

Research project report Nr 2 for the four-year period (2001-2004)

Project title:

Modeling of defects and surface-induced processes in advanced oxides

Project leader: Dr. habil. phys. E. A. Kotomin

Summary

The main task of the present project is to perform both detailed theoretical simulations as well as experimental studies of technologically advanced materials.

All participants of the project are scientists with the high qualification (1 Dr. habil. phys., 1 Dr. chem., 1 Dr. phys., 1 Dr. rer. nat. as well as 1 PhD student and 1 MS student). S. Piskunov received Dr. rer. nat degree from Osnabrück University (Germany) in 2003. His thesis title is "Electronic Structure of Perfect and Defective Perovskite Crystals by means of *ab initio* Hybrid Functional Theory". PhD thesis defense of MS D. Gryaznov is planned for 2005.

Publications and conference presentations published during the review period

Year	Publications	Conference presentations
2001	20	14
2002	15	16
2003	17	19
2004	16	22
2001-2004	68	71

MAIN RESULTS

1. *Ab initio* quantum chemical calculations have been performed for a number of *advanced ABO₃ materials and their solid solutions*, widely used in technological applications. In collaboration with *Osnabrück University, Germany* and *California Institute of Technology, Pasadena, USA*, we performed large scale first principles (CRYSTAL) calculations, in the framework of Density Functional Theory, DFT (including hybrid B3PW) methods as well as semi-empirical (INDO) calculations. We have studied the atomic relaxation of SrTiO₃(100) and (110) surfaces, which serve as substrates for growth of technologically important high T_c materials, as well as charge-transfer vibronic excitons in KNbO₃ and KTaO₃ ferroelectric crystals. We studied also theoretically the atomic and electronic nature of the polarons and excitons in perovskites and suggested an interpretation of commonly observed "green" luminescence (2.2-2.3 eV) as a radiative recombination of nearest electron and hole polarons localized on Ti(Nb) ion and neighboring O²⁻ ion. This theoretical study permits to make a choice between many hypothetical models of the green luminescence. We studied also the atomic structure of the KNb_xTa_{1-x}O₃ perovskite solid solutions and demonstrated that Nb impurities even at very low concentrations reveal a cooperative self-ordering effect, which drives *the phase transition* in incipient KTaO₃ ferroelectric.

2. One of particular purposes of our study is identification of point defects, in particular, those responsible for the blue-light-induced-infrared-adsorption devices (BLIIRA) effect which strongly affects efficiency of laser frequency doubling in KNbO₃-based devices. Using both CRYSTAL and VASP codes, in collaboration with *University of Barcelona, Spain*, and *Uppsala University, Sweden*, we have performed large scale first principles calculations on the *defective structures* of cubic SrTiO₃ using supercells containing up to 320 atoms. Due to existence of different kinds of chemical bonds in SrTiO₃, there is a competition between the tendency to trap two electrons associated with the missing oxygen atom and leaving a vacancy (*F center*) or to localize them on the nearest Ti 3d orbitals. We demonstrated how creation of a neutral O vacancy results in the new electronic state below the conduction band, which is consistent with the experimental estimate indicating small ionization energy for the neutral oxygen vacancy. The formation of oxygen vacancies is accompanied by a large relaxation of the first and second nearest neighbours. The localization of the electrons on titanium ions is consistent with photoemission studies on the surface of SrTiO₃, which indicate the formation of Ti³⁺ ions when surface defects are created under Ar⁺-ion bombardment.

3. Progress in *solid oxide fuel cells* needs search for new materials for cathodes. Of principal interest is O₂ molecule adsorption on cathode surface, its dissociation, O atom diffusion and penetration through the electrolyte to anode, where O meets with H atoms. In collaboration with *Max Planck Institute for Solid State Researches, Stuttgart, Germany* and *St. Petersburg University, Russia* we performed detailed *ab initio* and shell model calculations of the atomic and electronic structure of the (100) and (110) LaMnO₃ surfaces, with emphasis on the surface energies and

polarization. We have demonstrated that the electrostatic stabilization of the (110) surface could be achieved through its reconstruction by formation large concentration of O vacancies. This removes an infinite dipole moment and stabilizes polar surface. On the other hand, the polar (100) surface could be stabilized by the electronic charge redistribution nearby the surface. Both (100) and (110) polar surfaces reveal a strong increase of the Mn-O bond covalency in the first three planes nearest to the vacuum. These are first studies of LaMnO₃ surfaces.

4. In collaboration with *Antwerpen University, Belgium*, we elaborated a general theory of *bound polarons* in oxides. A continuum theory at arbitrary electron-phonon couplings is used for the calculation of the energies of thermal dissociation and photoionization optically induced release of an electron hole from the ground self-consistent state, as well as optical absorption to nonrelaxed excited states. Unlike the case of free strong-coupling polarons, where the ratio κ of the photoionization energy to the thermal dissociation energy was shown to be always equal to 3, here this ratio depends on the Fröhlich coupling constant α and the screened Coulomb interaction strength β . Reasonable variation of these two parameters has demonstrated that the magnitude of κ remains usually in the narrow interval from 1 to 2.5. This is in agreement with atomistic calculations and experimental data for hole O polarons bound to the cation vacancy in MgO. The thermal dissociation energy for the ground self-consistent state and the energy of the optically induced charge transfer process hops of a hole between O²⁻ ions have been calculated using INDO method. Results obtained within the two approaches for hole O⁻ polarons bound by the cation vacancies (V) in MgO and by the Mg²⁺ impurity (V_{Mg}) in corundum are compared to experimental data and to each other.

5. In collaboration with *Osnabrück University, Germany*, using CRYSTAL (DFT) calculations, we performed simulation of copper and silver adhesion on both regular and defective MgO(001) surfaces. We carefully studied adhesion and electronic properties of Ag/MgO(001) and Cu/MgO(001) interfaces which are very important for many technological applications. Using earlier optimized Ba, Cu, O and Ti atomic wave functions, we performed quantum chemical simulation for copper adhesion on the BaTiO₃(001) perovskite substrate (over both TiO₂- and BaO-terminated surfaces). In collaboration with *Ben Gurion University (Ber-Sheva, Israel)*, we combined results of the electronic structure calculations for regular and defective metal/oxide interfaces (including interatomic potentials) with a novel thermodynamic approach, and as a result explained the *mechanism of thin metal film growth* on several metal oxide surfaces.

6. In collaboration with *Uppsala University, Sweden*, we performed *ab initio* calculations on technologically advanced Ag/ α -Al₂O₃(0001) interface, for both Al- and O-terminated substrate. The main attention was paid to the analysis of substrate coverage by a metal (including adhesion energy) and *optimal adsorption sites* for Ag adatoms. We observe a qualitative difference in results for a silver adhesion on Al- and O-terminated corundum substrates. In the former case, which is an equilibrium state of corundum substrate, the small adhesion energies per Ag atom are accompanied with a negligible interfacial charge transfer, thus indicating a *physisorption*. In contrast, in the case of O-terminated corundum, substantial adhesion energies being combined with a noticeable charge transfer from silver towards a substrate clearly indicate a strong *ionic bonding*. In collaboration with *Max Planck Institute for Solid State Researches, Stuttgart, Germany* we particularly used the model of the Ag/ α -Al₂O₃(0001) interface for *ab initio* simulation on the AgCl/ α -Al₂O₃(0001) interface. We obtained the interfacial structure using VASP code. We found optimal interface configurations, as well as possible trajectories for silver ion migration inside the interface, and suggested the mechanism of ionic conductivity on this interface.

7. In collaboration with *Western Ontario University, London, Canada*, we completed a series of first principles DFT simulations on both *regular and stepped close-packed O/Al interfaces*, in order to clarify the mechanism of oxygen interaction with single-crystal aluminum surfaces. The initial stage of the interaction, which includes O₂ molecule approach to the substrate with further adsorption, is completed by almost spontaneous dissociation of molecular oxygen and arrangement of O_{ads} atoms above the hollow sites on the aluminum surface. It has been also shown that the less density of atomic packing on the aluminum surface, the energetically more favorable and faster is its reactivity towards oxygen, *i.e. oxygen adatom absorption* into the Al(001) substrate is more preferable than into Al(111). The energy gain following adsorption of molecular oxygen and its dissociation on the aluminum substrate favors this mechanism for the formation of Al₂O₃ units within the O/Al(111) interface and is sufficient to overcome the potential barriers for initial oxide growth. Together with mechanism of the initial growth of Al₂O₃ formula units on the Al(111) substrate, this study can be considered as the first attempt to describe atomistically the most important stage of metal oxidation between adsorption of molecular oxygen and oxide film growth.

8. In collaboration with *Physics and Chemistry Research Institute (RIKEN), Tokyo, Japan*, a *novel ultra fast luminescence* was found by measuring time-resolved luminescence spectra (resolution of 80 ps) of heavy-ion irradiated in alumina. Further measurements on single crystals of LiF, NaF, NaCl, KCl, KBr, KI, RbI, CsCl, CsBr, CsI, MgO, SiO₂, and diamond revealed the corresponding luminescence except for SiO₂ and diamond. The luminescence has the following common characteristics:

- 1) The ultra-short time (<100 ps)
- 2) The wavelength differs from all known bands and unusually broad bandwidths.
- 3) The super-linear increase in efficiency with an increase in the excitation density.
- 4) The decay rate and the efficiency invariant to temperature changes.

The results show that the luminescence does not arise from self-trapped excitons, free excitons, excited defects, and excited impurity centers, that is, it is not caused by the localized excited state, but multiply bound states among short-lived excited states.

9. In collaboration with *European Molecular Biology Laboratory, Grenoble, France*, and *King's College London, UK*, we have studied *neutron sensitive image plates* in a combination with a suitable scanning system, which exhibit excellent characteristics. *Storage phosphor imaging plate (IP)* are widely used as a two-dimensional integrating position-sensitive detector based on the effect of photo-stimulated luminescence (PSL). By admixture of Gd_2O_3 the storage phosphor can be sensitized to thermal neutrons utilizing the extremely high absorption cross section of gadolinium in this energy range. We have performed comparative measurements PSL recorded using a Molecular Dynamics 'Storm' scanner (635 nm) after neutron irradiation of a number of new combinations of converter/storage phosphors. Measurements have been made for a number of advanced materials, in order to characterize the intrinsic fading of the PSL signal with time after neutron irradiation. The X-ray sensitivity and fading of several of these compounds have also been measured. We have prepared image plates by layering Eu^{2+} doped BaSrFBr phosphor alternately with Gd_2O_3 converter. Prototype image plates have been constructed and tested using a spraying technique for the phosphor/converter. We used optical spectroscopy for the characterization of radiation defect aggregation in oxide materials.