Exercise on symmetry

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1 Introduction

Sodium chloride (NaCl) crystallizes in the well-known *rock salt* (halite) structure, which is a face-centered cubic lattice with a two-atom basis (Na^+ and Cl^-). This crystal belongs to the $Fm\bar{3}m$ space group (No. 225)[1], indicating a highly symmetric structure (octahedral symmetry). Each Na is octahedrally coordinated by Cl and vice versa, resulting in a highly regular structure. Such symmetry has important consequences for the material's physical properties.

NaCl is an ionic solid with predominantly ionic bonding. In this compound, Na donates its $3s$ valence electron to Cl, resulting in closed-shell ions (Na^+ and Cl^-)[2]. As a result, the valence electron states (derived largely from Cl $3p$ orbitals) are fully occupied, and the conduction states (derived from Na $3s$ orbitals) are empty. This leads to a wide energy band gap on the order of 8.5[3]. Thanks to this large band gap, NaCl is a good electrical insulator and is transparent to visible light. In summary, NaCl's crystal structure and bonding give it a highly symmetric lattice and the electronic characteristics of a wide-band-gap insulating material.

2 Methodology

The high symmetry of NaCl was taken into account at the band structure analysis. NaCl's space group $Fm\bar{3}m$ implies a cubic Bravais lattice (fcc) with a high-symmetry Brillouin zone (BZ). To efficiently explore the electronic structure, we focused on the *irreducible section* of the Brillouin zone, using symmetry to reduce redundant k-points. The Brillouin zone for the fcc lattice (rock-salt structure) is a truncated octahedron, and it contains several high-symmetry points of interest as it is shown in Figure 1.

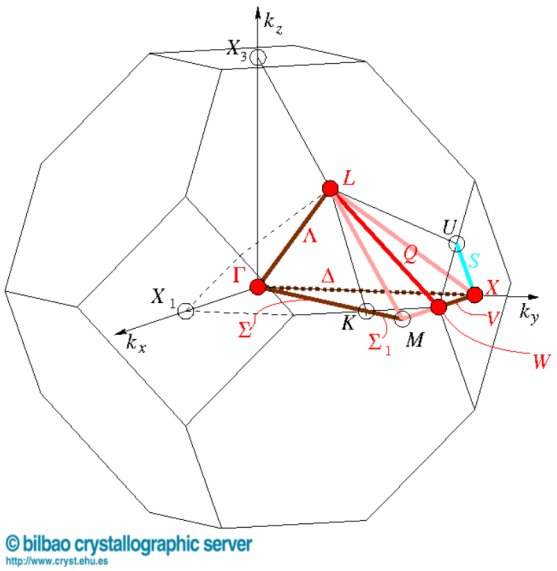

Figure 1: Brillouin zone of the NaCl

Using the k-vector database of the Bilbao Crystallographic Server[1] we identified the key

high-symmetry k-points and paths for NaCl. The electronic band structure was computed along the following high-symmetry path in the Brillouin zone:

$$\Gamma \to L \to X \to K \to \Gamma.$$

These points and directions correspond to high-symmetry lines where band extrema and degeneracies are often found. It is important to note that the segment $\Gamma \to X$ is particularly significant as it represents the bonding direction between the ions, capturing the essential interactions between the cations and anions. Ten points of k were used in the sampling, since it was observed that with fewer points the results did not converge adequately.

The electronic band structure was computed using the Python-based program `simpleTB`. This tool implements a tight-binding model to calculate the electronic bands of crystalline materials. It reads an input file in FDF format, where key parameters such as the unit cell, supercell, lattice vectors, and orbital definitions (s, p_x, p_y, and p_z) are specified, along with the interaction parameters. Based on this information, `simpleTB` constructs the Hamiltonian of the system and performs diagonalization along high-symmetry paths in the Brillouin zone. This approach not only simplifies the calculation by exploiting crystal symmetry but also provides clear insights into the origin and dispersion of the bands.

3 Results and Discussion

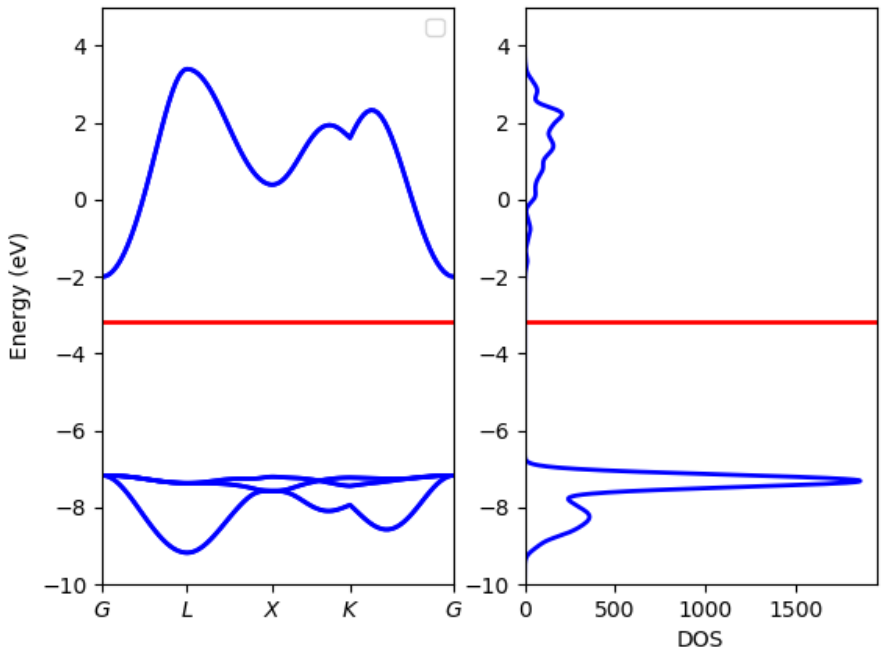

Figure 2: Band diagram and density of states (DOS) of the NaCl

Band Structure and Orbital Character

The calculated band structure of NaCl is shown in Figure 2. The Fermi level is represented by a red horizontal line. The bands below the Fermi level correspond to the valence bands, which are relatively flat, indicating low dispersion. In contrast, the band above the Fermi level corresponds to the conduction band, which exhibits greater dispersion. By examining the orbital-projected band structure, these bands can be attributed to specific atomic orbitals:

- **Valence Bands (Cl $3p$ orbitals):** The top of the valence band primarily arises from the chlorine $3p$ orbitals (p_x, p_y, p_z). Owing to the highly symmetric (octahedral) environment around each Cl, these p orbitals are nearly degenerate in energy at the Γ point. Because the overlap between $3p$ orbitals on neighboring Cl ions is relatively small, the valence bands exhibit a narrow bandwidth, appearing fairly flat near the valence-band maximum. Any slight dispersion that does occur is due to limited hopping of electrons between adjacent Cl $3p$ orbitals.

- **Conduction Band (Na $3s$ orbital):** The lowest conduction band derives mainly from the Na $3s$ orbital, which is more spatially extended than the Cl $3p$ orbitals. This increased extension leads to a stronger overlap with neighboring orbitals, resulting in a more dispersive (wider) conduction band. Because NaCl is highly ionic, this $3s$ band is empty in the ground state. The conduction-band minimum occurs at k-point Γ.

These results align with the chemical intuition for NaCl. The chlorine $3p$-derived valence bands, being fully occupied and less dispersive, are lower in energy and relatively flat because the electrons are tightly bound to the more electronegative Cl^- ions. The sodium $3s$-derived conduction band is higher in energy and shows greater dispersion, reflecting the more delocalized nature of an empty cation state.

Band Types and Dispersion Origins

In the context of solid-state band terminology, the Cl $3p$ valence bands in NaCl can be considered the *valence band* complex, while the Na $3s$ band is the bottom of the *conduction band*. The valence band in NaCl is relatively flat (especially near its top at Γ) because of the limited overlap of p orbitals – this indicates a large effective mass for holes and localized electronic states. In contrast, the conduction band exhibits more curvature in the E-k diagram, signifying more dispersive states (lighter effective mass for electrons). The origin of this dispersion difference lies in the symmetry and bonding: the p-orbitals on Cl point toward neighboring Na^+, but since those neighbors have no valence electrons (Na^+ has an empty $3s$), the p–p overlap between adjacent Cl ions is minimal. On the other hand, the empty $3s$ orbitals on Na can overlap (through the medium of the Cl ions) in a way that spreads out the conduction band in energy.

Conducting vs. Insulating Behavior

From the band structure interpretation, it is evident that NaCl is a classic band insulator. All bands up to the valence band maximum are occupied and there is a large energy separation

to the next available band. There are no partially filled bands crossing the Fermi level. In a conductor (metal), we would expect to see a band crossing the Fermi energy or a very small gap allowing electrons to be thermally excited into the conduction band. NaCl, by contrast, shows a completely filled valence band and an empty conduction band separated by a wide gap, which means there are no carriers available for electrical conduction at ordinary temperatures. This explains why solid NaCl does not conduct electricity in its pure crystalline form. Only by adding energy (for example, via a high-energy photon to excite an electron across the gap, or via thermal activation at extremely high temperatures) could NaCl generate free carriers, and even then, the required energy (8.5) is so large that NaCl remains insulating under virtually all practical conditions. In summary, the band structure analysis, grounded in the crystal's symmetry and orbital composition, clearly indicates that NaCl is an insulator.

4 Conclusions

In this report, we examined the crystal symmetry and electronic band structure of NaCl (rock-salt structure) and discussed how symmetry influences its electronic properties. NaCl's $Fm\bar{3}m$ symmetry gives rise to a highly symmetric Brillouin zone, which allowed us to focus on high-symmetry k-points when computing the band structure. By using the Bilbao Crystallographic Server for Brillouin zone.

The results show that NaCl's valence band is derived from the chlorine $3p$ orbitals and is fully occupied, while the conduction band is derived from the sodium $3s$ orbital and is completely empty. The large difference in energy between these bands (a wide band gap) confirms that NaCl is an electrical insulator.

References

[1] Aroyo, M. I., Pérez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A., & Wondratschek, H. (2006). *Bilbao Crystallographic Server: I. Databases and crystallographic computing programs*. Zeitschrift für Kristallographie - Crystalline Materials, **221**(1), 15–27.

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