

2. SYMMETRY ASPECTS OF EXCITATIONS

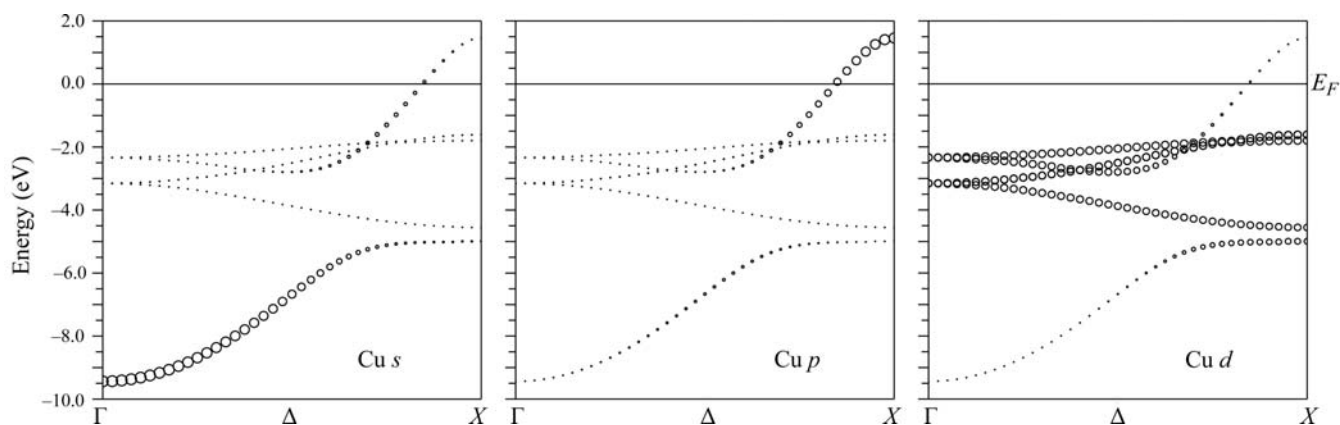


Fig. 2.2.16.1. Character of energy bands of f.c.c. copper in the Δ direction. The radius of each circle is proportional to the respective partial charge of the given state.

and thus is not occupied, leading to a smaller p_z charge of 0.91 e, in contrast to the fully occupied nonbonding states with occupation numbers around 1.2 e. (Note that only a fraction of the charge stemming from the oxygen 2p orbitals is found inside the relatively small oxygen sphere.) This anisotropy causes a finite asymmetry count [(2.2.15.18)] that leads – according to (2.2.15.19) – to a corresponding EFG.

In this simple case, the anisotropy in the charge distribution, given here by the different p occupation numbers, is directly proportional to the EFG, which is given with respect to the crystal axes and is thus labelled V_{aa} , V_{bb} and V_{cc} (Table 2.2.15.1). The principal component of the EFG is in the direction where the p occupation number is smallest, *i.e.* where the density has its highest anisotropy. The other oxygen atoms behave very similarly: O2, O3 and O4 have a near neighbour in the a , b and c direction, respectively, but not in the other two directions. Consequently, the occupation number is lower in the direction in which the bond is formed, whereas it is normal (around 1.2 e) in the other two directions. The principal axis falls in the direction of the low occupation. The higher the anisotropy, the larger the EFG (compare O1 with the other three oxygen sites). Excellent agreement with experiment is found (Schwarz *et al.*, 1990). In a more complicated situation, where p and d contributions to the EFG occur [see (2.2.15.17)], which often have opposite sign, the interpretation can be more difficult [see *e.g.* the copper sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$; Schwarz *et al.* (1990)].

The importance of semi-core states has been illustrated for rutile, where the proper treatment of 3p and 4p states is essential to finding good agreement with experiment (Blaha *et al.*, 1992). The orthogonality between ℓ -like bands belonging to different principal quantum numbers (3p and 4p) is important and can be treated, for example, by means of local orbitals [see (2.2.12.4)].

In many simple cases, the off-diagonal elements of the EFG tensor vanish due to symmetry, but if they don't, diagonalization of the EFG tensor is required, which defines the orientation of the principal axis of the tensor. Note that in this case the orientation is given with respect to the local coordinate axes (see Section 2.2.13) in which the LM components are defined.

2.2.16. Examples

The general concepts described above are used in many band-structure applications and thus can be found in the corresponding literature. Here only a few examples are given in order to illustrate certain aspects.

2.2.16.1. F.c.c. copper

For the simple case of an element, namely copper in the f.c.c. structure, the band structure is shown in Fig. 2.2.16.1 along the Δ

symmetry direction from Γ to X . The character of the bands can be illustrated by showing for each band state the crucial information that is contained in the wavefunctions. In the LAPW method (Section 2.2.12), the wavefunction is expanded in atomic like functions inside the atomic spheres (partial waves), and thus a spatial decomposition of the associated charge and its portion of ℓ -like charge (s -, p -, d -like) inside the Cu sphere, $q_\ell^{Cu}(E_{\mathbf{k}}^i)$, provides such a quantity. Fig. 2.2.16.1 shows for each state $E_{\mathbf{k}}^i$ a circle the radius of which is proportional to the ℓ -like charge of that state. The band originating from the Cu 4s and 4p orbitals shows an approximately free-electron behaviour and thus a k^2 energy dependence, but it hybridizes with one of the d bands in the middle of the Δ direction and thus the ℓ -like character changes along the Δ direction.

This can easily be understood from a group-theoretical point of view. Since the d states in an octahedral environment split into the e_g and t_{2g} manifold, the d bands can be further partitioned into the two subsets as illustrated in Fig. 2.2.16.2. The s band ranges from about -9.5 eV below E_F to about 2 eV above. In the Δ direction, the s band has Δ_1 symmetry, the same as one of the d bands from the e_g manifold, which consists of Δ_1 and Δ_2 . As a consequence of the 'non-crossing rule', the two states, both with Δ_1 symmetry, must split due to the quantum-mechanical interaction between states with the same symmetry. This leads to the avoided crossing seen in the middle of the Δ direction (Fig. 2.2.16.1). Therefore the lowest band starts out as an 's band' but ends near X as a 'd band'. This also shows that bands belonging to different irreducible representations (small representations) may cross. The fact that Γ_{12} splits into the subgroups Δ_1 and Δ_2 is an example of the compatibility relations. In addition, group-theoretical arguments can be used (Altmann, 1994) to show that in certain symmetry directions the bands must enter the face of the BZ with zero slope.

Note that in a site-centred description of the wavefunctions a similar ℓ -like decomposition of the charge can be defined as $1 = \sum_t \sum_\ell q_\ell^t$ (without the q^{out} term), but here the partial charges have a different meaning than in the spatial decomposition. In one case (*e.g.* LAPW), q_ℓ^t refers to the partial charge of ℓ -like character inside sphere t , while in the other case (LCAO), it means ℓ -like charge coming from orbitals centred at site t . For the main components (for example Cu d) these two procedures will give roughly similar results, but the small components have quite a different interpretation. For this purpose consider an orbital that is centred on the neighbouring site j , but whose tail enters the atomic sphere i . In the spatial representation this tail coming from the j site must be represented by the (s , p , d etc.) partial waves inside sphere i and consequently will be associated with site i , leading to a small partial charge component. This situation is sometimes called the off-site component, in contrast to the on-site component, which

2.2. ELECTRONS

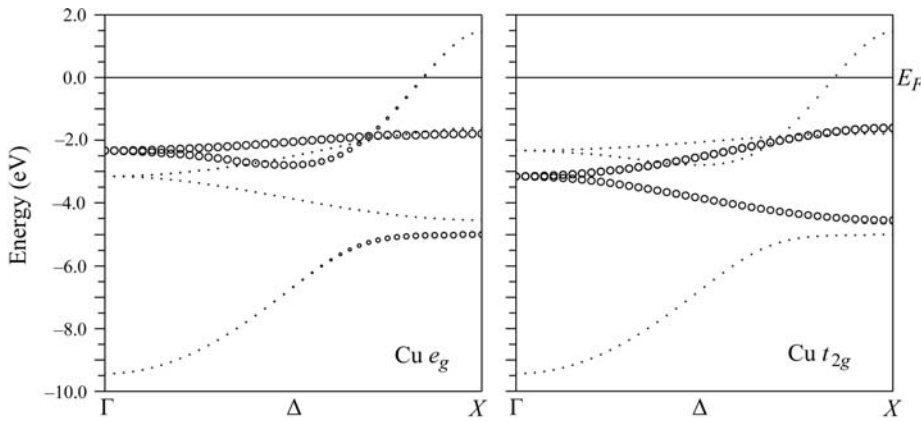


Fig. 2.2.16.2. Decomposition of the Cu d bands into the e_g and t_{2g} manifold. The radius of each circle is proportional to the corresponding partial charge.

will appear at its own site or in its own sphere, depending on the representation, site-centred or spatially confined.

2.2.16.2. The rutile TiO_2

The well known rutile structure (e.g. TiO_2) is tetragonal (see Fig. 2.2.16.3) with the basis consisting of the metal atoms at the $2a$ Wyckoff positions, $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and anions at the $4f$ position, located at $(\pm u, \pm u, 0)$ and $(\frac{1}{2} \pm u, \frac{1}{2} \mp u, \frac{1}{2})$ with a typical value of about 0.3 for the internal coordinate u . Rutile belongs to the non-symmorphic space group $P4_2/mmm$ (D_{4h}^{14}) in which the metal positions are transformed into each other by a rotation by 90° around the crystal c axis followed by a non-primitive translation of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The two metal positions at the centre and at the corner of the unit cell are equivalent when the surrounding octahedra are properly rotated. The metal atoms are octahedrally coordinated by anions which, however, do not form an ideal octahedron. The distortion depends on the structure parameters a , c/a and u , and results in two different metal–anion distances, namely the apical distance d_a and the equatorial distance d_e , the height (z axis) and the basal spacing of the octahedron. For a certain value u^* the two distances d_a and d_e become equal:

$$u = u^* = \frac{1}{4} [1 + \frac{1}{2}(c/a)^2]. \quad (2.2.16.1)$$

For this special value u^* and an ideal c/a ratio, the basal plane of the octahedron is quadratic and the two distances are equal. An ideal octahedral coordination is thus obtained with

$$d_a = d_e, \quad c = \sqrt{2}(1 - 2u)a \quad (2.2.16.2)$$

$$u_{\text{ideal}} = \frac{1}{2}(2 - \sqrt{2}) = 0.293 \quad (2.2.16.3)$$

$$(c/a)_{\text{ideal}} = 2 - \sqrt{2} = 0.586. \quad (2.2.16.4)$$

Although the actual coordination of the metal atoms deviates from the ideal octahedron (as in all other systems that crystallize in the rutile structure), we still use this concept for symmetry arguments and call it *octahedral coordination*.

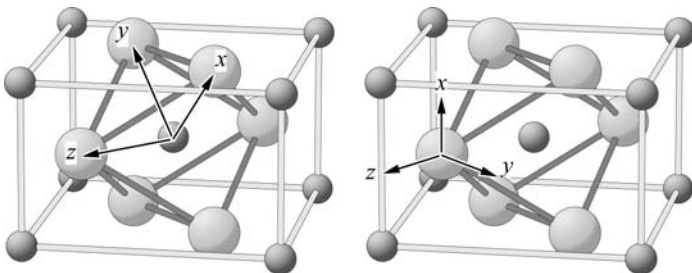


Fig. 2.2.16.3. The local coordinate system in rutile for titanium (small spheres) and oxygen (large spheres).

The concept of a local coordinate system is illustrated for rutile (TiO_2) from two different aspects, namely the crystal harmonics expansion (see Section 2.2.13) and the interpretation of chemical bonding (for further details see Sorantin & Schwarz, 1992).

(i) The expansion in crystal harmonics.

We know that titanium occupies the Wyckoff position $2a$ with point group mmm . From Table 2.2.13.1 we see that for point group mmm (listed under the orthorhombic structure) we must choose the x axis parallel to $[\bar{1}10]$, the y axis parallel to $[110]$ and the z axis parallel to $[001]$. We can transform the global coordinate system (i.e. that of the unit cell) into the local coordinate system around Ti. The following first LM combinations

appear in the series (2.2.12.5): $(LM) = (0, 0), (2, 0), (2, 2), (4, 0), (4, 2), (4, 4), \dots$, etc.

(ii) *The interpretation of bonding.* The second reason for choosing a local coordinate system is that it allows the use of symmetry-adapted orbitals for interpreting bonding, interactions or crystal-field effects. For this purpose, one likes to have the axes pointing to the six oxygen ligands, i.e. the x and y axes towards the oxygen atoms in the octahedral basal plane, and the z axis towards the apical oxygen (Fig. 2.2.16.3). The Cartesian x and y axes, however, are not exactly (but approximately) directed toward the oxygen ligands due to the rectangular distortion of the octahedral basal plane.

For oxygen in TiO_2 with point group $mm2$, the two types of local systems are identical and are shown in Fig. 2.2.16.3 for the position $(\frac{1}{2} - u, \frac{1}{2} + u, \frac{1}{2})$. The z axis coincides with that of the Ti atom, while it points to the neighbouring oxygen of the basal plane in the octahedron around Ti at the origin. Only in this local coordinate system are the orbitals arranged in the usual way for an octahedron, where the d orbitals split (into the three orbitals of t_{2g} and the two of e_g symmetry) and thus allow an easy interpretation of the interactions, e.g. one of the two e_g orbitals, namely the $\text{Ti } d_{z^2}$ can form a σ bond with the $\text{O } p_z$ orbital.

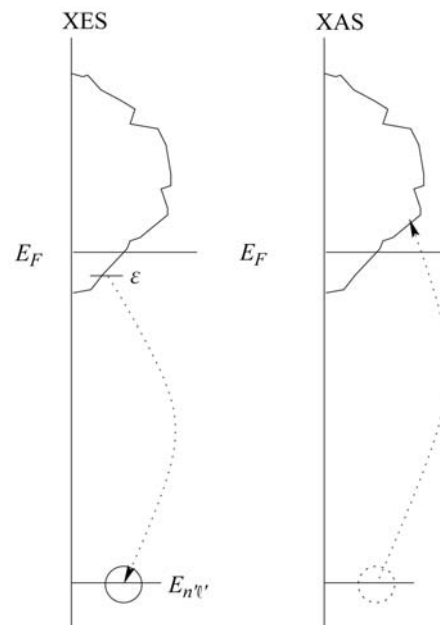


Fig. 2.2.16.4. Schematic transitions in X-ray emission and absorption spectra.

2. SYMMETRY ASPECTS OF EXCITATIONS

Table 2.2.16.1. $W_{\ell\ell'}$ factors for X-ray emission spectra showing the $\Delta\ell = \pm 1$ selection rule

ℓ'	ℓ				
	0	1	2	3	4
0					
1	1	1/3	2/5		
2		2/3		3/7	
3			3/5		4/11

2.2.16.3. Core electron spectra

In excitations involving core electrons, simplifications are possible that allow an easier interpretation. As one example, (soft) X-ray emission (XES) or absorption (XAS) spectra are briefly discussed. In the one-electron picture, the XES process can be described as sketched in Fig. 2.2.16.4. First a core electron of atom A in state $n'\ell'$ is knocked out (by electrons or photons), and then a transition occurs between the occupied valence states at energy ε and the core hole (the transitions between inner core levels are ignored).

According to Fermi's golden rule, the intensity of such a transition can be described by

$$I_{An'\ell'}(\nu) = \nu^3 \sum_{\ell} W_{\ell\ell'} n_{\ell}^A(\varepsilon) M_A(\ell, n'\ell', \varepsilon)^2 \delta(\varepsilon - E_{n'\ell'}^A - h\nu), \quad (2.2.16.5)$$

where $W_{\ell\ell'}$ comes from the integral over the angular components (Table 2.2.16.1) and contains the $\Delta\ell = \pm 1$ selection rule, $n_{\ell}^A(\varepsilon)$ is the local (within atomic sphere A) partial (ℓ -like) DOS, $M_A(\ell, n'\ell', \varepsilon)^2$ is the radial transition probability [see (2.2.16.6) below], and the last term takes the energy conservation into account.

The $M_A(\ell, n'\ell', \varepsilon)^2$ are defined as the dipole transition (with the dipole operator r) probability between the valence state at ε and the core state characterized by quantum numbers $n'\ell'$,

$$M_A(\ell, n'\ell', \varepsilon)^2 = \frac{[\int_0^{R_A} u_{\ell}^A(r, \varepsilon) r^3 R_{n'\ell'}^{A \text{ core}}(r) dr]^2}{\int_0^{R_A} [u_{\ell}^A(r, \varepsilon)]^2 r^2 dr}. \quad (2.2.16.6)$$

In this derivation one makes use of the fact that core states are completely confined inside the atomic sphere. Therefore the integral, which should be taken over the entire space, can be restricted to one atomic sphere (namely A), since the core wavefunction $R_{n'\ell'}^{A \text{ core}}(r)$ and thus the integrand vanishes outside this sphere. This is also the reason why XES (or XAS) are related to $n_{\ell}^A(\varepsilon)$, the local DOS weighted with the ℓ -like charge within the atomic sphere A .

The interpretation of XES intensities is as follows. Besides the ν^3 factor from Fermi's golden rule, the intensity is governed by the $\Delta\ell = \pm 1$ selection rule and the energy conservation. In addition, it depends on the number of available states at ε which reside inside sphere A and have an ℓ -like contribution, times the probability for the transition to take place from the valence and to the core hole under energy conservation. For an application, see for example the comparison between theory and experiment for the compounds NbC and NbN (Schwarz, 1977).

Note again that the present description is based on an atomic sphere representation with partial waves inside the spheres, in contrast to an LCAO-like treatment with site-centred basis functions. In the latter, an equivalent formalism can be defined which differs in details, especially for the small components (off-site contributions). If the tails of an orbital enter a neighbouring sphere and are crucial for the interpretation of XES, there is a semantic difference between the two schemes as discussed above in connection with f.c.c. Cu in Section 2.2.16.1. In the present framework, all contributions come exclusively from the sphere where the core hole resides, whereas in an LCAO representation 'cross transitions' from the valence states on one atom to the core

hole of a neighbouring atom may be important. The latter contributions must be (and are) included in the partial waves within the sphere in schemes such as LAPW. There is no physical difference between the two descriptions.

In XES, spectra are interpreted on the basis of results from ground-state calculations, although there could be relaxations due to the presence of a core hole. As early as 1979, von Barth and Grossmann formulated a 'final state rule' for XES in metallic systems (von Barth & Grossmann, 1979). In this case, the initial state is one with a missing core electron (core hole), whereas the final state is close to the ground state, since the hole in the valence bands (after a valence electron has filled the core hole) has a very short lifetime and is very quickly filled by other valence electrons. They applied time-dependent perturbation theory and could show by model calculations that the main XES spectrum can be explained by ground-state results, whereas the satellite spectrum (starting with two core holes and ending with one) requires a treatment of the core-hole relaxation. This example illustrates the importance of the relevant physical process in experiments related to the energy-band structure: it may not always be the just the ground states that are involved and sometimes excited states must be considered.

2.2.17. Conclusion

There are many more applications of band theory to solids and thus an enormous amount of literature has not been covered here. In this chapter, an attempt has been made to collect relevant concepts, definitions and examples from group theory, solid-state physics and crystallography in order to understand symmetry aspects in combination with a quantum-mechanical treatment of the electronic structure of solids.

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