Final technical report for grant #DE-FG03-02ER45986; Design of the first magnetic piezoelectric

Nicola Spaldin
Materials Department, University of California,
Santa Barbara, California 93106-5050

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The following achievements were made during the course of this grant:

We developed a thorough understanding of piezoelectricity in antiferromagnetic wurtzite structure MnO.

We explained the absence of ferromagnetism in high quality samples of transition-metal-doped ZnO, and proposed a scheme for obtaining robust ferromagnetism in ZnO-based systems.

We demonstrated that the MgO-ZnO-CdO system is a promising candidate for the production of polarization field-effect transistors.

Seven journal articles were published and nine talks presented on this work. The grant supported one graduate student who successfully received her PhD degree.

Magneto-structural coupling in wurtzite structure MnO. During the first year of the project, we calculated the magneto-structural properties of wurtzite structure MnO, within the local spin density approximation (LSDA) to density functional theory. We found an insulating, antiferromagnetic ground state, with strong magneto-structural coupling and a large piezoelectric response. This was an important result since it demonstrated, for the first time to our knowledge, that piezoelectricity and magnetism could coexist. We then extended our studies of wurtzite MnO using two "beyond-LDA" methods; the LDA+U (within the VASP implementation) and our own pseudopotential self-interaction corrected scheme.[1] Our

[1] A. Filippetti and N. A. Spaldin, *Self-interaction corrected pseudopotential scheme for magnetic and strongly-correlated systems*, Phys. Rev. B **67**, 125109 (2003)

motivation is three-fold. First, the LSDA calculations for piezoelectricity posed a significant technical difficulty, in that the LSDA ground state has overlapping conduction and valence bands at one point (Γ) in k-space. Since a metallic system can not sustain a polarization, we employed cheating and calculated the polarization on a shifted k-point grid that avoided the offending Γ-point. Clearly we needed to test the validity of this trick. Second, developing an understanding of the origin of the large piezoelectric response in this simple idealized structure will allow us to optimize the piezoelectric response in more complex systems. And finally, this is a simple system in which to compare the results of LDA+U calculations (over a range of U values) with our pseudopotential self-interaction corrected (pseudo-SIC) method. We found [2]:

i) the method used to calculate the polarization within the LSDA was indeed valid;

ii) inclusion of either a U or self-interaction corrections reduces the piezoelectric response slightly, with a larger U giving a larger reduction. This suggests that the piezoelectricity might be driven by O $2p$ - Mn $3d$ hybridization (as we previously determined for ZnO)[3] since this hybridization is also reduced by increasing U; and

iii) the LDA+U method is unable to reproduce the amount of gap-opening obtained within the pseudo-SIC formalism even at U values of 7 eV. We believe that the reason for this is that the gap lies between a mixed Mn $3d$ / O $2p$ valence band, and a conduction band edge composed of Mn s states, rather than the $d-d$ gap for which the LDA+U method is designed. The pseudo-SIC method is able to correct the valence band appropriately, whereas the LDA+U pushes up the empty d states, but leaves s states unaffected.

Search for ferromagnetism in doped ZnO. The first component of our theoretical study was been the search for ferromagnetism in transition metal doped ZnO-based semiconductors. In year 1 we predicted the occurrence or absence of ferromagnetism in a range of structures by calculating the relative stability of the likely magnetic phases of candidate materials within the local spin density approximation (LSDA). We specifically explored two transition metals (Mn and Co) over a range of doping concentrations and containing a variety of likely defect structures. We found that, for most experimentally accessible doping profiles and defect concentrations, the ground states of (Zn,Mn)O and (Zn,Co)O were in fact antiferromagnetic, and that a ferromagnetic state could only be achieved by p-type doping. This was of tremendous interest since it contradicted earlier theoretical results[4] and also because

[2] P. Gopal, N. A. Spaldin and U. V. Waghmare, *First-principles study of wurtzite-structure MnO*, Phys. Rev. B **70**, 205104 (2004)

[3] N. A. Hill and U. V. Waghmare, *First principles study of strain/electronic interplay in ZnO; Stress and temperature dependence of the piezoelectric constants*, Phys. Rev. B **62**, 8802 (2000)

[4] K. Sato and H. Katayama-Yoshida, *Material design for transparent ferromagnets with ZnO-based magnetic semiconductors*, Jpn. J. Appl. Phys. II Lett. **39** L555-L558 (2000); K. Sato and H. Katayama-Yoshida, *Stabilization of Ferromagnetic States by Electron Doping in Fe-, Co- or Ni-Doped ZnO*, Jpn. J. Appl. Phys. **40**, L334-L336, (2001)

it suggested that the mechanism for the ferromagnetism could be the same as in the more well-studied transition metal-doped III-V semiconductors. Our computational predictions have subsequently been verified by accurate experiments on carefully grown bulk samples.[5]

Subsequently we extended our study to more sophisticated exchange-correlation functionals (the LSDA+U and the pseudo-SIC methods, as described above) and additional dopants/defects [6]. Our results confirmed our earlier qualitative conclusions that ferromagnetism should only exist in transition-metal-doped ZnO in the presence of p-type carriers.

Motivated by our discovery that the presence of holes is desirable for the production of ferromagnetism, we explored avenues for p-type doping of ZnO. The ability to p-dope ZnO will have far-reaching consequences beyond the magnetic properties since it will allow ZnO to compete with GaN in the wide band gap optoelectronics market. Our calculations [7] suggest that substitution of Zn by Cu is likely to produce holes in the valence band, since the Cu ion adopts a +1 configuration, with localized empty states just above the valence band edge.

Polarization, piezoelectric constants and elastic constants of ZnO, MgO and CdO. Over the past decade, nitride-based III-V semiconductors have emerged as leading contenders for many technological applications, particularly in optoelectronics and microelectronics. Their utility in optoelectronics stems in large part from their wide range of direct band gaps - 0.7 eV in InN, 3.4 eV in GaN, and 6.3 eV in AlN - combined with their ability to form complete solid solutions, which provides the entire spectrum of emission wavelengths from 1800 nm (infra-red) to 200 nm (ultra-violet). In addition, the macroscopic polarization associated with the wurtzite crystal structure plays an important role in determining the electrical and optical properties. This is particularly important in heterostructures where a difference in polarization between layers induces an electric field at the interface, which in turn is screened by the formation of a two-dimensional electron gas (2DEG). The electron mobility in such polarization-induced 2DEGs can be much higher than that in traditional impurity-doped systems; Thus high speed transistors known as POLFETs can be produced.

Presently, there is growing interest in ZnO-based materials as alternatives to the nitrides. Indeed many properties of ZnO are similar, if not superior to those of GaN. Perhaps most importantly, and in striking contrast to GaN, single crystals of ZnO can be grown readily, and used as substrates for the growth of thin film devices. This facilitates the production of much higher quality films using homoepitaxy, and circumvents the problems associated with dislocation formation from epitaxial mismatch that plagues GaN growth. The band gap of ZnO (3.4 eV) is very close to that of GaN, and it can likewise be varied systematically by alloying with MgO or CdO. However, since MgO and CdO do not occur in the

[5] A. S. Risbud, N. A. Spaldin, Z. Q. Chen, S. Stemmer, and Ram Seshadri, *Magnetism in polycrystalline cobalt-substituted zinc oxide*, Phys. Rev. B **68**, 205202 (2003)

[6] P. Gopal and N. A. Spaldin, *Magnetic interactions in transition-metal-doped ZnO: An ab initio study*, Phys. Rev. B **74**, 094418 (2006)

[7] N. A. Spaldin, *Search for ferromagnetism in transition-metal-doped piezoelectric ZnO*, Phys. Rev. B **69**, 125201 (2004).

wurtzite structure, values of the electronic and elastic properties, crucial for the modeling of heterojunction device performance, cannot be obtained experimentally.

Motivated by the potential for producing ZnO-based POLFETs, and the absence of available experimental information, we calculated the spontaneous polarizations, piezoelectric coefficients and elastic constants of wurtzite-structure MgO, ZnO and CdO. We calculate optimized structures of the materials using the standard local density approximation (LDA) to density functional theory as implemented in the VASP package. We then used the pseudo-SIC method described above to calculate the electronic properties, because the LDA fails to obtain a band gap for wurtzite-structure CdO, preventing the calculation of its polarization. We calculated the polarizations using the Berry phase method, and the piezoelectric coefficients and elastic constants were obtained from the calculated dependence of polarization and energy on the appropriate strain.

We found that the polarization gradients in the ZnO-based system are larger than those in the GaN-based system, suggesting ZnO as a promising candidate for the development of polarization field-effect transistors [8].

Educational component. Graduate student, Priya Gopal, was supported for the duration of her thesis work by this grant. She received her PhD in June 2006, and is now a postdoctoral researcher at UT Austin in the group of Prof. Kleinman working on multiferroic materials.

Failures. Our proposed collaboration with Dr. Giulia Galli's group on finite-size effects on piezoelectricity was thwarted by Lawrence Livermore National Lab.'s restrictions on hosting foreign students (Gopal is in Indian citizen).

Publications supported by this grant

Magnetic interactions in transition-metal-doped ZnO: An ab initio study, P. Gopal and N. A. Spaldin, Phys. Rev. B **74**, 094418 (2006).

Polarization, piezoelectric constants and elastic constants of ZnO, MgO and CdO, P. Gopal and N. A. Spaldin, J. Elec. Mat. **35**, 538 (2006).

Understanding ferromagnetism in Co-doped TiO_2 anatase from first principles, R. Janisch and N. A. Spaldin Phys. Rev. B **73**, 035201 (2006).

Transition metal-doped TiO_2 and ZnO – present status of the field, R. Janisch, P. Gopal and N. A. Spaldin, J. Phys.: Condens. Matter **17**, R657 (2005).

[8] P. Gopal and N. A. Spaldin, *Polarization, piezoelectric constants and elastic constants of ZnO, MgO and CdO*, J. Elec. Mat. **35**, 538 (2006)

First-principles study of wurtzite-structure MnO, P. Gopal, N. A. Spaldin and U. V. Waghmare, Phys. Rev. B **70**, 205104 (2004).

Search for ferromagnetism in transition-metal-doped piezoelectric ZnO, N. A. Spaldin, Phys. Rev. B **69**, 125201 (2004).

Magnetism in polycrystalline cobalt-substituted zinc oxide, A. S. Risbud, N. A. Spaldin, Z. Q. Chen, S. Stemmer, and R. Seshadri, Phys. Rev. B **68**, 205202 (2003).

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Materials Research Society Fall Meeting, Boston, MA, 2006 (Janisch)
Ab initio calculation of magnetic interactions in oxide-based diluted magnetic semiconductors

American Physical Society March meeting, Baltimore, 2006 (Gopal)
Computational investigation of MgO, CdO and ZnO in the wurtzite structure

Electronic Material Conference, Santa Barbara, CA, 2005 (Gopal)
Polarization, piezoelectric and elastic constants of ZnO, MgO and CdO in the wurtzite structure

American Physical Society March meeting, Los Angeles, 2005 (Gopal)
Magnetic interactions in transition metal doped ZnO

American Physical Society March meeting, Los Angeles, 2005 (Janisch)
Ab initio calculation of magnetic interactions in oxide-based diluted magnetic semiconductors

Materials Research Society Fall meeting, Boston, MA, 2004 (Invited, Spaldin)
Computational design of multifunctional oxides.

University of Lancaster, Physics Dept. Colloquium, 2004 (Invited, Spaldin)
New materials for nanospintronics

American Physical Society March meeting, Montreal, 2004 (Gopal)
First-principles study of wurtzite structure MnO

Fritz-Haber Insitute, Berlin, 2004 (Invited, Janisch)
Interfaces in Co-doped TiO_2 anatase - the key to understanding this new class of diluted magnetic semiconductors?