Computational Materials Science Network
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In the last few years, our CMSN effort has focused on core-excitation spectra of semiconductors and insulators. Calculations were performed at two different levels of approximation: a) inclusion of a static core hole in a particular atom, which is then treated like an impurity, modifying the available states for an electron that would otherwise go into the conduction-band Bloch states; b) modeling the core hole by actually using an impurity atom with atomic number $Z+1$, where Z is the atomic number of the host element. We demonstrated that electron-hole interaction dominate the spectra, with a significant shift of oscillator strength to lower energies even in cases where no core excitons appear below the threshold for excitations to the conduction-band continuum, e.g., in Si. In addition to Si, we investigated SiO_2 , and MgO . These studies were carried out in the context of experimental data, especially spatially resolved energy-loss spectroscopy by Steve Pennycook's microscopy group at ORNL. For example, we investigated the Si $L_{2,3}$ spectrum across the Si- SiO_2 interface from which we attempted to extract information about the local bonding of Si by effectively inverting the experimental spectra.

During the last year, we turned our attention to transition metal oxides. In our first example, ZrO_2 , we found that electron-hole interactions give rise to bound exciton states below the Zr 3d continuum. These calculations demonstrated a phenomenon that occurs frequently: if the core hole is neglected, the resulting spectrum (Z spectrum), after suitable broadening, is essentially indistinguishable from the $Z+1$ spectrum if the first peaks are lined up. It is this kind of coincidence that has led to claims in many cases that the Z spectra fit the data (by freely sliding the theoretical spectra on the energy axis), thus signifying absence of significant electron-hole interactions.

In the last year, we examined a particular feature of the core spectra of transition metals in various "oxidation states". The formal "oxidation state" of a transition metal in oxides is defined as the number of electrons that must be donated to the O atoms in order to complete their 2p valence shell. For example, Mn in MnO , Mn_2O_3 , MnO_2 , CaMnO_3 is considered to have a formal oxidation state of +2, +3, +4, and +4. In Mn_3O_4 , the formal oxidation state is $8/3$, which is usually interpreted to mean two Mn^{+3} atoms and one Mn^{+2} atom. These formal oxidation states are widely believed to be true charge states, indicating the ionic character of the materials. This belief is supported by a well-known correlation of the so called L_2/L_3 ratios (ratio of areas under first peak of the L_2 and the L_3 spectra) with the occupancy of the transition-metal d orbitals, as shown in Fig. 1. This correlation has

Fig.1 Correlation of L_2/L_3 ratio with occupancy of d orbital according to the formal oxidation state rule. From Ref. X.

Fig. 2 The Mn L_2/L_3 ratio in $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ as measured by atomically-resolved EELS by Varela and Pennycook at ORNL.

so that one expects 2/3 of the Mn atoms to be Mn^{+4} and 1/3 to be Mn^{+3} . Indeed, electron diffraction data show a tripling of the cell in the [001] direction, with two Mn planes being equivalent and the third being inequivalent. The phenomenon is usually interpreted in terms of “charge ordering”. Recently, Maria Varela and Steve Pennycook, using samples fabricated by Dave Mandrus’s group at ORNL obtained *atomically resolved* electron-energy loss spectra (EELS), showing unambiguously that the L_2/L_3 ratio of two Mn atoms looks like that of CaMnO_3 , suggesting Mn^{+4} , while the L_2/L_3 ratio of the third Mn atom looks like that of LaMnO_3 , suggesting Mn^{+3} (Fig. 2). “Charge ordering” is generally attributed to strong electron correlations that are described by Hubbard models that are fit to the data.

We have performed density-functional calculations for the ground state of $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$, modeling the doping by Bi by simply adding an extra electron per tripled CaMnO_3 unit cell, compensating it with a positive background. We found that, if the unit cell is also doubled in the other two directions, a spontaneous distortion occurs and a band gap opens up at the tripled-cell’s

Fig. 3 a) The distorted tripled unit cell of $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ as calculated by density functional theory. b) the energy bands in the Brillouin zone corresponding to the tripled cell, showing the Peierls gap at the cone boundary. c) The electron density integrated in the plane perpendicular to the direction in which the unit cell is tripled, d) the electron density around a Mn atom within a radius, plotted as a function of this radius, in Mn metal and several Mn oxides discussed in the text.

been often understood to mean that the formal oxidation state indeed corresponds to a true charge state. The correlation has intriguing consequences in “mixed-valence” cases, as in Mn_3O_4 mentioned earlier. One can create mixed-valence systems by doping. For example, though CaMnO_3 has Mn^{+4} , the doped material $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ has one extra electron per three Mn atoms

Comment: I am not sure Mn_3O_4 is known as a mixed-valence system.

Comment: The point I wanted to make is that BiCaMnO_3 is only one of many materials commonly described as “charge ordered”.

Brillouin zone edge, signaling a Peierls-like instability (Fig. 3). The resulting structure indeed has two equivalent and one inequivalent Mn atoms and is in agreement with the electron diffraction data. However, a calculation of the electron density revealed that all three Mn atoms are effectively neutral! In Fig. 3d we show the electron density integrated in a sphere of radius R

centered about a Mn atom, plotted as a function of R . The electron density is identical in Mn metal, where Mn atoms are guaranteed to be neutral (0 oxidation state) and all the Mn oxides of interest! This result actually confirms what Ewing and Seitz found in 1936 in the first-ever self-consistent electronic structure calculation for LiF. They found minimal charge transfer from Li to F! The point here is that in $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ there is no “charge ordering”, merely a structural distortion driven by a Peierls-like instability.

What then of the correlation of L_2/L_3 ratios with the formal occupation of the d orbital? The explanation is quite straightforward: in crystals, the O 2p energy bands always lie low and thus are always full. Thus, simple electron counting accounts for *nominal* orbital occupation that corresponds to the *formal* oxidation state. The question of the electron density distribution is a totally different issue, however. In a self-consistent calculation, bands hybridize so that the O 2p Bloch functions have contributions from cation orbitals. Self-consistency seems to ensure that hybridization is just what it takes to make all atoms effectively neutral! When there are inequivalent cations, one can do the same book-keeping of nominal orbital occupations by invoking atomic-like Wannier functions that inevitably have amplitudes about other atoms. Thus, one out of three Mn atoms in $\text{Bi}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ has one more 3d-like Wannier function nominally occupied than the others, but self-consistency ensures that the 3d Wannier functions of inequivalent Mn atoms are different by just what it takes to keep all atoms effectively neutral. This nominal occupation of 3d-like Wannier functions is reflected in the $L_{2,3}$ spectra and the L_2/L_3 ratios.

Calculation of the L_2/L_3 ratios presents a major challenge, however. A standard $Z+1$ calculation does not distinguish between the L_2 and the L_3 spectrum and would therefore yield the statistical L_2/L_3 ratio of 2.0. Clearly, a true core-hole calculation including spin polarization and spin-orbit interactions is essential. We initiated calculations including spin polarization and spin-orbit interactions. Results for Ni metal show a definitive departure from 2.0, roughly 2.2, close to the experimental value. John Rehr’s group has been calculating L_2/L_3 ratios for monatomic transition metals. A collaboration is under way to explore the L_2/L_3 ratios of manganites and other transition-metal oxides using complementary approaches.