Abstract. The one-electron level structure of NaCl, NaF, LiF and LiCl crystals containing F centers is calculated using the INDO method in the molecular cluster (MC) approximation. Spin-polarization is considered in the Unrestricted Hartree-Fock (UHF) formulation of the method and F-band transition energies are estimated through limited configuration interaction (CI).

Resumo. Os esquemas de níveis monoeletrônicos do centro F em cristais de LiF, NaF, LiCl e NaCl são obtidos utilizando o método INDO na aproximação de aglomerados. Considera-se a polarização de spin no esquema Hartree-Fock Não Restrito (UHF) e calcula-se a energia de transição da banda F através da Interação de configurações com os primeiros estados excitados.

* Work partially supported by FINEP and CNPq.
Standard parameterisation of semiempirical LCAO methods has shown to be inadequate for the description of important electronic properties of both perfect and defective ionic crystals [1-4]. New parameterisation schemes have been used by Itoh et al [2] and Schluqer et al [3] who employed a molecular cluster (MC) CNDO method in the study of F centers in KCl [2] and NaCl [3]. More recently, another parameterisation scheme has been proposed [4] and its applicability in the study of alkali halides successfully tested [5]; the present investigation of F centers intends to corroborate further its adequacy.

We have used the INDO/1 version [6] of the Intermediate Neglect of Differential Overlap method, in the MC approximation, to investigate the electronic structure of undistorted F centers in LiF, NaF, LiCl and NaCl crystals, with special consideration of the F-band transition energy. A valence basis set of Slater type orbitals (STO) was used, including 1s and 2p type vacancy-centered orbitals. Two-electron integrals were directly evaluated with s-type functions [7] and the open-shell nature of the system was taken into account with the use of the Unrestricted Hartree-Fock (UHF) formulation of the method. The MC consisted of a 27-atom cube centered at the anionic vacancy and was embedded in the field of a finite set of point charges which neutralizes the whole cluster, while preserving its symmetry and providing correct Madelung energies in all cluster sites [4,5]. F center empirical parameters for all crystals were determined through a direct fit to experimental data for NaCl. The F-band transition energy $\Delta E_p$ was estimated from the difference between the total energies of ground and first excited states obtained within a limited
configuration interaction (CI) calculation. This procedure takes into account electron-hole correlation and reduces the simple one-electron eigenvalues difference by an amount of the order of 4.5 eV. All host atom parameters had the values determined in reference [5] and are presented in Table 1.

In the Fock equations corresponding to the defect electron five quantities must be determined, namely: $1s (\xi_{1s})$ and $2p (\xi_{2p})$ orbital exponents of the vacancy-centered STO's, the corresponding one-center integrals $U_{\mu\mu}$ and the F-center bonding parameter $\beta_p$. Since no attractive center is associated with the vacancy, $U_{\mu\mu}$ is simply given by:

$$U_{\mu\mu} = \frac{1}{2} \xi_{2p}^2$$  \hfill (1)

The remaining parameters for NaCl were determined in the following way:

(i) $\xi_{1s} = 0.46\text{a.u.}$: value used in reference [6] to reproduce ENDOR results;

(ii) $\beta_p = -0.85\text{eV}$: fitting of the F center ground-state energy $(\Delta E_c)$ relative to the conduction band edge [3];

(iii) $\xi_{2p} = 0.65\text{a.u.}$: fitting of the F-band transition energy $(\Delta E_F)$

In reference [3] $\xi_{1s}$ is obtained from a separate point-ion variational calculation, $\beta_p$ is calculated through a relation with cationic parameters and $U_{\mu\mu}$ is determined so that the one-electron eigenvalues difference is close to the experimental F-band transition energy. In reference [4] ion-size corrections are included in the variational calculation which determines $\xi_{1s}$, $U_{\mu\mu}$ is calculated from Eq. (1) and $\beta_p$ empirically adjusted simultaneously with host atoms parameters. In both references the basis set does not include a 2p-type vacancy-centered orbital.
Figure 1 shows our results for NaCl. It is observed that the presence of the defect does not appreciably affect the crystalline band structure while spin-polarisation effects are noticeable for the forbidden gap defect levels. The amount of charge inside the vacancy is estimated to be -0.84 a.u. through a Mulliken population analysis [9].

The vacancy-centered orbital exponents, $\xi_{1s}$ and $\xi_{2p}$, for the other three crystals were obtained through the scaling transformation suggested in reference [5], which assumes that, in units of lattice constant, a given STO exponent does not depend on the particular crystal. This leads to the relation:

$$\xi_d = \xi_d'$$

(2)

where $\xi(\xi')$ is the exponent of a given STO in a crystal with lattice constant $d(d')$. Calculations were then performed for the F center in LiF, NaF and LiCl in which the preceding value for $\xi_F$ is used and the vacancy-centered STO’s exponents are scaled according to Eq. (2). Table 2 presents the values of these parameters together with the estimates for the electronic charge inside the vacancy and the F-band transition energy. The later is seen to agree with experiment within 8%. The one-electron energy level structures are very similar to the one obtained for NaCl.

Calculations were performed using a basis set not including the vacancy-centered $2p-t_{1g}$ STO. They led to only slight changes in the one-electron levels structure but to significantly different estimates for $\Delta E_p$ (11% in NaCl, 20% in LiCl, and 9% in NaF and LiF, relative to the extended basis calculation), probably due to different calculated values for the
Coulomb integrals appearing in the CI calculation.

The present investigation indicates that the parameterisation scheme proposed in references [4,5] for ionic crystals may be successfully used in the study of defective systems and suggests that an independent parameterisation for the perfect crystal should precede the defect parameterisation. In the case of F centers we may remark that for an accurate estimate of the F-band transition energy one is led to:

(i) include the contribution from electron-hole correlation, probably because the one-electron excited molecular orbital involved in the transition is still quite localised;

(ii) extend the basis set in order to include a vacancy-centered 2p-type STO.
REFERENCES

4. Matos, M., Maffeo, B. and Zerner, M.C., to be published.
**TABLE CAPTIONS**

Table 1. INDO parameters for LiF, NaF, LiCl and NaCl crystals [5]
- $\beta$: bonding parameter in eV.
- $\xi$: STO exponents in a.u.

Table 2. Results of MC-UHF-INDO calculations of F center in LiF, NaF and LiCl crystals. Quantities are defined in the text. Energies in eV and other quantities in a.u.
<table>
<thead>
<tr>
<th></th>
<th>LiF</th>
<th></th>
<th>LiCl</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_{\text{Li}} / \delta_{\text{F}} )</td>
<td>(-3.25/-39.0)</td>
<td>( \delta_{\text{Li}} / \delta_{\text{Cl}} )</td>
<td>(-3.25/-12.2)</td>
<td></td>
</tr>
<tr>
<td>( \xi_{\text{Li}} (2s) / \xi_{\text{Li}} (2p) )</td>
<td>(1.40/1.40)</td>
<td>( \xi_{\text{Li}} (2s) / \xi_{\text{Li}} (2p) )</td>
<td>(1.09/1.09)</td>
<td></td>
</tr>
<tr>
<td>( \xi_{\text{F}} (2s) / \xi_{\text{F}} (2p) )</td>
<td>(2.60/2.07)</td>
<td>( \xi_{\text{Cl}} (3s) / \xi_{\text{Cl}} (3p) )</td>
<td>(2.34/1.77)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaF</td>
<td></td>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>( \delta_{\text{Na}} / \delta_{\text{F}} )</td>
<td>(-1.75/-39.0)</td>
<td>( \delta_{\text{Na}} / \delta_{\text{Cl}} )</td>
<td>(-1.75/-12.2)</td>
<td></td>
</tr>
<tr>
<td>( \xi_{\text{Na}} (3s) / \xi_{\text{Na}} (3p) )</td>
<td>(1.23/1.23)</td>
<td>( \xi_{\text{Na}} (3s) / \xi_{\text{Na}} (2p) )</td>
<td>(1.01/1.01)</td>
<td></td>
</tr>
<tr>
<td>( \xi_{\text{F}} (2s) / \xi_{\text{F}} (2p) )</td>
<td>(2.25/1.79)</td>
<td>( \xi_{\text{Cl}} (3s) / \xi_{\text{Cl}} (3p) )</td>
<td>(2.13/1.61)</td>
<td></td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th></th>
<th>LiF</th>
<th>NaF</th>
<th>LiCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\xi_{1s})</td>
<td>0.65</td>
<td>0.56</td>
<td>0.50</td>
</tr>
<tr>
<td>(\xi_{2p})</td>
<td>0.91</td>
<td>0.79</td>
<td>0.71</td>
</tr>
<tr>
<td>(\Delta E_F^{(\text{calc.})})</td>
<td>5.3</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>(\Delta E_F^{(\text{exp.})})</td>
<td>5.1</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Q</td>
<td>-1.02</td>
<td>-1.20</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

(a) Bartram et al. Ref[10]
FIGURE CAPTION

Figure 1. UHF electronic level structure of F center in NaCl crystal.