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A theoretical study of the aggregation of divalent impurities in NaCl:Mn, Pb and KCl:Mn, Pb

Jacques Soullard
Instituto de Física, Universidad Nacional Autónoma de México
Apartado postal 20-364, 01000 México, D.F., Mexico

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The formation energy of small clusters has been calculated in NaCl:Mn, Pb and KCl:Mn, Pb by means of a static simulation of ionic crystals; the results are used to study quantitatively the structure of the equilibrium state of crystals in the temperature range 600 K–425 K. In these systems the equilibrium state at high temperature is characterized by isolated impurities and dipoles. In NaCl:Mn, Pb dimers are found to nucleate on $\{110\}$, $\{100\}$ and $\{111\}$ planes, at 475 K the cluster population consists of $3/4$ dimers and $1/4$ trimers; about 30% of clusters have a mixed character. In the system KCl:Mn, Pb, the nucleation planes are $\{100\}$ and $\{110\}$. At about 475 K the equilibrium state is characterized by a high concentration of dipoles and the formation of dimers. Only 14% of dimers have a mixed character. This difference in mixed clusters concentration between the two systems agree qualitatively well with the results obtained from fluorescence experiments. This difference can be understood by considering the relative solubility of impurities.

Keywords: Defect structure; defect energy; mass action law

Se calcula la energía de formación de pequeños agregados en los sistemas NaCl:Mn, Pb y KCl:Mn, Pb utilizando una simulación estática de cristales iónicos; se utilizan los resultados para estudiar cuantitativamente la estructura del estado de equilibrio de los cristales en el intervalo de temperatura 600 K–425 K. En estos sistemas el estado de equilibrio a alta temperatura es caracterizado por impurezas aisladas y dipolos. En NaCl:Mn, Pb se encuentra que los dimeros se forman sobre planos $\{110\}$, $\{100\}$ y $\{111\}$; a 475 K la población de agregados consta de 75% de dimeros y 25% de trimeros; alrededor de 30% de agregados tienen un carácter mixto. En el sistema KCl:Mn, Pb los planos de nucleación son $\{100\}$ y $\{110\}$. A 475 K el estado de equilibrio se caracteriza por una alta concentración de dipolos y la formación de dimeros. Solamente 14% de dimeros tienen un carácter mixto. Esta diferencia en la concentración de agregados mixtos entre los dos sistemas está en buen acuerdo cualitativo con los resultados de los experimentos de fluorescencia. Esta diferencia en la concentración de agregados mixtos entre los dos sistemas está en buen acuerdo cualitativo con los resultados de los experimentos de fluorescencia. Esta diferencia se puede entender considerando la solubilidad relativa de las impurezas.

Descriptores: Estructura de defectos; energía de defecto; ley de acción de masa

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1. Introduction

Co-doped insulators have been developped for several decades in order to design materials suitable for solid state lasers and phosphors [1, 2]. Two types of impurity, generally metal transition or rare earth ions are introduced in an insulating matrix; one acts as a sensitizer (or donor) it absorbs incoming radiation, transfers the absorbed energy to the second impurity, the activator (or acceptor) which emits light with a wave length different from that of the incoming radiation.

In order to study experimentally the transfer mechanisms between the impurities in simple situations where the impurity sites are easily identified, alkali halide single crystals were used as host crystals. The acceptor is very often the doubly charged manganese ion whereas, as sensitizer ions like Eu^{2+}, Pb^{2+}, Cu^{+}, and Ag^{+} are found. The efficiency of energy transfer mechanisms has been recognized for a long time as being strongly dependent on impurity pairs (or dimers) formation [3] and this problem has been studied recently in details and intensively [4–17]. The dependence of energy transfer between sensitizer and activator upon impurity distribution has been studied also theoretically [18–20].

In doubly doped crystals three types of dimer are possible, two types are homogeneous, they contain like impurities, the other one is heterogenous. A criterion based on a comparison between the ionic radii of the impurities and the host cation radius has been proposed to predict the type of dimer which is likely going to form at the beginning of the aggregation process [7, 11, 17]. If r_1 and r_2 are the radii of impurities, the dimer whose formation is more likely is that where the ratio $(r_1 + r_2)/2\, r_c$ is closest to unity, r_c is the host cation radius.

On the other hand, the aggregation state of doubly charged impurites in alkali halide crystals has been studied theoretically in the passed when only one type of impurity is present in the crystal. The energy of impurity clusters, is calculated by means of an atomistic calculation, the most stable aggregates are determined and an aggregation path is proposed [21–23] (Ref. 22 will be cited later as Ref. I). More recently, the aggregation of Mg in LiF has been studied by a combination of a classical atomistic simulation and a quantum mechanical calculation [24]. The aim of the present work is to extend this type of study (when a classical simulation is used) to the case where two types of impurity are present at the same time in the host crystal. Our choice has been directed to the systems NaCl:Mn, Pb and KCl:Mn, Pb which optical properties have been studied experimentally [4–6, 10] and for which the necessary interionic potentials are available [25].

For these systems, the ionic radius criterion predicts that the formation of mixed clusters is more propitious in NaCl than in KCl. When the defect energies are known, the reaction energies for aggregation are determined and the concentration of defects is given by the mass action law. This calculation allows one to determine the dominant defects and the results can be compared to the predictions of the ionic radius criterion. A quantitative description of the defect structure of the equilibrium state at a given temperature is also helpful in determining the aggregation path of impurities in these systems, this determination is another outcome of this work.

2. Method and potential

The defect energies in the systems NaCl:Mn, Pb and KCl:Mn, Pb were calculated by using the static simulation of ionic lattice PDINT [26, 27]. The energy of a defect is defined as the energy difference between the defective and the perfect crystal. To calculate these energies, the potential function between two ions is summed up over all lattice points, but in the case of a defective crystal the equilibrium position of ions has to be determined. This is achieved after dividing the crystal into two regions. In the inner region (of radius R_1), the relaxation to equilibrium is obtained by means of numerical methods. The relaxation of the outer region (of radius R_2) is described in a continuum approximation. In the present calculation R_1 and R_2 were taken equal to 4.1 r_o and 6.1 r_o respectively (r_o = half lattice parameter). This procedure to calculate the defect energy is known as the generalized Mott-Littleton method [28].

The crystal bonding is assumed to be fully ionic and the potential function is the sum of a long range Coulomb potential and of a short-range potential, which describes the overlap of the electronic wave functions between two ions. The cut-off radius to calculate the short-range repulsion energy is taken equal to 1.8 r_o. The quality of the results depends on the potential model chosen to represent the short-range interaction. For the host crystals, the potential model known as CDN-set I developed by Catlow *et al.* is used [25]. These potentials have non-integral ion charges and the impurity charges were taken equal to twice the host ion charges in order to ensure the electrical neutrality of clusters [21]. The short range potential parameters were considered independent of the ion charge and taken equal to those derived with integral charges on the ions. This simplification of the potential model has also been used to study the aggregation process of divalent ions in alkali halides [21] as well as in studies relative to oxides where the cation presents several charge states [29, 30] and in both cases this approximation has been proved to be appropriate. The impurity ions were assumed unpolarizable, this assumption was shown to have an insignificant effect on the defect energy [31]. The impurity-ion host-ion potentials are of Born type, they are calculated independently from the model potential by using electron gas methods and were taken from Ref. I. The contribution of the repulsion between to like impurities to the defect energy is negligible and the repulsion Mn-Pb was not taken into account.

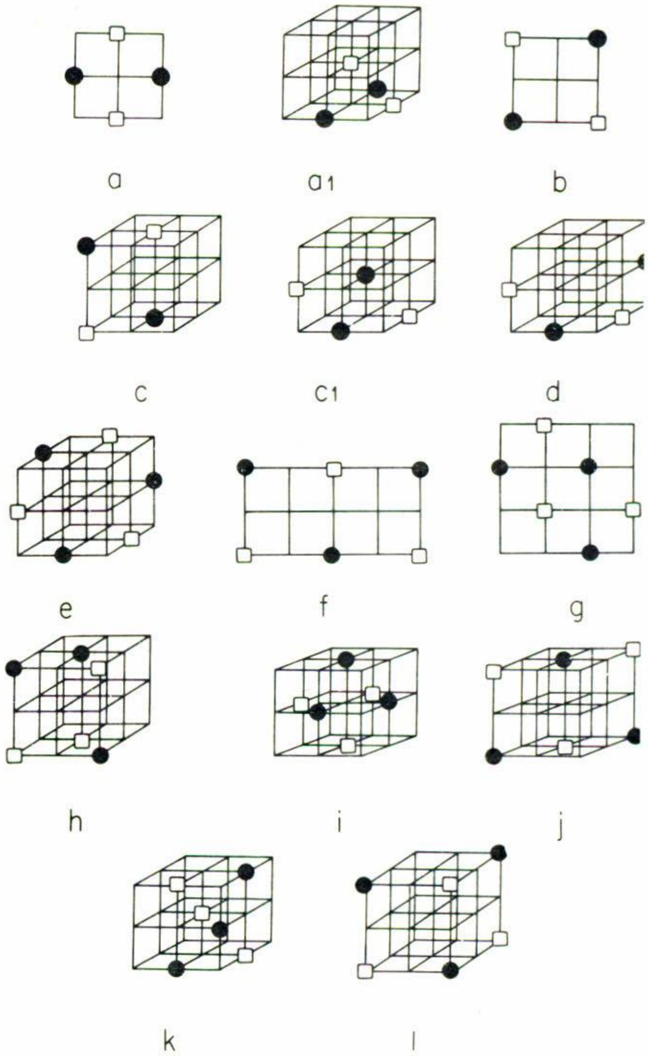

FIGURE 1. Dimer and trimer configurations.

3. Defect structure

In crystals doped with two types of impurity, the diversity of defects is increased by the presence of heterogenous clusters composed by unlike impurities and owing to the fact that a particular cluster has several possible configurations. The morphology of small clusters of divalent impurities in alkali halides has been described essentially in Ref. I and is given in Fig. 1.

Configurations a and b represent dimers in $\{100\}$ planes formed by n.n. dipoles and n.n.n. dipoles, respectively. The defect has only two different configurations whether the im-

TABLE I. Energy of basic defects and binding energy of dipoles (in eV).

System	Cation vacancy	Divalent impurity	n.n. dipole	n.n.n. dipole	Binding energy n.n.	Binding energy n.n.n.
$NaCl{:}Mn^{2+}$	5.1572	−10.1214	−5.5832	−5.4863	−0.619	−0.522
$NaCl{:}Pb^{2+}$	5.1572	−7.8724	−3.4182	−3.1799	−0.703	−0.465
$KCl{:}Mn^{2+}$	4.9301	−11.8735	−7.5770	−7.5731	−0.634	−0.63
$KCl{:}Pb^{2+}$	4.9301	−9.8632	−5.6218	−5.5082	−0.689	−0.575

purities are similar or not. The dimer with configuration $a1$ proposed by Gavartin *et al.* [24] is a variation of configuration a. The dimer with configuration c nucleates in $\{110\}$ planes and has three different configurations. It presents a particular interesting feature, it can be formed either by two n.n. dipoles or by two n.n.n. dipoles. The $\{110\}$ dimer $c1$ [24] can only be formed from n.n. dipoles. Two n.n. dipoles can bind together in a $\{111\}$ plane to form a dimer of configuration d, this defect has two distinct configurations with like impurities and three different configurations when the impurities are unlike.

In the systems NaCl:Mn, Pb and KCl: Mn, Pb four types of trimer can form; those where manganese impurities only are present (T111), those composed with lead impurities only (T222), those formed with two manganese impurities (T121) or with two lead impurities (T212). There are three ways to add a dipole to a dimer in order to form a trimer, the third dipole can be located in the dimer plane, in a plane parallel to the dimer plane or perpendicular to that plane. In the last two cases, trimer configurations resulting from the addition of an impurity pair or a vacancy pair to a planar defect where three vacancies or three impurities respectively are present are avoided because these configurations are not energetically favored.

The $\{111\}$ trimer e has two possible configurations but the most stable one is achieved when the two types of defect alternate. The trimers f, g, h, i, and l are formed from a dimer in a $\{100\}$ plane. In the configurations f and g, the third dipole is located in the dimer plane, 8 distinct configurations were studied for irregular trimers and 3 distinct configurations were found in the case of regular trimers. In configuration i the third dipole is perpendicular to the dimer plane, 2 and 4 configurations were studied for the homogeneous and heterogenous trimers respectively. The trimers h and l are formed by addition of a dipole parallel to the dimer plane, the number of distinct configurations studied for the regular and irregular complexes are 4 and 12 respectively for the configuration h; in the case of trimer l one and two configurations were studied respectively. The configurations of trimers j and k are based on the $\{110\}$ dimer. In the first case the three n.n.n. dipoles are in the same plane (3 homogeneous and 8 heterogeneous configurations were studied), in configuration k a n.n. dipole is added perpendicular to the $\{110\}$ dimer plane, 2 homogeneous and 4 heterogeneous configurations were studied. In the case of dimers and trimers, a given configuration can be realized in various ways. In the next section, the configuration which is reported is that of minimum energy.

4. Defect energies

4.1. Dipoles

The calculated dipole energies as well as the energies of isolated defects and the corresponding binding energies are given in Table I. The results show that the n.n. configuration is more stable than the n.n.n. one. The energy difference between the two configurations depends on the host crystal and on the impurity size. It is smaller in KCl than in NaCl and for impurities of smaller radius.

These results are similar to those obtained in Ref. I though the number of ions in region I in the present simulation (257) is greater than in the previous work and though the interionic repulsive potentials are slightly different. The agreement with experiments is fair, an improvement of the Mn^{2+}-Cl-potential is desirable [23]. When the binding energy of dipoles is calculated in the frame of a point ion model the same trends are observed but, in this case the theoretical binding energy is higher [32].

4.2. Dimers

Divalent impurities in doped alkali halide crystals are known to aggregate to form small clusters called dimers and trimers. On the other hand, these divalent impurities are charged defects which are neutralized by a cation vacancy which can be found close to the impurity or not depending on the temperature. When the impurity aggregation is studied, two cases have to be distinguished. If the temperature is high enough so that the divalent impurity-cation vacancy dipoles can dissociate, the encounter of a dipole with a defect (which can be an other dipole or a cluster) occurs when both defects are in an excited state, the dipole does not have a particular configuration, the new defect is also in an excited state and will reach its configuration of minimum energy (reported later in this work) after some rearrangements. The binding energy is given by the difference between the energy of the new defect and the sum of energies of isolated defects. The binding energies are given in Table II, second row for each dimer type. At

TABLE II. Energy of dimers in NaCl and KCl (in eV, first row), binding energies with respect to isolated defect energies (in eV, second row) and reaction energies with respect to isolated dipoles energy (in eV, third row) for each dimer type.

NaCl

Dimer Configuration	a	$a1$	b	c	$c1$	d
Type 11	−11.3477	−11.3072	−11.4114	−11.5268	−11.4028	−11.4080
	−1.419	−1.379	−1.483	−1.598	−1.474	−1.480
	−0.181	−0.141	−0.439	−0.360, −0.554	−0.236	−0.242
Type 22	−7.0999	−7.1750	−6.6678	−7.0751	−7.0536	−7.1254
	−1.669	−1.745	−1.237	−1.645	−1.623	−1.695
	−0.263	−0.339	−0.308	−0.239, −0.715	−0.217	−0.289
Type 12	−9.2789	−9.2994	−9.0473	−9.2918	−9.2425	−9.2978
	−1.600	−1.620	−1.368	−1.612	−1.563	−1.618
	−0.277	−0.298	−0.381	−0.290, −0.626	−0.241	−0.296

KCl

Dimer Configuration	a	$a1$	b	c	$c1$	d
Type 11	−15.0627	−15.2893	−15.7105	−15.6451	−15.3921	−15.36
	−1.176	−1.402	−1.824	−1.758	−1.505	−1.473
	−0.091	−0.135	−0.564	−0.491, −0.499	−0.238	−0.206
Type 22	−11.4769	−11.4024	−11.4757	−11.6094	−11.5257	−11.4967
	−1.611	−1.536	−1.609	−1.743	−1.659	−1.630
	−0.233	−0.159	−0.459	−0.366, −0.593	−0.282	−0.253
Type 12	−13.3043	−13.3659	−13.5977	−13.6254	−13.4756	−13.4551
	−1.428	−1.489	−1.721	−1.749	−1.599	−1.579
	−0.105	−0.167	−0.516	−0.427, −0.544	−0.277	−0.256

low temperature, the dipoles do not dissociate, they keep their identity (n.n. type or n.n.n type) during the encounter dipole-defect, the reaction energy is equal to the difference between the energy of the newly formed cluster and the sum of the dipole energy and that of the cluster which absorbs it. The reaction energies are given in Table II, third row for each dimer type.

When the temperature is greater than the dissociation temperature of dipoles, the calculated binding energies of dimers reported in Table II for the system NaCl:Mn, Pb show that nucleation in the $\{110\}$ plane (configuration c) for the Mn impurities is favored, whereas lead impurities nucleate preferentially in the $\{100\}$ plane (configuration $a1$) however, nucleation of Pb impurities on $\{111\}$ planes can also be considered because the binding energy of dimer d is close to that of dimer $a1$. Nucleation of Mn impurities on $\{110\}$ planes is consistent with the formation of a Suzuki phase in NaCl:Mn; Raman spectroscopy and X ray diffraction methods have provided strong evidences of the formation of this phase in this system [33].

Our result for lead nucleation is consistent with the analysis of luminesence polarization experiments obtained with lead doped NaCl single crystals indeed, these experiments exhibit the presence of two types of aggregate in samples anneled at 300 K for 1000 h after quenching [34]. One has a C3 symmetry and corresponds to aggregates form from $\{111\}$ dimers. The second one has a D4h symmetry and can result from the growth of $\{100\}$ dimers with configuration $a1$. For NaCl crystals singly doped with Mn or Pb our theoritical predictions are in agreement with the overall experimental facts. The results presented in Table II for homogenous dimers reproduce those obtained in Ref. I (except for configurations $a1, c, c1$ which were not studied). The predicted nucleation planes for mixed dimers are $\{111\}$, $\{110\}$ and $\{100\}$ the binding energies of dimers d, c, $a1$ and a being very close.

For the system KCl:Mn, Pb (Table II), there is a preferential aggregation of Mn impurities on $\{100\}$ and $\{110\}$ planes to form dimers b and dimers c respectively, their binding energies being close. In the case of Pb impurities, the $\{110\}$ nucleation plane only is expected, the binding energy of dimer c and $c1$ are greater than the binding energy of other dimers. The presence of this dimer is consistent with the development, in the system NaCl:Pb, of a Suzuki phase as proposed by Benci, Chiari and Fermi [35] or of a phase with a "Suzuki phase like structure" [33]. A model of this phase has been suggested recently by Gavartin *et al.* in LiF:Mg [24]. The results presented in Table II for homogenous dimers reproduce those obtained in Ref. I (except for configuration $a1, c, c1$). In the system KCl:Mn, Pb, the mixed dimers adopt mainly the configuration c and b.

At low temperature ($T \leq 425$ K), the reaction energies are given in Table II, for the dimer c two reaction energies are possible, they correspond to the association of two n.n. dipoles or two n.n.n dipoles.

In NaCl:Mn, Pb, a dimer c is expected to form by association of 2 n.n.n. dipoles in the three cases. The n.n. dipoles are found to associate to form a dimer with configuration c in the case of manganese; in the case of lead and mixed dimers, the most favorable configurations are $a1$ and d. The introduction of $\{110\}$ plane as nucleation plane where both types of dipoles can cluster, avoid the need to introduce an interconversion mechanism to explain the aggregation of the dipole type which does not correspond to the dimer of lowest energy.

In the system KCl:Mn, Pb, the n.n. manganese dipoles form a dimer c whereas, a dimer b results from the association of two n.n.n. manganese dipoles. Lead dimers and mixed dimers with configuration c result from the association of both types of dipoles.

4.3. Trimers

When the NaCl:Mn, Pb system is considered, the most stable trimer has the configuration e whatever the type is (Table III). This is the dimer configuration which is expected to form at high temperature.

In the low temperature case ($T \leq 425$ K), the energies corresponding to the following reactions are reported in Table III:

$$\text{n.n.n.} + a \rightarrow i, \qquad \text{n.n.} + a \rightarrow g;$$

$$\text{n.n.n.} + b \rightarrow h, \qquad \text{n.n.n.} + b \rightarrow f, \qquad \text{n.n.n.} + b \rightarrow l;$$

$$\text{n.n.n.} + c \rightarrow j, \qquad \text{n.n.} + c \rightarrow k;$$

$$\text{n.n.} + d \rightarrow e.$$

From the previous results relative to the formation of dimer from dipole aggregation, we conclude that the dimer c is expected to grow in $\{110\}$ planes to form a trimer j for the four trimer types. Lead and mixed trimers are also expected to form by the aggregation of n.n. dipoles in $\{111\}$ planes. When two reactions are possible to form a trimer ($a1 \rightarrow i$ and $a \rightarrow i$ or $b \rightarrow h$ and $c \rightarrow h$) the most fovorable one ,from an energetic point of view is only reported.

In KCl crystals doped with Mn and Pb impurities, the most stable trimer configurations at high temperature are f for T111 and T121 and e for T222 and T212 (Table III).

In the low temperature range ($T \leq 425$ K) the reactions studied previously in the case of NaCl crystals were also found to occur in KCl crystals, their energies are reported in Table III. The manganese dimers b are found to grow in $\{100\}$ planes to form trimers f. The lead and mixed dimers which nucleate in $\{110\}$ planes develop in these planes to form trimers with configuration j. The n.n. dipoles aggregate to form trimer e.

5. Defect concentration

5.1. General

In this section the equilibrium state of crystals containing two types of impurity is described quantitatively. The concentration of each defect type is calculated in the quasi-chemical approach when the long-range interaction between charged defects is not taken into account. The defect concentrations are then given by the ideal mass action law valid for small impurity concentration.

5.2. Defect model

The defect model includes the defects and clusters which concentration is defined below:

$$\begin{array}{ll}
x(1) = [\dot{\mathrm{F}}^{1}_{\mathrm{M}}] & x(8), x(9) = [(2\mathrm{F}^{1}_{\mathrm{M}} 2V_{\mathrm{M}})^{\times}]_{\alpha} \\
x(2) = [\dot{\mathrm{F}}^{2}_{\mathrm{M}}] & x(10), x(11) = [(2\mathrm{F}^{2}_{\mathrm{M}} 2V_{\mathrm{M}})^{\times}]_{\alpha} \\
x(3) = [V'_{\mathrm{M}}] & x(12), x(13) = [(\mathrm{F}^{1}_{\mathrm{M}} \mathrm{F}^{2}_{\mathrm{M}} 2V_{\mathrm{M}})^{\times}]_{\alpha} \\
x(4) = [(\mathrm{F}^{1}_{\mathrm{M}} V_{\mathrm{M}})^{\times}] & x(14) = [(3\mathrm{F}^{1}_{\mathrm{M}} 3V_{\mathrm{M}})^{\times}] \\
x(5) = [(\mathrm{F}^{1}_{\mathrm{M}} - V_{\mathrm{M}})^{\times}] & x(15) = [(3\mathrm{F}^{2}_{\mathrm{M}} 3V_{\mathrm{M}})^{\times}] \\
x(6) = [(\mathrm{F}^{2}_{\mathrm{M}} V_{\mathrm{M}})^{\times}] & x(16) = [(2\mathrm{F}^{1}_{\mathrm{M}} \mathrm{F}^{2}_{\mathrm{M}} 3V_{\mathrm{M}})^{\times}] \\
x(7) = [(\mathrm{F}^{2}_{\mathrm{M}} - V_{\mathrm{M}})^{\times}] & x(17) = [(\mathrm{F}^{1}_{\mathrm{M}} 2\mathrm{F}^{2}_{\mathrm{M}} 3V_{\mathrm{M}})^{\times}]
\end{array}$$

where M = Na or K, $\dot{\mathrm{F}}^{1}_{M} = \mathrm{Mn}^{2+}$, $\dot{\mathrm{F}}^{2}_{M} = \mathrm{Pb}^{2+}$ and α = 1,2, represents the 2 configurations of a defect or a cluster.

In the notation of Kröger [36], $x(1)$ and $x(2)$ represent the concentration of substitutional doubly charged manganese and lead impurities with an effective charge $+1$ whereas $x(3)$ is the concentration of negatively charged cation vacancies. The concentration of manganese and lead dipoles in their n.n. and n.n.n. configurations are given by $x(i)$ for $4 \leq i \leq 7$.

In KCl:Mn, Pb the concentrations $x(8)$, $x(9)$ and $x(10)$, $x(11)$ are associated to the two configurations of lowest energy for the manganese dimer (b and c) and lead dimer (c and $c1$) respectively; the concentrations of mixed dimers b and c are $x(12)$ and $x(13)$, respectively. The manganese trimers T111 (f), the lead trimers T222 (e) and the mixed trimers T121 (f) and T212 (e) have concentrations $x(14), x(15)$ and $x(16), x(17)$ respectively. The system of equations include 14 non-linear equations of type

$$x(1)^{p} x(2)^{q} x(3)^{r} = x(s) \exp(-\Delta G_{s}/RT), \qquad 4 \leq s \leq \nu,$$

where $p+q+r$ is the number of defects in the cluster s. ΔG_{s} is the energy difference between the cluster energy and that

TABLE III. Energy of trimers in NaCl and KCl (in eV, first row), binding energies with respect to isolated defect energies (in eV, second row) and reaction energies with respect to isolated dipoles energy and dimer energy (in eV, third row) for each trimer type.

NaCl

Trimer Configuration	e	f	g	h	i	j	k	l
Type 111	−17.4647	−17.2067	−16.9714	−17.0959	−16.8913	−17.3590	−17.1300	−17.1362
	−2.572	−2.314	−2.079	−2.203	−1.999	−2.466	−2.237	−2.244
	−0.473	−0.309	−0.040	−0.198	−0.057	−0.346	−0.02	−0.238
Type 222	−11.0889	−10.0002	−10.6810	−10.4502	−10.3999	−10.7311	−10.5481	−9.9394
	−2.943	−1.855	−2.535	−2.305	−2.254	−2.585	−2.395	−1.794
	−0.545	−0.152	−0.163	−0.602	−0.12	−0.476	−0.055	−0.092
Type 121	−15.3398	−14.8288	−14.9858	−14.9035	−14.9066	−15.1812	−15.0557	−14.7676
	−2.696	−2.185	−2.342	−2.26	−2.263	−2.538	−2.412	−2.124
	−0.459	−0.295	−0.124	−0.37	−0.14	−0.403	−0.181	−0.234
Type 212	−13.2150	−12.4464	−12.9028	−12.7108	−12.7795	−12.9567	−12.8031	−12.3852
	−2.820	−2.052	−2.508	−2.316	−2.385	−2.562	−2.408	−1.991
	−0.499	−0.219	−0.206	−0.484	−0.32	−0.485	−0.093	−0.158

KCl

Trimer Configuration	e	f	g	h	i	j	k	l
Type 111	−23.3411	−23.7077	−22.4530	−23.1022	−22.6963	−23.4998	−23.0976	−23.6347
	−2.511	−2.877	−1.623	−2.272	−1.866	−2.67	−2.267	−2.804
	−0.404	−0.424	−0.187	−0.181	−0.060	−0.282	−0.124	−0.3511
Type 222	−17.6156	−17.3019	−17.1690	−17.2306	−17.1027	−17.5022	−17.2967	−17.2358
	−2.816	−2.503	−2.37	−2.431	−2.303	−2.703	−2.497	−2.436
	−0.497	−0.318	−0.07	−0.247	−0.118	−0.385	−0.065	−0.2519
Type 121	−21.4321	−21.5964	−20.7808	−21.1779	−20.9989	−21.5267	−21.3333	−21.5297
	−2.612	−2.776	−1.961	−2.358	−2.179	−2.707	−2.513	−2.71
	−0.4	−0.426	−0.1	−0.007	−0.121	−0.328	−0.135	−0.359
Type 212	−19.5241	−19.4811	−18.9806	−19.2221	−19.2080	−19.5154	−19.2101	−19.4151
	−2.714	−2.671	−2.171	−2.412	−2.398	−2.706	−2.4	−2.605
	−0.447	−0.375	−0.054	−0.116	−0.395	−0.382	−0.037	−0.309

of the $p+q+r$ isolated basic defects. The reaction entropy is not taken into account. The system is completed by 3 equations which express the conservation of the total number of each basic defect, the total number of equations being $\nu = 17$:

$$\sum_{i=l}^{\nu} n_1^i x(i) = x_1 \qquad \sum_{i=l}^{\nu} n_2^i x(i) = x_2$$

$$\sum_{i=l}^{\nu} n_v^i x(i) = x_1 + x_2.$$

n_1^i and n_2^i are the number of manganese and lead impurities in the defect or cluster i whereas n_v^i is the number of extrinsic vacancies. The initial concentrations of manganese and lead impurities are x_1 and x_2, respectively.

In the case of NaCl:Mn, Pb system, a slightly different model has been developed in order to give a correct account of the dimer population. It consists in one manganese dimer (c), two lead dimers $(a1, d)$ and four mixed dimers $(a, a1, c$ and $d)$. Preliminary calculations which did not include trimers have shown that the Mn dimer population is well represented by only one dimer whereas in the case of mixed dimers, the four configurations have to be taken into account because their binding energies are very close. The number of equations in that case is $\nu = 18$. The four trimers have the configuration (e).

This model applies when the diffusion of divalent impurities is sufficient to produce associations of two or three impurities which form with the corresponding number of cation vacancies the neutral clusters called dimers and trimers. A high mobility of the divalent impurity is achieved if the charge compensating cation vacancy spends a relatively large fraction of its time close to the impurity (generally in n.n. or n.n.n. position), this means that the dipole concentration is significant or that the degree of association (defined as the ratio between the dipole concentration and the impurity concentration) is not too small. A quantitative estimate of the impurity diffusion is obtained by considering for instance the diffusion coefficient at saturation which correspond to a degree of association equal to unity (Nowick [37]). In that model, the equilibrium concentration of dipoles results from the competition between the association and dissociation reactions of divalent impurity-cation vacancy pairs, the diffusion of impurities being sufficient to reach the thermodynamical equilibrium state. The same method is used to calculate the defect concentrations in metal oxides at high temperature and to study the thermodynamic properties of these materials (Tomlinson, Catlow and Harding [38]; Soullard [30]). This model presents two limitations, at high temperature and low temperature respectively.

At high temperature ($T \leq 1000$ K), the degree of association is too small and clusters do not form; intrinsic defects (Schottky pairs and vacancy pairs) have to be taken into account; this is domain where the ionic conductivity is studied (Fuller [39]).

At temperature lower than the temperature where the dipole concentration is maximum the dissociation of dipoles does not take place, the dipoles are captured by small clusters (they can be greater than dimers and trimers) which are fixed and which cannot dissolve. The dipole concentration results in that case from the interaction of mobile dipoles with fixed obstacles and the concentration of various defects is given by a set of chemical rate equations (Cook and Dryden 1962 [40, 41]; Unger and Perlman [42]).

5.3. Results of calculations

When the atomic concentration is the same for both types of impurity ($x_1 = x_2 = 4.2 \times 10^{-6}$ [6]), the variation of defect concentrations in the temperature range 600 K–425 K is given in Figs. 2a, 2b, 3a, and 3b. In both cases, a decrease in the concentration of isolated defects and an increase of the dipole concentrtion are observed; dimers and trimers also form.

For NaCl crystals, the maximum dipole concentration is obtained at 450 K and 500 K for the Mn and Pb impurities, respectively (Figs. 2a and 2b). At equilibrium, the proportion of n.n. and n.n.n. dipoles is different for each impurity: at 500 K, 10% of the dipole population is of n.n.n. type in the case of Mn impurities whereas, for Pb impurities the concentration of n.n.n. dipoles can be neglected (less than 1%).

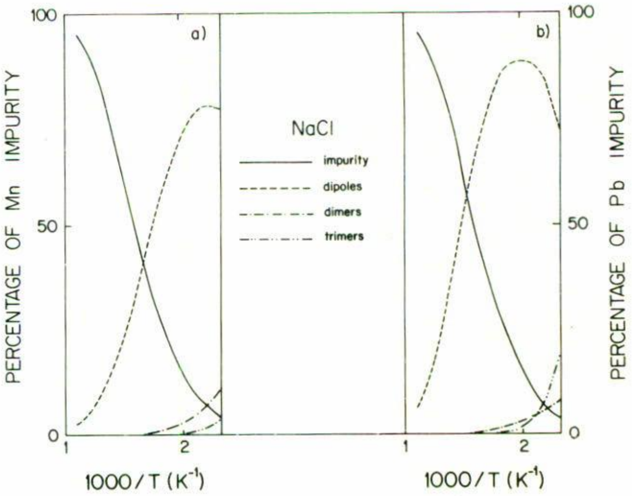

FIGURE 2. (a) Manganese concentration in the various defects as a function of temperature in NaCl:Mn, Pb. (b) Lead concentration in the various defects as a function of temperature in NaCl:Mn, Pb.

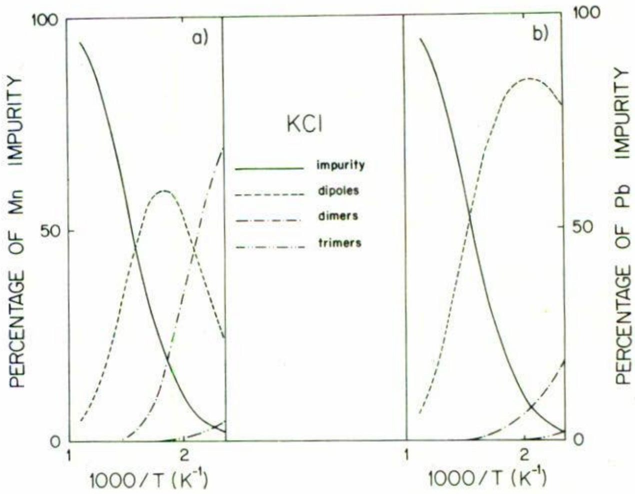

FIGURE 3. (a) Manganese concentration in the various defects as a function of temperature in KCl:Mn, Pb. (b) Lead concentration in the various defects as a function of temperature in KCl:Mn, Pb.

For KCl crystals, manganese is found to be less soluble than lead (a situation opposite to that found for NaCl); the maximum dipole concentration is obtained at 550 K and 500 K for the Mn and Pb impurities, respectively (Figs. 3a and 3b). The equilibrium state at 500 K is characterized by 50% of each dipole type with Mn impurities, only 10% of Pb form dipoles where defects are in next nearest neighbouring positions.

As mentioned in Sect.3, various cluster types are in principle present in the samples, to characterize the equilibrium state the cluster distribution must be considered, it is given in Table IV at 475 K. For the system NaCl:Mn, Pb, the dimers constitute 3/4 of the cluster population while the trimers represent 1/4 of this population and 29% of clusters show a mixed charcter. In the case of KCl:Mn, Pb, the dimers is the dominant cluster, only 14% of dimers have a mixed character.

TABLE IV. Cluster distribution (in percent) at 475 K in NaCl: Mn, Pb and KCl:Mn, Pb.

System	NaCl:Mn, Pb	KCl:Mn, Pb
Dimers 11	23	76
Dimers 22	28	8
Dimers 12	22	14
Trimers 111	-	2
Trimers 222	19	-
Trimers 212	2	-
Trimers 121	5	-

The results shown in Figs. 2a, 2b, 3a, and 3b allow to improve our knowledge relative to the solubility of Mn and Pb in the two host crystals. By considering the temperature at which the maximum concentration of dipoles is obtained, Manganese is found to be less soluble in KCl than in NaCl whereas the lead solubility is similar in both crystals consequently, the solubility difference between Mn and Pb is greater in KCl than in NaCl. As a consequence of this difference in Mn solubility in both crystals, a strong precipitation of manganese alone is observed in KCl which prevents the formation of mixed clusters.

6. Conclusion

In both systems, at equilibrium at high temperature, only isolated defects (doubly charged substitutional impurities, cation vacancies and dipoles) are present in the crystals. The manganese dipoles are generally found in two configurations (n.n. and n.n.n.), the ratio of their concentrations being dependent on the host matrix and on the impurity radius. For the lead dipoles the n.n. configuration is dominant in both systems.

In the system NaCl:Mn, Pb, the Mn dimers nucleate in $\{110\}$ planes, the lead dimers in $\{100\}$ and $\{111\}$ planes whereas the mixed dimers nucleate on $\{110\}$, $\{100\}$ and $\{111\}$ planes. In the system KCl:Mn, Pb the manganese dimers nucleate on $\{100\}$ planes, those of lead on $\{110\}$ planes and the mixed dimers nucleate in the two previous planes.

The aggregation processes in the two systems differ in three ways. The nucleation planes for the dimers are different. The main characteristic of the cluster distribution at a given temperature is not the same, at 475K in NaCl:Mn, Pb trimers represent 1/4 of the cluster population, at the same temperature dimers are only found in KCl:Mn, Pb. Finally, in NaCl:Mn, Pb, the concentration of mixed clusters (29%) is more important than in the system KCl:Mn, Pb (14%). This result is in agreement with the prediction of the ionic radius criterion and with the results of fluorescence experiments; the system where the concentration of close Mn-Pb pairs is the highest is the most efficient to transfer energy from Pb to Mn consequently, for the same doping the system NaCl:Mn, Pb exhibits a fluorescence intensity greater than the system KCl:Mn, Pb [6, 10].

The formation of mixed clusters is related to the solubility difference of impurities in each host matrix. The matrix where the solubility is smaller is less favorable to form mixed clusters; KCl is thus less favorable than NaCl to form mixed clusters, as observed experimentally. In KCl, the manganese dimers nucleate at a temperature (550 K) higher than the temperature where lead dimers form (500 K) and this prevents the formation of mixed clusters; in NaCl on the contrary, the condensation of both impurities occurs at the same temperature (500 K) and the formation of mixed dimers is favored.

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