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Wavefunction character of the F-center in table salt

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Abstract

The wave character of an F-type color center in sodium chloride has been investigated using *ab initio* band structure calculations in the super-cell approach. Although the F-center, consisting of a zero-charge nucleus and an electron, can be regarded as the most delocalized 'atom', calculations show a localized character of its 1s state. The influence of the F-center extends over 12 Å. The wave character of the defect band originates mainly from the chlorine 4s states rather than the sodium 3s states, in line with the available experimental results.

1. Introduction

Sodium chloride is the archetype of an ionic compound. It is an insulator with a wide energy gap of about 8.5 eV. The valence bands are dominated by chlorine 3s and 3p states. The bottom of the conduction band of sodium chloride is generally believed to originate from sodium 3s states [1–3].

Recent work showed that in sodium chloride not only the valence bands, but also the conduction bands, are primarily derived from chlorine states. Specifically, the lower parts of the conduction bands are dominated by chlorine 4s states while the sodium 3s states play a role at higher energies only [4, 5]. Indications for the role of the anion in the conduction band in sodium chloride go back to an analysis by Slater and Shockley [6].

A phenomenon in wide-gap insulators is the existence of color centers. They have been intensively investigated and are even considered for applications, e.g. a sodium chloride color center laser (CCL) [7]. The simplest form of color centers is F-centers: electrons trapped at vacant anion sites [1–3, 8, 9]. They are produced chemically or physically, for example by heating a sodium chloride crystal in sodium vapor, electron or γ -irradiation [1, 2, 8, 9], or laser pulses [10]. Many experimental [8–13] and theoretical [14–16] efforts have been made to understand the F-centers in insulators. The description of the wavefunction character of the F-centers is generally given as finite extensions of the alkaline ion wavefunctions neighboring the center, while the other ions are treated as point charges [1, 8, 9, 14]. In view of the dominance of the anions in the proper description of the conduction bands of alkali halides found recently, it is timely to re-investigate the wave character

of the F-center in sodium chloride. The conclusions will help to understand the origin of the conduction bands [4, 5] as well as the color centers in insulators [2, 13–18].

2. Details of calculations

The electronic structure of the F-center was calculated in the super-cell approach. In order to avoid interactions between defects, a unit cell of $7 \times 7 \times 7$ times the conventional unit cell containing 2744 atoms was employed. The F-center is introduced by replacing one chlorine atom by an 'atom' without nuclear charge. No structural relaxations were considered, since experiments and theoretical analysis showed that lattice distortions are small [8, 9]. *Ab initio* band structure calculations were performed with the localized spherical wave (LSW) method [19], using the scalar-relativistic Hamiltonian. We used the local-density exchange–correlation potential [20] inside space-filling and therefore overlapping spheres around the atomic constituents. The self-consistent calculations were carried out including all core electrons. Iterations were performed with k -points distributed uniformly in the irreducible part of the Brillouin zone, corresponding to a volume of the BZ per k -point of about $3 \times 10^{-7} \text{ \AA}^{-3}$. Self-consistency was assumed when the changes in the local partial charges in the atomic sphere decreased to less than 1×10^{-5} .

In the construction of the LSW basis [19, 21], the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomic-like symbols 3s, 3p for sodium and 4s, 3p for chlorine. The internal l summation used to augment a Hankel function at surrounding atoms was

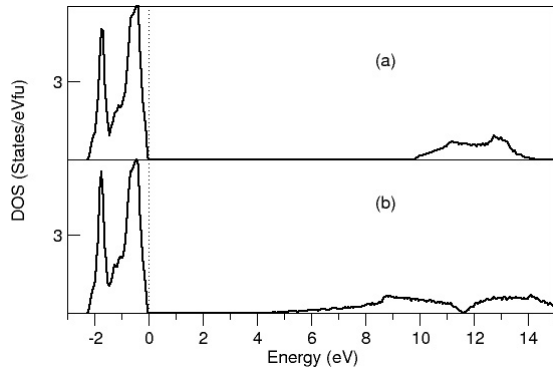


Figure 1. Total DOS for sodium chloride calculated using the LSW method: without chlorine 4s orbitals (a) and with chlorine 4s orbitals (b).

extended to $l = 2$, resulting in the use of 3d orbitals for both sodium and chlorine. The F-center is treated as if it were an atom. This means that a local Schrodinger equation is solved with 1s and 2p as Hankel and Bessel functions, and 3d as an extension for the expansion of wavefunction tails of adjacent ions. The Wigner–Seitz radii used are 2.01 Å for chlorine and the color center and 1.37 Å for sodium, close to the ionic values [22].

3. Results of the calculations

3.1. Electronic structure of bulk sodium chloride

Sodium chloride has a face-centered cubic structure with space group $Fm\bar{3}m$ (no. 225). The removal of a chlorine atom reduces the symmetry of the super-cell to $Pm\bar{3}m$ (no. 221). Though the electronic structure of sodium chloride, including the effects of chlorine 4s orbitals, has been reported [4, 5], we show the density of states in figure 1 for comparison.

The calculated electronic structure of sodium chloride without chlorine 4s orbital has a large energy gap of about 9.8 eV as shown in the density of states plot (DOS) in figure 1(a). Remarkably, this band gap is larger than the experimental value (8.5 eV) [5, 23]. The valence bands are mainly composed of chlorine 3p states and the conduction band is of sodium 3s character. The energy gap is indirect, with the top of the valence band at Γ while the bottom of the conduction band is at the X point, in disagreement with optical measurements [5, 23]. The direct energy gap at Γ is about 12.5 eV, which is significantly larger than the experimental value. DFT calculations generally *underestimate* band gaps of semiconductors or insulators [24].

Figure 1(b) shows the DOS of sodium chloride calculated with chlorine 4s states. The shape of the valence bands is very close to those without chlorine 4s states. However, the conduction band differs strongly from those exempt from chlorine 4s states. Strong mixing occurs between chlorine 4s and sodium 3s states. The chlorine 4s states dominate the lower part of the conduction band, ranging from 4.5 to about 11.5 eV above the Fermi level (which is arbitrarily set to be the top of the valence band). The sodium 3s character is noticeable

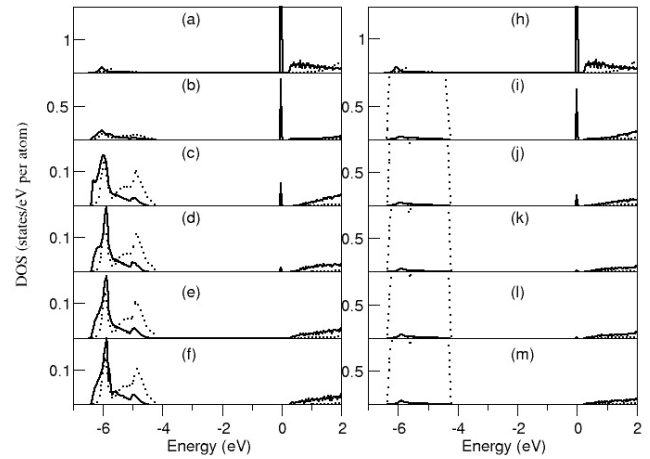


Figure 2. Partial DOS for sodium and chlorine atoms and the F-center in the sodium chloride super-cell. The s-like (Va 1s, Na 3s and Cl 4s) states are represented the solid lines and the p-like (Va 2p, Na 3p and Cl 3p) states by dotted lines. (a) and (h) are the same for the F-center, (b)–(f) for sodium ions with distance from the F-center $a_o/2$ (b), $\sqrt{3}a_o/2$ (c), $3a_o/2$ (d), $3\sqrt{3}a_o/2$ (e) and bulk-like (f); (i)–(m) for chlorine ions with distance from the F-center $a_o\sqrt{2}/2$ (i), a_o (j), $\sqrt{3}a_o$ (k), $2a_o$ (l) and bulk-like (m).

from about 8.5 eV upwards and dominates the upper part of the conduction band (from about 11.5 eV up). The energy gap is about 4.5 eV, which is smaller than the experimental value (8.5 eV) [5, 23]. The calculated energy gap with chlorine 4s states at the bottom of the conduction band is direct at the Γ point of the Brillouin zone, in agreement with experiment. The size of the calculated band gap follows the general trend of band gaps in the LDA [24].

3.2. The F-center

Figure 2 shows the local DOS for the F-center and several neighboring ions. The total DOS of the super-cell is almost identical to that of the primitive cell, except for the 1s level of the color center forming a narrow peak about 0.34 eV below the bottom of the conduction band. The Fermi level is in the middle of the narrow band. The 2p level of the F-center is located about 1.5 eV above the Fermi level, as shown in figure 2 (dotted line).

Comparing figures 1 and 2 it is clear that the DOSs of the neighboring sodium and chlorine ions are basically the same as those of the bulk. There are also some differences. The states of the color center also reside to some extent on neighboring ions. It is interesting to note that the contributions from the neighboring sodium and chlorine ions are comparable in spite of the fact that the sodium is closer to the defect site than the chlorine. The figure also shows the partial DOS of the atoms more distant from the color center.

The calculations show there are about 0.64 electrons in the sphere of the F-center with a radius the same as that of the chlorine sphere. This number is just about 0.13 electrons less than the charge (0.77 electrons) in the sphere of chlorine in the unperturbed crystal. Each of the adjacent Na ions ($a_o/2$ from the defect, a_o is the lattice parameter of the conventional

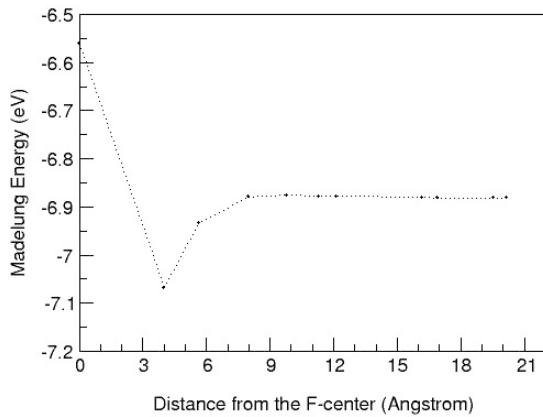


Figure 3. Dependences of Madelung energy (E_m , in eV) of chlorine atoms on the distance from the F-center.

cell) loses about 0.78 electrons, slightly more than those in the perfect case (about 0.77 electrons).

Figure 3 shows the Madelung energy at various sites as a function of the distance from the F-center. There is a potential valley around the F-center. The sodium ions adjacent to the F-center have a Madelung potential about 0.26 eV lower than those in the bulk. One adjacent chlorine ion (which is $\sqrt{2}a_o/2$ away from the F-center) has a Madelung energy about 0.19 eV lower than that in the bulk as well. The Madelung energy of the sodium ion about $\sqrt{3}a_o/2$ away from the F-center is about 0.06 eV lower than that of bulk sodium ions as well. The Madelung energy becomes more or less constant beyond about 12 Å (≤ 0.01 eV). So, the specific band originating from the F-center can still be recognized in the partial DOS of atoms at $2a_o$ (a_o is the lattice parameter of the conventional cell) or over 12 Å, as shown in figure 2.

3.3. Discussion and comparison with available experimental data

Based on electron spin resonance (ESR) measurements, Hutchison discovered in the late 1940s resonance effects in crystals of alkaline halides after neutron irradiation and related them to F-centers [25]. Feher reported detailed measurements of the ESR spectra of a potassium chloride single crystal bombarded by electrons [26]. He used the electron spin double-resonance technique to resolve the hyperfine structure of the spectra. This technique can provide information about the F-center. The magnetic field was parallel to [100], in which direction the nearest neighbor is a potassium atom at a distance of half the lattice parameter. The next-nearest neighbor of the F-center in this direction is a chlorine atom at a distance of the lattice parameter. The measured spectra showed contributions from adjacent chlorine atoms, as well as from potassium. So the wavefunction of the color center has chlorine character in spite of the fact that the distance between the F-center and the adjacent chlorine along the [100] direction is twice that between the F-center and the adjacent potassium atom. Systematic study on alkaline halides by Holton and Blum confirmed these conclusions [27].

Table 1. Experimental band gaps (E_g) [5, 23] and excitation energies (E_{cc}) [9] of F-centers and their differences (Diff) for various alkali chlorides.

Chloride	E_g (eV)	E_{cc} (eV)	Diff (eV)
LiCl	9.4	3.22	6.2
NaCl	8.5	2.67	5.8
KCl	8.4	2.21	6.2
RbCl	8.2	1.98	6.2
CsCl	8.3	2.06	6.2

The optical transition of the F-centers in alkaline metal halides occurs between the 1s state and the 2p states according to the dipole selection rule. The energy gap between the occupied 1s states and the unoccupied 2p states of the F-centers in NaCl is calculated to be about 1.5 eV, which is lower than the experimental value (about 2.7 eV from the maximum absorption) [9, 27]. The energy gaps of insulators/semiconductors are in general underestimated by the DFT-LDA method [24].

Let us consider the trend in both band gaps and excitation energies of F-centers for the alkali chloride series (table 1). The first observation considering the band gaps of the series is their invariance. This directly reflects the fact that the band gap is in first approximation a property of the chlorine exclusively. The slight cation dependence is strongest in the reduction in band gap going from lithium to sodium, after which the band gaps are constant and slightly increases at the end of the series. Three effects are of importance here. First of all, there is the influence of the cation through its influence of the lattice constant. This affects the band gaps in two ways. First, there is the influence through the band widths. This leads to a gradual decrease of the band gap through an increase of band widths from lithium to cesium. A competing effect is the increase of the band gap through the increase of the energy separation between chlorine 3p states (forming the top of the valence band) and the chlorine 4s states (forming the bottom of the conduction band). This is because the radial wavefunctions of the 4s states having three nodes are much more delocalized and are consequently much more sensitive to repulsion by neighboring chlorine states as compared with the 3p states with just one radial node. The effect is particularly important in the case of lithium chloride, where the chlorine–chlorine inter-ionic distance is slightly *smaller* than twice the ionic radius of the chlorine ion. This explains the (slight) composition dependence of the band gaps of the alkali chlorides (and alkali halides in general). A complication is the fact that cesium chloride crystallizes in a different crystal structure, named after it.

The F-center behaves identically. Here the 1s valence-band and 2p conduction-band states play an identical role to the 3p and 4s states of the chlorine it replaces. This is summarized in the table. The dependences of the band gap and color center absorption on the cation are *identical*, reflecting the dominant role of the anions in both cases. Sodium shows a deviation, possibly due to the *a*-symmetrical shape of the peak of the color center [9, 27].

4. Conclusions

First-principles band structure calculations were performed for an F-center in a large unit cell. The calculations showed that there are about 0.64 electrons in the sphere of the F-center, close to that of a Cl atom. This indicates that the ionic model is a good first-order approximation. The F-center has a localized character of the 1s state; it is located about 0.34 eV below the bottom of the conduction band. The gap between the localized 1s and rather delocalized 2p states is calculated to be about 1.5 eV. Considering alkali chlorides ACl (A = Li to Cs), the dependences on cation of both the band gap and the color center absorption are identical, consistent with the dominant role of the anions (Cl 4s) in both cases. The calculations also showed that the electrostatic influence of an F-center in an insulator has a considerable range (12 Å).

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