Design of new ferromagnetic materials with high spin moments by first-principles calculation

Design of new ferromagnetic materials with high spin moments by first-principles calculation

Masaaki Geshi, Koichi Kusakabe and Naoshi Suzuki

Division of Frontier Materials Science, Department of Materials Engineering Science,
Graduate School of Engineering Science, Osaka University, 1-3, Machikaneyama-cho, Toyonaka
560-8531, Japan

Abstract
We have searched for a new highly spin-polarized ferromagnet which has a
higher spin moment than that of known half-metallic transition metal pnictides
with the zinc-blende structure by first-principles calculations. To generate the
high spin moment we focus on Gd compounds. Our calculation shows that
a $(GdN)_1/(CrAs)_1$ structure is a ferromagnetic material. The total magnetic
moment of this ferromagnet is over 9.9 μ_B per chemical formula.

Highly spin-polarized materials are one of the most fascinating materials for spintronics
devices. In particular, 3d-transition-metal (TM)–sp-semiconductor compounds in the zinc-
blende (ZB) structure have been extensively studied because they have completely spin-
polarized states, called half-metallic states, and have been experimentally fabricated [1, 2].
The mechanism of magnetism of the 3d-TM–sp-semiconductor compounds has been revealed,
but the maximum spin moment in this series of compounds is at most 4 μ_B for ZB-MnAs as
shown in the literature [3]. If the ferromagnetic (FM) state were realized, ZB-MnA (A = S,
Se, Te) would have the spin moment of 5 μ_B. Unfortunately this possibility is denied by a
theoretical work [4]. The high spin moment is an advantage for application to practical devices.
Thus, our aim is to search for new FM materials that have higher spin moment than 4 μ_B. For
this purpose we have focused on rare-earth metals. f orbitals can accommodate more electrons
than d orbitals and a larger magnetic moment can be expected.

However, because the strongly localized spin states of f electrons, it may be difficult to
make dispersive bands across the Fermi level. In the case of ZB-CrAs, one of three electrons
occupying d orbitals is accommodated in the $d\varepsilon$ band which is dispersive. It is an itinerant
electron and can make the double-exchange mechanism switch on. The spins of those three
electrons align in parallel due to Hund's rule. The existence of both factors may be an origin
of the high spin-polarizability of the system.

Based on the above consideration we have designed a $(RN)_1/(CrAs)_1$ (R = rare earth)
superlattice structure based on the ZB structure. Why we choose nitrogen in pnictogen is that

rare-earth nitrides have more potential to become FM than rare-earth phosphides or rare-earth arsenides or rare-earth antimonides [5] though the ground state structure of RN compounds is rock-salt. This system has itinerant electrons coming from Cr and high spin localized moment coming from the rare-earth metals. This system satisfies the two factors as mentioned above. In the rare-earth metals we have focused on Gd, because it has seven f electrons and is expected to yield the maximum spin moment in lanthanides. Moreover, to form the ZB structure six electrons per formula unit are required. For example, in ZB-CrAs, three electrons $(3d^2 4s^1)$ of Cr and three electrons $(3p^3)$ of As mainly contribute to the bond formation. For GdN, $(5d^1 6s^2)$ of Gd and $(2p^3)$ of N may contribute to form the structure. In these compounds, due to the strong Hund coupling, 4f electrons on the Gd atom have the same parallel spin in the low energy states. These considerations may allow us to treat the 4f electrons and the others independently, or we may say that 4f states should not be hybridized with the other states from these physical viewpoints. Thus, we use an LSDA + U method [6] to divide the 4f states and the other states. The LSDA + U method including the SO coupling effect is one of the standard treatments of 4f elements [7]. We have calculated electronic structures of $(GdN)_1/(CrAs)_1$ and discuss them in this paper.

A full potential linearized augmented plane wave method based on the density functional theory was used to calculate the electronic structure. The calculation has been carried out with the WIEN2k code [8]. We performed spin-polarized calculations and employed a generalized gradient approximation (GGA) [9] for an exchange–correlation functional (spin-GGA calculation). The muffin-tin (MT) radii are $0.22a_{cubic}$, $0.18a_{cubic}$, $0.18a_{cubic}$, and $0.18a_{cubic}$ for Gd, Cr, N, and As, respectively, for calculations not to optimize atomic positions, where a_{cubic} is a lattice constant of the cubic cell. The $R_{MT}K_{max}$ value is fixed at 7.00, where R_{MT} is a minimum MT radius and K_{max} is a maximum reciprocal lattice vector. 100 **k**-points were sampled in the first Brillouin zone. In all calculations a spin–orbit (SO) coupling effect is included.

We calculated the system having four inequivalent atoms as shown in figure 1(a). These x and y axes are rotated by 45° from the ZB structure. This structure can be considered as one monolayer of ZB-CrAs in the conventional cell being replaced by a GdN monolayer. The lattice constants are given as $a = a_{cubic}/\sqrt{2}$ Å and $c = a_{cubic}$ Å. Calculations were performed for several lattice constants, 5.45, 5.65, 5.75, 5.8, 5.9 and 6.27 Å. For each lattice constant an FM, an antiferromagnetic (AFM), and a paramagnetic (PM) state between the spins of Gd and Cr were calculated. In all lattice constants total energies of FM states are lower than those of AFM ones. These differences are about 0.02 eV. The PM states are rather higher energy states than FM or AFM ones.

At 5.75 Å total energy is minimum, and at this lattice constant an optimization of four atomic positions has been done within the spin-GGA calculation. In this calculation the MT radii are 2.39, 1.96, 1.50, and 1.8 au for Gd, Cr, N, and As, respectively, to avoid overlap among their MT radii. The lattice constant, 5.75 Å, is an optimized lattice constant of ZB-GaAs in our GGA calculation, although this is overestimated against an experimental value, 5.65 Å, within a well known trend of the GGA calculation. At the starting atomic positions which are the same as the ZB structure, the nearest neighbour distance is 2.49 Å (figure 1(a)). After the optimization the nearest neighbour distance between Gd and N, d_{Gd-N}, is 2.30 Å. In the same way, d_{Gd-As}, d_{Cr-N}, and d_{Cr-As} are 3.25, 2.16, and 2.48 Å, respectively (see figure 1(b)). d_{Gd-As} is rather larger than d_{Gd-N}, d_{Cr-N}, and d_{Cr-As}. This is caused by the unit cell being fixed as cubic. We optimized the lattice constant c without optimizing the internal parameters, which is based on the assumption of growing the layer epitaxially to the c axis. Finally, the optimized lattice constant c is 4.876 Å as shown in figure 1(c). d_{Gd-N}, d_{Gd-As}, d_{Cr-N}, and d_{Cr-As} are 2.23, 2.96, 2.12, and 2.36 Å, respectively. The energy difference between the cubic
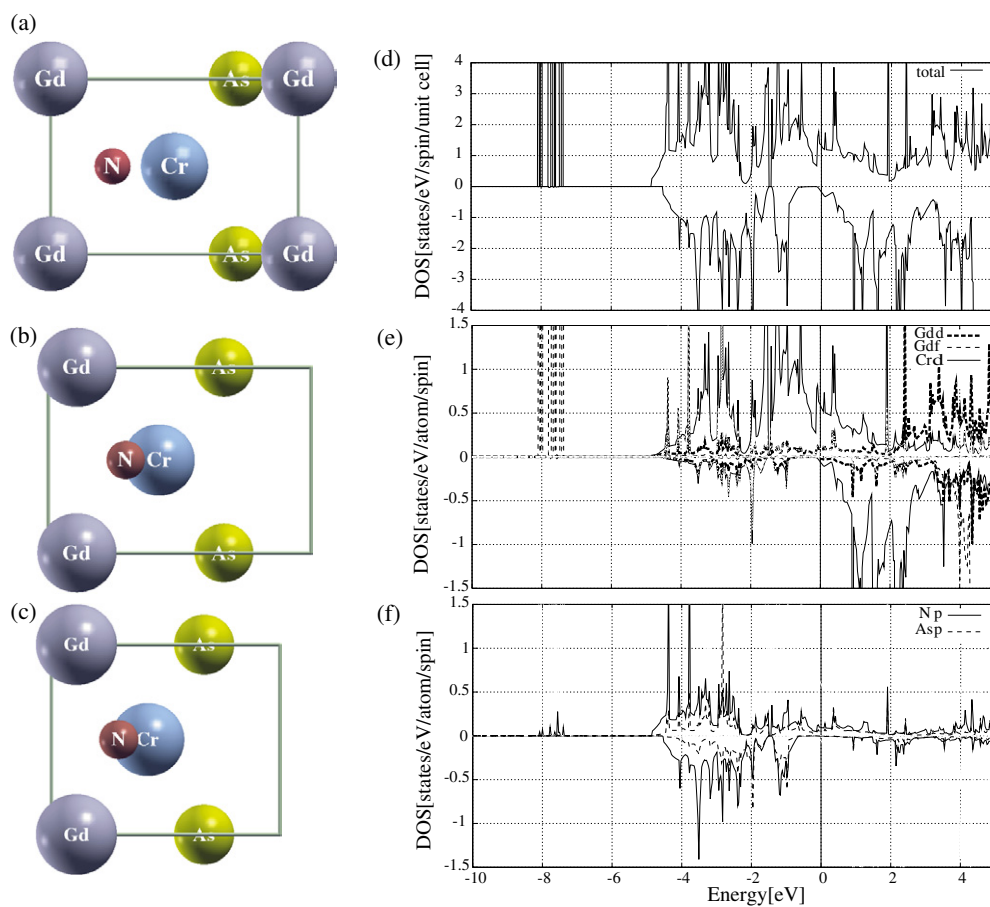
Figure 1. The calculated structure of $(GdN)_1/(CrAs)_1$: (a) before optimization, (b) the structure whose internal parameters are optimized, and (c) the structure whose lattice constant of c is optimized. The DOS of (d) total, d, and f states of Gd, (e) the d states of Cr, and (f) the p states of N and the p states of As are plotted for (c) with the LSDA $+\,U$ method. U is 0.6 Ryd.

(This figure is in colour only in the electronic version)

cell and the optimized cell is about 0.47 eV. This strongly suggests that this system must be distorted tetragonally. At this optimized state electronic structures are investigated.

Total and partial electronic densities of states (DOSs) are shown in figures 1(d)–(f) when U is 0.6 Ryd. U is determined by checking each occupation number of the 4f states being $\sim$1 and the DOS. The f states are at -8 eV and do not hybridize with the other states. The electronic states located in the vicinity of the Fermi level are mainly d states of magnetic ions (Gd and Cr) and p states of N and As. The main components at the Fermi level are obviously the d states of Cr. This means that the electronic conductivity is taken by the d electrons of Cr.

The value of the total magnetic moment is quite large and more than 9.9 μ_B. That is slightly dependent on including effects; however, the difference among them is quite small (for the GGA, the GGA $+$ SO, and the LSDA $+\,U+$ SO ($U = 0.6$ Ryd) calculations, 10.00, 9.98, and 9.99 μ_B, respectively).

To summarize the present work, we have searched for a highly spin-polarized FM which has a high spin moment greater than 4 μ_B based on the ZB structure. It is found that the

$(GdN)_1/(CrAs)_1$ superlattice structure is FM and the total magnetic moment becomes more than 9.9 μ_B per formula unit. The structure is optimized and the unit cell prefers to distort the tetrahedral structure. The present result suggests that there is a possibility to make high spin FM materials if 3d TM and rare-earth metals are suitably synthesized. The LSDA + U calculation realizes our required electronic structure; however, we have not examine closely the quantity of U. A more suitable treatment of this system may be needed.

Acknowledgments

References

[1] Shirai M, Ogawa T, Kitagawa I and Suzuki N 1998 *J. Magn. Magn. Mater.* **177–181** 1388
[2] Akinaga H, Manago T and Shirai M 2000 *Japan. J. Appl. Phys.* **39** L1118
[3] Galanakis I and Mavropoulos P 2003 *Phys. Rev.* B **67** 104417
[4] Wei S H and Zunger A 1987 *Phys. Rev.* B **35** 2340
[5] Gshneidner K A Jr and Eyring L 1978 *Handbook on the Physics and Chemistry of Rare Earths* vol 1 *Metals* (Amsterdam: North-Holland) p 532
[6] Anisimov V I, Solovyev I V, Korotin M A, Czyzyk M T and Sawatzky G A 1993 *Phys. Rev.* B **48** 16929
    Lichitenstein A I, Anisimov V I and Zaanen J 1995 *Phys. Rev.* B **52** R5467
[7] Gotsis H J and Mazin I I 2003 *Phys. Rev.* B **68** 224427
[8] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria)*
[9] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865