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Condensed matter physics in the 21st century: The legacy of Jacques Friedel

Insulating oxide surfaces and nanostructures

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ABSTRACT

This contribution describes some peculiarities of the science of oxide surfaces and nanostructures and proposes a simple conceptual scheme to understand their electronic structure, in the spirit of Jacques Friedel's work. Major results on the effects of non-stoichiometry and polarity are presented, for both semi-infinite surfaces and ultra-thin films, and promising lines of research for the near future are sketched.

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R É S U M É

Cet article décrit quelques particularités de la science des surfaces d'oxydes et des nanostructures, et propose un schéma conceptuel simple permettant de comprendre leur structure électronique, dans l'esprit des travaux de Jacques Friedel. Des résultats majeurs quant aux effets de non-stœchiométrie et de polarité sont présentés, à la fois pour les surfaces semi-infinies et les films ultra-fins, et des perspectives de recherche prometteuses pour un future proche sont esquissées.

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1. Introduction

Understanding the characteristics of surfaces, which are the contact zones between a solid and its environment, is of crucial interest from many points of view. However, while metal surfaces have been studied for more than fifty years with techniques of increasing sophistication, the science of oxide surfaces has only emerged in the late 1990s [1]. This delay was due more to experimental difficulties and theoretical disinterest than to the materials themselves. As a matter of fact, it took a long time to realize that very specific protocols of sample preparation were needed to control the surface stoichiometry and thus to achieve surface reproducibility. Moreover, the insulating character of numerous oxides induces charging effects when electrons are sent to or collected from their surfaces during spectroscopic experiments, making it difficult to correctly calibrate the sought information. The use of scanning tunneling microscopy (STM) is also impossible,

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unless oxides are sufficiently doped or deposited as thin films on a metal substrate. From the point of view of theory, a description of insulating oxides in terms of classical charges has long been considered as sufficient, driving the interest of theorists to more fashionable materials. Eventually, experimental and theoretical advances have been made, highlighting novel structural and electronic effects not met in more traditional materials. This has revived activity in various disciplinary fields, such as mineralogy, geochemistry, toxicology, catalysis, electronics, spintronics, and has even led to the emergence of the recent “all-oxide” electronics.

For a long time, all insulating oxides have been described by classical electrostatic models, in which the ionic charges play the major role. This has led to the development of the Born model of cohesion in which the leading interatomic forces result from Coulomb charge–charge interactions, to which short-range repulsion and weak van der Waals terms are added [2]:

$$E = \frac{1}{2} \sum_{i \neq j} \left(\frac{Q_i Q_j}{r_{ij}} + B_{ij} e^{-\frac{r_{ij}}{\rho}} - \frac{C_{ij}}{r_{ij}^6} \right) \quad (1)$$

Such models have been widely used in the past, for example to predict inorganic crystal structures, relaxation effects at oxide surfaces but also lattice dynamics or point defect properties [3,4]. Even now, they remain useful to understand complex mineral bulk or surface structures [5] or to derive structural phase diagrams of mixed oxides [6]. However, because they include no information on the electronic structure, their parameters determined for bulk atom environment are not necessarily transferable to surfaces or nano-objects.

The development of concepts such as local electronegativity or site specific acid/base character [1], has led to the recognition that, even in highly ionic materials, the electronic structure is not frozen but may vary as a function of the local environment of the atoms. Methods intermediate between fully classical and fully quantum methods have emerged, such as those based on the electronegativity equalization principle [7–9] which yield environment dependent ionic charges. They are very efficient to address issues in which large systems are involved. This was, for example, the case in the impressive molecular dynamic simulation of the oxidation of an aluminum nanoparticle, in which interactions between more than eight hundred thousand atoms were accounted for [10]. However, these methods still disregard many essential electronic characteristics.

In particular, they are unable to give an interpretation of the forbidden gap in insulating oxides. The latter may be associated either with a transfer of electron from an oxygen ion to a cation ($X^{n+} + O^{2-} \rightarrow X^{(n-1)+} + O^-$) or with an exchange of electrons between two cations ($X^{n+} + X^{n+} \rightarrow X^{(n-1)+} + X^{(n+1)+}$). In the first case, the excitation energy Δ_{CT} is equal to the difference between the oxygen second electronic affinity A_2 and the cation n th ionization potential I_n , while in the second case, the excitation energy Δ_U is related to the difference between the $(n+1)$ th and n th cation ionization potentials I_{n+1} and I_n . According to whether $\Delta_{CT} < \Delta_U$ or $\Delta_{CT} > \Delta_U$, the insulators are of charge-transfer or of Mott–Hubbard type [11]. Simple oxides such as MgO, Al₂O₃, SiO₂ and d⁰ transition metal oxides, such as TiO₂ or SrTiO₃ are charge-transfer insulators, while most other transition metal oxides are Mott–Hubbard ones. These latter usually require more advanced simulation methods to account for their electronic structure than the former.

In the last decades, the description of the electronic structure of materials has impressively improved, at a level of quasi-chemical accuracy [12,13]. Density Functional Theory (DFT), in its various implementations, is a widely used tool which, in most cases, satisfactorily predicts atomic structures but may fail in correctly accounting for some electronic properties. The reasons why it largely under-estimates the gap width of insulators and is unable to yield good quasi particle spectra have been assigned to the lack of correct treatment of exchange [14] which yields erroneous self-interaction energy terms [15]. In the following section, in the spirit of Jacques Friedel’s work, we will present a simplified description of the electronic structure of insulating oxides, which only retains the key ingredients and may thus be used to interpret the mechanisms taking place at their surfaces or around low-coordinated atoms in nano-objects.

2. Simple approach to the electronic structure of insulating oxides

In transition metals and tetrahedral semi-conductors, the tight-binding method – which is the equivalent of the Linear Combination of Atomic Orbitals (LCAO) in chemistry – has been very successful to predict band structures, density of states (DOS) and Fermi level position, before the advent of ab initio methods. It is based on the resolution of an effective one-electron Schrödinger equation, projected on a minimal basis set made of atomic orbitals which are assumed orthogonal. In its simplest form, only two types of Hamiltonian matrix elements are kept: the diagonal ones which represent the (effective) atomic orbital energies ϵ_i , and the non-diagonal ones β_{ij} , named resonance or hopping integrals, which involve orbitals on neighboring atoms. The latter are responsible for the formation of bands and electron delocalization. Generic features of the local DOS (LDOS) may then be obtained, such as its center of gravity related to the ϵ_i and its width $W \propto \beta\sqrt{Z}$, which was shown to scale as the square root of the local atomic coordination number Z [16].

Application of this method allowed for example J. Friedel to analyze the dependence of the bulk cohesion energy of transition metals as a function of the d band filling, within a rectangular model of the density of states (DOS) [17]. It is also the essence of a very successful model of surface reactivity [18]. The so-called second moment approximation (SMA), in which the DOS is represented by its first and second moments only [16], and the local neutrality condition have allowed

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