100) plane occupied by the impurity ions in the unrelaxed configuration relax upwards out of the plane by about $0.15a$. The lattice ion originally at $0, 0, +0.5$ and the third interstitial newly added to the cluster form a pair of " $\langle 111 \rangle$ interstitials" located approximately at $\pm 0.5, \pm 0.5, +1.0$. In fact they relax inwards to about $\pm 0.35, \pm 0.35, +0.8$, the extent of this relaxation depending on the host crystal and on the dopant ion (Table VII). The F⁻ ion originally at the lat-

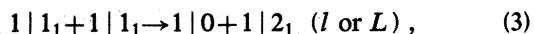
TABLE VII. Ion positions in the minimum energy configuration of the $2|3_1$ clusters. The ion coordinates refer to the origin shown in Fig. 2(b). The cluster contains three pairs of ions: For CaF_2 and SrF_2 the relaxed position of only one member of each of these pairs is given since the coordinates of the other member of the pair may be obtained from the coordinates quoted and those of the second ion in the column headings. For BaF_2 the final configuration of this cluster has lower symmetry than in CaF_2 and SrF_2 , so the coordinates of both ions in each pair are given for the impurity ions and $\langle 111 \rangle$ interstitials. A minimum energy configuration could not be located for $\text{BaF}_2:\text{Y}^{3+}$.

System	Impurity ions relaxed from $\pm 0.5, \pm 0.5, 0$	F^- interstitials relaxed from $\pm 0.5, \mp 0.5, 0$	" $\langle 111 \rangle$ interstitials" approximately at interstitial sites $\pm 0.5, \pm 0.5, + 1.0$	F^- lattice ion relaxed from the site $0, 0, -0.5$
$\text{CaF}_2:\text{Y}^{3+}$	0.478, 0.478, 0.038	0.349, -0.349, 0.147	0.368, 0.368, 0.847	-0.000, -0.000, -0.629
$\text{CaF}_2:\text{Yb}^{3+}$	0.485, 0.485, 0.027	0.356, -0.356, 0.157	0.370, 0.370, 0.864	-0.000, -0.000, -0.623
$\text{CaF}_2:\text{Tb}^{3+}$	0.488, 0.488, 0.028	0.360, -0.360, 0.155	0.369, 0.369, 0.868	-0.000, -0.000, -0.630
$\text{CaF}_2:\text{Gd}^{3+}$	0.488, 0.488, 0.028	0.360, -0.360, 0.156	0.369, 0.369, 0.868	-0.000, -0.000, -0.629
$\text{CaF}_2:\text{La}^{3+}$	0.490, 0.490, 0.024	0.364, -0.364, 0.156	0.369, 0.369, 0.873	0.000, 0.000, -0.630
$\text{SrF}_2:\text{Y}^{3+}$	0.462, 0.462, 0.085	0.324, -0.321, 0.117	0.358, 0.358, 0.811	-0.215, -0.215, -0.619
$\text{SrF}_2:\text{Yb}^{3+}$	0.469, 0.469, 0.037	0.338, -0.325, 0.147	0.368, 0.368, 0.829	-0.063, -0.063, -0.603
$\text{SrF}_2:\text{Tb}^{3+}$	0.470, 0.470, 0.047	0.338, -0.333, 0.151	0.370, 0.370, 0.839	-0.029, -0.029, -0.603
$\text{SrF}_2:\text{Gd}^{3+}$	0.470, 0.470, 0.047	0.339, -0.332, 0.151	0.370, 0.370, 0.839	-0.032, -0.032, -0.603
$\text{SrF}_2:\text{La}^{3+}$	0.473, 0.473, 0.041	0.339, -0.339, 0.153	0.372, 0.372, 0.847	-0.000, -0.000, -0.601
$\text{BaF}_2:\text{Yb}^{3+}$	0.479, 0.479, 0.090 -0.426, -0.426, 0.055	0.303, -0.290, 0.145	0.347, 0.346, 0.762 -0.318, -0.318, 0.763	-0.118, -0.118, -0.573
$\text{BaF}_2:\text{Tb}^{3+}$	0.481, 0.481, 0.098 -0.426, -0.426, 0.057	0.302, -0.296, 0.148	0.347, 0.347, 0.757 -0.320, -0.320, 0.765	0.113, -0.113, -0.575
$\text{BaF}_2:\text{Gd}^{3+}$	0.481, 0.481, 0.096 -0.427, -0.427, 0.056	0.303, -0.295, 0.148	0.346, 0.346, 0.758 -0.320, -0.320, 0.765	-0.113, -0.113, -0.575
$\text{BaF}_2:\text{La}^{3+}$	0.471, 0.471, 0.080 -0.444, -0.444, 0.052	0.307, -0.296, 0.158	0.344, 0.344, 0.774 -0.328, -0.328, 0.773	-0.083, -0.083, -0.568

tice site $0, 0, -0.5$ relaxes downwards very nearly in the $[00\bar{1}]$ direction in CaF_2 and also in SrF_2 apart from $\text{SrF}_2:\text{Y}^{3+}$. In this system, as well as in the $\text{BaF}_2:\text{M}^{3+}$ systems that we investigated, the relaxation is unsymmetrical and involves some x, y displacement as well. (See Table VII for a more detailed amplification of these generalizations: In $\text{SrF}_2:\text{Yb}^{3+}$, for example, the x, y relaxation is not much less than in $\text{BaF}_2:\text{La}^{3+}$.)

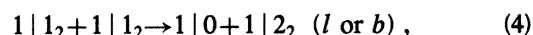
D. Cluster reactions in fluorites

In Secs. IVC and IVD we have seen that both the monomer and dimer clusters can capture free interstitials. However, the source of these interstitials is presumably the monomer and dimer clusters themselves. Our results can be used to discuss the reactions

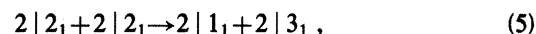


where l denotes the linear configuration and L the

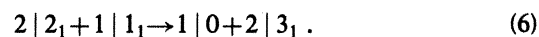
right-angled (\perp) configuration of the $1|2_1$ cluster comprising a $1|1_1$ complex and an extra F_i^- , and



where l and b denote the linear or bent configurations of the $1|1_2$ complex that has trapped an extra F_i^- . Similarly, $2|2_1$ dimers may undergo the disproportionation reaction



or $2|2_1$ dimers may trap an interstitial produced by dissociation of a $1|1_1$ monomer



The energy changes associated with these possible reactions (3)–(6) have been calculated and are given in Table VIII. We see that reaction (3), the disproportionation of two $1|1_1$ NN monomers, is highly improbable, except in $\text{CaF}_2:\text{Y}^{3+}$ where L-shaped complexes comprising an Y^{3+} ion and two NN F_i^- may exist in equilibrium with $1|1_1$ monomers. Similarly, reaction (4), the disproportiona-

TABLE VIII. Energy changes (in eV) associated with the disproportionation of a $1|1_1$ monomer to form $1|0$ and $1|2_1$ in either the linear (l) or L configuration, with the disproportionation of a $1|1_2$ monomer to form $1|0$ ion and $1|2_2$ in either the linear (l) or bent (b) configurations, with the disproportionation of a $2|2_1$ cluster to form $2|1_1$ and $2|3_1$ clusters, and with the transfer of a F_i^- ion from a $1|1_1$ monomer to a $2|2_1$ cluster to form a $1|0$ substitutional impurity ion and a $2|3_1$ cluster. (Omissions in the table indicate that the calculations were not performed since trends had already been sufficiently established. A dash indicates that the energy of one of the defects could not be established due to excessive displacement of one of the lattice F^- ions.)

System	Reaction Product	(3)		(4)		(5)	(6)
		$1 2_1(l)$	$1 2_1(L)$	$1 2_2(l)$	$1 2_2(b)$	$2 3_1$	$2 3_1$
	$\text{CaF}_2:\text{Y}^{3+}$	0.772	-0.034	0.411	0.453	-0.093	-0.787
	$\text{CaF}_2:\text{Yb}^{3+}$	0.824	0.224			-0.433	-0.775
	$\text{CaF}_2:\text{Tb}^{3+}$	0.787	0.318			-0.455	-0.697
	$\text{CaF}_2:\text{Gd}^{3+}$	0.794	0.313	0.462	0.495	-0.457	-0.703
	$\text{CaF}_2:\text{La}^{3+}$	0.802	0.431	0.480	0.506	-0.220	-0.485
	$\text{SrF}_2:\text{Y}^{3+}$	0.659	0.162	0.325	0.414	+ 0.319	-0.308
	$\text{SrF}_2:\text{Yb}^{3+}$	0.654	0.515			+ 0.097	-0.330
	$\text{SrF}_2:\text{Tb}^{3+}$	0.646	0.524			+ 0.016	-0.300
	$\text{SrF}_2:\text{Gd}^{3+}$	0.650	0.525	0.344	0.427	+ 0.020	-0.320
	$\text{SrF}_2:\text{La}^{3+}$	0.666	0.542	0.351	0.429	-0.099	-0.318
	$\text{BaF}_2:\text{Y}^{3+}$	0.807	0.424	0.348	-	-	-
	$\text{BaF}_2:\text{Yb}^{3+}$	0.503	0.427			+ 0.559	-0.200
	$\text{BaF}_2:\text{Tb}^{3+}$	0.534	0.450			+ 0.554	-0.172
	$\text{BaF}_2:\text{Gd}^{3+}$	0.532	0.450	0.339	0.398	+ 0.547	-0.174
	$\text{BaF}_2:\text{La}^{3+}$	0.552	0.476	0.338	0.397	+ 0.180	-0.282

tion of two $1|1_2$ monomers, will not occur. Reaction (5), the disproportionation of $2|2_1$ dimers, is most interesting. This is strongly favored for all the five dopants in CaF_2 that we investigated, except for Y^{3+} for which an equilibrium between $2|2_1$ dimers and $2|3_1 + 2|1_1$ complexes should exist. In SrF_2 , in which both $1|1_1$ and $1|1_2$ monomers may be found, the disproportionation reaction (5) is marginal, except in $\text{SrF}_2:\text{Y}^{3+}$ where it is not expected to occur. In BaF_2 this reaction would not occur but $1|1_2$ monomers are in any case favored over $1|1_1$ monomers in BaF_2 (Table III). Reaction (6) describes the ability of $2|2_1$ complexes to take F^- interstitials from $1|1_1$ monomers, and we see from Table VIII that this process is strongly favored in CaF_2 and less so in SrF_2 and BaF_2 .

E. Orientation of dipolar clusters

A considerable effort was devoted to finding the mechanism of the orientation of $1|1_1$ and $1|1_2$ dipolar clusters since these relaxation processes may

be studied experimentally. Two mechanisms for the orientation of $1|1_1$ clusters were examined: the interstitialcy noncollinear (INC) mechanism shown in Fig. 5(a) and the direct jump through a cube edge aided by the $\langle 111 \rangle$ relaxation of the two F^- lattice ions nearest to the mobile interstitial in its saddle-point configuration, Fig. 5(b). It turned out that this second mechanism required an activation energy larger than that for the INC mechanism by amounts varying from 0.11 eV in $\text{CaF}_2:\text{La}^{3+}$ to 0.42 eV in $\text{SrF}_2:\text{Yb}^{3+}$. It is most important in these calculations to use an adequate size for region I, that is, the inner region in which the relaxation of each individual ion is followed explicitly. The results for the orientation of $1|1_1$ monomers by the INC mechanism Δu_{11} in Table IX were obtained with 111 ions in region I; for 53 ions in region I the calculated values of Δu_{11} were considerably higher, 0.632 eV for $\text{CaF}_2:\text{Y}^{3+}$ and 0.758 eV for $\text{CaF}_2:\text{Gd}^{3+}$, for example.

Three mechanisms for the orientation of $1|1_2$ complexes were examined. These were the relaxation via NN sites ($1|1_2 \rightarrow 1|1_1$) shown in Fig. 5(c),

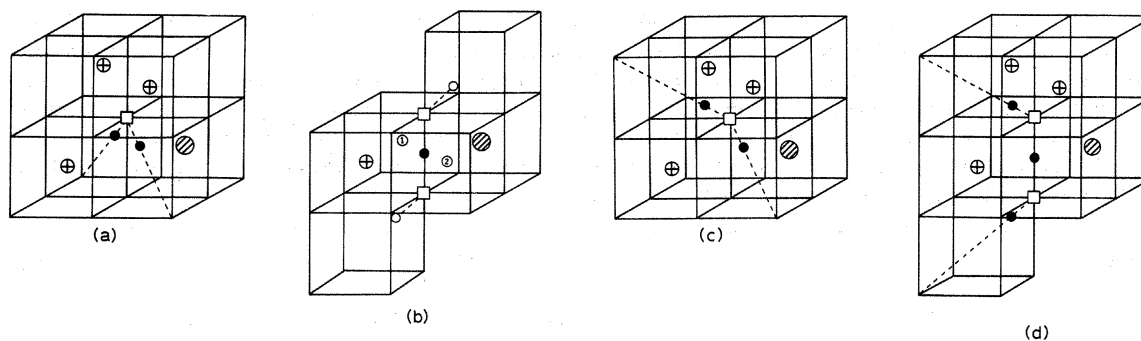


FIG. 5. (a) w_{11} saddle point for the interstitialcy noncollinear mechanism; (b) w_{11} saddle point for the direct jump from interstitial site 1 to the interstitial site marked 2 along $\langle 110 \rangle$; (c) w_{21} saddle point for the interstitialcy noncollinear mechanism; (d) w_{22} saddle point, double interstitialcy mechanism.

TABLE IX. Energy changes (in eV) associated with the reorientation of $1|1_1$ and $1|1_2$ clusters. Δu_{11} is the activation energy for the orientation of a $1|1_1$ monomer by the INC mechanism; Δu_{21} is the activation energy for the conversion of a $1|1_2$ monomer to a $1|1_1$ monomer, by the INC mechanism. A minimum-energy configuration could not be located for the Δu_{21} saddle point in $\text{BaF}_2:\text{Y}^{3+}$.

	Δu_{11}	Δu_{21}
$\text{CaF}_2:\text{Y}^{3+}$	0.569	0.734
$\text{CaF}_2:\text{Lu}^{3+}$	0.677	0.771
$\text{CaF}_2:\text{Yb}^{3+}$	0.579	0.769
$\text{CaF}_2:\text{Er}^{3+}$	0.678	0.772
$\text{CaF}_2:\text{Tb}^{3+}$	0.618	0.769
$\text{CaF}_2:\text{Gd}^{3+}$	0.616	0.770
$\text{CaF}_2:\text{Eu}^{3+}$	0.692	0.770
$\text{CaF}_2:\text{La}^{3+}$	0.637	0.769
$\text{SrF}_2:\text{Y}^{3+}$	0.580	0.729
$\text{SrF}_2:\text{Lu}^{3+}$	0.589	0.764
$\text{SrF}_2:\text{Yb}^{3+}$	0.560	0.775
$\text{SrF}_2:\text{Er}^{3+}$	0.586	0.765
$\text{SrF}_2:\text{Tb}^{3+}$	0.565	0.758
$\text{SrF}_2:\text{Gd}^{3+}$	0.564	0.760
$\text{SrF}_2:\text{Eu}^{3+}$	0.585	0.756
$\text{SrF}_2:\text{La}^{3+}$	0.558	0.747
$\text{BaF}_2:\text{Y}^{3+}$	(0.493)	
$\text{BaF}_2:\text{Lu}^{3+}$	0.359	0.757
$\text{BaF}_2:\text{Yb}^{3+}$	0.366	0.778
$\text{BaF}_2:\text{Er}^{3+}$	0.380	0.761
$\text{BaF}_2:\text{Tb}^{3+}$	0.327	0.746
$\text{BaF}_2:\text{Gd}^{3+}$	0.334	0.750
$\text{BaF}_2:\text{Eu}^{3+}$	0.393	0.749
$\text{BaF}_2:\text{La}^{3+}$	0.387	0.757

the relaxation via third-NN sites (not illustrated) and the jump from $\text{NNN} \rightarrow \text{NNN}$ sites which involves a double INC mechanism [Fig. 5(d)]. The second and third of these alternatives proved to have much higher activation energies than the first one, so only the results for Δu_{21} , the activation energy associated with the change $1|1_2 \rightarrow 1|1_1$, are given in Table IX. In this calculation it was necessary to fix the positions of the two interstitials in the saddle point to prevent the saddle point reverting to the more stable $1|1_2$ configuration. This consideration does not apply to the calculation of Δu_{11} where the collapse of the saddle point to the $1|1_1$ configuration is prevented by symmetry.

Experimental values of the activation energies for the relaxation of $1|1_1$ and $1|1_2$ complexes are given in Table X. Also shown is the activation energy for the so-called R_{IV} relaxation which is associated with a larger cluster, probably $2|3_1$. Fontanella *et al.*³¹ have shown the R_I relaxations in the dielectric spectra of CaF_2 double-doped with the pairs of ions Er^{3+} , Sm^{3+} , Nd^{3+} , and Dy^{3+} ; Nd^{3+} and Tb^{3+} show only the R_I relaxations of the singly doped species, thus confirming that this is the relaxation of a monomer cluster. On the other hand, the R_{IV} relaxation in double-doped CaF_2 shows, in addition to that characteristic of singly doped samples, a new relaxation that lies between the two R_{IV} peaks that are characteristic of the individual rare-earth dopants.³² This result strongly suggests that the R_{IV} relaxation is associated with a dimer cluster containing two rare-earth ions. The R_I relaxation is unambiguously identified with the $1|1_1$ NN monomer of tetragonal symmetry from the fact that the relaxation fre-

quencies of the tetragonal centers obtained from EPR line broadening in $\text{CaF}_2:\text{Gd}^{3+}$ lie on the same Arrhenius line as the R_1 frequencies found from dielectric relaxation measurements.^{33,34}

Several activation energies (particularly for CaF_2) have been determined independently by a number of different investigators. For the most part the agreement is satisfactory. For the sake of uniformity and to avoid too large a table, we have shown only the data from a single group. Thus, for example, the RI relaxation in CaF_2 has been measured for many of M^{3+} ions by the ionic thermocurrent (ITC) technique by Kitts and Crawford³⁵ with results very similar to those obtained from measurements of ϵ'' by Fontanella *et al.*^{6,7} The experimental results are most complete for the R_1 relaxation of $1|1_1$ monomers in CaF_2 . Our results for the favored INC mechanism are all higher than the experimental numbers by about 0.2 eV. We have no explanation of this fact. It is true that our calculations were made under the harmonic approximation, but it seems unlikely that lattice expansion can account for the difference, as the dipolar relaxations are observed at relatively low temperatures. In any case, while $\Delta u(T)$ decreases with T the corresponding enthalpy increases with T so our calculated values are lower bounds to the quasiharmonic enthalpies. At first we suspected the $M^{3+}\text{F}_i^-$ potential, but arbitrary quite severe changes in the $\text{Y}^{3+}\text{F}_i^-$ potential, for example,

failed to rectify the matter. A softening of the $\text{Y}^{3+}\text{F}_i^-$ potential did in fact reduce Δu_{11} slightly but at the cost of reversing the sign of $\Delta u(1-2)$. Since our potentials give the correct order of stability for the $1|1_1$ and $1|1_2$ monomers in all three host crystals, we feel that the fault probably does not lie with the $M^{3+}\text{-F}^-$ potentials. It also seems unlikely that the INC mechanism of dipolar relaxation is incorrect. Our calculations of Δu_{11} in SrF_2 are in rather better agreement with the experimental results of van Weperen and den Hartog.¹⁰ These authors allowed for dipole-dipole interactions, which have the effect of reducing the activation energy for dipole relaxation. If their analysis is correct, then activation energies that have not been corrected for dipole-dipole interactions may be too low by perhaps 0.01–0.05 eV. Quantitative results for $\text{BaF}_2:M^{3+}$ exist only for La^{3+} . Here our calculated result for Δu_{11} is in excellent agreement with the experimental (ITC) values obtained by Ong and Jacobs.³⁶ The ITC of $\text{BaF}_2:\text{La}^{3+}$ has also been measured by Laredo, Puma, and Figueroa¹³ and their results of 0.39 ± 0.02 and 0.50 ± 0.02 eV for the relaxation of $1|1_1$ and $1|1_2$ complexes agree satisfactorily with those of Ong and Jacobs.³⁶ Also the relative strengths of the $1|1_2$ and $1|1_1$ relaxations^{13,36} agree quite well with the ϵ'' measurements of Andeen *et al.*⁴ and with the relative stability predicted by our calculations (Table III).

TABLE X. Experimental results for the activation energy associated with the relaxation of small-defect clusters in CaF_2 , SrF_2 , and BaF_2 . (Reference numbers in parentheses.)

Z	M^{3+}	$R/\text{\AA}$ (37)	CaF_2		SrF_2		BaF_2	
			$1 1_1$	R_{IV}	$1 1_1$	$1 1_2$	$1 1_1$	$1 1_2$
39	Y^{3+}	1.019	0.409 (7)	0.552 (7)	0.471 (10)			
57	La^{3+}	1.160	0.443 (7)				0.391 (36)	0.544 (36)
58	Ce^{3+}	1.143	0.431 (6)		0.48 (10)			
59	Pr^{3+}	1.126	0.432 (6)	0.91 (6)	0.472 (10)			
60	Nd^{3+}	1.109	0.429 (6)	0.89 (6)	0.479 (10)			
62	Sm^{3+}	1.079	0.403 (6)	0.793 (6)				
63	$\text{Eu}^{3+\text{a}}$	1.066	0.414 (6)	0.757 (6)				
64	Gd^{3+}	1.053	0.414 (6)	0.723 (6)	0.471 (10)	0.64 (38)		
65	Tb^{3+}	1.040	0.404 (6)	0.645 (6)	0.457 (10)	0.52 (38)		
66	Dy^{3+}	1.027	0.406 (6)	0.604 (6)	0.451 (10)	0.53 (38)		
67	Ho^{3+}	1.015	0.409 (6)	0.580 (6)		0.57 (38)		
68	Er^{3+}	1.004	0.406 (6)	0.543 (6)		0.59 (38)		
69	Tm^{3+}	0.994	0.384 (35)	0.48 (6)		0.59 (38)		
70	Yb^{3+}	0.985	0.390 (35)			0.58 (38)		
71	Lu^{3+}	0.977				0.57 (38)		

^aMay be mainly Eu^{2+} in CaF_2 .

Experimental results for the relaxation of $1 | 1_2$ clusters exist only for $\text{BaF}_2:\text{La}^{3+}$ and for the ions $\text{Gd}^{3+} \rightarrow \text{Lu}^{3+}$ in SrF_2 (Table X). In the six cases for which they may be compared with experiment the calculated values of Δu_{21} are too high by 0.12–0.24 eV. Again no explanation is forthcoming as to why this should be so, except to note that it is the calculation of activation energies in the pure fluorites which is most sensitive to the details of the $\text{F}^- - \text{F}^-$ potential.²⁰

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