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Electronic structure of fluorite-type crystals

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Abstract. The results of the electronic structure calculations made in the large-unit-cell complete neglect of differential overlap approach are given for the crystals MF_2 (M ≡ Ca, Sr, Ba, Cd, Pb or Sn) and $PbSnF_4$. The same approach is used for the impurity centre MF_2:Cd (M ≡ Ca, Sr, Ba or Pb) and the lattice distortion introduced by the symmetrical shift of the nearest cation neighbour. It is shown that the influence on the band structure of this lattice distortion is not large.

1. Introduction

Ionic crystals with a fluorite-type structure have been widely studied in the last 10 years. These are prospective optical materials in the vacuum ultraviolet area which have an anomalously high ionic conductivity (superionic solids). Fluorine conductive solid electrolytes are used in gas sensors, ion-selective electrodes and opto-ionic devices.

The calculation of the electronic structure is the first step in the theoretical investigation of crystals. It is the electronic structure that mainly determines both the properties of a perfect crystal and its interaction with point defects.

Systematic calculations of the band structure of the fluorides of rare-earth metals were started only in the 1970s (Salamon 1979, Hayes 1974).

The use of the LCAO basis and quantum chemical calculational schemes in solid state theory allows one to understand the connection between the crystal properties and the behaviour of the atoms which form the crystal (Evarestov 1982).

The application of the large-unit-cell (LUC) model in a quantum chemical scheme (Evarestov *et al* 1983) permits one to describe pure and defect crystals in the limits of the same approach. It is important to understand the nature of defects.

The mechanism of ionic transport is one of the most interesting problems in solid state theory. The phenomenon of superionic conductivity is qualitatively explained by quasi-melting of one of the sublattices in crystal. This determines the transition from the dielectric phase to the electrolyte phase.

A certain number of ions in the crystal are displaced from their regular positions after dopants have been introduced (heterovalent solid solutions) or by increasing the temperature, which causes structure irregularity. It is of great interest to understand the connection between the superionic properties of the crystal and the change in its electronic structure when the crystal turns into the electrolyte phase.

In this work, we give the electronic structure calculations of a number of inorganic fluorides MF_2 (M ≡ Ca, Sr, Ba, Cd, Pb or Sn) and $PbSnF_4$. These calculations were

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Table 1. The main electronic structure characteristics of the crystalline fluorides: ΔE_g, the energy gap; E_v, the top of upper valence band; ΔE_v, the valence band width; Q_M, metal effective charge; Q_F, fluorine effective charges.

Crystal		ΔE_g	E_v	ΔE_v	Q_M	Q_F
CaF_2	Ca_8F_{16} (I)	14.40	−8.20	4.84	1.99	−0.99
	$Ca_{32}F_{64}$ (I)	14.30	−8.19	4.84	1.99	−0.99
	Ca_8F_{16} (II)	13.62	−8.82	4.86	1.99	−0.99
	Experiment[a]	12.10	−12.30	4.8	—	—
	TB method[b]	17.09	−14.04	2.73	—	—
	TB method[c]	—	−8.78	8.75	—	—
	LCAO method[d]	9.8	−11.66	2.01	—	—
SrF_2	Sr_8F_{16} (I)	11.27	−8.49	4.47	1.99	−0.99
BaF_2	Ba_8F_{16} (I)	11.20	−9.33	3.35	1.99	−0.99
CdF_2	Cd_8F_{16} (I)	9.67	−9.25	5.26	1.99	−0.99
	TB method[b]	14.26	−13.7	3.5	—	—
SnO_2	Sn_8O_{16} (II)	3.78	−1.39	10.53	3.20	−1.60[e]
SnF_2	Sn_8F_{16} (II)	8.40	−6.90	6.52	1.84	−0.92
	$Sn_{16}F_{32}$ (II)	8.01	−7.05	6.37	1.77	−0.88
PbF_2	Pb_8F_{16} (I)	15.20	−9.07	9.50	1.98	−0.98
	$Pb_{32}F_{64}$ (I)	14.70	−8.31	9.54	1.98	−0.98
	Pb_8F_{16} (II)	9.04	−8.44	6.74	1.77	−0.88
$PbSnF_4$	$Pb_{16}Sn_{16}F_{64}$ (II)	3.73	−4.47	8.21	1.80	−0.89

[a] Poole *et al* (1975).
[b] Albert *et al* (1977).
[c] Starostin and Ganin (1973).
[d] Heaton and Lin Chun (1980).
[e] On O atoms.

made by the complete neglect of differential overlap (CNDO) method in the LUC approach (Evarestov 1982). We also calculated the impurity MF_2:Cd centres (M ≡ Ca, Sr, Ba or Pb) and PbF_2 and CaF_2 crystals with a structure irregularity, i.e. a symmetric shift of the first-coordination sphere of cations in crystals. We estimated the influence of the quasi-melting of the anion sublattice on the electronic structure. This melting is given by Kristofel (1985) for cationic superionics.

2. The band structure of pure crystals

Up to the present time the electronic structure of the crystal CaF_2 has been investigated fully compared with those of other fluorite-type crystals. The main results obtained in the band-structure calculations of CaF_2 are the following.

(i) The upper valence band (UVB) consists of F^- ion states; the top of the UVB (TUVB) and the bottom of the UVB have X_2 and X_1 symmetry respectively; the Γ_{15}-state one-electron energy is higher than that of $\Gamma_{25'}$.

(ii) The bottom of conduction band (BCB) is s type (symmetry, Γ_1) which consists mainly of Ca^{2+} 4s states with some addition of F^- 2s states.

The quantitative results of band-structure calculations obtained by the LCAO and the tight-binding (TB) methods differ both from each other and from experimental data (table 1).

The non-self-consistent calculation (Albert *et al* 1977) in the TB approach with local exchange gives a very narrow UVB. TB calculations with non-local exchange (Starostin and Ganin 1973) give an UVB twice as large as the experimental one (Poole *et al* 1975). The OPW and APW methods (Starostin and Shepilov 1975, Nemoshkalenko *et al* 1976) give too narrow an UVB. So no band calculations have been made in which the experimental width of the UVB was obtained. The various calculated values of the band gap in CaF_2 are given in table 1. From the experimental investigation (Poole *et al* 1975) the band structures of the crystals SrF_2 and BaF_2 are similar to that of CaF_2. The same conclusion can be made from our results in table 1.

In the paper by Albert *et al* (1977) the band-structure calculations of CaF_2 and CdF_2 crystals were performed by the TB method for the valence band and by the pseudopotential method for the conduction band; the UVB in CdF_2 is a little wider than in CaF_2, and the d states of Cd^{2+} ions situated under the UVB form a very narrow band (0.7 eV). As shown experimentally (Berger 1974), the band gap obtained is wider in CaF_2 than in CdF_2.

The band structure of β-PbF_2 has been calculated for the first time by Evarestov *et al* (1984). It follows from experiment (Scrocco 1982) that the TUVB in PbF_2 consists of s states of Pb^{2+}, while the BCB is formed by p states of Pb^{2+}. The TB calculation of PbF_2 (Velicky and Masek 1986) agrees with experiment.

The experimental band gap in the fluorite modification of $PbSnF_4$ crystals is known (3.5 eV) (Vashishta *et al* 1979).

For $PbSnF_4$ and SnF_2 crystals, electronic structure calculations were made in this work for the first time. The simulation of the electronic structure of the above-mentioned crystals was done using a quasi-molecule in a cyclic model. The calculation scheme will be given below.

3. Calculation scheme

In our calculations, we have used the LUC CNDO approximation (Evarestov 1982). The matrix elements of the one-electron Hamiltonian for the LUC model in the CNDO approximation are as follows:

$$F_{\mu\mu} \doteq U_{\mu\mu} + \beta_{\mathrm{AA}} \sum_{j} (S^{0j}_{\mu\mu} - \delta_{0j}) - \sum_{j,\mathrm{B}} Z_{\mathrm{B}}(1 - \delta_{\mathrm{A}}\delta_{0j})\, \gamma^{0j}_{\mathrm{AB}}$$

$$+ \sum_{j,\mathrm{B}} P_{\mathrm{B}} \gamma^{0j}_{\mathrm{AB}} - \tfrac{1}{2} P_{\mu\mu} \gamma^{00}_{\mathrm{AA}} \tag{1}$$

$$F_{\mu\nu} = \beta_{\mathrm{AB}} \sum_{j} S^{0j}_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \sum_{j} f(\bar{R}_{\mathrm{A}} - \bar{R}_{\mathrm{B}} + \bar{R}_j)\gamma^{0j}. \tag{2}$$

Here

$$f(\bar{R}_{\mathrm{A}} - \bar{R}_{\mathrm{B}} + \bar{R}_j) = \frac{1}{V_{\mathrm{B}}} \int_{V_B} \exp[\mathrm{i}\bar{K}(\bar{R}_{\mathrm{A}} - \bar{R}_{\mathrm{B}} + \bar{R}_j)]\, \mathrm{d}K \tag{3}$$

is the Brillouin δ function of the crystal. In (1) and (2) the atomic orbitals (AOs) μ and ν belong to atoms A and B in the LUC, respectively. The subscript j runs over the LUCs in the crystal, and S^{0j} and J^{0j}_{AB} are the overlap and Coulomb integrals calculated with the atomic functions in the zeroth and jth cells. Equations (1) and (2) contain a core integral $U_{\mu\mu}$, a resonance integral β and a core charge Z. The gross atomic population P_{B} and

Table 2. Parameters of the CNDO scheme used in fluorite-type crystal calculations. The orbital exponents were taken from the tables in the papers by McLean and McLean (1981) and Clementi and Roetti (1974).

	β (eV)	$-U_{ss}$ (eV)	$-U_{pp}$ (eV)	$-U_{dd}$ (eV)
F (I)	35	129.544	108.933	—
F (II)	9	129.544	108.933	—
Ca (I)	3.3	9.842	—	—
Ca (II)	0.27	9.842	—	—
Sr(I)	3.35	9.43	—	—
Ba (I)	3.6	10.49	—	—
Pb (I)	10	51.13	26.62	—
Pb (II)	2	51.13	26.62	—
Cd (I)	6.5	97	—	125.47
Sn (II)	1	26.98	21.87	—

the density matrix elements $P_{\mu\nu}$ are calculated using the basis set of AOs. Integration in (3) is carried out over the small Brillouin zone which corresponds to the LUC chosen. The Coulomb integrals γ_{AA}^{00} are calculated from the Hartree–Fock ionisation potentials for neutral and charged atoms:

$$\gamma_{AA}^{00} = I_\mu(A^+) - I_\mu(A^0). \tag{4}$$

The core integrals $U_{\mu\mu}$ are calculated according to the following relation;

$$U_{\mu\mu} = -I_\mu(A^0) - (Z_A - 1)\gamma_{AA}^{00}. \tag{5}$$

The two-centre integrals γ_{AB}^{0j} are calculated from the Ohno (1967) expression using γ_{AA}^{00}.

The resonance integrals β in the CNDO scheme were considered in our calculations as fitting parameters. When the basis set I is used (wavefunctions of neutral atoms), the integrals β_{AA}, β_{AB} and β_{BB} were chosen to represent the experimental values ΔE_v (width of the UVB) and ΔE_g (band gap) and the symmetry of band.

For the basis set II (wavefunctions of charged ions), β_A and β_B were fitted, and β_{AB} was set equal to

$$\beta_{AB} = 1.3(\beta_A\beta_B)^{1/2}. \tag{6}$$

All the parameters used are given in table 2. For CaF_2 crystals with these parameters, the relative positions of the different symmetry levels and the atomic composition of the corresponding molecular orbitals were reproduced correctly.

The effective atomic charges obtained correspond to the ionic bond. When the size of the quasi-molecule was increased, the calculation results did not change considerably. This means that a relatively small LUC (Ca_8F_{16}) reproduced rather well the Γ, X and L states in the band structure.

We showed that the band structure of PbF_2 differs from those of rare-earth and cadmium fluorides. The TUVB has a symmetry X_1 and is formed from s states of Pb^{2+}; the BCB with a symmetry $\Gamma_{4'}$ is formed from p states of Pb^{2+}.

To calibrate the parameter βSn–Sn which is necessary for the following simulations, we calculated the electronic structure of SnO_2 crystals (space group, D_{4h}^{14}; rutile structure).

Table 3. The band-structure characteristics of imperfect crystals: ΔE_d, the distε nce from the bottom of the UVB to the level.

Crystal	ΔE_g	E_v	ΔE_v	ΔE_d
CaF_2, pure (I)	12.50	−8.21	4.84	—
CaF_2, irregular (I)	12.34	−8.18	4.87	—
PbF_2, pure (I)	14.74	−8.31	9.54	—
PbF_2, irregular (I)	14.52	−8.01	9.74	—
$CdCa_7F_{16}$ (I)	15.63	—	4.86	3.86
$CdSr_7F_{16}$ (I)	14.46	—	4.48	5.78
$CdBa_7F_{16}$ (I)	14.15	—	3.35	7.58
$CdPb_7F_{16}$ (I)	15.20	−8.80	8.54	0.87
$CdPb_{31}F_{64}$ (I)	14.76	−8.34	9.40	1.65
$Cd_4Pb_{28}F_{64}$ (I)	14.80	−7.91	9.0	—
$Cd_8Pb_{24}F_{64}$ (I)	14.87	−8.38	7.4	—

We found from our calculations that in this crystal the UVB was formed by 2p states of O and 5s states of Sn, the TUVB has an M_5 symmetry and the BCB has a Γ_1+ symmetry and was formed by 5p states of Sn. Earlier, the SnO_2 band structure had been calculated by the approximate TB method (Robertson 1979). In this calculation the symmetries of the TUVB and BCB were Γ_3+ and Γ_1+, respectively. We have also fitted β for SnO_2 to experimental values of ΔEg and ΔEv.

α-SnF_2 has the space group $C2/c$ with a monoclinic body-centres lattice. There are eight molecules of SnF_2 in a primitive cell. For SnF_2, the use of only the Γ point for the self-consistent process have given good results for the electronic structure. Even when other points were added, there were no significant changes.

The TUVB in SnF_2 is formed by s states of cations, and this band is too wide. The dispersion of bands in Γ–Y and Γ–M directions is not large. The effective atomic charges correspond to the ionic crystal but are less than in fluorite-type crystals.

We have studied γ-$PbSnF_4$ crystals which possess cubic symmetry.

Calculations were carried out for the cyclic system $Pb_{32}F_{64}$ corresponding to the LUC of PbF_2 crystals with cubic symmetry. We have calculated the cyclic system $Pb_{16}Sn_{16}F_{64}$ with the correct stoichiometry of $PbSbF_4$. The local group of cations in this model is O_h.

As a result of our calculations, it was shown that in $PbSbF_4$ the TUVB is formed by s states of Sn, and the BCB is formed by p states of Sn. The atomic charge of Sn is less than that of Pb. The calculated band gap (3.7 eV) is in good agreement with the experimental value. We had no fitted parameters for calculations of $PbSnF_4$ and SnF_2.

4. Defects in fluorides

Defects in fluoride crystals were calculated in using the LUC model with the parameters of the CNDO scheme calibrated for perfect crystals.

When the Cd^{2+} ion is placed in the cation site of MF_2 ($M \equiv$ Ca, Sr or Ba), the band gap is increased and there is no influence on the UVB. On increasing the atomic number of the metal in the fluoride, the narrow band of Cd is lowered.

We have investigated PdF_2:Cd defects more carefully, because in the PbF_2–CdF_2 system there is essentially an increase in the ionic conductivity as shown experimentally (Murin and Chernov 1982). Table 3 gives the calculation results of the centre PbF_2:Cd.

The defect period in the cyclic model was changed from $2R\sqrt{2}$ ($CdPb_7F_{16}$) to $4R$ ($CdPb_{31}F_{64}$) where R is the inter-atomic distance. The results given in table 3 show that

(i) the widths ΔE_g and ΔE_v change insignificantly and
(ii) the defect local level (Cd d type) is situated above the UVB and is not split by the crystal field.

Shifting symmetrically the nearest anion to the impurity atom anions in PbF_2:Cd the total energy of the quasi-molecule $CdPb_{31}F_{64}$ was minimised. The energy minimum corresponds to the case when anions move to the dopant from their regular positions and are fixed at a distance of 90% of the inter-atomic distance in a pure PbF_2 crystal.

We have investigated three impurity ion concentrations (P_{Cd}): 3, 14 and 33%, which correspond to the LUCs $CdPb_{31}F_{64}$, $Cd_4Pb_{28}F_{64}$ and $Cd_8Pb_{24}F_{64}$. If P_{Cd} increases, the width of the UVB decreases; the d level of Cd splits into a narrow d band; ΔE_g changes very little.

The coordinates of atoms displaced from their regular positions in fluorite-type crystals have been given by Hutchings *et al* (1984), on the bases of neutron scattering experiment. We have simulated this displacement in the quasi-molecule $M_{32}F_{64}$ ($M \equiv Ca$ or Pb) by shifting eight fluorine atoms from the nearest coordination sphere of cations. Thus the concentration of shifting ions was taken to be 12.5%. From the results given in table 3, one can see that the main characteristics of the band structure of these crystals change insignificantly. When fluorine atoms were shifted, the change in Coulomb interaction also was too small, because the shift was only a few per cent.

The F concentration in fluorite in the superionic state was estimated by Catlow and Hayes (1982) and appeared to be about 2%. Even such a high concentration (12.5%) gave no localised levels, which is not what occurs in cationic superionics.

The influence of the atomic irregularity on the band structure of fluorite-type crystals despite some differences in electronic structure is not large.

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