Structure and interaction of impurity–vacancy (Mg^{2+}–V_c^-) dipoles in crystalline LiF

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Abstract. Both the spatial and electronic structure of Mg^{2+}, V_c^- and $(Mg^{2+}-V_c^-)_n$ centres ($n = 1, 4$) in a LiF crystal have been calculated by semiempirical techniques of pair potentials and INDO. Crystal polarization was taken into account in a self-consistent way in terms of the Mott–Littleton approach. It is shown that a consistent choice of parametrization of both methods gives rather close values for displacements of ions surrounding the centres under study. The Mg^{2+} compensation by a cation vacancy located in its nearest surrounding along the $\langle 110 \rangle$ axis is found to be most energetically favourable. It is shown that the aggregation of impurity–vacancy dipoles can lead to the formation of a phase with a periodical structure differing from the traditional Suzuki phase.

1. Introduction

The lattice of insulating crystals is strongly disturbed by charged impurities. Therefore, to study them theoretically it is necessary to take into account the displacements of ions surrounding such defects and the polarization of a whole crystal. At present the basic achievements in the modelling of a spatial structure of these defects (Colbourn and Mackrodt 1982, Catlow 1989) are connected with the application of pair potentials (PP) realized in a form of shell model (Stoneham and Harding 1986, Catlow *et al* 1982). At the same time, their electronic structure and spectroscopic characteristics are theoretically rarely studied. The reliability of results depends, in its turn, on the accuracy of ionic displacement calculations. However, a direct accuracy displacement calculation of a large number of atoms using quantum-chemical methods is a rather difficult problem, at least for the time being. Furthermore, the direct use of atomic coordinates obtained by the PP method in the electronic structure calculations may lead to incorrect results due to inconsistent use of both methods.

The novel approach to the cluster model for the crystal with point defects proposed by Shluger and Kantorovich allows the successful combination of the advantages of both methods in the case where a model of the so called 'embedded molecular cluster' (EMC) type (Kantorovich 1983–1988, Shluger *et al* 1986) can be applied and essential redistribution of the electron density in the defect region (in comparison with an ideal lattice) does not take place. The most reasonable results can be expected when approximations based on a zero differential overlap between atomic orbitals are used in the

electronic structure calculations (Pople and Beveridge 1970). In this case, a quantum-chemical description of the interactions is of two-body character and, therefore, there is a complete analogy between the method of pair potentials (Stoneham *et al* 1986) and the quantum-chemical calculation in the EMC model with a self-consistent treatment of polarization of the rest of the crystal (Shluger *et al* 1986). Actually, in both cases a cluster model for a crystal with a defect, a pair approximation for describing interactions between ions, a shell model for describing ion deformation in the defective region, and a long wave length approximation for describing the polarization of the rest of the crystal have been used. As both calculation schemes are semiempirical, it is possible to coordinate their parametrization schemes. Such an approach was first used by Itoh *et al* (1977); a successful combination of quantum-chemical methods and a method of pair potentials was also used later by Williams *et al* (1986) to model self-trapped excitons in alkali halides, as well as by Grimes *et al* (1989) to determine the energies of intrinsic and impurity defects in MgO.

The present paper deals with the studies of spatial and electronic structure of $(Mg^{2+}-V_c^-)$ centres and their interaction in crystalline LiF and with the application and comparison of the two aforementioned methods.

2. Calculation scheme

To calculate the spatial structure of the centres by the method of pair potentials we have used a computer code MOLSTAT (Kolmogorov and Varaksin 1989) analogous to the widely spread simulation code HADES (Norgett 1974, Catlow *et al* 1982). (From the point of view of the questions in which we are interested, there are minor differences in complexes of programs, so we do not consider them in the present article.) The parameters of the Born–Mayer short-range potentials between Li^+ and F^- were taken from the paper by Sangster and Atwood (1978). The interaction $Mg^{2+}-F^-$ was described by potentials with parameters given in the handbook of interionic potentials (Stoneham 1981) for the rutile structured MgF_2, in which the coordination number for Mg^{2+} is equal to 6, but the Mg–F distance is very close to the interionic distance in LiF ($a = 1.99$ Å). The non-Coulomb contribution to the interaction between the impurity and host cations has been neglected.

The quantum-chemical computer code CLUSTER that we have devised allows us to make INDO calculations of the band structure of perfect crystals as well as to determine optical and ESR parameters of point defects therein (Shluger 1985, Shluger *et al* 1986, 1988). The structure and properties of perfect crystals can be studied using the large unit cell model (LUC) (Evarestov and Lovchicov 1979), whereas the defects can be investigated by LUC and EMC. The CLUSTER is a modification of the MONSTER program, the possibilities of which are described by Shluger *et al* (1986). Its program makes it possible to study the defect structure with a self-consistent account of polarization of the crystal.

The parameters of both methods have been obtained independently, but on the basis of analogous ideas. Thus the parameters of the PP method, which have been used to study defects in crystals, were fitted to reproduce the spatial structure of perfect crystals, consisting of relevant ions, their lattice and elasticity constants, phonon spectra and static and high frequency dielectric permittivity (Catlow *et al* 1977, Stoneham 1981). At the same time, the parameters of the INDO method used in these calculations were obtained by Shluger (1985) in order to reproduce both the spatial structure and the

Table 1. Displacements (in % of a) of ions surrounding the Mg^{2+}, V$_c^-$ and Mg^{2+}–V$_c^-$ centres in LiF, calculated by the pair potentials method (a), and INDO (b) using a different approximation for ion relaxation. Δ_1, displacements of the anions in the first coordination sphere of the Mg^{2+} ion; Δ_2, the same for the anions surrounding of V$_c^-$; σ, the displacement of Mg^{2+} towards V$_c^-$; and Δ_3, displacements of two anions belonging to the Mg^{2+}–V$_c^-$ dipole environment.

Type of defect		Frozen lattice		Small displacements		Full relaxation
		(a)	(b)	(a)	(b)	(a)
Mg^{2+}	Δ_1	-2.5	-3.0	-2.1	-2.0	-0.9
V$_c^-$	Δ_2	7.1	10.0	6.4	7.0	5.4
Mg^{2+}–V$_c^-$	σ	7.0	5.7	4.2	4.2	4.2
	Δ_1	-1.7	—	-1.6	—	1.2
	Δ_2	5.0	—	5.1	—	5.2
	Δ_3	7.3	8.0	6.6	4.0	5.2

lattice constants of LiF and MgO crystals as well as the basic parameters of their electronic structure, forbidden gap, valence band width and mid-point, electronic density distribution with the highest possible accuracy. To ensure the possibility of studying the impurities in various charge states, while optimizing the parameters, we were aiming for an adequate description of the potential energy curves of the relevant diatomic molecules F_2, F_2^-, MgF, Mg^{2+}, Mg$_2$, LiMg and Li$^+$Mg^{2+}.

The next section deals with the comparison of the results obtained by both methods using a Mg^{2+} impurity compensation model in the LiF crystal as example.

3. The embedding of a Mg^{2+} ion in a LiF lattice

3.1. Isolated defects

We assumed the existence of single Mg^{2+} and V$_c^-$ centres in the lithium fluoride, grown from the LiF:MgF$_2$ melt. We shall discuss their spatial structure in this section, and calculate their interaction and the structure of the forming centre. Section 4 deals with a mechanism of impurity aggregation.

In table 1 the values of displacements of nearest anions of Mg^{2+} and V$_c^-$ centres calculated both by the method of PP and INDO are plotted. In the table we have compared the results obtained by the three most widespread methods used to calculate the lattice deformation around the defect:

(i) nearest ion relaxation in the otherwise frozen lattice;

(ii) the same relaxation taking into account the polarization of the rest of a crystal in terms of the Mott–Littleton (1938) approach of small displacements;

(iii) a full realization of the PP method, where the region I of explicit two-body interactions consists of five spheres of surrounding ions.

The methods (i) and (ii) have been used for the quantum-chemical calculations performed for a cluster containing three spheres of ions around the defect. As we have

already pointed out, there are practically no quantum-chemical calculations with a more detailed account of surrounding-ion relaxation.

The approach (i) leads to a considerable overestimation of the nearest-ion displacements: the long wave length approach (small displacements) is useful only for long distances from charged defects. Therefore, for a reliable determination of lattice deformation, an explicit incorporation of approximately four spheres of surrounding ions is necessary. At the same time the displacements of the second-sphere cations surrounding V_c^- constitute $5.7\%a$ towards a vacancy, unlike Mg^{2+}, where the $5.8\%a$ outward displacement takes place. The Löwdin population analysis (Pople and Beveridge 1970) shows that the ion's effective charges in LiF are $0.94e$ (e is electron charge), but an effective ion Mg^{2+} charge is equal to $1.93e$ and its substitution for a host cation does not essentially result in a redistribution of the electron density. This latter point and similar principles of parametrization of both methods have led to good agreement of the results obtained. They prove that when the formation of a defect is not accompanied by a considerable redistribution of electron density in a crystal, the use of ion displacements obtained by the PP method in quantum-chemical electron structure calculations can be quite successful. On the other hand, the quantum-chemical calculation of the electron density distribution in a crystal allows us to reach a conclusion about the legitimacy of the PP method, the effective charge of the impurity and, correspondingly, about the number of vacancies necessary to compensate it.

3.2. The Mg^{2+}–V_c^- dipole

Calculations carried out for a series of bivalent cation impurities in alkali halide crystals (Corish *et al* 1981, Bannon *et al* 1985, Jacobs 1989) show that the compensation of impurity charge by a cation vacancy can take place either in the nearest cation sphere along the $\langle 110 \rangle$ axis (NN) or along the $\langle 100 \rangle$ axis in the second sphere (NNN), depending on the relation of effective radii of impurity and host cations. The calculated binding energies for dipoles (Mg^{2+}–V_c^-) are equal 0.6 and 0.4 eV for (NN) and (NNN) configurations, respectively. Since their energy difference is rather small, the two configurations can coexist at relatively high temperatures.

The displacements of nearest ions surrounding the (Mg^{2+}–V_c^-) dipole obtained by the three methods discussed above, are displayed in table 1. It is seen that the tendency of the absolute displacement value to decrease with increasing number of displaced ions remains in this case too. It is most obvious in the almost twofold reduction of the Mg^{2+} ion displacement.

The displacements of ions surrounding the NN dipole are close to the vector sum of the component displacements. The main difference arises due to a displacement of the Mg^{2+} ion towards a vacancy. The additivity of displacements is again a result of the pair character of the interaction, and is fulfilled with good accuracy within the PP method applicability. It should be noted that the slight difference in the ion displacements obtained by two methods does not affect the electronic structure of the centre. The wave function of a local state formed in the crystalline forbidden gap has been almost completely defined by 3S atomic orbitals (AO) of Mg^{2+}. The relaxation of ions surrounding V_c^- gives rise to the one-electron states near the top of the valence band. The relevant molecular orbitals are linear combinations of AOs centred on displaced anions. The anion relaxation around Mg^{2+} also leads to the states with wave functions represented by linear combinations of AOs centred on these anions only. Their one-electron states are near the bottom of the valence band. Besides, cation displacements lead to

the formation of analogous localized states with energies falling in the conduction band. In cluster calculations the wave functions of the states spread through the whole cluster can be provisionally called 'delocalized', while those with wave functions localized in the defect region and with one-electron energies falling in the valence (conduction) band can be called 'quasilocal'. It is clear that such classification is relative. As is shown by Kristofel (1984), another criterion which distinguishes between the two kinds of states is that the oscillator strengths of the optical transitions from the quasi-local states into the local ones be greater than for transitions from band (delocalized through a cluster) states.

We have calculated the energies and matrix elements of optical transitions by the method of restricted configuration interaction (RCI) taking into account about a hundred single-excited configurations. The wave function of the excited state in this method is presented by a linear combination of MO LCAO determinants corresponding to these single excitations. In the calculated excitation spectrum there exist transitions both from the quasi-local and band states from the valence band into the local defect state. It should be noted that the matrix elements of transitions from the latter are of more than two orders of magnitude less than those from the states with the wave functions localized near the Mg^{2+} and the vacancy. Thus the 'quasilocality' of these states is also proved. The oscillator strengths of these transitions are small and constitute an order of 10^{-4} for the states near a vacancy and 10^{-3} for the transitions from the states localized on anions near Mg^{2+}, whereas the energies range between 4 eV and 7.3 eV, respectively. They have not been observed experimentally yet, which could be due both to the small oscillator strengths and to the fact that in the energy region above 5.5 eV there is absorption of a series of oxygen-containing centres usually present in lithium fluoride (Nepomnyaschikh *et al* 1984).

To conclude, let us consider the role of crystal polarization in the electronic structure calculations. First, as was said above, it determines ionic displacements directly. The calculation proves that both the absolute values of the potential induced by a polarized lattice at ideal crystalline sites and its change in the defect region are rather great. However, in our case of an ionic system with almost closed shells the potential does not result in a considerable charge redistribution among them. Thus, the effective Mg^{2+} ion charge, when taking into account the polarization, only increases from $1.82e$ to $1.89e$ (unlike the case of a $[Li^0]$ centre in MgO where the charge redistribution is much greater (Shluger *et al* 1986)). The difference between one electron energies of the local state and those of the states near the top of the valence band, without taking into account the polarization, is 7.1 eV, but taking the polarization into account increases this to 11 eV. In this way the crystal polarization has an essential influence on the defect's energy spectrum. It should also be stressed that the energies of optical transitions obtained by RCI are considerably smaller than one-electron energies. This is mainly because of the strong interaction between the excited electron localized in the defect region with the hole below.

4. Studies of dipole aggregation

Since the first experimental studies on the metastable phase of Ca^{2+} and Cd^{2+} ions in NaCl, published by Suzuki (1955, 1961), the aggregation of impurity–vacancy dipoles in alkali halides has been a subject under permanent theoretical and experimental study. In the studies of Bannon *et al* (1985), Corish *et al* (1981) and Jacobs (1989) the aggregation
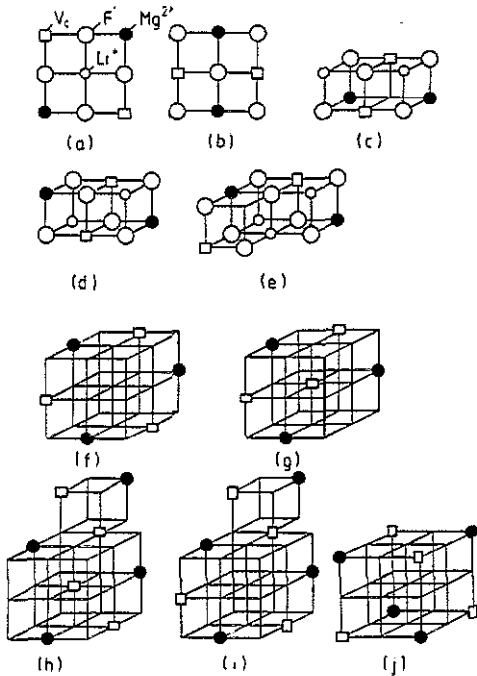
Figure 1. Configurations of the most energetically favourable dimers (a)–(e), trimers (f), (g) and tetramers (h)–(j) $(Mg^{2+}-V_c^-)_n$ in the LiF lattice.

of vacancy–impurity dipoles was modelled by the PP method. Conclusions were drawn on the basis of calculations in the different systems (e.g. KCl, KBr, NaBr, Cd^{2+}, Pb^{2+}, Mn^{2+}) concerning the connection between the structure of complexes consisting of 2, 3 and 4 dipoles and the possibility of forming the Suzuki phase with a relationship between effective radii of impurity and host cations in alkali halides.

In the LiF:Mg system the Mg^{2+} effective radius slightly exceeds that of Li^+ and in accordance with above rule—that Mg^{2+} compensation by V_c^- in the nearest neighbours is expected to be energetically favourable (which is confirmed by our calculations discussed above), but the metastable phase is not formed. Our results make the last conclusion rather doubtful.

4.1. Interaction of two dipoles (dimers)

The most energetically favourable dimer $(Mg^{2+}-V_c^-)_2$ configurations, calculated by the PP method, are shown in figure 1(a)–(e). In table 2 we have plotted the energies of the LiF crystal with a pair of dipoles, U, as well as energies of dimer formation from isolated ones, U_1, and from isolated Mg^{2+} ions and cation vacancies, U_2. The compact configurations of dimers in figure 2 provide the possibility of dipoles approaching each other without dissociation. Less evident is the advantage of the configuration (c) in which a strong Coulomb repulsion of vacancies is compensated by a considerable lattice relaxation around a dimer. Thus, the shift of an anion located between two Mg^{2+} ions constitutes $0.09a$ along the defect symmetry axis. The value of the energy barrier between the configurations (b) and (c) has not been studied. The barrier being small makes possible the rotation of vacancies in a plane perpendicular to the $Mg^{2+}-Mg^{2+}$ axis, which leads to the peculiarities in the vibrational spectrum.

Table 2. Calculated defect and binding energies (in eV) for dimers, trimers and tetramers. The binding energies were calculated according to the formulae: $U_1(n) = U(n) - n^*U_{mono}$ and $U_2(n) = U(n) - n^*(U_{vac} + U_{Mg})$. $U(n)$ is the total energy of the crystal with defect LiF: $(Mg^{2+}-V_c^-)_n$; U_{mono} is the total energy of the crystal LiF with a dipole $(Mg^{2+}-V_c^-)$ in an NN configuration; U_{vac} is the energy of the crystal with a cationic vacancy; U_{Mg} is the energy of the crystal LiF with a single Mg^{2+} ion on a cationic site; and $U_2(n)$ is the binding energy of an n-dipole aggregate from the isolated impurities and cationic vacancies in LiF.

	Dimers					Trimers		Tetramers		
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
U	−10.01	−10.58	−10.58	−10.83	−10.54	−16.09	−15.92	−21.86	−21.54	−19.84
U_1/n	0.12	−0.17	−0.17	−0.29	−0.15	−0.24	0.19	−0.34	−0.26	
U_2/n	−0.47	−0.76	−0.89	−0.74	−0.74	−0.83	−0.78	−0.93	−0.85	−0.14
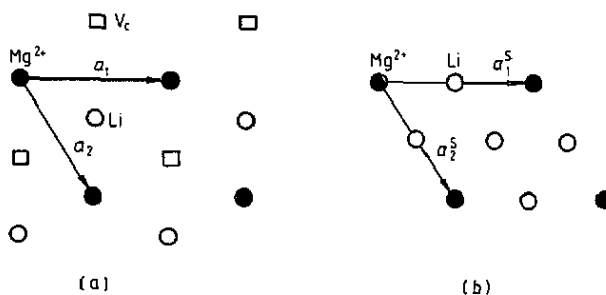
Figure 2. Possible structures of the Mg^{2+} ion aggregation in the LiF crystal $\langle 111 \rangle$ plane. (a) Assumed model; (b) Suzuki phase model.

The dipole interaction also leads to a change of the electron structure of the crystal. Calculations of the one-electron spectrum of the dimer $(Mg^{2+}-V_c^-)_2$ in the most energetically favourable configuration (figure 1(d)) show that the local state in the forbidden gap, determined by the 3S AO of the Mg^{2+} ion, shifts closer to the bottom of the conduction band in relation to its state in a crystal with a single dipole. This shift is connected with the change in the Coulomb potential with the appearance of the second dipole in the vicinity of the Mg^{2+} ion. Estimations predict that the value of the Coulomb shift slowly depends on the compact configuration of the dimer in the crystal and constitutes 2.1 eV which, in its turn, results in the shift of the absorbtion spectrum to higher energies.

The energies of configurations (b) and (c) are 0.6 eV lower than the energy of a dimer in configuration (a), which Bannon et al (1985) thought to be a precursor of the Suzuki phase. Therefore, the growth of such a phase does not seem to be energetically favourable, and the dipole aggregation can take place through the low energy dimer configurations as shown, e.g. in figure 1(d), (e).

4.2. Formation of trimers and the impurity metastable phase

When studying the aggregation there arises one main question: whether the growth of associates is limited or whether in certain conditions a metastable impurity phase is

formed in the matrix of the basic crystal. It was shown by Bannon *et al* (1985) that further linking of dipoles to the precursor with the configurations (*b*) and (*e*) is indeed limited for Mn^{2+}, Cd^{2+} and Pb^{2+} in $NaCl$, Pb^{2+} and KCl. It turned out that the most stable dipole aggregate is a trimer such as that presented in figure 1(*f*), but the subsequent growth results in a decrease in the binding energy of the system. It can be assumed that the situation of Mg in lithium fluoride is generally the same, and the final products of the aggregation in LiF should be trimers $(Mg^{2+}-V_c^-)_3$. The experiments proving such assumptions were carried out by McKeever and Lilley (1982) and Yuan and McKeever (1988). However, direct experimental observation of trimers is complicated by their zero spin and small oscillator strength.

Our simulations show that, to agree with the above conclusions, the most stable magnesia-vacancy trimer in LiF has the structure shown in figure 1(*f*) and the formation of tetramers with a Suzuki phase precursor structure (figure 1(*j*)) is energetically unfavourable (see table 2). However, analysing the different possible ways of joining the (NN) dipoles to trimers (*f*) and (*g*), we have come to a conclusion about the possibility of the formation of tetramers more stable than these trimers. For example, the binding energy of the (*h*) tetramer to a dipole is 0.1 eV greater than the corresponding energy of trimer (*f*). Hence, the trimer formation is not a limiting process to magnesium-vacancy aggregation in lithium fluoride. The geometrical analysis shows that a linking of dipoles to the tetramers (*h*) and (*i*) can result in the redistribution of vacancies and the further formation of a periodical structure with translation vectors in the $\langle 111 \rangle$ plane $a1(2, 1, -1)$ and $a2(1, 2, 1)$ and stoichiometric formulae $7LiF:MgF_2$—unlike $6LiF:MgF_2$ in the Suzuki phase (see figure 2(*a*), (*b*)). Furthermore, it would be interesting to perform the analysis of the possible growth of such a phase and to determine the most favourable relative position of the $\langle 111 \rangle$ planes.

5. Discussion

Let us enumerate features of the defects we have studied, which, in our opinion, are common to all defects considerably changing the lattice of insulators.

(i) As a rule such defects produce quasilocal states in the one-electron crystal spectrum (Kristofel 1984). The optical transitions from and to these states have to be taken into account when analysing the excitation spectra of the crystals with defects (e.g. using the RCI approach).

(ii) The energies, the degree of localization and the symmetry of wave functions of these states (and, consequently, the oscillator strengths of relevant optical transitions) are greatly affected by the deformation of ions surrounding the defect.

(iii) The values of calculated ionic displacements around the defects from the regular sites of the ideal lattice strongly depend on whether all the other ions are 'allowed' to relax, and they reduce with the growth of the number of ions included in the calculation of the relaxation.

(iv) The aggregation of $(Mg^{2+}-V_c^-)$ dipoles in LiF can lead to the formation of a periodical phase which differs from the traditional Suzuki phase. The conditions of formation require further studies based on statistical methods.

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