

Polarization around an Eu^{++} impurity in alkali halides

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Abstract. We calculate the polarization energy of a complex for all the alkali halides containing Eu^{++} impurities. Ten nearest neighbors of the complex are considered, and it is assumed that the field on each dipole is produced by the charge of the complex and by the field produced by the other induced dipoles. We concluded that previous calculations have to be revised.

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1. Introduction

Recently, Ruíz Mejía and Oseguera [1] have proposed a method for calculating the polarization energy of a complex. This procedure is different from the one that followed in earlier studies, where the field produced by induced dipoles is neglected [2, 3, 4, 5, 6, 7]. The purpose of this paper is to extend the recent calculations in order to include all the alkali halides, and also to present some details of the procedure.

2. Theory

The method is based on the familiar Mott-Littleton [8] approach, in which the crystal consists of two regions, an inner region containing the complex in which the ions are specifically relaxed and an outer region which is treated as a dielectric continuum.

In this first approach the inner region was considered as the complex and its ten nearest neighbors (see Fig. 1). The dipole moments μ_i (see Fig. 2) are determined from the solution of n equations with n unknowns. That is:

$$\mu_i = \alpha_i \left| \frac{eq_i}{R_{vi}} - \frac{eq_i}{R_{Ii}} - \sum_j \nabla_i \left(\mu_j \cdot \nabla_i \frac{1}{|\mathbf{r}|} \cdot \frac{\mathbf{r}_i}{r} \right) \right|. \quad (1)$$

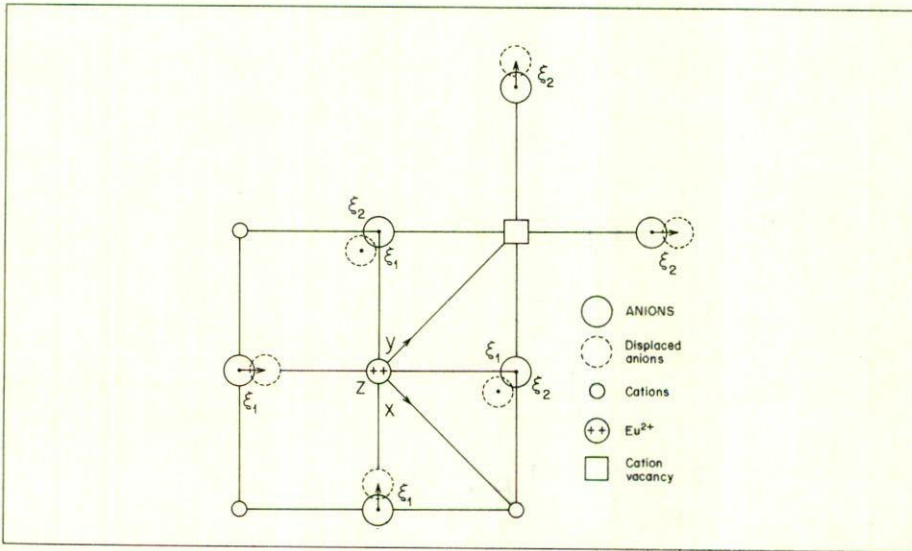


FIGURE 1. Nearest cation vacancy complex of Eu^{++} in the alkali halides.

This is an exact formulation of the problem. In equation (1), α_i is the electric polarizability of the i -th ion, R_{vi} is the distance from the ion i to the vacancy, R_{Ii} is the distance from ion i to the divalent impurity, q_i is the charge of the defect and μ_i and μ_j are the dipole moments associated with the i -th and j -th ions, respectively, and $r = r_i - r_j$, where r_i and r_j are the positions of the μ_i and μ_j dipoles.

The set of equations given by (1) leads to an infinite set with an infinite number of unknowns. Attempts to obtain exact solutions have been unsuccessful and therefore all solutions obtained represent approximations of various orders.

It is important to point out that this method uses the dielectric concept to determine the dipole moment μ , on each ion, but in the final calculation of the polarization work the crystal is treated as an array of induced point dipoles rather than as a continuum. Specifically, the region I consists of the complex and dipole moments at the lattice sites (001) , $(00\bar{1})$, (111) , $(11\bar{1})$, (120) , (210) , $(0\bar{1}0)$, $(\bar{1}00)$, (010) and (100) .

From the symmetry of the problem we have only five different moments. In order to obtain the polarization energy one proceeds as follows: the final dipole moment μ_{1i} induced on ion i , is the one coming from the effective field of the impurity which is located at (000) , and from the other dipoles induced by this ion (see Fig. 2), while μ_{2i} is due to the corresponding field produced by the vacancy. These components are treated separately in the calculation.

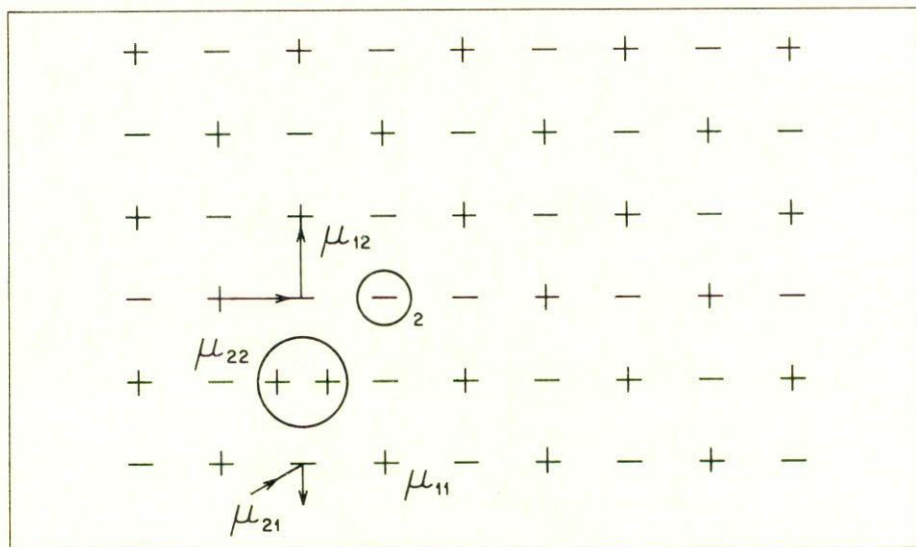


FIGURE 2. Dipole moments induced on ion i by the adjacent polarizing charges 1 and 2, the m_{11} is localized at (001) and $(00\bar{1})$, m_{12} at (010) and (100) , m_{13} at (111) and $(\bar{1}\bar{1}\bar{1})$, m_{14} at (120) and (210) , and m_{15} at (010) and (100) . The m_{2i} are localized in the positions of the m_{1i} but they have a different direction.

The equation for the total work of polarization is:

$$W' = \frac{1}{2}(-e)\phi'_1 + \frac{1}{2}(+e)\phi'_2, \quad (2)$$

where ϕ'_1 is the potential in position 1 (see Fig. 2), and ϕ'_2 that at position 2. That is

$$\phi'_1 = \sum' \left(-\frac{\mu_{1i}}{r_{1i}^2} + \frac{\mu_{2i} \cos \gamma_i}{r_{1i}^2} \right), \quad (3)$$

$$\phi'_2 = \sum' \left(\frac{\mu_{2i}}{r_{2i}^2} - \frac{\mu_{1i} \cos \gamma_i}{r_{2i}^2} \right). \quad (4)$$

The prime indicates the omission of points 1 and 2 in the sums, and γ_i is the angle between μ_{1i} and μ_{2i} . If the first ten neighbors to the complex are fixed

(zero approximation), equation (2) becomes:

$$W' = \frac{1}{2}e^2a^2 \left| \sum'_{\substack{i \\ \text{odd}}} M_- \left(\frac{1}{r_{1i}^4} + \frac{1}{r_{2i}^4} - \frac{2 \cos \gamma_i}{(r_{1i}^2 r_{2i}^2)} \right) + \sum'_{\substack{i \\ \text{even}}} M_+ \left(\frac{1}{r_{1i}^4} + \frac{1}{r_{2i}^4} - \frac{2 \cos \gamma_i}{(r_{1i}^2 r_{2i}^2)} \right) \right|. \quad (5)$$

This result is in accordance with the Mott-Littleton idea [8], since

$$\mu_{1i} = \frac{M_i a^3 e}{r_{1i}^2}, \quad \mu_{2i} = \frac{M_i a^3 e}{r_{2i}^2}, \quad (6)$$

M_- refers to the negative (odd) ions,

$$M_- = \frac{2\alpha_-}{\alpha_- + \alpha_+} \frac{1}{4\pi} \left(1 - \frac{1}{K_0} \right), \quad (7)$$

and M_+ to the positive (even) ions

$$M_+ = \frac{2\alpha_+}{\alpha_+ + \alpha_-} \frac{1}{4\pi} \left(1 - \frac{1}{K_0} \right), \quad (8)$$

where K_0 is the optical dielectric constant, α_+ is the polarizability of the positive ions, and α_- the polarizability of the negative ions. In our case (first order approximation):

$$W_T = \frac{1}{2} \left[\frac{2}{a^2} (\mu_{11} + \mu_{12} + \mu_{15}) + \frac{2\mu_{13}}{3a^2} + \frac{2\mu_{14}}{5a^2} - \frac{2}{a^2} \left(\frac{\mu_{21}}{\sqrt{3}} + \frac{2\mu_{25}}{\sqrt{5}} \right) - \frac{2\mu_{23}}{\sqrt{3} 3a^2} - \frac{4\mu_{24}}{5\sqrt{5} a^2} + \phi_{1L} \right] + \frac{1}{2} (-e) \left[-\frac{2}{a^2} (\mu_{22} + \mu_{23} + \mu_{24}) - \frac{2\mu_{21}}{3a^2} - \frac{2\mu_{25}}{5a^2} + \frac{2\mu_{12}}{3a^2} \frac{1}{\sqrt{3}} + \frac{2\mu_{13}}{\sqrt{3} a^2} + \frac{2\mu_{14}}{a^2} \frac{2}{\sqrt{5}} + \frac{2\mu_{15}}{5 a^2} \frac{2}{\sqrt{5}} + \phi_{2L} \right] + W_I, \quad (9)$$

where W_I is the polarization energy due to the impurity; the terms containing μ_{ij} are due to the dipoles around the complex (see Fig. 2); ϕ_{1L} represents the contribution of the rest of the lattice, beyond the set of ten nearest neighbors, to the potential field at point 1, and ϕ_{2L} represents the contribution of the lattice

beyond the ten nearest neighbors, to the potential field at point 2. Finally, W_T is the total polarization energy, and is similar to W' of equation (2).

The sum ϕ_{1L} is obtained from equation (3) for the dipole moments which are beyond the first ten neighbors complex. In this case

$$\mu_{1i} = M_i a^3 \frac{e}{r_{1i}^2}$$

and

$$\begin{aligned} \phi_{1L} = \frac{1}{2} e^2 a^3 \left[\sum'_{\substack{i \\ \text{odd}}} M_- \left(\frac{1}{r_{1i}^4} \right) - \sum'_{\substack{i \\ \text{even}}} M_+ \left(\frac{1}{r_{1i}^4} \right) \right. \\ \left. + M_- \sum'_{\substack{i \\ \text{odd}}} \frac{\cos \gamma_i}{r_{1i}^2 r_{2i}^2} + M_+ \sum'_{\substack{i \\ \text{even}}} \frac{\cos \gamma_i}{r_{1i}^2 r_{2i}^2} \right], \end{aligned} \quad (10)$$

$$\begin{aligned} \phi_{2L} = \frac{1}{2} e^2 a^3 \left[\sum'_{\substack{i \\ \text{odd}}} M_- \left(\frac{1}{r_{2i}^4} \right) + \sum'_{\substack{i \\ \text{even}}} M_+ \left(\frac{1}{r_{2i}^4} \right) \right. \\ \left. - M_- \sum'_{\substack{i \\ \text{odd}}} \frac{\cos \gamma_i}{r_{1i}^2 r_{2i}^2} + M_+ \sum'_{\substack{i \\ \text{even}}} \frac{\cos \gamma_i}{r_{1i}^2 r_{2i}^2} \right]. \end{aligned} \quad (11)$$

The prime indicates the omission of the set of the ten nearest neighbors to the complex, and

$$\cos \gamma_i = \frac{r_{1i}^2 + r_{2i}^2 - 2a^2}{2r_{1i} r_{2i}}. \quad (12)$$

According to equations (2) and (9) the contribution of the lattice can be written as

$$W_L = \frac{1}{2} e (\phi_{2L} - \phi_{1L}). \quad (13)$$

From equations (10) and (11) one can see that $\phi_{2L} - \phi_{1L}$ can be obtained carrying out the sums

$$A = \sum'_{\substack{i \\ \text{odd}}} \left(\frac{1}{r_{1i}^4} + \frac{1}{r_{2i}^4} - \frac{2 \cos \gamma_i}{r_{1i}^2 r_{2i}^2} \right) a^4, \quad (14)$$

and

$$B = \sum'_{\substack{i \\ \text{even}}} \left(\frac{1}{r_{1i}^4} + \frac{1}{r_{2i}^4} - \frac{2 \cos \gamma_i}{r_{1i}^2 r_{2i}^2} \right) a^4, \quad (15)$$

for all the lattice points (except $r_{1i} = r_{2i} = 0$). It is then found that:

$$A = 3.5961 \quad \text{and} \quad B = 10.9190.$$

The expressions for A and B require that the sums include the whole lattice, excluding the ten nearest neighbors and the points 1 and 2. These ten ions are all negative and their contribution was found to be equal to 9.6337. Inserting this value, it is found that

$$W_L = \frac{e^2}{a} \left(\frac{A}{2} M_+ + \frac{B - 9.6337}{2} M_- \right), \tag{16}$$

and

$$W_T = W + W_L + W_I, \tag{17}$$

where

$$W = \frac{1}{2}(-e)\phi_1 + \frac{1}{2}e\phi_2, \tag{18}$$

$$\begin{aligned} \phi_1 = & -\frac{2}{a^2}(\mu_{11} + \mu_{12} + \mu_{15}) - \frac{2\mu_{13}}{3a^2} - \frac{2\mu_{14}}{5a^2} \\ & + \frac{2}{a^2} \left(\frac{\mu_{21}}{\sqrt{3}} + \frac{2\mu_{25}}{\sqrt{5}} \right) + \frac{2\mu_{23}}{\sqrt{3}3a^2} - \frac{4\mu_{24}}{5\sqrt{5}a^2}, \end{aligned} \tag{19}$$

$$\begin{aligned} \phi_2 = & - \left[\frac{2}{a^2}(\mu_{22} + \mu_{23} + \mu_{24}) - \frac{2\mu_{21}}{3a^2} - \frac{2\mu_{25}}{5a^2} \right. \\ & \left. + \frac{2\mu_{12}}{3a^2\sqrt{3}} + \frac{2\mu_{13}}{\sqrt{3}a^2} + \frac{2\mu_{14}}{a^2} \frac{2}{\sqrt{5}} + \frac{2\mu_{15}}{5a^2} \frac{2}{\sqrt{5}} \right], \end{aligned} \tag{20}$$

and

$$W_I = -\frac{e^2\alpha_I}{4a^4}. \tag{21}$$

To obtain numerical values for ϕ_1 and ϕ_2 it is necessary to find μ_{1i} and μ_{2i} [9, 10] from a set of equations of the type of (1):

$$\begin{aligned} 1 - 1.8283M_+ - 0.2552M_- = & \left(\frac{1}{\beta_-} + 0.25 \right) m_{11} + 1.0606m_{12} + 0.3219m_{13} \\ & + 0.1521m_{14} + 1.0606m_{15}, \end{aligned} \tag{22}$$

$$1 - 1.6124M_+ - 0.3198M_- = 1.0606m_{11} + \left(\frac{1}{\beta_-} + 0.5305 \right) m_{12} + 0.4082m_{13}$$

$$- 0.3393m_{14} + 0.7803m_{15}, \quad (23)$$

$$\frac{1}{3} - 1.5390M_+ - 0.5830M_- = 0.321m_{11} + 0.4082m_{12} + \left(\frac{1}{\beta_-} + 0.1666\right)m_{13} \\ + 0.5477m_{14} + 0.2357m_{15}, \quad (24)$$

$$\frac{1}{5} - 1.2417M_+ - 0.5988M_- = 0.1521m_{11} - 0.3393m_{12} + 0.5477m_{13} \\ + \left(\frac{1}{\beta_-} + 0.3889\right)m_{14} + 0.1292m_{15}, \quad (25)$$

$$1 - 1.8821M_+ - 0.2552M_- = 1.0606m_{11} + 0.7803m_{12} + 0.2357m_{13} \\ + 0.1299m_{14} + \left(\frac{1}{\beta_-} + 0.5303\right)m_{15}. \quad (26)$$

The m_{1i} are related to the μ_{1i} by the equation:

$$\mu_{1i} = eam_{1i}, \quad (27)$$

and $\beta_- = \alpha_-/a^3$, where α_- is the polarizability of the displaced ions. The five equations with five unknowns corresponding to m_{21} , m_{22} , m_{23} , m_{24} and m_{25} are:

$$1 - 0.2552M_- - 1.8283M_+ - \frac{0.1361\alpha_I}{a^3} = \left(\frac{1}{\beta_-} + 0.25\right)m_{23} \\ + 1.0606m_{22} + 0.3219m_{21} + 0.1521m_{25} + 1.0606m_{24}, \quad (28)$$

$$1 - 0.3198M_- - 1.6124M_+ - \frac{0.3536\alpha_I}{a^3} = 1.0606m_{23} \\ + \left(\frac{1}{\beta_-} + 0.5303\right)m_{22} + 0.4082m_{21} - 0.3393m_{25} + 0.7803m_{24} \quad (29)$$

$$\frac{1}{3} - 0.5830M_+ - 1.5390M_- - \frac{0.4082\alpha_I}{a^3} = 0.3219m_{23} \\ + 0.4082m_{22} + \left(\frac{1}{\beta_-} + 0.1666\right)m_{21} + 0.5477m_{25} + 0.2357m_{24} \quad (30)$$

$$1 - 0.5988M_+ - 1.2417M_- + \frac{0.4743\alpha_I}{a^3} = 0.1521m_{23} \\ - 0.3393m_{22} + 0.5477m_{21} + \left(\frac{1}{\beta_-} + 0.3889\right)m_{25} + 0.1299m_{24} \quad (31)$$

and

$$1 - 0.2835M_- - 1.8821M_+ - \frac{0.0822\alpha_I}{a^3} = 1.0606m_{23}$$

$$-0.7803m_{22} + 0.2357m_{21} + \left(\frac{1}{\beta_-} + 0.5303\right)m_{24}, \quad (32)$$

where the terms in α_I are due to the dipole moment of the Eu^{++} ion.

To determine the coefficients of M_+ and M_- in equations (22–31), it should be noted that Mott and Littleton have performed these lattice sums for 23 shells of the lattice, excluding the first four shells. The coefficients require the sums for the whole lattice, excluding the ten nearest neighbors to the complex, and the points 1 and 2. Hence, it was necessary to add to the Mott–Littleton [8] sums, the contributions of the following ions:

$(\underline{110})$, $(\underline{1}\underline{1}0)$, $(\underline{200})$, $(\underline{1}0\underline{1})$, $(\underline{1}0\underline{1})$, $(0\underline{1}\underline{1})$, $(0\underline{1}\underline{1})$, $(0\underline{1}\underline{1})$, $(0\underline{1}\underline{1})$, $(\underline{1}0\underline{1})$, $(\underline{1}0\underline{1})$, $(\underline{1}\underline{1}0)$, $(\underline{200})$, $(0\underline{2}0)$, $(00\underline{2})$, $(0\underline{2}0)$, $(00\underline{2})$ which are negative and $(\underline{1}\underline{1}\underline{1})$, $(\underline{1}\underline{1}\underline{1})$, $(\underline{1}\underline{1}\underline{1})$, and $(\underline{1}\underline{1}\underline{1})$ which are positive.

The ions (120) and (210) , which correspond to the first ten neighbors, are outside the first four shells and require a special treatment.

3. Conclusions

We have calculated the polarization energy of a Eu^{2+} -cation vacancy complex in all alkali halides. Table IV gives the values of ϕ_1 , ϕ_2 , W_L , W_I , W_T and W'_T taken from a previous work [2]. There are some differences with respect to reference 1, in which the values of M_- and M_+ are incorrect; those values are given in Table I. Table II gives the values of m_{1i} and Table III the values of m_{2i} .

As can be seen from Table IV, the values of W_T are slightly bigger than those of W'_T , that is, the polarization energy calculated in this work is greater than that calculated by the traditional method [2, 3, 4, 5, 6, 7]. This energy is positive, so the corresponding calculated work to create a nearest positive ion vacancy near an Eu^{++} ion in the alkali halides is decreased by these values of W_T . While there are no experimental values for W_T in the case of the Eu^{++} impurity, we can conclude that this result is not too good. This is because in the case of impurities such as Mg^{++} and Sr^{++} the theoretical values are smaller than the experimental ones [11, 12, 13, 14]. There are no experimental values for the polarization energy. The binding energy for the complex is the quantity that can be compared with experiment.

In general the polarization energy is given by

$$\frac{e \sum_k \alpha_k \mathbf{E}_k \cdot \mathbf{r}}{r^3} \quad (33)$$

	α_+	α_-	K_0	M_+	M_-	R
LiCl	0.03	2.96	2.75	0.0010	0.1003	2.5700
NaCl	0.44	2.96	2.25	0.0107	0.0777	2.8100
KCl	1.33	2.96	2.13	0.0261	0.0582	3.1400
RbCl	1.98	2.96	2.19	0.0346	0.0518	3.2700
LiBr	0.03	4.16	3.16	0.0007	0.1080	2.7450
NaBr	0.41	4.16	2.62	0.0088	0.0896	2.9805
KBr	1.33	4.16	2.33	0.0220	0.0688	3.2930
RbBr	1.98	4.16	2.33	0.0293	0.0615	3.4270
LiI	0.03	6.43	3.80	0.0005	0.1167	3.0000
NaI	0.41	6.43	2.91	0.0062	0.0982	3.2310
KI	1.33	6.43	2.69	0.0171	0.0829	3.5260
RbI	1.98	6.43	2.63	0.0232	0.0754	3.6630
LiF	0.03	0.64	1.92	0.0034	0.0728	2.0086
NaF	0.41	0.64	1.74	0.0264	0.0412	2.3100
KF	1.33	0.64	1.85	0.0494	0.0237	2.6700
RbF	1.98	0.64	1.93	0.0579	0.0187	2.8200

TABLE I. Values of the constants used in the calculations.

	m_{11}	m_{12}	m_{13}	m_{14}	m_{15}
LiCl	0.1185	0.1190	0.0249	0.0218	0.1185
NaCl	0.0963	0.0968	0.0221	0.0170	0.0963
KCl	0.0724	0.0731	0.0172	0.0118	0.0723
RbCl	0.0646	0.0653	0.0152	0.0100	0.0645
LiBr	0.1305	0.1312	0.0252	0.0239	0.1305
NaBr	0.1088	0.1093	0.0232	0.0191	0.1087
KBr	0.0852	0.0859	0.0193	0.0140	0.0851
RbBr	0.0766	0.0773	0.0174	0.0121	0.0764
LiI	0.1455	0.1465	0.0249	0.0271	0.1454
NaI	0.1249	0.1257	0.0246	0.0226	0.1248
KI	0.1020	0.1028	0.0215	0.0171	0.1019
RbI	0.0928	0.0936	0.0199	0.0150	0.0926
LiF	0.0644	0.0644	0.0169	0.0112	0.0643
NaF	0.0433	0.0436	0.0115	0.0071	0.0432
KF	0.0280	0.0284	0.0072	0.0041	0.0280
RbF	0.0237	0.0241	0.0054	0.0032	0.0236

TABLE II. Values of m_{1i} for the alkali halides.

where the sum is carried over the ions which are displaced. $\alpha_k E_k$ is the induced dipole in the k -th ion, whose electric polarizability is α_k , and \mathbf{r} is the vector from the k -th ion to the point where one wishes to calculate the polarization energy.

The difference between the traditional method and the one used in this work

	m_{21}	m_{22}	m_{23}	m_{24}	m_{25}
LiCl	0.0201	0.1160	0.1177	0.1182	0.026
NaCl	0.0193	0.0950	0.0958	0.0960	0.0201
KCl	0.0158	0.0720	0.0721	0.0722	0.0134
RbCl	0.0141	0.0645	0.0643	0.0643	0.0112
LiBr	0.0207	0.1285	0.1299	0.1303	0.0290
NaBr	0.0205	0.1076	0.1083	0.1085	0.0222
KBr	0.0178	0.0848	0.0849	0.0849	0.0157
RbBr	0.0163	0.0765	0.0763	0.0763	0.0135
LiI	0.0207	0.1443	0.1450	0.1453	0.0317
NaI	0.0220	0.1242	0.1245	0.1247	0.0256
KI	0.0200	0.1018	0.1017	0.1018	0.0189
RbI	0.0187	0.0927	0.0925	0.0925	0.0164
LiF	0.0125	0.0611	0.0633	0.0638	0.0163
NaF	0.0096	0.0421	0.0428	0.0429	0.0093
KF	0.0064	0.0278	0.0278	0.0278	0.0050
RbF	0.0053	0.0236	0.0235	0.0235	0.0039

TABLE III. Values of m_{2i} for the alkali halides.

	ϕ_1	$-\phi_2$	W	W_L	W_I	W_T	W'_T
LiCl	5.2842	1.3524	3.3183	0.3588	0.2344	5.5368	4.3930
NaCl	3.8553	1.3192	2.5873	0.4498	0.1640	4.3510	3.0680
KCl	2.5437	1.1029	1.8233	0.6200	0.1052	3.3274	2.2480
RbCl	2.1477	1.0192	1.5834	0.7215	0.0894	3.0821	2.0850
LiBr	5.4342	1.2775	3.3559	0.3955	0.1801	5.7343	4.7430
NaBr	4.1227	1.2413	3.6820	0.4229	0.1296	4.6087	3.3780
KBr	2.8641	1.1205	1.9923	0.5491	0.0869	3.5817	2.4530
RbBr	2.4919	1.0415	1.7667	0.6266	0.0741	3.2811	2.2440
LiI	5.5157	1.1722	3.3440	0.3461	0.1263	5.8613	5.2810
NaI	4.2381	1.1937	2.7159	0.3694	0.0938	4.8052	3.8220
KI	3.2195	1.0882	2.1538	0.4710	0.0661	3.8565	2.7800
RbI	2.7968	1.0449	1.9209	0.5275	0.0568	3.5203	2.5660
LiF	3.7522	1.2465	2.4993	0.4070	0.6284	3.7042	3.0558
NaF	2.0839	1.0091	1.5465	0.7852	0.3592	2.8063	2.4000
KF	1.1194	0.6857	0.9025	1.0966	0.2012	2.3565	2.1060
RbF	0.9168	0.5456	0.7312	1.1908	0.1617	2.2583	2.0800

TABLE IV. Values of ϕ_1 , ϕ_2 , W , W_L , W_I , W_T and W'_T for the alkali halides. The values W'_T is obtained from a previous work. All energies are given in electron volts.

is the way in which the field E_k on each dipole is calculated. The field produced by the dipoles, which are displaced, and the field produced by the dipoles corresponding to the rest of the crystal are not considered in earlier works [2, 3, 4, 5, 6, 7].

These dipole fields are taken into account in the present paper. It is evident that the dipole field must be considered in the calculation of E_k . In this way our results should, in principle, be better than earlier calculations. Because the values obtained by us for the polarization energy lead to values of the complex energy which are in bad agreement with the experimental results, several possibilities that can explain this fact may be given.

1. The size of our region must be increased.
2. The other terms, which appear together with the polarization energy in the calculation of the complex energy, need to be revised.
3. In earlier calculations [2, 3, 4, 5, 6, 7], the first neighbors of the complex and the second and third neighbors of the vacancy are taken into account. There is no clear justification for this way of choosing the ions which contribute to the energy.
4. Finally, in earlier calculations [2, 3, 4, 5, 6, 7] it was considered that the electric field E_k depends on the variation in the electric field produced by the displacements of the first neighbors to the complex. This field was not taken into account in the present calculations, since we followed the procedure of Rittner *et al.* [10], who studied the polarization energy in the divacancy case.

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Reference

1. C. Ruíz Mejía and U. Oseguera, *Cryst. Latt. Def. and Amorph. Mat.* **11** (1985) 259.
2. C. Ruíz Mejía, U. Oseguera, H. Murrieta and J. Rubio, *J. Chem. Phys.* **73** (1980) 60.
3. C. Ruíz Mejía and U. Oseguera, *Crys. Latt. Def.* **10** (1984) 125.
4. F. Bassani and F.G. Fumi, *Nuovo Cimento* **11** (1954) 274.
5. G. Airoldi and M.P. Tosi, *Nuovo Cimento* **8** (1958) 584.
6. T. Iwasaki and H. Wakabayasi, *The 90th Anniversary Bulletin of Chuo University* (unpublished) (1975) p. 79.
7. J.R. Reitz and J.L. Gammel, *J. Chem. Phys.* **19** (1951) 894.
8. N.F. Mott and M.J. Littleton, *Trans. Faraday Soc.* **53** (1957) 206.
9. E.S. Rittner, R.A. Hunter and F.K. Du Pre, *J. Chem. Phys.* **17** (1949) 198.
10. E.S. Rittner, R.A. Hunter and F.K. Du Pre, *J. Chem. Phys.* **17** (1949) 204.
11. R.W. Dreyfus and A.S. Nowick, *Phys. Rev.* **126** (1962) 1367.
12. N. Brown and I.M. Hoodless, *J. Phys. Chem. Solids* **28** (1967) 2297.
13. J.H. Beanmoht and P.W.M. Jacobs, *J. Chem. Phys.* **45** (1966) 1496.
14. A.R. Allnatt, P. Pantelis and S.J. Sime, *J. Phys.* **C4** (1967) 1778.

Resumen. Se calcula la energía de polarización de un complejo para todos los halogenuros alcalinos que contienen impurezas de Eu^{++} . Se consideran diez vecinos cercanos del complejo y se supone que el campo de cada dipolo es el producido por la carga del complejo y por el campo producido por otros dipolos inducidos. Concluimos que los cálculos obtenidos previamente deben ser revisados.