

## Materials design for new functional semiconductors by *ab initio* electronic structure calculation

–Prediction vs. experiment–

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The use of *ab initio* calculation for materials design is an interdisciplinary research that bridges between computational physics and applied physics. It will become indispensable for future generations in the 21st century where there will be a major shift in the structure of industry as industrialized societies evolve into information societies. Based on the successful application of materials design to the development of new spin control methods for semiconductor spintronics and new valence electron control methods known as simultaneous codoping in wide band-gap semiconductors, it is expected that *ab initio* calculation will prove to be a powerful tool with considerable future potential.

**Keywords:** *ab initio* calculation, materials design, codoping, semiconductor spintronics, wide band-gap semiconductors, valence control, magnetic semiconductors, Spin-FET, Spin transistor

### 1. Materials Design and Industrial Structure Change

In the electronics industry, devices are produced based on materials, and software is then developed to run on these devices. This corresponds to a three-layer hierarchical structure (materials → devices → software). As industrialized societies evolve into information societies in the 21st century, industries will shift the emphasis of their work from materials to devices, and from devices to software. To develop software based on new concepts, new devices must be made to implement these concepts, and new materials that possess new functions are needed for the fabrication of these new devices. Con-

versely, the discovery of new materials with new functions has a far-reaching impact not only on science and technology but also on economics and culture, and thus even in the 21st century the efficient research and development of materials with new functions will greatly influence the future of humanity. For the efficient discovery and development of advanced materials with novel properties, it is essential to design materials based on new theoretical procedures without relying solely on experiment instead of adopting the trial-and-error approach to development that has hitherto been the mainstream.

In recent years, great advances have been made in computers and computational physics procedures, and by performing *ab initio* calculations based on quantum mechanics (the basic laws at the quantum level of matter), it has become possible to quantitatively predict the physical properties of diverse systems with only atomic numbers as the input parameters. Compared with conventional theory based on simple models whose parameters have to be determined experimentally, *ab initio* calculation is perhaps the only theoretical framework that can quantitatively predict electronic states and physical properties for virtual materials and new materials that do not yet exist in the real world. Therefore, *ab initio* calculation is called as “the standard model of the condensed matters”. Previous papers have already discussed the feasibility and practicality of materials design based on the prediction of physical properties by *ab initio* calculation.<sup>1-5)</sup> Osaka University is at the forefront of this work, where this grand challenge is being met by combining novel ideas with the prediction of physical properties by *ab initio* calculation. Spe-

cifically, these research on materials design is being carried out at the Institute of Scientific and Industrial Research by Hiroshi Katayama-Yoshida, Hisatomo Harima and Koun Shirai, at the Graduate School of Science by scientific researchers Hisazumi Akai and Takeo Kotani, and at the Graduate School of Engineering Science by Masafumi Shirai and Naoshi Suzuki. This research is recognized all over the world as originating from Osaka, and the computational physics software for materials design that was developed here with the assistance of public finance has been made publicly available and is provided free of charge to many researchers and technologists.<sup>6-8)</sup>

To clarify the great usefulness and future prospects of this research, this paper describes how *ab initio* calculation is used in the design of new valence electron control methods and new spin control methods for semiconductor spintronics, and compares the predictions with experimental results.

### 2. The Design of Valence Electron Control Methods for Wide Band-Gap Semiconductors

Wurtzite ZnO ( $E_g = 3.3$  eV) and GaN ( $E_g = 3.4$  eV) have a direct transition band gap ( $E_g$ ) and are transparent to visible light. Since these materials contain N and O, which are highly electronegative, they are readily doped with electrons, but are very difficult to dope with holes. This property is known as unipolarity. Due to the electronic excitation that arises from the shift of the Fermi level corresponding to  $E_g$  due to doping with a high density of holes, the acceptor atoms leave atomic vacancies behind and undergo atomic

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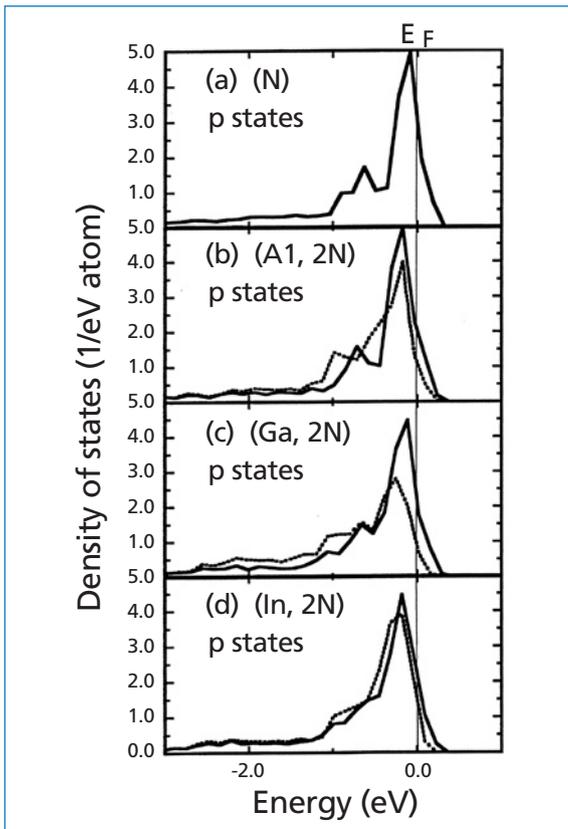


Fig. 1: Local density of states in ZnO (a) when doped only with N, and when codoped with N acceptors and (b) Al, (c) Ga or (d) In donors (1:2). As the dotted lines show, codoping has the effect of shifting the N impurity band toward lower energies. This band also becomes broader, and the effective mass decreases.<sup>9)</sup>

transfer to interstitial sites. This gives rise to a compensatory effect whereby acceptors turn into donors. To prevent this, it is necessary to use a doping method that increases the solubility of acceptor atoms by stabilizing them at substitution sites. Also, a wide band-gap semiconductor generally has a small dielectric constant; in ZnO:N (300 meV) and GaN:Mg (200 meV) the acceptor level is very deep, and at room temperature ( $\approx 30$  meV) the activation rate is extremely low. To achieve lower resistance it is necessary to use a doping method in which the acceptor level itself is made shallower.

To solve these problems at a stroke, we have developed a valence electron control method called codoping based on *ab initio* calculation, and we have applied it to numerous systems.<sup>9,11-22)</sup> Codoping involves using non-equilibrium crystal growth technique at a low temperature where diffusion is restricted to simultaneously dope the crystal with donors and acceptors in a 1:2 density ratio. This technique exploits the electrostatic repulsion between acceptors (A) and the at-

traction between acceptors (A) and donors (D) to form a meta-stable A-D-A complex which is frozen in the thin-film crystal. Using atomic layer epitaxial growth, it is possible to form an A-D-A complex alternately doped with A and D in atomic layer epitaxy (ALE). The formation of an A-D-A complex results in strong ionic properties, so that the Madelung energy is reduced. And since the lattice is relaxed by doping with two types of atom having different ionic radii, the solubility greatly increases under thermal non-equilibrium conditions. Codoping also has the effect of screening the impurity potential and changing the scattering mechanism from a long-range Coulomb scattering mechanism to a short-range multipole scattering mechanism, and thus lead to substantially increased mobility.

Due to the structure of the A-D-A complex, the wave functions of the acceptors and donors are strongly hybridized, causing the acceptor levels (bonding states) to shift toward lower energies while the donor levels (antibonding states) shift toward higher energies. As a result, the acceptor levels become to be shallower, and the activation rate of the carriers is greatly increased.

ZnO is very environmentally friendly material whose exciton bound energy of 60 meV is greater than that of GaN (24 meV) and allows excitons to exist stably even at room temperature. It is therefore also a promising material for use in light-emitting devices and next-generation short-wavelength semiconductor lasers that

use exciton light-emission mechanisms. In practice, polycrystalline ZnO has been shown to undergo CW laser action under optical excitation.<sup>10)</sup> To examine ways of producing low-resistance p-type ZnO, we have performed *ab initio* materials design calculations to study the effects of codoping ZnO with Ga, Al and In donors and N acceptors.<sup>9-11)</sup> Codoping ZnO with Ga donors and N acceptors in a 1:2 ratio results in a metastable N-Ga-N complex in the ZnO. When doped only with N, the wave function of the acceptors is strongly localized at the positions of the N atoms and a deep acceptor level (300 meV) is formed, but when an N-Ga-N complex is formed, the strong hybridization between the N and Ga wave functions causes the N acceptor levels to shift toward lower energies and the wave function spreads out. The impurity band is also made wider due to the presence of the N acceptors, and the effective mass of the acceptors becomes smaller (see Fig. 1). When doped only with Ga, the Madelung energy decreases, and with N it increases, giving rise to unipolarity. On the other hand, the N-Ga-N complex formed by codoping has a much smaller Madelung energy (see Table 1) and can thus be doped with a high density of N acceptors.<sup>11)</sup>

Based on our materials design method, Tabata, Kawai et al. have successfully produced low-resistance p-type ZnO with a carrier density of  $4 \times 10^{19} \text{ cm}^{-3}$  and a resistivity of  $2 \Omega \cdot \text{cm}$  by laser MBE with ECR-excited  $\text{N}_2\text{O}$  and  $\text{Ga}_2\text{O}_3$  as the codoping sources.<sup>12)</sup> The low-resistance p-type and n-type ZnO pro-

Table 1 The change in Madelung energy (relative to non-doped ZnO) when doping with pure donors and acceptors, and when codoping with donors and acceptors.

Doping type	Change in Madelung energy relative to non-doped ZnO (eV)
ZnO: Al	-6.44
ZnO: Ga	-13.72
ZnO: In	-9.73
ZnO: N	+0.79
ZnO: 2N	+0.91
ZnO: [Al+2N]	-4.74
ZnO: [Ga+2N]	-12.06
ZnO: [In+2N]	-7.79

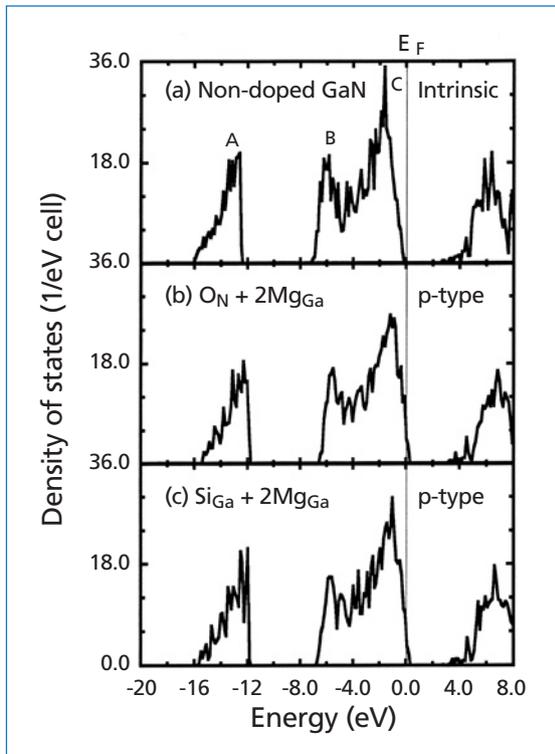


Fig. 2: Density of states in GaN.<sup>14)</sup> (a) Non-doped GaN, in which there are no doped holes. (b) GaN codoped with O donors and Mg acceptors in the ratio 1:2. (c) GaN codoped with Si donors and Mg acceptors in the ratio 1:2.

duced by codoping is transparent to visible light and electrically conductive, and is thus ideal for the electrodes of efficient solar cells and for transparent electronic devices. These materials also have important potential applications in ultraviolet light-emitting devices and short-wavelength optoelectronic devices with p-n junctions.<sup>12)</sup>

We have also managed to stabilize high densities of acceptors in GaN by codoping with Mg and Be acceptors and Si and O donors to produce the complexes Mg-Si-Mg, Mg-O-Mg, Be-Si-Be and Be-O-Be, and we have designed materials in which the formation of these A-D-A complexes makes the acceptor levels shallower, resulting in p-type semiconductors with lower resistance (Fig. 2).<sup>14-22)</sup> Compared with single doping, codoping increases the number of carriers and the electrical conductivity by approximately two orders of magnitude.<sup>15)</sup>

Many of the predicted effects of codoping<sup>13-22)</sup> have subsequently been verified ex-

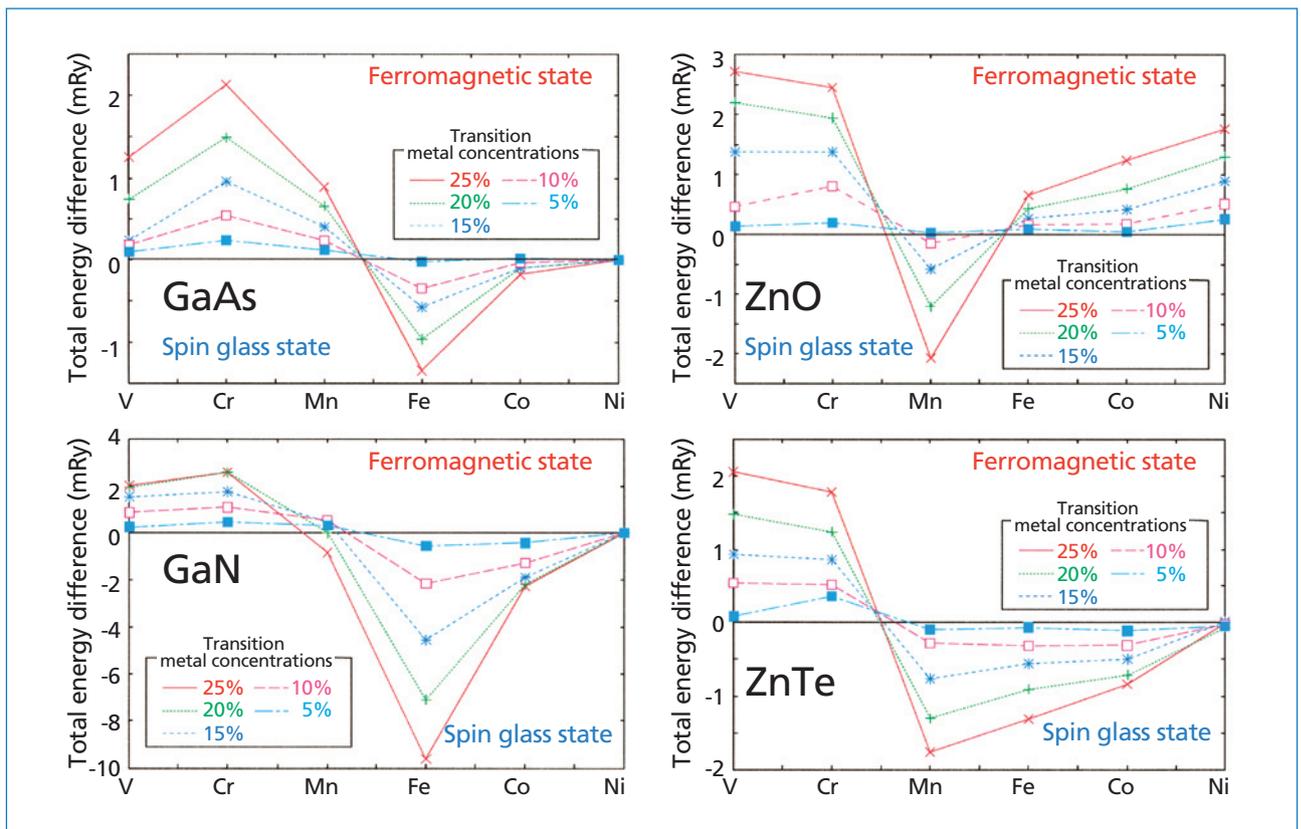


Fig. 3: Total energy difference between the ferromagnetic state and the antiferromagnetic spin glass state in GaAs, GaN, ZnO and ZnTe containing a solid solution of 5–25% transition metal ions.

perimentally. Ploog et al. experimentally verified the codoping of GaN:(2Be+O).<sup>23)</sup> When doping GaN with Be acceptors, they discovered by chance that it can be made p-type simply by performing MBE with the addition of O donors. Subsequent secondary ion mass spectroscopy (SIMS) experiments showed that the Be and O had been codoped with high densities (Be =  $2 \times 10^{21} \text{ cm}^{-3}$ , O =  $1 \times 10^{21} \text{ cm}^{-3}$ ), and as a result the carrier density ( $5 \times 10^{18} \text{ cm}^{-3}$ ) and mobility ( $150 \text{ cm}^2/\text{Vs}$ ) increased, causing the semiconductor to turn into a low-resistance p-type (resistivity  $0.02 \text{ } \Omega\text{-cm}$ ). Recently, they have also made low-resistance p-type materials by codoping with controlled quantities of Be and H<sub>2</sub>O.<sup>23)</sup>

The fact that low-resistance p-type semiconductors can be produced by codoping is also clear from the results of SIMS measurements of commercial high-brightness white LEDs with the structure /AlGaIn (n-type:  $E_g = 3.6 \text{ eV}$ )/InGaIn (MQW:  $E_g = 3.2 \text{ eV}$ )/AlGaIn (p-type:  $E_g = 4.1 \text{ eV}$ ), where the p-type regions

are found to be doped with O and Mg densities of a similar order ( $O \approx 10^{20} \text{ cm}^{-3}$ ;  $Mg \approx 2 \times 10^{20} \text{ cm}^{-3}$ ). A patent application in which the density of Mg acceptors is increased by approximately two orders of magnitude by codoping with Si or O donors to reduce the resistivity by approximately two orders of magnitude was submitted by Nichia Corporation<sup>24,25)</sup> 1-2 months after our own patent application.<sup>15)</sup>

Recently, Wessels et al. used MOCVD to perform systematic tests of codoping with Mg acceptors and O donors, and reported that the resistivity decreases from  $8 \text{ } \Omega\text{-cm}$  by a factor of approximately 40 while the acceptor levels drop to 135 meV and the p-type carrier density and mobility increase by at least an order of magnitude.<sup>26)</sup> According to our materials design method, codoping with 2Mg+O increases the p-type carrier density to  $8 \times 10^{20} \text{ cm}^{-3}$  and reduces the resistivity to less than  $0.01 \text{ } \Omega\text{-cm}$ .<sup>15)</sup>

Codoping is a generally applicable tech-

nique, and is widely applied to cases where it is difficult to control valence electrons in thermal equilibrium conditions or conventional crystalline deposition,<sup>17,30)</sup> such as low-resistance p-type  $\text{CuInS}_2:(\text{V}_{\text{Cu}}+\text{In}_{\text{Cu}}+2\text{P})$ ,<sup>22)</sup> low-resistance p-type  $\text{ZnSe}:(2\text{N}+\text{In})$ ,<sup>22)</sup> low-resistance p-type  $\text{AlN}:(2\text{C}+\text{O})$ ,<sup>27)</sup> low-resistance p-type GaN:(2C+O), low-resistance p-type  $\text{SrTiO}_3:(2\text{N}+\text{Nb})$ <sup>28)</sup> and low-resistance n-type diamond:(2P+H, 2N+B, H+S).<sup>29)</sup> A background of the designs relating to codoping and more elaborate descriptions of codoping in materials such as GaN and ZnO can be found in the references.<sup>31)</sup>

### 3. Design of Spin Control Methods for Transparent Ferromagnetic Semiconductors

Electrons in a semiconductor have two degrees of freedom: charge and spin. In the conventional electronics, the charge is controlled in the semiconductor devices in the valence and conduction electrons. Semiconductor spintronics (spin electronics) is a new branch of electronics in which the spin degree of the freedom is also controlled. The interaction between localized spin states doped into a semiconductor depends on (1) the density  $N$  and type (p-type or n-type) of carriers upon doping, (2) the scale size ( $L$ ) which is correlated to the spin coherent length, and (3) the dimensionality of the semiconductor structure ( $d = 0, 1, 2, 3$ ) fabricated by nanotechnology. It is possible to control these spin states in any way one likes by means of subminiature processing and charge control, which are both readily achieved in semiconductor materials. Here, with regard to the interaction between spin states in semiconductors, we will use *ab initio* calculation to predict the spin state interactions in different host semiconductor materials (the group II-VI semiconductors ZnO, ZnS, ZnSe and ZnTe, and the group III-V semiconductors GaAs and GaN), and their dependence on the type and doping density of transition metals (V, Cr, Mn, Fe, Co, Ni) and the type (p-type or n-type) and density of carriers in these materials. Figure 3 shows the results obtained by using the KKR-CPA method to calculate the total energy difference between the ferromagnetic state and the

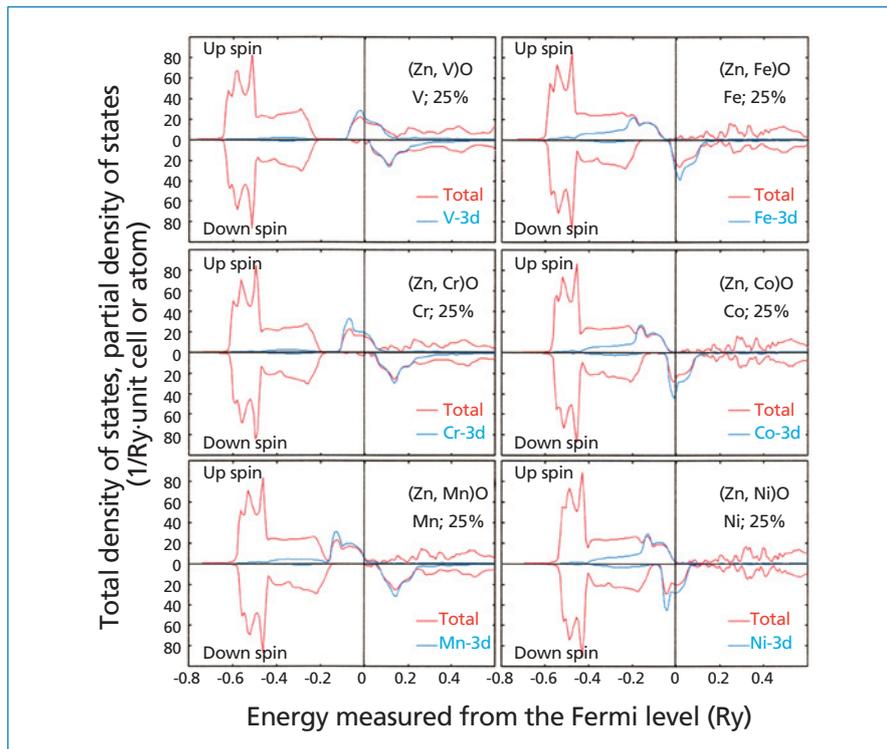


Fig. 4: The density of states produced when a transition metal (V, Cr, Mn, Fe, Co, Ni) is incorporated as a 25% solid solution in ZnO in a ferromagnetic state. Red lines show the total density of states per unit cell, and blue lines show the partial density of states for each atom with a 3d orbital. The d band, which exhibits prominent exchange splitting, occupies an increasingly large proportion as the atomic number of the transition metal impurity increases, and thus the transition metal ions are in high spin states. For Mn it can be seen that this corresponds to  $d^5$ .

antiferromagnetic spin glass state in GaAs, GaN, ZnO and ZnTe including a 5–25% solid solution of transition metal ions.<sup>32)</sup> Due to lack of space, the results for ZnS and ZnSe are omitted.

In group II-VI semiconductors, V and Cr all form ferromagnetic half-metal states (where a spin in one direction has a metallic state and a spin in the opposite direction has an insulating state), and it is possible to produce and extract 100% spin-polarized electrons from the Fermi surface (see Fig. 4).<sup>32)</sup> With V and Cr, the Fermi level is situated at the  $t_2$  state, which is the strong anti-bonding state of p-d hybridization (between the transition metal's 3d $\epsilon$  orbital (d(xy), d(yz), d(zx)) and the p orbital of the host material ( $p_x, p_y, p_z$ )). This p-d hybridization causes the band energy to decrease by allowing 3d holes with spin-up states (majority spin) to migrate through the crystal, and stabilizes

the ferromagnetic half-metal state because the ferromagnetic double exchange interaction overcomes the antiferromagnetic superexchange interaction. This mechanism for the expression of magnetism has already been proposed and discussed by Akai for the case of (In, Mn)As.<sup>35)</sup> From the viewpoint of materials design, strong ferromagnetism can be expected from V and Cr in group II-VI semiconductors.

When Mn is present in a group II-VI semiconductor, the Zn<sup>2+</sup> is substituted with Mn<sup>2+</sup> (d<sup>5</sup>) to form an insulator, the carriers are not doped, and the antiferromagnetic superexchange interaction predominates so that the ground state is an insulating antiferromagnetic spin glass. If holes are doped into these systems by N acceptors, most of the holes enter  $t_2$  states with strong p-d hybridization, the Mn<sup>2+</sup> (d<sup>5</sup>) changes into Mn<sup>3+</sup> (d<sup>4</sup>), the 3d holes in up spin states migrate

through the crystal via the strong p-d hybridization, and the ferromagnetic double exchange interactions become predominant resulting in a ferromagnetic half-metal state (Fig. 4).<sup>34)</sup> The possibility that ZnO or GaN that has been doped with a high density of Mn and holes may have a high Curie temperature ( $T_c$ ) has also been discussed in terms of the mean field approximation due to p-d interactions.<sup>35)</sup> On the other hand, in the case of electron doping with a Ga donor (Mn<sup>2+</sup> + electrons), the electron states in the vicinity of the Fermi level for down-spin states are located at the bottom of the conduction band. These states includes almost no Mn 3d components, and since the doped electrons enter the Zn 4s orbitals (which are in the conduction band of the ZnO host material), the 3d electrons are unable to migrate and remain as Mn<sup>2+</sup> (d<sup>5</sup>) so that the antiferromagnetic superexchange interaction predominates and the antiferromagnetic spin glass state is maintained<sup>34)</sup> (Figs. 4, 5).

For Fe, Co and Ni in ZnS, ZnSe and ZnTe, the Fermi level is situated at the localized e states (in the band gap) where the p-d hybridization (between 3d  $\gamma$  orbitals and p orbitals) is weak. This results in weak migration properties, and thus the antiferromagnetic superexchange interaction predominates and an antiferromagnetic spin glass state is achieved. On the other hand, for Fe, Co and Ni in ZnO, exchange splitting causes the down-spin states to enter the conduction band. As a result, the 3d electrons migrate through the crystal due to the s-d hybridization between the conduction band (Zn 4s) and 3d orbitals (e states), and the ferromagnetic double exchange interaction predominates so that the ferromagnetic half-metal state assumes the ground state<sup>34)</sup> (Fig. 4). In ZnO, since it is very easy in practice to produce a low-resistance n-type semiconductor by doping with a donor such as Ga, Al or In, it is possible to achieve a stable transparent ferromagnetic state with a high  $T_c$  by electron doping with Fe, Co or Ni (Fig. 5).<sup>34)</sup> When V, Cr, Mn + holes, Fe, Co or Ni is doped into ZnO, exchange splitting outweighs crystal field splitting, resulting in a high spin state and a large saturated magnetic moment.<sup>34)</sup> Such systems absorb long infrared light, but

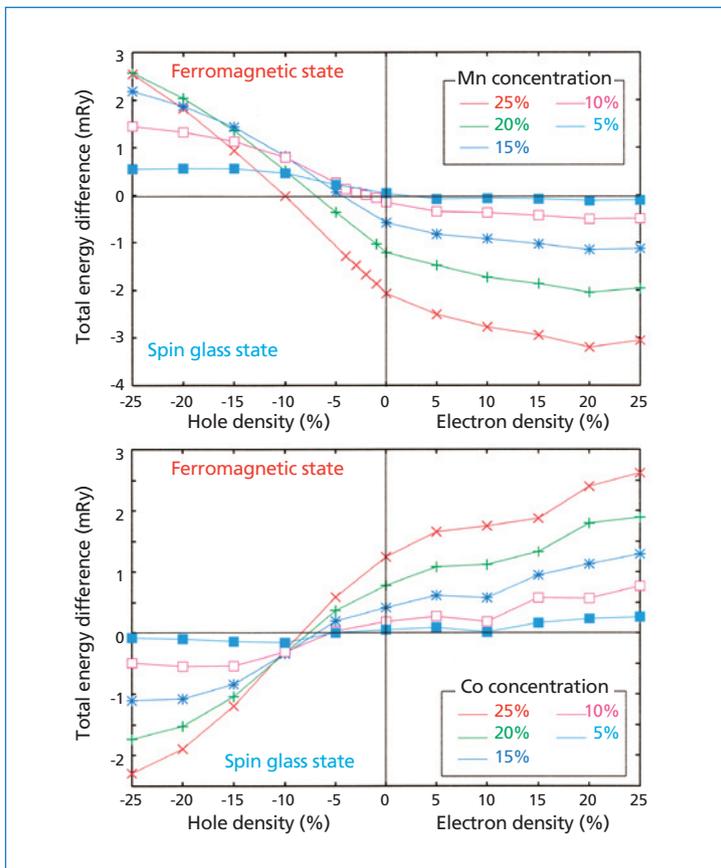


Fig. 5: The dependence of the total energy difference between the ferromagnetic state and antiferromagnetic spin glass state on the hole and electron densities in solid solutions of 5–25% transition metal ions (Mn, Co) in ZnO.

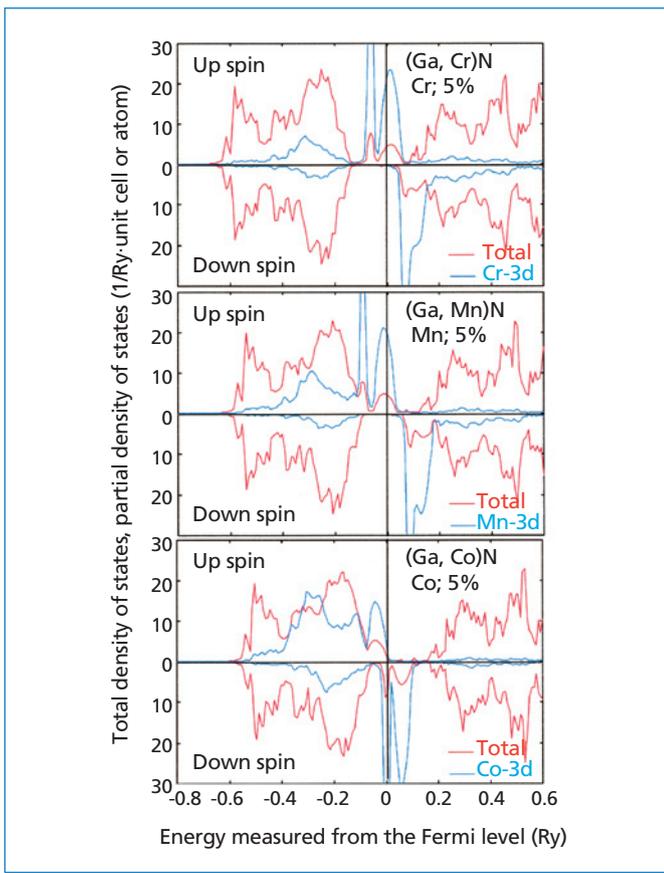


Fig. 6: The density of states obtained by forming a 5% solid solution of transition metal ions (Cr, Mn, Co) in GaN in a ferromagnetic state. Red lines show the total density of states per unit cell, and blue lines show the partial density of states for each atom with a 3d orbital. In the case of Cr and Mn, the Fermi level is situated in a band originating from spin-up  $t_2$  states, whereas in the case of Co the Fermi level is situated in a band of down-spin  $e$  states.

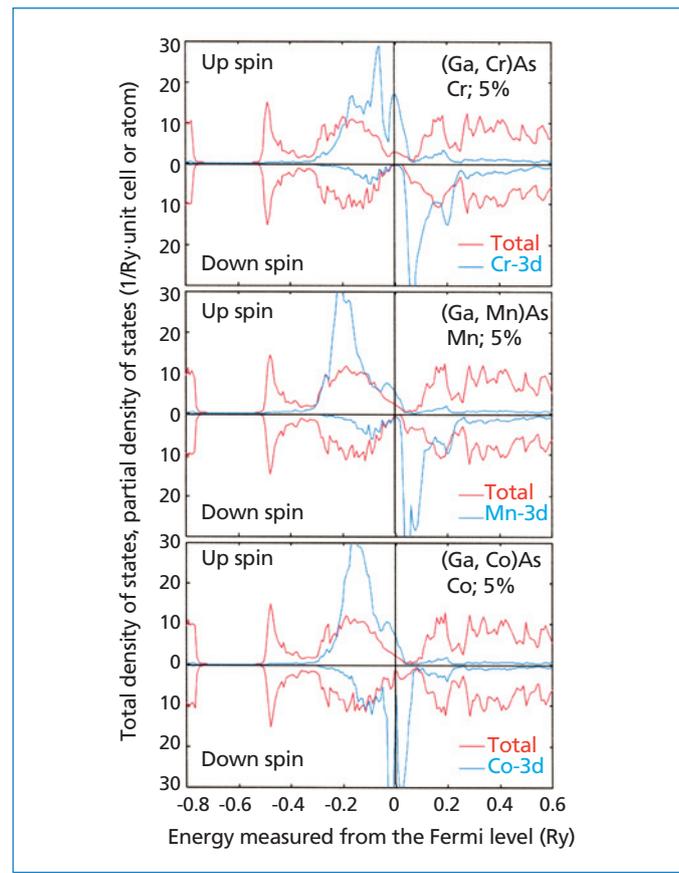


Fig. 7: The density of states obtained by forming a 5% solid solution of transition metal ions (Cr, Mn, Co) in GaAs in a ferromagnetic state. Red lines show the total density of states per unit cell, and blue lines show the partial density of states for each atom with a 3d orbital. In the case of Cr and Mn, the Fermi level is situated in a band originating from spin-up  $t_2$  states, whereas in the case of Co the Fermi level is situated in a band of down-spin  $e$  states.

in the visible light region they hardly absorb any light except for absorption by the excitation of inner-shell 3d orbitals in the transition metal, resulting in a transparent ferromagnetic material. For example, Co produces a skeleton transparent ferromagnetic semiconductor material with a cobalt blue color.

Doping GaN or GaAs with V, Cr or Mn has the effect of introducing holes into the semiconductor. Spin-up 3d holes that are close to the Fermi level mainly enter a  $t_2$  state with strong p-d hybridization (between 3d  $\epsilon$  orbitals and p orbitals), which allows them to migrate through the crystal, resulting in a ferromagnetic half-metal state due to the so-called double-exchange interaction arising from the reduction of band energy. In particular, the most stable ferromagnetic states are achieved with V and Cr<sup>36,37</sup> (see Figs. 3, 6 and 7). When GaN is doped with Mn, the Mn exhibits ferromagnetism when it is doped with a low concentration and occupies few

sites. But as its concentration increases, the number of antiferromagnetic superexchange interactions between closest-neighbor Mn-N-Mn atoms increases, causing it to switch from the ferromagnetic state into an antiferromagnetic spin glass state<sup>36</sup>) (see Fig. 3). If the holes are compensated by doping these systems with the O donors, the antiferromagnetic spin glass state becomes more stable.<sup>30</sup> When Fe<sup>3+</sup> ( $d^5$ ) is doped into GaN or GaAs, the carriers are undoped and the antiferromagnetic spin glass becomes stable due to the antiferromagnetic superexchange interaction. Doping Co and Ni into GaAs and GaN causes the states close to the Fermi level to have opposite spins, weakening the p-d hybridization (between the 3d  $\gamma$  orbitals [ $d(3z^2-\gamma^2)$ ,  $d(x^2-y^2)$ ] and p orbitals [ $p_x$ ,  $p_y$ ,  $p_z$ ]) and causing localized  $e$  states to appear in the band gap. This weakens the migration properties and allows the antiferromagnetic superexchange interaction to predominate over

the ferromagnetic double exchange interaction, resulting in an antiferromagnetic spin glass state.<sup>37</sup>)

These results correspond well with the results of experimental measurements. For example, recent measurements of optical transmittance in ZnO doped with transition metals synthesized by laser MBE have shown that it forms a transparent material.<sup>38</sup>) ZnO doped with 15% Co exhibits ferromagnetism above room temperature (Curie temperature  $T_c = 280$  K),<sup>38</sup>) while Ni-doped ZnO is ferromagnetic at low temperature and superparamagnetic at room temperature, and the existence of ferromagnetic interaction has been observed.<sup>30</sup>) For the (Ga,Mn)As system, experiments conducted before the materials design have shown that it forms a ferromagnetic material with a  $T_c$  of about 100 K, which agrees well with the calculated results.<sup>40</sup>) Experiments have also been performed recently with (Ga,Cr)As, Yoshino et al. have reported

that it exhibits ferromagnetism.<sup>41)</sup> Shirai<sup>42)</sup> has used a full-potential linearized augmented-plane-wave (FLAPW) super-cell method to design (Ga,Cr)As and CrAs materials with a zinc-blende structure that exhibit ferromagnetism, and a zinc-blende type ferromagnetic CrAs half metal with a  $T_c$  of over 400 K was recently synthesized by Akinaga et al.<sup>43)</sup> There are other systems apart from these on which no experiments have been performed so far, so further experimental investigations are expected. Materials design methods of this sort have recently been extended to the design of other materials such as group III-V/II-VI superlattice magnetic semiconductors,<sup>44)</sup>

Si, Ge, perovskite SrTiO<sub>3</sub>,<sup>45)</sup> chalcopyrite-type CuGeP<sub>2</sub>, CuAlS<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>.

Some possible device applications of this technology are as follows. A crystalline mixture of Mn (antiferromagnetic) and Fe (ferromagnetic) in ZnO (ZnO:Fe<sub>x</sub>Mn<sub>1-x</sub>) or of Cr (ferromagnetic) and Mn (antiferromagnetic) in ZnO (ZnO:Cr<sub>x</sub>Mn<sub>1-x</sub>) can be produced so as to keep the material in a paramagnetic state on the threshold of ferromagnetism. This mixture is deposited on a substrate such as GaAs or Si. Since it is transparent, it allows visible light to pass through and strike the substrate, where it stimulates electrons and holes. By applying a bias voltage, the holes

and electrons can be guided to the paramagnetic region, and if this can be done in sufficient quantities to produce a ferromagnetic half-metal state by optical excitation, then this structure can be made magnetic simply by shining light onto it. It is also possible to fabricate transistors from Mn-doped ZnO (ZnO:Mn). Although this is an antiferromagnetic material, it can be changed from an antiferromagnetic insulator into a ferromagnetic half-metal state by using semiconductor superstructure techniques to fabricate a /metal/insulator/semiconductor/ superstructure consisting of /p-type ZnO/insulating ZnO/ZnO:Mn/ and doping the ZnO:Mn layer with

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holes by applying a bias voltage. This allows a 100% spin-polarized current to flow, and it is thus possible to make spin-FETs and spin-transistors.<sup>46)</sup> It seems likely that semiconductor spintronics devices of this sort will soon be realized.

#### 4. Conclusion

In the 21st century, the most important problems that need to be addressed on a worldwide scale are the energy problems, environmental problems, and the problems of addressing the medical needs of an aging society. Materials design can help to solve these problems, and the future of human-

ity depends strongly on whether or not it is possible to efficiently develop highly efficient energy conversion materials, environmentally harmonious materials, and materials for medical care applications. *Ab initio* materials design is likely to play an important role in this effort. So when taxpayers ask us why we are studying *ab initio* materials design, we tell them it is for the distant future of humanity.

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Onward and upward

#### Note added in proof

**Added note (1):** Complex nature of very shallow acceptor levels of 14 meV from the valence band maximum in Mg doped p-type  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  (band-gap energy is 4.1 eV) is observed and its acceptor is activated even at 100K. [Y. Zohta, Y. Iwasaki, S. Nakamura, and T. Mukai, *Jpn. J. Appl. Phys.* 40, L423 (2001)]. See the discussion of the codoping (O+2Mg, Si+2Mg) for the fabrication of the low-resistive p-type GaN in the recent review paper [H. Katayama–Yoshida, T. Nishimatsu, T. Yamamoto, and N. Orita, *J. Physics: Condens. Matter* 13, 8901 (2001)].

**Added note (2):** Room temperature ferromagnetism in Mn doped GaN (Curie temperature  $T_c \sim 940\text{K}$ ), [S. Sonoda, S. Shimizu, T. Sasaki, Y. Yamamoto, and H. Hori, *J. Crystal Growth*, in press], and Cr doped GaN ( $T_c > 400\text{K}$ ) [M. Hashimoto, Y.-K. Zhou, M. Kanamura, and H. Asahi, *Solid State Commun.* 122, 37 (2002).] are fabricated based upon the materials design. However, the predicted  $T_c$  from the *ab initio* calculation is  $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{N}$  ( $T_c=350\text{K}$ ),  $\text{Ga}_{0.95}\text{Cr}_{0.05}\text{N}$  ( $T_c=500\text{K}$ ),  $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$  ( $T_c=260\text{K}$ ), and  $\text{Ga}_{0.95}\text{Cr}_{0.05}\text{As}$  ( $T_c=520\text{K}$ ), [K. Sato, P. H. Dederichs, and H. Katayama–Yoshida, to be published.].

**Added note (3):** Higher  $T_c$  ( $T_c \sim 15\text{K}$ ) in Cr doped ZnTe is reported [H. Saito, W. Zaets, S. Yamagata, Y. Suzuki, and K. Ando, *J. Appl. Phys.* 91, 8085 (2002)]. However, the predicted  $T_c$  from the *ab initio* calculation is  $\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Te}$  ( $T_c=350\text{K}$ ),  $\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Se}$  ( $T_c=300\text{K}$ ),  $\text{Zn}_{0.95}\text{V}_{0.05}\text{Te}$  ( $T_c=200\text{K}$ ), and  $\text{Zn}_{0.95}\text{V}_{0.05}\text{Se}$  ( $T_c=400\text{K}$ ), [K. Sato, P. H. Dederichs, H. Katayama–Yoshida, to be published.].

**Added note (4):** Higher  $T_c$  ( $T_c > 350\text{K}$ ) in V doped n-type ZnO is reported [H. Saeki, H. Tabata and T. Kawai, *Solid State Commun.* 120, 439 (2001)]. However, the predicted  $T_c$  from the *ab initio* calculation is  $\text{Zn}_{0.85}\text{V}_{0.15}\text{O}$  ( $T_c=480\text{K}$ ), [K. Sato, P. H. Dederichs, H. Katayama–Yoshida, to be published.].

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