Crystal Orbital Schemes for Solids*

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The crystal orbital (CO) scheme is demonstrated for vanadium carbide and vanadium nitride. The scheme shows in simple terms orbital interactions, bonding properties of states, and covalency/ionicity relations. In contrast with traditional representations, such as total DOS, band structure, and partial DOS, the CO scheme indicates the "chemical" information, and therefore stands for the chemical representation of the electronic structure of solid compounds. Examples are followed by the instruction how the CO scheme is constructed.

Solid silicon is shown as an example with rather complex 2:2 pattern of the bonding. The CO scheme shows that hybridization is an obsolete concept conflicting with the real shape of the DOS spectrum. No intraatomic hybridization of AOs occurs as previously expected. There is only slight interatomic mixing of s and p orbitals producing states with increased ionicity.

The CO scheme represents a new concept of the presentation of chemical bonding in solids. Applications to vanadium carbide, vanadium nitride, and silicon demonstrate that the scheme displays many features and relations useful on our way to the global understanding of the bonding.

Leading role in developing theories and computational methods for solids belongs to physicists. They have been using solid state language and displaying electronic structures *via* representations which usually show little chemical information, if any. Chemists, however, would prefer representations showing information relevant from the chemical point of view. In this contribution a chemical representation called "crystal orbital scheme" is introduced. The scheme in fact is a simplified interaction diagram for solids integrating many particular features of the bonding. It is simple and well understandable and therefore the scheme can be useful especially to those who are not practicing calculations but wishing to understand electronic reasons behind properties of materials.

THEORETICAL

Traditional Representations

Fig. 1 shows several typical representations used to present results of electronic structure calculations. First place among them belongs to the total density of states (DOS). The DOS, displayed in Fig. 1a, is a universal representation containing all information about the system. It represents an envelope curve showing how energy states are distributed on the one-dimensional energy scale. In spite of the usefulness and the completeness the DOS is often difficult to interprete.

The band structure (Fig. 1b) shows how energy levels move up and down on the energy scale when going throughout the momentum space. Especially this representation is very unappealing and discouraging to chemists because it says nothing about the chemical bonding.

The effective bonding is usually driven by the overlap of atomic orbitals (AO). Orbital interactions are easily identified by means of the decomposition of the total electron density into orbital components. The components projected on the energy scale are called partial DOS (Fig. 1c). An effective mixing of AOs exhibits a mirroring of partial DOS. Fig. 1c shows that in vanadium nitride (VN) mirroring of states occurs within each of three valence bands.

As soon as orbital interactions are identified on the energy scale, they can be transformed into the direct space. The location of AOs into atomic positions in the structure shows overlaps which are responsible for the final distribution of states characterized by the total DOS. p-to-d Interactions identified in Fig. 1c are in the direct space displayed in Fig. 1d. The decomposition of AOs into symmetry components shows further details. In VN there are two kinds of the p-to-d interaction [6]: p—d (σ) (left) and p—d (π) (right).

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*Presented at the *Solid State Chemistry* '96 Conference, Bratislava, July 6—12, 1996.
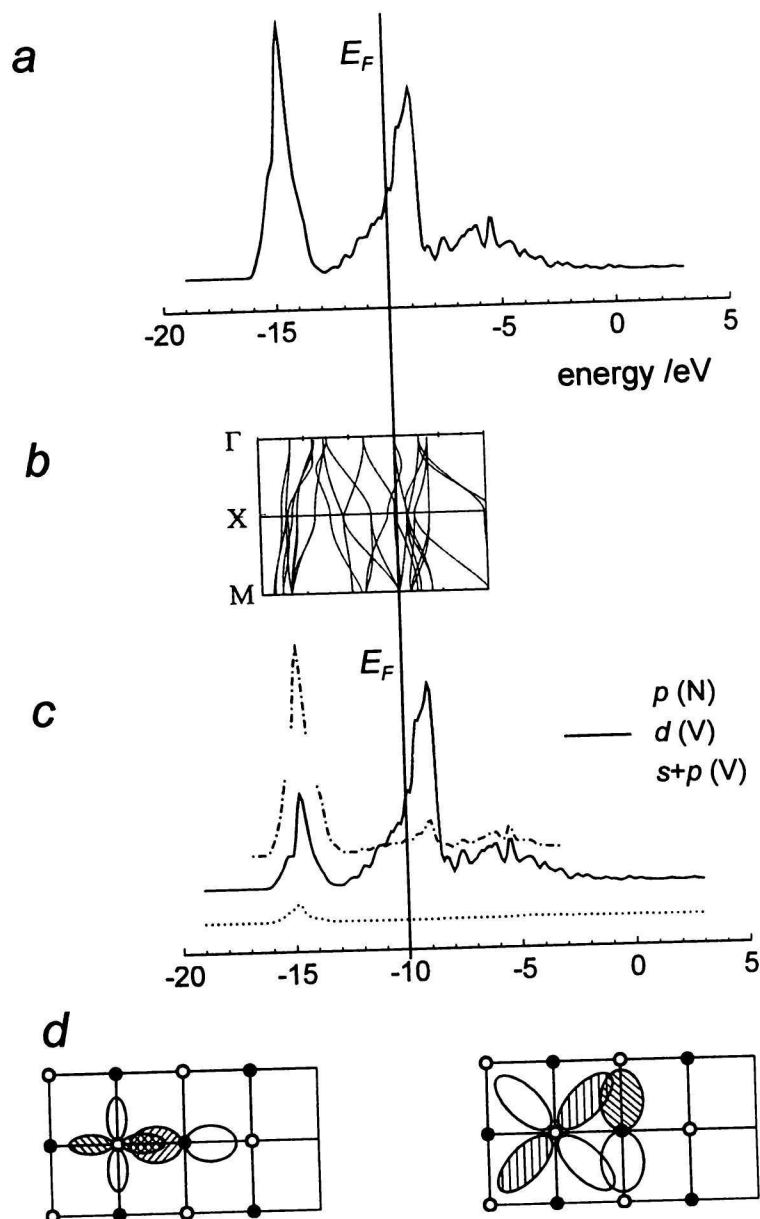
Fig. 1. Traditional representations of electronic structures, *a*) the total DOS, *b*) the band structure, *c*) partial DOS, and *d*) orbital interactions. Cubic VN is sampled within the experimental geometry [1, 2] using the EHT method for extended systems [3, 4]. Figs. *a—c* [5] are displayed on the same energy scale. Orbital interactions, displayed in Fig. 1*d* [6], show in the direct space the overlap of AOs responsible for the bonding (cross-hatched area indicates the positive overlap of atomic orbitals; empty and full circles represent the metal and the nonmetal atom, respectively).

Crystal Orbital Scheme

The crystal orbital (CO) scheme is a simplified interaction diagram [7]. It is based on the DOS distribution (of any origin, from the theory or from experiment) and contains also atomic energy levels and interaction lines. The idea of the interaction scheme is not new at all. It has been used by many authors, but always only in a schematic form [6, 8—10]. New feature of the CO scheme is that it displays the real DOS on the real energy scale [7]. Atomic levels and interaction lines make the scheme self-explanatory. It shows in simple terms main factors driving the final

distribution of states into the total DOS.

In Fig. 2 the interaction scheme of VN is compared to that of vanadium carbide (VC). How such schemes can be constructed? As soon as the calculation of the electronic structure is done only a small effort is necessary to set up the scheme. Add positions of atomic levels to the total DOS displayed on the real energy scale (DOS and atomic levels must be consistent, *i.e.* experimental DOS needs experimental atomic levels). Then draw interaction lines which show the splitting of atomic states into their final positions in the total DOS (according to the partial DOS). This requires the setting of some threshold to distinguish which levels
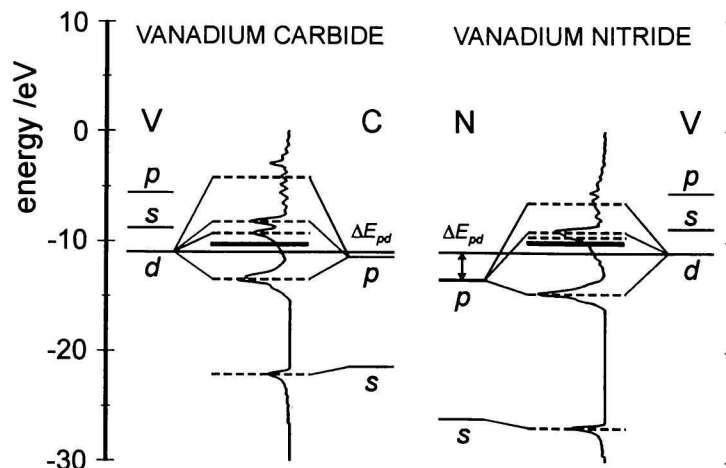
Fig. 2. Crystal orbital schemes for VC and VN [7, 11]. The distribution of states (DOS, central curve of the scheme) is completed with positions of atomic levels (side horizontal lines; full lines within the DOS indicate the Fermi level). Interaction lines connecting atomic positions and band positions (dashed horizontal lines) indicate orbital interactions and bonding properties of states. The energy difference between interacting levels (ΔE) indicates the covalency/ionicity of final states.

are relevant to the bonding and which are not (this is why the scheme is a simplified interaction diagram). For example in VC and VN the metal s and p levels are considered not relevant because of their negligible contribution to the bonding states (see the summary $s + p$ partial DOS in Fig. 1c). The bonding in VC and VN is therefore driven by one strong p-to-d orbital interaction. What can the CO scheme say about the bonding [11]?

1. **Orbital interactions.** Interaction lines instructively show orbital interactions thus indicating the number of levels taking part in the bonding. In VC and VN only one level from nonmetal interacts with one level from the metal atom (the p-to-d interaction). Note that the recognition of levels relevant to the bonding allows one to classify compounds according to the number of interacting levels. This is quite important because increased number of levels increases the complexity of the bonding.

2. **Bonding properties of states.** They are identified according to the direction of interaction lines. The line going down indicates the stabilization. States in the DOS, which such line is pointing at, are bonding. Lines going up show destabilized (antibonding) states. Horizontal (or nearly horizontal) interaction lines demonstrate that states are neither stabilized, nor destabilized. Such states are usually nonbonding.

3. **Covalency/ionicity of the bonding.** In the scheme the covalency/ionicity of states is indicated simultaneously by several features.

a) Covalent states are indicated by at least two interaction lines. Keep in mind that the covalency is a synonym to mixing of electron densities coming from different centres. States in the diagram indicated by one line only are either ionic (usually deeper lying), or nonbonding (situated near the E_F). In VC and VN (Fig. 2) s states are ionic. Valence states situated near

the Fermi level (≈ -15 eV to ≈ 0 eV) are covalent. A fraction of states within the bonding/antibonding multiplet is nonbonding. Located just above the Fermi level these states are only slightly destabilized compared to their atomic position (metal d level). Note that in VC the nonbonding states are distinguished in a separate subband (≈ -9 eV).

b) Covalent states result from mixing of states of similar electronegativities. In the scheme the difference in electronegativities is characterized by the energy difference between interacting atomic levels (ΔE). A large value of ΔE indicates a large difference in electronegativities. Mixing of states with the large ΔE gives rise to increased ionicity of final states. Values of ΔE_{pd} (indicated in Fig. 2) are 0.4 eV and 2.4 eV for VC and VN, respectively. States raised by the p-to-d interaction (pd states) are therefore in VN much more ionic than those in VC. Note that for the s-to-d interaction the value of ΔE_{sd} exceeds 10 eV (in both, VC and VN). s States are therefore typical ionic states taking part only in electrostatic interactions.

c) Another feature showing the covalency degree of bonding states is the bonding-antibonding splitting. The stronger covalent bonding gives rise to the larger splitting. In VC and VN these splittings look similar. Keep in mind, however, that the value of the splitting is obtained as an energy difference between two band positions, diminished by the value of ΔE. For the p-to-d (t_{2g}) interaction the bonding-antibonding splitting equals 4.7 and 3.4 eV for VC and VN, respectively [11].

d) Finally, bands due to the covalent interaction (small ΔE) have larger bandwidth than bands due to more ionic interactions [4]. In the spectrum of carbide (Fig. 2) the width of the main bonding band (at ≈ -13 eV) is approximately 4 eV, contrary to 3 eV in nitride [11].
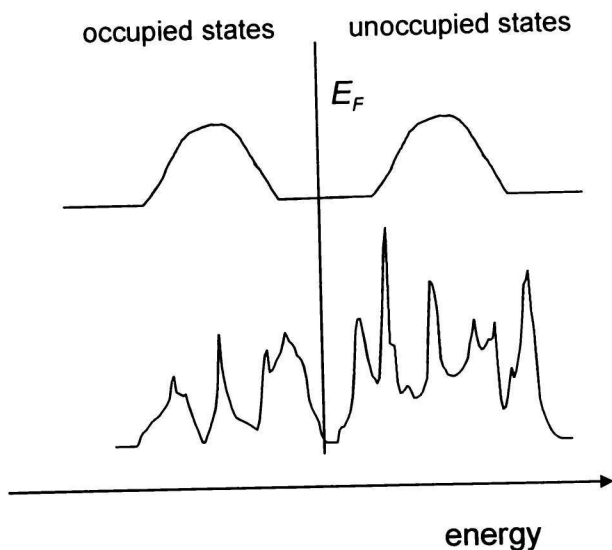
occupied states   unoccupied states

E_F

energy

Fig. 3. The spectrum of states in silicon. The upper curve sketches two bands predicted for the interaction of hybridized sp^3 orbitals. The reference spectrum (down) is the first principles FP-LAPW total DOS [15].

SOLID SILICON

energy /eV

E_F

Fig. 4. The crystal orbital scheme of solid silicon. Three subbands distinguished below the Fermi level originate from orbital interactions within tetrahedra (ss, sp, and pp states). ss and pp states are perfectly covalent ($\Delta E = 0$). The sharp peak of the sp band indicates increased ionicity ($\Delta E = 6.7$ eV). Note that sp states are s-to-p bonding and s-to-s antibonding at the same time.

Bonding in Silicon

Silicon is often referred to as a textbook example of the simple bonding [12]. It has a diamond-like structure, where each atom has the tetrahedral surrounding. The bonding in solid silicon has been explained by means of sp^3 hybridization. One s electron is supposed to be promoted to the p orbital and one s and three p orbitals are mixed to form four equivalent sp^3 hybrids pointing towards the corners of the tetrahedra and creating four σ bonds [13, 14]. If this is true, then the DOS should exhibit two bands, a band of occupied states being separated by a gap from a band of unoccupied states (Fig. 3, upper curve). Each state should consist of 25 % of the s component and 75 % of the p component. The total DOS displayed in Fig. 3 (lower curve), which mimics all details of experimental spectra [12], shows different features. The truth is that the curve consists of two broad bands, the states of the lower one being occupied. Both bands, however, display a characteristic structure. The DOS distribution of the lower band shows clear splitting into three subbands. This splitting, occurring in spectra of all tetrahedral compounds [12, 16], cannot be explained in terms of the hybridization. Moreover, partial DOS projections show that the composition of bands is completely different from that predicted within the concept of hybridization (1:3 mixing of s and p states). The lower subband consists of pure s states and the upper one of pure p states. States mixed of both, s and p components are situated only in the midband, which contains only 1.9 of the total 8 electrons.

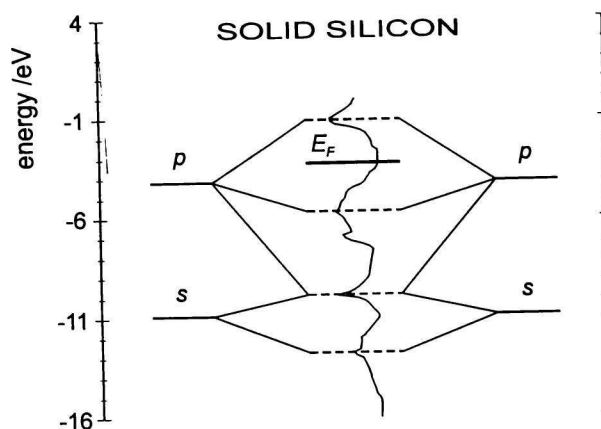The crystal orbital scheme displayed in Fig. 4 accounts for the DOS structures and also for their com-position. The scheme shows that in silicon two atomic levels interact with two levels of the neighbouring atom. This 2:2 bonding is much more complex compared to the simple 1:1 pattern in carbides and nitrides (see above). The shape of the DOS is driven by the interaction of individual atomic orbitals within the tetrahedra, not by the interaction of hybrids. There is no intraatomic hybridization of states. At least two reasons prevent atomic orbitals from mixing. The first reason is different symmetry of s and p orbitals and the second one is the large energy difference between two atomic levels ($\Delta E_{sp} = 6.7$ eV, see Fig. 4). Fig. 4 shows that the lowest valence subband is due to the s-to-s interaction and states of the subband situated just below the E_F come from the p-to-p interaction. States of these two subbands are perfectly covalent because $\Delta E_{ss} = \Delta E_{pp} = 0$. The states of the mid-band are due to the interatomic s-to-p interactions. Because of the large energy difference they show increased ionicity ($\Delta E_{sp} = 6.7$ eV). Interaction lines show that these states are not only s-to-p bonding but s-to-s antibonding at the same time. This is another feature which is in conflict with the concept of hybridization. The interaction of hybridized orbitals should produce only two kinds of s states, bonding (occupied) and antibonding (empty), cf. Fig. 3. None occupied s antibonding states are expected.

CONCLUSION

Traditional representations of electronic structures are briefly compared and contrasted for cubic vanadium nitride. The chemical representation "crystal orbital scheme" is demonstrated for VN and VC. The instruction how to construct the scheme is followed by examples of "chemical" information contained in this

simple diagram. The scheme displays orbital interactions, bonding properties of states, covalency/ionicity relations, *etc.*

Solid silicon is demonstrated as an example of rather complex 2:2 pattern of the bonding. Its interaction scheme shows that a part of occupied states displays *s*-to-*s* antibonding character. No intraatomic hybridization of AOs occurs as previously expected. The slight interatomic mixing of *s* and *p* orbitals produces states with increased ionicity.

The crystal orbital scheme represents a new concept of the presentation of chemical bonding in solids, introduced only recently [7]. So far CO diagrams have been constructed for transition metal carbides and nitrides [7, 11], silicon nitride [17, 18], mineral lizardite [19], and for a series of zinc-blende structure semiconductors GaAs, GaN [20], and GaP [16]. In all applications the scheme provides interesting view of the bonding displaying many features and relations useful on the way to the global understanding of the bonding.

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