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The electrostatic model of the core level shifts in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$

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Abstract. The electrostatic model was applied to interpret the XPS core level spectra of $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$. The energy positions of the levels are governed by both the Madelung energy and the intraionic Coulomb interaction with the valence charge. Moreover, some aspects of the local structure of the mixed crystals were taken into account. It was shown that the effective charge of Pb is markedly greater than that of Cd ions ($e_{\text{Pb}}^* = 0.70e$, $e_{\text{Cd}}^* = 0.46e$). This is the main reason for the slight increase of the binding energy of all core levels investigated. This also explains the lack of broadening of the XPS spectra of the mixed crystals.

1. Introduction

$\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ is a specific mixed crystal. The blending of two highly ionic compounds with the same crystal structure but with markedly different lattice constants and electronic structures results in a ternary crystal with many interesting properties. These properties have been thoroughly investigated by means of many techniques. Quite often the results turned out to be unusual in the family of ionic crystals. The Raman spectra observed in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ are of 'two-mode' character (characteristic of rather covalent mixed crystals) [1]. The fundamental absorption edge is governed by the atomic-like $\text{Pb}^{2+}6s^2 \rightarrow 6s6p$ transition [2] which is directly connected with the character of the valence band edge dominated by the $\text{Pb}^{2+}6s$ states and the conduction band derived from the $\text{Pb}^{2+}6p$ states [3]. The complex ($\text{F}^-2p-\text{Pb}^{2+}6s$) character of the valence band (confirmed by photoemission measurements [4]) is exceptional in itself.

Apart from ultraviolet photoemission studies of the electronic structure of the valence bands, XPS measurements of core levels in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ were carried out [5,6]. The results are shown in figure 1. The presence of Pb in the alloy leads to a decrease of the binding energy of the F^-1s level by about 1 eV. The cation levels ($\text{Cd}^{2+}3d$, $\text{Pb}^{2+}4f$) are also bound more weakly in PbF_2 than in CdF_2 , but the change is smaller. It has already been shown [7] that the energy position of the valence bands of difluorides can be successfully described by the sum of the atomic binding energy and the Madelung energy of an electron in the crystal. The Madelung term was calculated for a cation sublattice occupied by $+2e$ charges and an anion sublattice built up of $-e$ charges. However, the XPS data mentioned above cannot be explained in this way. The simple Madelung model gives absolute binding energies of the anion level which are too high by about 20 eV, while for the cations the energies are too low by about 20 eV. In figure 1 changes of the binding energies in accordance with

the change of the Madelung energy at the cation and anion sites are shown by broken lines. Instead of the sum of the atomic energy and the Madelung term calculated for the binary crystal, the binding energy measured for $\text{Cd}_{0.929}\text{Pb}_{0.071}\text{F}_2$ is chosen as a reference energy. This enables us to compare easily the core level shifts measured as a function of x with those predicted by the Madelung model. This estimate suggests that the binding energies of cation core levels should decrease by 1.8 eV, while the anion level energies should increase by 1 eV if Pb ions are introduced into the crystal. A comparison with experimental data indicates that even relative changes of the binding energies could possibly be described in this way only for the $\text{F}^- 1s$ level, but this approach is inappropriate for the cation core shells. Thus, some additional factors must be taken into account to interpret properly the changes observed.

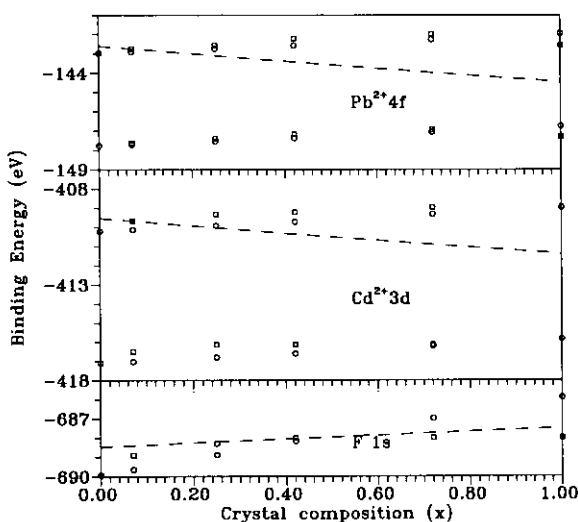


Figure 1. The binding energies of the core levels of $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$. The energy positions of the peaks observed in the XPS experiment are shown as squares (with a determination accuracy of 0.1 eV, while FWHM is about 1.5 eV). The binding energies calculated by means of the electrostatic model are shown as circles. The broken lines show the changes of the binding energies in accordance with the changes of the Madelung potential. The binding energy of the level in $\text{Cd}_{0.929}\text{Pb}_{0.071}\text{F}_2$ is kept as a reference energy.

In this paper the experimental facts are satisfactorily described by a model in which the binding energies of core levels are modified by the electrostatic interaction, with net charges placed in other lattice sites as well as with the changed electronic charge accumulated in the valence shell of the ion. Moreover, the difference between the Pb-F and Cd-F distances, and some aspects of the local structure of the mixed crystals were taken into account.

The observed shifts of the core levels in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ are shown to be a consequence of the marked difference between the effective charges of Pb and Cd ions, which are not equal to the formal charge of the cation in a difluoride ($+2e$). This also accounts well for the lack of broadening of the XPS spectra, which could be expected for mixed crystals.

2. Electrostatic model

The idea of an electrostatic model has been formulated for some time and it turned out to be useful in the interpretation of core level XPS spectra of chemical compounds [8, 9]. Lately, the same idea has been combined with modern methods of electronic charge distribution calculations, in order to predict the energy position of core levels in alloys [10].

The model is based on the assumption that a core electron is influenced, via the Coulomb interaction, by the presence of an additional electric charge in the valence shell (due to chemical bonding) and the rest of the crystal. Thus, the binding energy of the electron in the crystal is the sum of the atomic binding energy (E_{at}^M , E_{at}^F for metal and fluorine) and a correction term. The atomic binding energies have already been measured and published by several authors [9, 11–13]. Since some of the values given in these papers differ by about 1–2 eV, we have consistently used those collected by Ley and Cardona [13]. In order to describe the binding energies of a core electron in the crystal, we propose to use the following formulae:

$$E_{cr}^c = E_{at}^M + e \left(\frac{A_c \bar{e}_c^*}{2a} + \frac{16\bar{e}_c^*}{\sqrt{3}a} - \frac{(3\bar{e}_c^* + e_c^*)}{d_{c-a}} + \alpha \frac{e_c^*}{r_c} \right) \quad (1)$$

for core levels of a cation and

$$E_{cr}^a = E_{at}^F + e \left(\frac{A_a \bar{e}_c^*}{2a} - \frac{16\bar{e}_c^*}{\sqrt{3}a} + \sum_{i=1}^4 \frac{e_{c_i}^*}{d_{c_i-a}} - \alpha \frac{\bar{e}_c^*}{2r_a} \right) \quad (2)$$

for core levels of an anion.

The term added to the atomic binding energy describes the competition between two effects:

(i) the binding energy increases or decreases due to the change in the electrostatic interaction with the rest of the crystal, which is stronger or weaker according to electronic charges accumulated in the surrounding ions;

(ii) the binding energy decreases or increases due to the change in the interelectronic repulsion caused by an excess electronic charge in the valence shell.

The influence of the other ions of the crystal is usually described by the Madelung potential. It depends on the electric charges of the ions, the crystal structure, and the lattice constant. However, this method does not enable us to take into account the local structure occurring in mixed crystals. We know that the anion–cation distances in mixed materials are similar to those observed in the ‘parent’ crystals, and do not follow directly the change of the mean lattice constant measured by x-ray diffraction. These distances in $Cd_{1-x}Pb_xF_2$ have not been determined experimentally yet. However, it has been shown by means of EXAFS studies [14] that for ionic mixed crystals the nearest-neighbour distance can change by approximately 40% of the difference between the distances observed in the ‘parent’ binary crystals. Taking this into account, we can estimate the nearest-neighbour distance in $Cd_{1-x}Pb_xF_2$ from the lattice constants of the binary compounds [7]: $a = 5.388 \text{ \AA}$ ($d_{Cd-F} = 2.333 \text{ \AA}$) for CdF_2 and $a = 5.927 \text{ \AA}$ ($d_{Pb-F} = 2.566 \text{ \AA}$) for PbF_2 . We used the following formulae to extrapolate the cation–anion distances for an arbitrary x .

$$d_{Cd-F}(x) = d_{Cd-F}(CdF_2)(1-x) + x[d_{Cd-F}(CdF_2) + 0.4(d_{Pb-F}(PbF_2) - d_{Cd-F}(CdF_2))]$$

$$d_{Pb-F}(x) = d_{Pb-F}(PbF_2)x + (1-x)[d_{Pb-F}(PbF_2) - 0.4(d_{Pb-F}(PbF_2) - d_{Cd-F}(CdF_2))].$$

In the model proposed in this paper, the electrostatic interaction with nearest neighbours is calculated explicitly, taking into account both the real distances between the ions and their charges. This gives the terms $-(3\bar{e}_c^* + e_c^*)/d_{c-a}$ for a cation surrounded by eight fluorine anions and $+\sum_{i=1}^4 e_{ci}^*/d_{ci-a}$ for an anion surrounded by four cations (e.g. one Cd and three Pb). These terms are added to that describing the Madelung potential of all ions except the nearest neighbours: $A_c \bar{e}_c^*/2a + 16\bar{e}_c^*/\sqrt{3}a$ at the cation site and $A_a \bar{e}_c^*/2a - 16\bar{e}_c^*/\sqrt{3}a$ at the anion site. A_c and A_a are Madelung constants of the fluorite structure [7], a is the lattice constant, d_{ci-a} is the distance between the anion and the i th cation of the nearest neighbour, e_c^* is the effective charge of the cation and \bar{e}_c^* is the mean charge of the cations in the mixed crystal, determined from the linear approximation $\bar{e}_c^* = x e_{Pb}^* + (1-x)e_{Cd}^*$.

The last terms of equations (1) and (2) describe the interaction of the core electron with the charge existing in the valence shell of the ion. The charge is distributed on a spherical shell characterized by the radius r_c or r_a and the factor α . As the effective radii of the valence shells (r_c and r_a) we use the mean radii $\langle r \rangle$ [15] or the radii corresponding to the maxima of the radial wave functions [16] of Pb6s, Cd5s, and F2p shells. α results from the formula describing the Coulomb potential in the charged shell of outer radius r and inner radius nr :

$$\phi = \frac{3}{2}[(1-n^2)/(1-n^3)]q/r. \quad (3)$$

Thus, the α parameters are related to the thickness of the shell. Such an idea was proposed by Shevchik *et al* [17]. The limit values are $\alpha = 1$ for the charge distributed on a thin sphere of radius r and $\alpha = 1.5$ for a charged ball ($n = 0$). It was suggested by Shevchik *et al* that $n = 0.5$ gives the best description of the real charge distribution in the shells. However, it is difficult to determine α from first principles.

The excess electronic charge accumulated in the valence shell of the cation is just e_c^* . For the anion, the charge is determined by the chemical nature of the nearest neighbours. Thus, \bar{e}_c^* is the mean charge of the nearest cations. The number of Cd and Pb ions is determined by the crystal composition.

Discussing phenomena which influence the binding energies measured in XPS experiments, we should also address ourselves to the problem of relaxation effects. Since there is no precise information about their strength in $Cd_{1-x}Pb_xF_2$, we have made several assumptions. The atomic relaxation is assumed to be the same as in the atoms, we treated it as included in the atomic binding energies taken from XPS experiments. The extra-atomic relaxation energy cannot be easily estimated and taken into account, we know that it is typically 1–2 eV in ionic crystals [18]. Thus, some discrepancies between the measured and calculated binding energies can occur because these effects are not directly described by the formulae applied. In particular, this concerns the F⁻ 1s level because its atomic binding energy was measured for the gas phase (F₂) [13]. For Pb and Cd levels, these data were taken in metallic samples [13] and some extra-atomic relaxation energy is already included. Merely the difference between the relaxation energy in the metals and in $Cd_{1-x}Pb_xF_2$ can influence our results. Moreover, we expect that the dependence of the relaxation energies on the crystal composition is weak and does not influence strongly the changes of the binding energies observed.

Sometimes the binding energies measured by means of photoemission methods may be influenced by experimental conditions (e.g. charging of samples of high resistivity). Thus, the first basic step of our analysis (the determination of the model

parameters e_{Pb}^* , e_{Cd}^* and α) is based on the differences of the binding energies measured for different ions in the same sample—these are much less sensitive to external influence. For every crystal composition we can write two equations for $E_{Cr}^{Pb} - E_{Cr}^F$ and $E_{Cr}^{Cd} - E_{Cr}^F$, according to the formula

$$E_{Cr}^c - E_{Cr}^F = E_{at}^M - E_{at}^F + e \left\{ \frac{A_c \bar{e}_c^*}{2a} + \alpha \frac{e_c^*}{r_c} - \frac{A_a \bar{e}_c^*}{2a} + \frac{32\bar{e}_c^*}{\sqrt{3}a} - \frac{(3\bar{e}_c^* + e_c^*)}{d_{c-a}} - \sum_{i=1}^4 \frac{e_{c_i}^*}{d_{c_i-a}} + \alpha \frac{\bar{e}_c^*}{2r_a} \right\}. \quad (4)$$

The third is derived from the observation that the presence of different sets of nearest neighbours in the mixed crystal does not lead to the splitting or broadening of the core level peaks of the anion [5, 6]. This is described by the formula

$$-4 \frac{e_{Pb}^*}{d_{Pb-F}} + \alpha \frac{e_{Pb}^*}{2r_F} + 4 \frac{e_{Cd}^*}{d_{Cd-F}} - \alpha \frac{e_{Cd}^*}{2r_F} = 0. \quad (5)$$

Thus, we are able to determine three variables that cannot be easily calculated from first principles. These are e_{Pb}^* , e_{Cd}^* and α .

3. Effective charges

For each of the mixed $Cd_{1-x}Pb_xF_2$ crystals ($x = 0.071, 0.25, 0.42, 0.72$) we were looking for two sets of e_{Pb}^* , e_{Cd}^* and α . These correspond to the effective radii of the valence shells (r_a , r_c) equal to the mean radii (\bar{r}) of the shells, or to the radii corresponding to the maxima of the radial wave functions r_{max} , respectively. From the possible solutions we chose two which give both reasonable values for α and similar effective charges (see appendix). The results are as follows: $\alpha = 1.56 \pm 0.05$, $e_{Pb}^* = (0.68 \pm 0.02)e$, $e_{Cd}^* = (0.48 \pm 0.03)e$ for $r_i = \langle r_i \rangle$, and $\alpha = 1.08 \pm 0.02$, $e_{Pb}^* = (0.72 \pm 0.04)e$, $e_{Cd}^* = (0.44 \pm 0.03)e$ for $r_i = r_{i,max}$. Their dependence on the crystal composition is shown by the determination accuracy indicated. The α parameter depends strongly on the values of r_c and r_a assumed. However, its obtained value corresponds well to the justified limit values ($1 \leq \alpha \leq 1.5$). Thus, the mean radii of the shells and the radii corresponding to the maxima of the radial wave functions correspond to the limits of the acceptable length of the effective radii of the valence shells. Moreover, since r_c , r_a and α are coupled and their changes compensate each other, the effective charges are almost independent of them.

The effective charges obtained can be compared with data already known for similar as well as other materials. They correspond well to the trend determined by Shevchik *et al* [17] for less ionic (more covalent) materials. It was shown that the net transfer of electronic charge from the metallic cation to the anion occurs and the charge transferred is about $0.2e$ for III-V and $0.35e$ for II-VI crystals. The data were also extracted from XPS spectra.

For some highly ionic crystals, Falter *et al* [19] estimated values for the longitudinal effective charge (Z^L) introduced by Callen [20] into the theory of lattice vibrations. They were obtained on the basis of the results of the phonon spectrum investigation but could also be calculated from the charge density distribution [19]. Then, Falter

et al [21] showed that Z^L can be successfully compared with the charge transfer value obtained from the core level shifts using the electrostatic model of Shevchik *et al* [17]. Thus, we can also compare values for the effective charges determined for $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ with the longitudinal effective charges estimated for some other highly ionic compounds (e.g. for the oxides CdO ($Z^L = 0.539$), MgO (0.677) and CaO (0.826) or for the fluorides LiF (0.549) and NaF (0.594) [19, 21]). The qualitative correspondence seems to be fairly satisfactory.

4. Core level shifts

Using the values for charge transfer and α obtained on the basis of the relative positions of the XPS peaks (in a further analysis we will use the mean values $e_{\text{Pb}}^* = 0.70 \pm 0.06$ and $e_{\text{Cd}}^* = 0.46 \pm 0.06$), we can calculate the bare core level shifts in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$. Then, we can compare them directly with the energies measured. This enables us to show the relevance of the model to a description of the core levels, and to check some of our assumptions. The binding energies calculated for the $\text{F}^- 1s$, $\text{Cd}^{2+} 3d$ and, $\text{Pb}^{2+} 4f$ levels are shown together with the XPS peak positions in figure 1.

The calculated binding energies correspond well to those observed in experiment. No systematic difference is revealed, which could be caused by an external perturbation of the energy of the emitted electrons. Some discrepancies occur for the deeper states only (in particular, for $\text{F}^- 1s$). This can be possibly explained by some dependence of the ion charges on the crystal composition. This effect is not taken into account in the model presented. However, one can also argue that a more precise consideration of the relaxation effects and screening of the core levels by the outer shells of the ion could help us to describe the $\text{F}^- 1s$ level better.

The most striking feature, i.e. the increase of the binding energies of both anion and cation levels with an increase of x is still clearly reproduced by our model.

Thus, we can argue that the electrostatic model describes the observed shifts of core levels in $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ properly under the following conditions.

(i) The net effective charges of the ions interacting with the core electrons are markedly lower than the formal charge of the ions ($+Ze$ for cations and $-e$ for anions).

(ii) The charge accumulated on the Pb ion is greater than that on the Cd ion ($e_{\text{Pb}}^* = 0.70e$, $e_{\text{Cd}}^* = 0.46e$).

(iii) The cation-anion distances change in the mixed crystals (by up to 40%) but still $d_{\text{Cd-F}} < d_{\text{Pb-F}}$.

(iv) The effective radii of the valence shells of atoms are assumed to be longer than the radii corresponding to the maxima of the wave function and shorter than the mean radii of the shell.

The observed behaviour of the core levels is identified as a result of the marked difference between the charges accumulated on Cd and Pb. This inverts the direction of the change in the Madelung energy as a function of Pb content. Since the energy of interaction with the valence charge in the cation (Pb or Cd) is independent of the crystal composition, the change in the Madelung energy manifests itself directly in the energy shift of the cation core levels. The weak correction is added due to a change of the cation-anion distances in the mixed crystals.

For anions the Madelung energy changes are inverted also. However, this is overcompensated by the intraionic Coulomb interaction, modified according to the change of the mean effective charge of the cations in the mixed crystal.

The difference between the charges of Pb and Cd ions is also responsible for the lack of broadening of the XPS maxima. In mixed crystals the anions can be surrounded by neighbours of different chemical nature and placed at different distances from the anion. Thus, we could expect a splitting (or broadening) of the maxima into sets of peaks corresponding to levels influenced by different neighbours. However, in $Cd_{1-x}Pb_xF_2$ the decrease of the Coulomb potential caused by the longer $Pb^{2+}-F^-$ distance is compensated by its increase due to the greater charge of the Pb^{2+} ions.

Thus, the most important characteristics of the XPS spectra of core levels of $Cd_{1-x}Pb_xF_2$ are successfully described by the model applied, in spite of its simple physical assumptions.

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Appendix

The set of three non-linear equations we are dealing with was solved numerically. We concentrated upon the range of α values slightly wider than that corresponding to the physical meaning of this parameter ($1 \leq \alpha \leq 1.5$). The possible, approximate solutions were as follows: for $r_i = \langle r_i \rangle$, $\alpha \simeq 1.6$, $e_{Pb}^* \simeq 0.7e$, $e_{Cd}^* \simeq 0.5e$; $\alpha \simeq 1.2$, $e_{Pb}^* \simeq 1.1e$, $e_{Cd}^* \simeq 1.0e$; and for $r_i = r_{i,max}$, $\alpha \simeq 1.1$, $e_{Pb}^* \simeq 0.7e$, $e_{Cd}^* \simeq 0.4e$; $\alpha \simeq 0.8$, $e_{Pb}^* \simeq 0.9e$, $e_{Cd}^* \simeq 0.8e$. However, only the first and third possibilities seem to be satisfactory. They give consistent values for the effective charge and, simultaneously, the α values are close enough to those we expected, taking into account the physical assumptions of our model. Moreover, the values for α , e_{Pb}^* and e_{Cd}^* obtained are independent of the crystal compositions (taking into account the determination accuracy of the experimental peak positions) which is not the case for $\alpha \simeq 1.2$ and $\alpha \simeq 0.8$. In particular, for some values of x no solution can be found for $\alpha \simeq 0.8$. These arguments enabled us to choose the numbers listed in the text for further analysis.

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