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The polarization energy of a next nearest cation-vacancy complex in alkali halide crystals

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Abstract. The polarization energy of a next nearest cation-vacancy complex is calculated for all alkali halide crystals containing Cd^{++}, Mn^{++} and Ba^{++} impurities. We considered up to 48 nearest neighbors to the complex and assumed that the field of each dipole is the one produced by the charge of the complex and by the field due to the other induced dipoles. The effect of the displacement field is considered in the calculation of the polarization energy. For KCl and NaCl crystals containing Cd^{++}, Mn^{++} and Ba^{++} impurities, the polarization energy obtained in this paper is used to calculate the binding energy of the complex. This energy is compared with the binding energy of the nearest cation-vacancy complex. From this comparison we concluded that the next nearest neighbor complex is a more stable structure than the nearest neighbor complex only in the case of NaCl containing Ba^{++}.

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1. Introduction

The polarization of a complex in alkali halide crystals was studied by C. Ruíz-Mejía and U. Oseguera [1]. The problem was suggested after the review of the calculations of the association energy of cation-vacancy complex [2,3,4] to which the polarization energy is an important contribution. The Ruíz-Mejía and Oseguera method is more rigorous than that used in other papers [2,5,6,7]. Recently D. Cárdenas-García *et al.* [8] calculated the polarization energy of a complex from zero to fourth order. In that paper the interionic potential used by several researchers and the importance of the size of the relaxed region of the crystal are discussed. In order to compare the polarization energy obtained with the new method [1] with that used in other papers [2,5,6,7] the new values of the polarization energy were introduced together with the other contributions to the association energy of complexes doped with Cd^{++}, Mn^{++} and Ba^{++} impurities. This is not a rigorous procedure but it is useful in order to compare the new polarization energy with some experimental values. The association energy calculated in this way was not any closer to the experimental values. Because the new method [1,8,9] was more precise than the older ones [2,5,6,7] this fact was rather surprising. In order to clarify this point, we made a new study taking into account the effect of the displacement field in the calculation of the

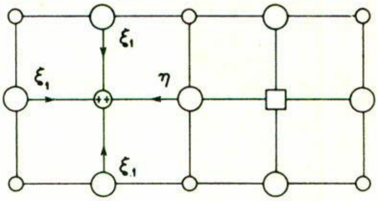

FIGURE 1. Next nearest cation-vacance complex and displacements (ξ_1 and η) of four of the nearest neighbors to the divalent impurity.

polarization energy of the complex [10], then a good agreement with experimental values of the association energy of the complex was obtained. In the calculation of the association energy of a complex [2,5,6,7] we always considered the impurity-first neighbor vacancy complex and the impurity-second neighbor vacancy complex. That is the reason why it is necessary a calculation of the polarization energy for the case of the impurity-second neighbor vacancy complex, which is the aim of this paper.

2. Calculations

As it was discussed before [1,9,10] the procedure to calculate the polarization energy is different from that followed in earlier papers [2,5,6,7]. The detail of the calculation have been given in other papers, so here we will describe very briefly the procedure. The solution to the problem requires to solve a system of n equations with n variables of the type:

$$\mu_i = \alpha_i \left(\frac{eq_i}{r_{Vi}} - \frac{eq_i}{r_{Ii}} - \sum_j \nabla_i' \left(\mu_j \cdot \nabla_i \frac{1}{r'} \right) \cdot \hat{r}_i \right), \tag{1}$$

where $\mathbf{r}' = \mathbf{r}_i - \mathbf{r}_j$, and μ_i and μ_j are the magnitudes of the dipole moments associated with the i-th and j-th ions respectively, and the number of equations depends on the desired order of aproximation. The vacancy and the divalent impurity in the case of a second neighbor complex are shown in Fig. 1. The expresion for the polarization work W_T is given by

$$W_T = \frac{e}{2}(\Phi_1' - \Phi_2') + W_I + W_L, \tag{2}$$

where $W_I = -\vec{\mu}_I \cdot \mathbf{E}$ is the polarization energy due to impurity; $\mathbf{E}$ is the electric field of the vacancy, and W_L is the polarization energy of the rest of the lattice beyond the nearest neighbors. The general expressions for Φ_1 and Φ_2 are

$$\Phi_1 = \sum_{i=0}^{\infty} \left(\frac{\mu_{1i}}{r_{1i}^2} - \frac{\mu_{2i} \cos \gamma_i}{r_{1i}^2} \right), \tag{3}$$

$$\Phi_2 = \sum_{i=0}^{\infty} \left(-\frac{\mu_{2i}}{r_{2i}^2} + \frac{\mu_{1i} \cos \gamma_i}{r_{2i}^2} \right). \tag{4}$$

We can write

$$\Phi_1 = \Phi_1' + \Phi_{1L}, \tag{5}$$

$$\Phi_2 = \Phi_2' + \Phi_{2L}, \tag{6}$$

where γ is the angle between μ_{1i} and μ_{2i}, Φ_{1L} and Φ_{2L} represent the contribution of the rest of the lattice beyond the set of nearest neighbors,Φ_1' and Φ_2' represent the contribution of the set of nearest neighbors to the complex (the number of neighbors depends on the aproximation). In appendix 1 we give the explicit expressions of Φ_1' and Φ_2' to fourth order for the impurity-second neighbor vacancy complex. There are two groups of equations that we have to solve. The first group is of the form

$$C_{e1}^i + C_{p1}^i M_+ + C_{n1}^i M_- = C_{11}^i m_{11} + C_{12}^i m_{12} + \ldots + \left(\frac{1}{\beta} + C_{1i}^i \right) m_{1i} + C_{1i+1}^i m_{1i+1} + \ldots + C_{124}^i m_{124}, \tag{7}$$

where i goes from 1 to 24.

For the second group we have

$$C_{e2}^i + C_{p2}^i M_+ + C_{n2}^i M_- + C_I^i \frac{\alpha_I}{a^3} = C_{21}^i m_{21} + C_{22}^i m_{22} + \ldots + \left(\frac{1}{\beta} + C_{2i}^i \right) m_{2i} + C_{2i+1}^i m_{2i+1} + \ldots + C_{2\,24}^i m_{2\,24}. \tag{8}$$

Equations (7) and (8) correspond to equation (1), where

$$\mu_{1i} = eam_{1i}, \tag{9}$$

$$\mu_{2i} = eam_{2i}, \tag{10}$$

and

$$\beta = \frac{\alpha_-}{a^3}. \tag{11}$$

The constants M_+, M_-, A and B were defined in other papers [1,9,10].

HA	$e\Phi_1$	$-e\Phi_2$	W_L	W_I	W_T	E_T
LiCl	7.2009	5.3664	0.9039	0.0953	6.1750	6.1750
NaCl	4.6793	4.1177	0.7005	0.0667	4.7515	4.7515
2KCl	2.1174	3.0162	0.5681	0.0428	3.5415	3.5415
RbCl	1.2443	2.7372	0.5442	0.0364	3.2451	3.2451
LiBr	7.4232	5.5232	0.9097	0.0732	6.3597	6.3597
NaBr	5.1888	4.3167	0.7414	0.0527	5.0055	5.0055
KBr	2.8320	3.2449	0.5941	0.0354	3.8037	3.8037
RbBr	1.9658	2.9223	0.5580	0.0301	3.4502	3.4502
LiI	7.5675	5.6373	0.8979	0.0513	6.4838	6.4838
NaI	5.6669	4.5308	0.7318	0.0382	5.2244	5.2244
KI	3.6229	3.4993	0.6228	0.0269	4.0952	4.0952
RbI	2.8048	3.1442	0.5810	0.0231	3.7021	3.7021
LiF	4.9530	3.8144	0.8629	0.2555	4.4218	4.4218
NaF	1.3708	2.6851	0.6048	0.1460	3.1439	3.1439
KF	−1.1302	2.1265	0.5182	0.0818	2.5629	2.5629
RbF	−1.8602	2.0415	0.5014	0.0658	2.4771	2.4771

TABLE I. The polarization energy calculated in all the alkali halides for a Cd^{++} impurity. The polarizability was taken as $\alpha = 1.80 \times 10^{-24}$ cm^3. The polarization energy due to first neighbors calculated in the impurity place is represented by $e\Phi_1'$; $-e\Phi_2'$ represents the polarization energy due to the first neighbors, calculated in the vacancy place which is forming the complex; W_I is the polarization energy due to the impurity; W_L is the polarization energy due to the rest of the lattice; W_T is the polarization energy and E_T is the polarization energy as a function of the polarizability α_I . All energies in eV.

3. Conclusions

The polarization energy of a next nearest cation-vacancy complex requires the formulation of a new set of equations (which is different from the case of first nearest neighbors) and the making of new computer programs to obtain the moments and the energy. The main purpose of this work is to calculate the complex polarization energy for alkali halide crystals in the case of next nearest neighbors. Tables I, II and III show the different contributions to the polarization energy for all the alkali halides containing Ba^{++}, Cd^{++} and Mn^{++} impurities respectively. In Fig. 1, it is shown the next nearest cation-vacancy complex. The displacement η corresponds to the ion which is first neighbor to the vacancy and to the divalent impurity. ξ is the displacement of the other ions which are first neighbors to the divalent impurity only. In Tables I, II and III, it was considered that $\eta = \xi_1 = 0$ in order to obtain the polarization energy. The calculated polarization energies can not be compared directly with experimental values. However, we can attempt to study how the binding energy of the divalent cation-vacancy complexes changes as a function of the polarization energy. Even though strictly speaking, we can not mixed the model used in [2] with our method (because the symmetry considered there is less accurate than ours) the procedured can be illustrative. This kind of calculation was done in [8] for the case of the polarization energy of the first nearest neighbor cation-vacancy complex.

HA	Φ_1	$-\Phi_2$	W_L	W_I	W_T	E_T
LiCl	7.1948	5.3616	0.9039	0.0890	6.1765	6.1765
NaCl	4.6715	4.1154	0.7005	0.0623	4.7536	4.7536
KCl	2.1104	3.0152	0.5681	0.0399	3.5433	3.5433
RbCl	1.2376	2.7365	0.5442	0.0339	3.2468	3.2468
LiBr	7.4181	5.5181	0.9097	0.0684	6.3600	6.3600
NaBr	5.1825	4.3144	0.7414	0.0492	5.0067	5.0067
KBr	2.8259	3.2439	0.5941	0.0330	3.8050	3.8050
RbBr	1.9600	2.9215	0.5580	0.0281	3.4514	3.4514
LiI	7.5635	5.6332	0.8979	0.0479	6.4831	6.4831
NaI	5.6622	4.5286	0.7318	0.0356	5.2248	5.2248
KI	3.6181	3.4982	0.6228	0.0251	4.0959	4.0959
RbI	2.8002	3.1434	0.5810	0.0216	3.7029	3.7029
LiF	4.9433	3.8098	0.8629	0.2385	4.4343	4.4343
NaF	1.3385	2.6833	0.6048	0.1363	3.1514	3.1517
KF	-1.1395	2.1255	0.5182	0.0764	2.5674	2.5674
RbF	-1.8682	2.0406	0.5014	0.0614	2.4806	2.4806

TABLE II. The polarization energy (in eV) calculated for Ba^{++} impurity. The polarizability was taken as $\alpha_I = 1.68 \times 10^{-24}$ cm^3. The meaning of the symbols is as in Table I.

HA	Φ_1	$-\Phi_2$	W_L	W_I	W_T	E_T
LiCl	7.1501	5.3261	0.0939	0.0424	6.1877	6.1877
NaCl	4.6144	4.0983	0.7005	0.0296	4.7691	4.7691
KCl	2.0592	3.0078	0.5681	0.0190	3.5568	3.5568
RbCl	1.1883	2.7308	0.5442	0.0162	3.2589	3.2589
LiBr	7.3804	5.4852	0.9097	0.0326	6.3623	6.3623
NaBr	5.1362	4.2976	0.7414	0.0234	5.0156	5.0156
KBr	2.7815	3.2362	0.5941	0.0157	3.8146	3.8146
RbBr	1.9172	2.9158	0.5580	0.0134	3.4604	3.4604
LiI	7.5342	5.6029	0.8979	0.0228	6.4780	6.4780
NaI	5.6279	4.5125	0.7318	0.0170	5.2274	5.2274
KI	3.5832	3.4904	0.6228	0.0120	4.1012	4.1012
RbI	2.7663	3.1376	0.5810	0.0103	3.7084	3.7084
LiF	4.8728	3.7764	0.8629	0.1135	4.5258	4.5258
NaF	1.2478	2.6697	0.6048	0.0649	3.2095	3.2095
KF	-1.2072	2.1183	0.5182	0.0364	2.6001	2.6001
RbF	-1.9274	2.0344	0.5014	0.0292	2.5065	2.5065

TABLE III. The polarization energy (in eV) calculated for Mn^{++} impurity. The polarizability was taken as $\alpha_I = 0.80 \times 10^{-24}$ cm^3. The meaning of the symbols is as in Table I.

Impurity	HA	$e\Phi'_{1d}$	$-e\Phi'_{2d}$	W_{TD}	W_T
Ba^{++}	NaCl	3.9672	1.7435	2.3773	4.7515
	KCl	1.5685	0.9356	1.4609	3.5415
Cd^{++}	NaCl	4.1849	2.5858	3.2240	4.7536
	KCl	1.7142	1.6043	2.1325	3.5433
Mn^{++}	NaCl	3.5605	1.8161	2.4870	4.7691
	KCl	1.3340	0.7352	1.2843	3.5568

TABLE IV. The polarization energy for next nearest neighbors taking into account the displacements ($\xi_1 \neq 0$; $\eta \neq 0$). The polarization energy due to the first neighbors taking into account the displacement calculated in the impurity place is represented by $e\Phi'_{1d}$; $-e\Phi'_{2d}$ represents the polarization energy due to he first neighbors taking into account the displacement, calculated in the vacancy place which is forming the complex; W_{Td} is the polarization energy taking into account the displacement. W_T is the polarization energy calculated as in Tables I, II and III. All energies in eV.

LiCl	$E_T = 6.197858 - 0.012704\alpha_I$	LiI	$E_T = 6.473301 - 0.005846\alpha_I$
NaCl	$E_T = 4.783158 - 0.017585\alpha_I$	NaI	$E_T = 5.229744 - 0.002948\alpha_I$
KCl	$E_T = 3.569046 - 0.015312\alpha_I$	KI	$E_T = 4.106047 - 0.006040\alpha_I$
RbCl	$E_T = 3.269913 - 0.013770\alpha_I$	RbI	$E_T = 3.713429 - 0.006282\alpha_I$
LiBr	$E_T = 6.364391 - 0.002610\alpha_I$	LiF	$E_T = 4.608958 - 0.103962\alpha_I$
NaBr	$E_T = 5.023674 - 0.010097\alpha_I$	NaF	$E_T = 3.262025 - 0.065650\alpha_I$
KBr	$E_T = 3.823341 - 0.010918\alpha_I$	KF	$E_T = 2.629869 - 0.037199\alpha_I$
RbBr	$E_T = 3.468543 - 0.010192\alpha_I$	RbF	$E_T = 2.530037 - 0.029419\alpha_I$

TABLE V. Equations for the polarization energy (E_T) as a function of the polarizability (α_I).

The results of the polarization energy for next nearest neighbors taking into account displacements ($\xi_1 \neq 0$, $\eta \neq 0$) are given in Table IV (NaCl and KCl containing Cd^{++}, Mn^{++} and Ba^{++}). Table V shows, the polarization energy as a function of the polarizability of the divalent impurity for all the alkali halides. Finally in Table VI, we show the binding energies obtained following the method reported in [2] with the only exception that the polarization energies calculated there are substituted by the polarization energies calculated in this paper (as they are given in Table IV). In this calculation we have used the polarization energy when the displacements of the first neighbors to the complex are different from zero because (as it was discussed in [8]) in this way the theoretical binding energies are in better agreement with the experimental ones. As we can see in Table VI, the theoretical prediction is more favorable to the next nearest neighbor cation-vacancy complex formation than to the nearest neighbor cation-vacancy complex formation only for NaCl:Ba^{++}.

In Table VII we reproduce the values of the different contributions to the work W_2 to create a next nearest positive ion vacancy near an Eu^{++} ion in the alkali chlorides [2]. $E_2^{C'P}$ is the term which is important to compare with our results. This term is equivalent to our W_{Td} in Table IV. The polarizability of the Cd^{++} was taken as $\alpha_I = 1.80 \times 10^{-24}$ cm^3 and for Eu^{++} (Table VII), $\alpha_I = 2.87 \times 10^{-24}$ cm^3. Even though we cannot compare $E_2^{C'P}$ and W_{Td} for the same impurity, we can see that W_{Td} increases with the value of α_I. For example, in Table IV, in NaCl, when α_I goes from 0.80×10^{-24} cm^3 (Mn^{++}) to 1.80×10^{-24} cm^3 (Cd^{++}) W_{Td} takes values from 2.4870 eV to 3.2240 eV. If we assume an equivalent change when α_I goes from 1.80×10^{-24} cm^3 (Cd^{++}) to 2.87×10^{-24} cm^3 (Eu^{++}) we can see that our W_{Td} would be near to 3.9 eV and in Table VII $E_2^{C'P}$ is equal to 3.40060.

The binding energy of the complex E_B is given by $E_B = W_0 - W_1$, where W_0 is the work needed to remove an alkali ion [2] and is given by $W_0 = -\frac{1}{2}(E_1^v + \Phi_1^v + E_2^v + \Phi_2^v)$. The work required to create a next nearest vacancy complex is $W_1 = -\frac{1}{2}(E_1^{C'} + \Phi_1^{C'} + E_2^{C'} + \Phi_2^{C'})$. $E_2^{C'P}$ is a negative number and it is contained in $E_2^{C'}$ (part of W_1), which has positive sign. In order to see how the values in Table VI were obtained, we give in Table VIII the values of $E_2^{C'P}$ ours W_{Td} and the E_B.

To obtain E_B^{nnn} (Table VI),we used the relation $E_B^{nnn} = \frac{1}{2}(W_{Td} - E_2^{C'P}) + E_B$.

In the present paper we have not done a study of the polarization energy as a function of the number of first neighbors to the complex. Table IX shows the polarization energies from zero order (W_{T0}) to fourth order (W_{T4}) [8] and the polarization energy W_T' obtained for Eu^{++} impurity from other work [2], in the case of a first nearest cation-vacancy complex. We have assume that the behavior of the polarization energy as a function of the number of first neighbors in that case is similar to the case of a next nearest cation-vacancy complex. As we can see from Table IX there are no significant changes in all alkali halides when going from second to fourth order. Our calculations, in the present paper, were done to fourth order.

Finally, in Table X, we reproduce the binding energies for next nearest neighbor complex for all the alkali halides and several impurities [4]. We can compare those values with the obtained from Table VI in which the polarization energy was obtained by a more rigorous method.

Impurity	HA	E_B^{nn}	E_B^{nnn}	$E_B^{\exp}$
Mn^{++}	NaCl	0.9310	0.3000	0.71 [11]
Cd^{++}	NaCl	0.8105	0.0936	0.47-1 [12]
Ba^{++}	NaCl	1.1473	0.9541	0.79 [13]
Mn^{++}	KCl	1.1108	0.5493	
Cd^{++}	KCl	0.9701	0.3036	
Ba^{++}	KCl	0.6848	1.1861	0.40 [14]

TABLE VI. Binding energies for nearest neighbor cation-vacancy complex (E_B^{nn}) and next nearest neighbor cation-vacancy complex (E_B^{nnn}) obtained following the method in [2]. $E_B^{\exp}$ are experimental values for comparison.

	LiCl	NaCl	KCl	RbCl
$-E_1^{C'R}(E_2^{C'R})$	6.9920	6.3820	5.7200	5.4920
$-E_1^{C'D}$	-0.0607	-0.1503	-0.2408	-0.2644
$-E_1^{C'P}$	2.9730	2.3730	1.9600	1.8910
$-\Phi_1^{C'}$	-0.8755	-0.7377	-0.7564	-0.8143
$-E_2^{C'D}$	-1.8920	-2.3860	-2.2000	-1.9410
$-E_2^{C'}$	-4.7300	-3.4060	-2.5490	-2.3800
$-\Phi_2^{C'}$	-0.5761	-0.3880	-0.3674	-0.4178
W_2	4.4114	4.0345	3.6432	3.5288

TABLE VII. Contributions to the work W_2 (in eV) to create a next nearest ion vacancy near an Eu^{++} ion in the alkali chlorides.

	$E_2^{C'P}$	W_{Td}	E_B
NaCl:(Mn^{++})	3.3800	2.4870	0.75
KCl:(Mn^{++})	2.5170	1.2843	0.76
NaCl:(Cd^{++})	2.5358	3.2240	0.71
KCl:(Cd^{++})	2.5538	2.1325	0.78
NaCl:(Ba^{++})	3.4398	2.4870	0.61
KCl:(Ba^{++})	2.5645	3.5568	0.69

TABLE VIII. The polarization energy $E_2^{C'P}$ obtained of other works [3,4,7], the polarization energy W_{Td} obtained in this paper and the binding energy E_B for next nearest neighbors complex [4]. All energies in eV.

HA	W_{T0}	W_{T1}	W_{T2}	W_{T3}	W_{T4}	W'_T
LiCl	7.6720	5.5368	5.5161	5.3043	5.3013	4.3930
NaCl	5.6737	4.3510	4.1279	3.9731	3.9476	3.0680
KCl	4.1984	3.3274	2.8202	2.7113	2.6615	2.2480
RbCl	3.8185	3.0821	2.4343	2.3390	3.2775	2.0850
LiBr	7.7866	5.7343	5.7204	5.5163	5.5139	4.7430
NaBr	6.1389	4.6087	4.4449	4.2767	4.2556	3.3780
KBr	4.5814	3.5817	3.1833	3.0611	3.0192	2.4530
RbBr	4.1240	3.2811	2.7644	2.6573	2.6056	2.2440
LiI	7.7452	2.8613	5.8534	5.6681	5.6663	5.2810
NaI	6.1747	4.8052	4.7042	4.5453	4.5289	3.8220
KI	5.0044	3.8565	3.5800	3.4446	3.4112	2.7800
RbI	4.5249	3.5203	3.1505	3.0286	2.9875	2.5600
LiF	6.8093	3.7042	3.6114	3.3722	3.3637	3.0558
NaF	4.0108	2.8063	2.1368	2.0219	1.9621	2.4000
KF	2.8890	2.3565	1.2556	1.1991	1.1013	2.1060
RbF	2.5508	2.2583	1.0294	0.9882	0.8786	2.0800

TABLE IX. Polarization energies from zero order (W_{T0}) to fourth order (W_{T4}) and the polarization energy W'_T obtained for Eu^{++} impurity from other work [8]. All energies in eV.

	Mg^{2+}	Zn^{2+}	Fe^{2+}	Mn^{2+}	Cd^{2+}	Eu^{2+}	Pb^{2+}	Ba^{2+}
LiF	0.29	0.24	0.19	0.28	0.27	0.26		
LiCl	0.68	0.56	0.56	0.54	0.51	0.39		
LiBr	0.72	0.60	0.55	0.57	0.56	0.50		
LiI	0.75	0.68	0.67	0.65	0.64	0.59		
NaF	0.82	0.61	0.56	0.60	0.60	0.63	0.58	0.50
NaCl	0.85	0.75	0.75	0.75	0.71	0.69	0.63	0.61
NaBr	0.71	0.74	0.73	0.72	0.70	0.68	0.59	0.60
NaI	0.84	0.70	0.70	0.69	0.67	0.64	0.59	0.59
KF	0.55	0.64	0.60	0.66	0.70	0.73	0.73	0.67
KCl	0.83	0.79	0.76	0.76	0.78	0.75	0.70	0.69
KBr	0.71	0.75	0.75	0.74	0.73	0.71	0.74	0.66
KI	0.63	0.71	0.73	0.70	0.69	0.65	0.63	0.62
RbF	0.54	0.71	0.67	0.72	0.77	0.82	0.81	0.76
RbCl	0.77	0.73	0.72	0.71	0.71	0.69	0.68	0.65
RbBr	0.69	0.70	0.69	0.68	0.68	0.65	0.67	0.61
RbI	0.61	0.67	0.66	0.65	0.65	0.63	0.61	0.59

TABLE X. Binding energies for *nnn*-dipoles in the alkali halides. All energies in eV.

Appendix 1

$$
\begin{aligned}
\Phi_1' = & \frac{\mu_{1,1}}{a^2} + \frac{4\mu_{1,2}}{a^2} + \frac{\mu_{1,3}}{a^2} + \frac{4\mu_{1,4}}{5a^2} + \frac{\mu_{1,5}}{9a^2} + \frac{4\mu_{1,6}}{2a^2} + \frac{4\mu_{1,6}}{2a^2} + \frac{4\mu_{1,7}}{2a^2} + \frac{4\mu_{1,8}}{2a^2} \\
& + \frac{4\mu_{1,9}}{6a^2} + \frac{4\mu_{1,10}}{10a^2} + \frac{4\mu_{1,11}}{3a^2} + \frac{4\mu_{1,12}}{3a^2} + \frac{4\mu_{1,13}}{11a^2} + \frac{\mu_{1,14}}{4a^2} + \frac{\mu_{1,15}}{a^2} \\
& + \frac{\mu_{1,16}}{2a^2} + \frac{\mu_{1,17}}{16a^2} - \frac{\mu_{2,1}}{a^2} - \frac{4\mu_{2,2}}{\sqrt{5}a^2} + \frac{\mu_{2,3}}{a^2} + \frac{4\mu_{2,4}}{\sqrt{5}a^2} - \frac{\mu_{2,5}}{a^2} \\
& - \frac{8\mu_{2,6}}{2\sqrt{5}a^2} - \frac{4\mu_{2,7}}{2\sqrt{3}a^2} - \frac{4\mu_{2,9}}{6\sqrt{3}a^2} - \frac{8\mu_{2,10}}{10\sqrt{5}a^2} - \frac{20\mu_{2,11}}{3\sqrt{33}a^2} - \frac{4\mu_{2,12}}{9a^2} \\
& - \frac{20\mu_{2,13}}{11\sqrt{33}a^2} - \frac{\mu_{2,14}}{4a^2} - \frac{\mu_{2,15}}{\sqrt{2}a^2} - \frac{\mu_{2,16}}{2\sqrt{2}a^2} + \frac{\mu_{2,17}}{16a^2} \\
\Phi_2' = & - \frac{\mu_{2,1}}{9a^2} - \frac{4\mu_{2,2}}{5a^2} - \frac{\mu_{2,3}}{a^2} - \frac{4\mu_{2,4}}{a^2} - \frac{\mu_{2,5}}{a^2} - \frac{4\mu_{2,6}}{10a^2} - \frac{4\mu_{2,7}}{6a^2} - \frac{4\mu_{2,8}}{2a^2} \\
& - \frac{4\mu_{2,9}}{2a^2} - \frac{4\mu_{2,10}}{2a^2} + \frac{4\mu_{2,11}}{11a^2} + \frac{4\mu_{2,12}}{3a^2} + \frac{4\mu_{2,13}}{3a^2} + \frac{\mu_{2,14}}{16a^2} + \frac{\mu_{2,15}}{2a^2} \\
& + \frac{\mu_{2,16}}{a^2} + \frac{\mu_{2,17}}{4a^2} + \frac{\mu_{1,1}}{9a^2} + \frac{4\mu_{1,2}}{5\sqrt{5}a^2} - \frac{\mu_{1,3}}{a^2} + \frac{4\mu_{1,4}}{\sqrt{5}a^2} + \frac{\mu_{1,5}}{a^2} \\
& + \frac{8\mu_{1,6}}{10\sqrt{5}a^2} + \frac{4\mu_{1,7}}{6\sqrt{3}a^2} + \frac{4\mu_{1,9}}{2\sqrt{3}a^2} + \frac{8\mu_{1,10}}{2\sqrt{5}a^2} - \frac{20\mu_{1,11}}{11\sqrt{33}a^2} - \frac{4\mu_{1,12}}{9a^2} \\
& + \frac{20\mu_{1,13}}{3\sqrt{33}a^2} - \frac{\mu_{1,14}}{16a^2} - \frac{\mu_{1,15}}{2\sqrt{2}a^2} - \frac{\mu_{1,16}}{\sqrt{2}a^2} - \frac{\mu_{1,17}}{4a^2}
\end{aligned}
$$

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Resumen. Se calcula la energía de polarización de un complejo vacancia-impureza divalente, a segundos vecinos, para cristales halogenuros alcalinos con impurezas Cd^{++}, Mn^{++} y Ba^{++}. Se considera que los primeros 48 vecinos al complejo pueden relajarse y se supone que el campo sobre cada dipolo es el producido por la carga del complejo y por los otros dipolos inducidos. Se estudia el efecto del campo de desplazamiento en el cálculo de la energía de polarización. Para la energía de polarización calculada en esta forma se determina la energía de amarre del complejo combinado al presente modelo con otro usado en trabajos anteriores. Al comparar resultados obtenidos con los del complejo a primeros vecinos se llega a la conclusión de que solamente en el caso del $NaCl{:}Ba^{++}$ el complejo a segundos vecinos es más estable.