**ENERGETICS, BONDING MECHANISM AND ELECTRONIC
STRUCTURE OF CERAMIC/CERAMIC AND
METAL/CERAMIC INTERFACES**

An Annual Progress Report for
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by

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Progress:

Work in this (short) period has continued along at a good clip - as seen also from the attached list of publications supported solely by the U.S. Department of Energy. New efforts have been undertaken to understand the electronic structure and properties of the metal/ceramic interface which was stimulated by, and undertaken in support, of the work of Seidman, Merkle and collaborators (supported by the DOE) who studied the Ag/CdO interface. To this end, we investigated the structure and electronic structure properties of the Ag/CdO (100) interface employing our total energy FLAPW thin film method. We showed (see attached preprint) that the preferred adsorption site for Ag is above the O site of the clean CdO(001) surface. The calculated equilibrium interlayer separation between the Ag overlayer and the CdO interface layer is 4.32 a.u. and the binding energy is 0.63 eV/atom. The charge transfer between Ag and the CdO substrate is small (0.02 electrons/atom) and the range of the interface effect on the CdO(001) surface is limited to the interface layer. The interfacial hybridization between the Ag and the O atoms makes a significant contribution to the binding of the Ag/CdO(001) interface.

In support of the research of Bader's group at ANL, we continued our investigation of magnetism at metal/ceramic interfaces. Stimulated by Felcher's neutron results, we studied the effects of a Au overlayer on the magnetic properties of Fe/MgO(001) (preprint attached). For the first time we predicted a substantial magnetic circular dichroism signal for Au with its sizeable spin moment ($0.069 \mu_B$) and orbital moment ($0.042 \mu_B$). Encouraged by this result and Yongsup Park's work on the Fe/MgO interface, we have in this period turned our attention to investigating overlayer induced reconstruction and possible magnetism of 4d elements on MgO (see preprint attached). The structural, electronic and magnetic properties of metal-ceramic interfaces, M/MgO(001) (M=Pd, Rh and Ru), were investigated using the FLAPW method. Ru and Rh monolayers were found to be able to retain large spin magnetic moments on MgO(001) ($1.95 \mu_B$ and $1.21 \mu_B$ for Ru and Rh, respectively) - indicating, in principle, the potential application of MgO(001) as a benign substrate for 4d monolayer magnetism. Significantly, according to our atomic force determinations, the metal overlayers induce a sizeable buckling reconstruction in the interfacial MgO layer, which enhances the M-Mg) binding energy by 0.1 eV. The weak M-O

interaction is mainly via tail effects; however, it affects the density of states at the Fermi level for Pd/MgO(001) significantly and completely eliminates the small magnetic moment of the free Pd monolayer ($0.34 \mu_B$).

Plans for Next Year:

1. Recently, Seidman, Merkle and collaborators used the atom-probe field-ion microscopy (APFIM) technique to study the Ag/CdO(222) interface. They found that the interface is atomically sharp, and that the sequence of planes through the interface is Ag|O|Cd... Stimulated by their results, we will set up a nine-layer slab model to study the Ag/CdO(111) system which consists of an eight-layer slab of CdO with four (polar) layers of O and four layers of Cd alternating with each other and a Ag monolayer adsorbed on either the upper or the lower side of the slab, where the sequence of the interface planes is Ag|O|Cd... or Ag|Cd|O... respectively. The FLAPW method will be employed to solve the Kohn-Sham equations self-consistently. The Ag site preference will be determined by total energy calculations and will be compared with the experimental result directly. The electronic structure of the interface will also be investigated. According to our previous calculations on Ag/CdO(001), the hybridization of Ag and O atoms plays an important role in the binding of the interface. For Ag/CdO(111), it is expected that this effect is enhanced for the terminating sequence Ag|O|Cd... and gives a significant contribution to the interfacial binding. The hybridization in Ag/CdO(111) will be studied by investigating the band structure and the density of states.

2. We have extended our studies of the ceramic-ceramic VO_2/TiO_2 interface done previously in collaboration with Lam at ANL. Whereas previously we considered both VO_2 and TiO_2 in their rutile phases each with 3 layers, we have now investigated the superlattice with 1 - 2 layers each and with VO_2 in its low temperature monoclinic phase. Problems of interpreting the interface were found because of uncertainty about the actual ground state of rutile VO_2 . To counter this, we discuss below our plans for continuing these studies.

In order to understand correctly the electronic structure of the TiO_2/VO_2 interface, we first need to obtain a reliable description of the band structure of VO_2 itself. This turns out to be a

challenging problem. Only few publications are available on this matter [1,2], where the LDA approach is applied for the description of the electronic structure of two phases of VO₂: the high-temperature rutile structure and the low-temperature monoclinic structure. The nature of the metal-insulator transition in VO₂ is still unclear. The authors of [2] argue that LDA gives the correct description for this transition. In order to verify this we have performed FLMTO total energy calculations for VO₂ in different phases - rutile and monoclinic - in both spin-restricted and spin-polarized modes. For the spin polarized case we investigated possible ferromagnetic and several antiferromagnetic ordering possibilities. Although the calculations are not completely finished yet, we already see that including the magnetic degree of freedom changes the simple picture proposed in [2].

First of all, the hypothetical ferromagnetic phase turns out to be more stable (has lower total energy) than the nonmagnetic phase. This appears to cast doubt on the speculation of [2], that LDA gives the correct result for the metal-insulator transition, since they did not consider this possibility. Second, our results indicate that probably the most stable phase is an antiferromagnetic one with a very small ($0.1 - 0.2 \mu_B$) magnetic moment; this result probably accounts in a simplified way for spin correlations in this system. And such a small antiferromagnetism should favor opening the gap at the Fermi energy once the rutile structure gets monoclinically distorted.

We plan to carry out highly precise FLMTO total energy calculations of such an "antiferromagnetic" phase of VO₂ starting from the rutile structure and going through the monoclinic distortion in order to find the equilibrium crystal structure. Once the correct and precise band and crystal structure is established, we will continue our investigation of VO₂/TiO₂ interface in terms of interfacial relaxation and possible peculiarities of magnetic ordering.

References:

1. P.B. Allen, R.M. Wentzcovitch, W.W. Schulz and P.C. Canfield, Phys. Rev. B **48** (1993) 4395.
2. R.M. Wentzcovitch, W.W. Schulz and P.B. Allen, Phys. Rev. Lett **72** (1994) 3389.

Post docs and Students:

Fangyi Rao, Graduate Student
Oleg Mryasov, Research Associate (part time)

Estimate of Unobligated Balance

We estimate that there will be no unobligated balances at the end of this fiscal period.

Publications Supported by DE-FG02-88ER45372 - 1994

1. "Electronic Structure of Noble-Metal Monoxides: PdO, PtO and AgO", (with Key-Taeck Park, D.L. Novikov and V.A. Gubanov), Phys. Rev. B **49**, 4425 (1994).
2. "Magnetism at Metal-ceramic Interfaces: Effects of a Au Overlayer on the Magnetic Properties of Fe/MgO(001)", (with Ruqian Wu), J. Magn. Magn. Mater. **137** (1994) 127.
3. "Electronic Structure and Relaxed Geometry of the TiO₂ Rutile (110) Surface", (with D. Vogtenhuber, R. Podlousky, A. Neckel and S.G. Steinemann), Phys. Rev. B **49**, 2099 (1994).
4. "Electronic Structure of VO₂ and TiO₂ Thin Films and Multilayers", (with V.A. Gubanov, D.L. Novikov and D.J. Lam), Phys. Rev. B (1994) (to appear).
5. "LDA Calculations of the Pressure Induced Structural Changes and Phase Transitions in PbTiO₃", (with O.N. Mryasov and D.L. Novikov), Ferroelectrics (to appear).
6. "Optimized Geometry, Static Potential, Electronic Structure and Ferroelectric Instability in PbTiO₃", (with O.N. Mryasov, D.L. Novikov, K.T. Park and G. Li), Phys. Rev. B (submitted).
7. "Electronic Structure and Metal-Ceramic Bonding of the Al₂O₃-Pd Interface", (with Key-Taeck Park), Phys. Rev. B (submitted).
8. "Structure and Bonding at Metal-Ceramic Interfaces: Ag/CdO(001)", (with Fangyi Rao and Ruqian Wu), Phys. Rev. B (submitted).
9. "Metal-Ceramic Interfaces: Overlayer Induced Reconstruction and Magnetism of 4d Transition Metal Monolayers", (with Ruqian Wu), Phys. Rev. B (Rapid Commun.) (submitted).

Conferences, Seminar, Workshops, etc.

"LDA Calculations of the Pressure Induced Structural Changes and Phase Transitions in PbTiO₃", (with O.N. Mryasov and D.L. Novikov), paper presented at the Third Williamsburg Workshop on First-Principles Calculations for Ferroelectricity, Williamsburg, VA, Feb. 6-9, 1994.

"Pressure Induced Structural and Phase Transformations in Ferroelectric PbTiO₃", (with O.N. Mryasov and D.L. Novikov), paper presented at the APS Mtg., Pittsburgh, PA, March 21-25, 1994.

"Electronic Structure of the Ag/CdO(001) Interface", (with Fangyi Rao and Ruqian Wu), paper presented at the APS Mtg., Pittsburgh, PA, March 21-25, 1994.

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