Above Room Temperature Ferromagnetism in Gd_2B_2 Monolayer with High Magnetic Anisotropy

Taylan Gorkan,[†] Erol Vatansever,[‡] Ümit Akıncı,[‡] Gökhan Gökoglu,[¶] Ethem Aktürk,[*,†,§] and Salim Ciraci[*,‖]

[†]*Department of Physics, Adnan Menderes University, 09100 Aydın, Turkey*

[‡]*Dokuz Eylül University, Faculty of Science, Physics Department, Tınaztepe Campus, 35390 İzmir, Turkey*

[¶]*Department of Mechatronics Engineering, Faculty of Engineering, Karabuk University, 78050 Karabuk, Turkey.*

[§]*Nanotechnology Application and Research Center, Adnan Menderes University, 09100 Aydın, Turkey*

[‖]*Department of Physics, Bilkent University, Ankara 06800, Turkey*

E-mail: ethem.akturk@adu.edu.tr; ciraci@fen.bilkent.edu.tr

Phone: +902562130835-1894. Fax: +902562135379

Abstract

In this Supplementary Material, we present all the details of Computational Method regarding Density Functional Theory (DFT), ab-initio molecular dynamics and Monte Carlo simulations.

Computational Method

DFT Calculations

Total energy and structure optimization calculations have been carried out within Density Functional Theory (DFT) using the plane-wave basis set and projector augmented wave (PAW) potentials[1] as implemented in VASP package.[2,3] The exchange-correlation potentials are represented by the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)[4] exchange-correlation functional including van der Waals (vdW) correction in DFT-D2 level.[5] Kinetic energy cutoff for plane-wave basis set is taken as 550 eV. Brillouin zone integration is performed by a 12×12×1 **k**-point grid. The convergence criterion of self-consistent field total energy calculations is taken to be 10^{-6} eV. The partial occupancies are determined using the Gaussian scheme with the smearing width of 0.01 eV. We consider SOC effect and also use PBE+U method to reveal the magnetic ground state.

In the calculations of the magnetic ground state we use PBE including Hubbard U correction for on-site Coulomb interaction,[6] i.e. PBE+U, which is necessary for atoms including 4f orbitals,[7–9] with interaction parameters of U= 6.7 eV and J=0.7 eV. The average cohesive energy (per atom) of Gd_2B_2 is calculated by using the expression, $E_c = (2E_{Gd} + 2E_B - E_{Gd_2B_2})/4$, where $E_{Gd_2B_2}$ is the optimized total energy per unit cell. The total energies of free B and Gd atoms, E_{Gd} and E_B, respectively are calculated in the same unit cell.

Phonon dispersion spectra are computed using force constants of the supercell within the framework of DFT perturbation theory as implemented in the VASP code combined with PHONOPY package[10] using an improved energy convergence criterion as 10^{-8} eV. Phonon calculation have been performed using a 3×3×1 supercell and 4×4×1 grid for **k**-point. All MD calculations have been performed using a 2×2×1 supercell and 5×5×1 **k**-point grid. A Nosé thermostat was used, and Newton's equation of motion were integrated through the Verlet algorithm with time steps of 2 fs.

In the analysis of bonding through the charge density isosurfaces, the difference charge

density $\Delta\rho$ is calculated by subtracting the atomic charge densities, i.e. ρ_B and ρ_{Gd} situated at the corresponding atomic site, from the total charge density, ρ_T. The spin density, ρ_S is calculated from the difference of charge densities of occupied spin-up and spin down states.

Monte Carlo Simulations

Monte Carlo simulation method has repeatedly proven its reliability. Very recently, electronic and magnetic properties of monolayer and bulk $\alpha - RuCl3$ have been investigated by means of first-principles and Monte-Carlo simulations. It is a known fact that $\alpha - RuCl3$ is in antiferromagnetic phase at the relatively lower temperature regions ranging from 6.5K to 15.6K.[11,12] Monte-Carlo simulation results strongly support this fact with a critical temperature 10.21K. Moreover, in Ref. 13, dynamic phase transition properties of a ferromagnetic thin film system under the influence of both bias and time-dependent magnetic fields have been used by benefiting from the Metropolis algorithm with local spin update. The numerical data given in Ref. 13 well qualitatively reproduce the previously published experimental findings[14] where time dependent magnetic behavior of a uniaxial cobalt films is studied in the neighborhood of dynamic phase transition point. The numerical tools used in the papers mentioned above are the same with the method we consider in the present paper. These works also suggest that Monte-Carlo simulation method with local spin-update scheme is a good candidate to model the real magnetic systems and to understand the underlying physics by properly adjusting the system parameters.

We investigate magnetic features of Gd_2B_2 monolayer under both biaxial compressive and tensile strains for selected directions. The spin Hamiltonian of system can be described by the following $J_1 - J_2 - J_3$ classical Heisenberg Hamiltonian:

$$\mathcal{H}_{total} = \mathcal{H}_{ex} + \mathcal{H}_{anisotropy} \tag{1}$$

here, $\mathcal{H}_{ex}$ and $\mathcal{H}_{anisotropy}$ terms refer to the energy contributions to the system originating

from the spin-spin interactions between neighbor spins up to third nearest neighbor and single-ion anisotropy, respectively:

$$\mathcal{H}_{ex} = -J_1 \sum_{\langle ij \rangle} \mathbf{S_i} \cdot \mathbf{S_j} - J_2 \sum_{\langle ik \rangle} \mathbf{S_i} \cdot \mathbf{S_k} - J_3 \sum_{\langle il \rangle} \mathbf{S_i} \cdot \mathbf{S_l} \tag{2}$$

$$\mathcal{H}_{anisotropy} = k_x \sum_i (S_i^x)^2 + k_y \sum_i (S_i^y)^2 + k_z \sum_i (S_i^z)^2 \tag{3}$$

where $\mathbf{S_i}$ denotes the classical spin (with a magnitude $S = |\mathbf{S_i}| = 7/2$ for each Gd atom) located on the ith position of the lattice. J_1, J_2 and J_3 correspond to the spin-spin interactions between nearest, second- and third-nearest spin pairs in the system. First, second and third summations in Eq. (2) are over the first, second and third nearest neighbor spin pairs, respectively. k_x, k_y and k_z terms given in Eq. (3) denote the magnetic anisotropy coefficients.

By mapping the DFT energies related to the different magnetic configurations denoted as E_{FM}, E_{AFM-1}, E_{AFM-2}, E_{AFM-3}, which are displayed in Fig. 3, the numerical values of the exchange interactions J_1, J_2, J_3 can be calculated by solving equation system

$$\begin{aligned} E_{FM} &= E_0 - 2S^2 (J_1 + J_2 + J_3) \\ E_{AFM-1} &= E_0 - 2S^2 (J_1 - J_2 - J_3) \\ E_{AFM-2} &= E_0 - 2S^2 (-J_1 - J_2 + J_3) \\ E_{AFM-3} &= E_0 - 2S^2 (-J_1 + J_2 - J_3) , \end{aligned} \tag{4}$$

where E_0 is the energy contribution that does not include magnetic interactions. On the other hand, the numerical values of the anisotropy coefficients (in Eq. 3) are calculated by making use of the magnetic anisotropy energies supported by the DFT data, which is given in Table 1. The calculated values of the exchange interactions can be found in Table S1.

We perform Monte Carlo simulation with local spin update Metropolis algorithm[15,16] to elucidate the magnetic properties of the Gd_2B_2 monolayer on a $L \times L$ square lattice.

Table S1: Exchange interaction values (in units of meV) under compressive and tensile strains for selected directions.

Strain (%)	J_1	J_2	J_3
-8	4.724	0.995	1.642
-6	4.428	0.901	1.509
-4	4.348	0.872	1.471
-2	4.420	0.907	1.396
0	4.452	0.997	1.367
2	4.379	1.086	1.306
4	4.210	1.058	1.170
6	4.025	0.969	0.981
8	2.006	2.575	-1.059

Here L is the linear size of the lattice, and it is fixed as $L = 128$ throughout this work. Periodic boundary conditions are imposed in all directions. We implemented 112 different initial realizations to obtain thermodynamic observable with high accuracy. For each initial configuration, the simulation starts at the relatively high temperature region corresponding to the paramagnetic phase, and then the temperature is gradually decreased until it reaches to the lower temperature regions. For each temperature steps, the first 2×10^4 Monte Carlo step per site (MCSS) have been discarded for the thermalization process and the numerical data have been collected over the next 8×10^4 MCSS for the thermodynamic quantities of interest. Our test calculations indicate that this amount of transient steps are found to be sufficient for the thermalization process for each applied controllable strain values. During the simulation, the following thermodynamic quantities of interest have been measured:

- Instantaneous magnetization components of the total magnetization

$$m_\alpha(t) = \frac{1}{N} \sum_i^N g\mu_B S_i^\alpha, \tag{5}$$

  here $N(= L \times L)$ is the total number of spin in the system, g is the Lande-g factor and μ_B is the Bohr magneton. Using Eq. (5), we can obtain the thermal average of the magnitude of the total magnetization according to the following definition:

$$\langle M_T \rangle = \left\langle \sqrt{\sum_{\alpha=x,y,z} m_\alpha(t)^2} \right\rangle. \tag{6}$$

- In order to determine the phase transition point, we use thermal variations of specific heat;

$$C(T) = N\left(\langle E^2 \rangle - \langle E \rangle^2\right)/k_B T^2, \tag{7}$$

and magnetic susceptibility;

$$\chi(T) = N\left(\langle M_T^2 \rangle - \langle M_T \rangle^2\right)/k_B T, \tag{8}$$

here k_B and T denote the Boltzmann constant and temperature, respectively.

References

(1) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.

(2) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.

(3) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(4) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(5) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

(6) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **1998**, *57*, 1505–1509.

(7) Oroszlány, L.; Deák, A.; Simon, E.; Khmelevskyi, S.; Szunyogh, L. Magnetism of gadolinium: a first-principles perspective. *Phys. Rev. Lett.* **2015**, *115*, 096402.

(8) Anisimov, V. I.; Aryasetiawan, F.; Lichtenstein, A. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA+ U method. *J. Phys. Condens. Matter* **1997**, *9*, 767.

(9) Turek, I.; Kudrnovskỳ, J.; Bihlmayer, G.; Blügel, S. Ab initio theory of exchange interactions and the Curie temperature of bulk Gd. *J. Phys. Condens. Matter* **2003**, *15*, 2771.

(10) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **2015**, *108*, 1–5.

(11) Sears, J.; Songvilay, M.; Plumb, K.; Clancy, J.; Qiu, Y.; Zhao, Y.; Parshall, D.; Kim, Y.-J. Magnetic order in α- RuCl 3: A honeycomb-lattice quantum magnet with strong spin-orbit coupling. *Phys. Rev. B* **2015**, *91*, 144420.

(12) Johnson, R. D.; Williams, S.; Haghighirad, A.; Singleton, J.; Zapf, V.; Manuel, P.; Mazin, I.; Li, Y.; Jeschke, H. O.; Valentí, R., et al. Monoclinic crystal structure of α-RuCl 3 and the zigzag antiferromagnetic ground state. *Phys. Rev. B* **2015**, *92*, 235119.

(13) Vatansever, E.; Polat, H. Dynamic phase transitions in a ferromagnetic thin film system: A Monte Carlo simulation study. *Thin Solid Films* **2015**, *589*, 778–782.

(14) Berger, A.; Idigoras, O.; Vavassori, P. Transient behavior of the dynamically ordered phase in uniaxial cobalt films. *Phys. Rev. Lett.* **2013**, *111*, 190602.

(15) Landau, D. P.; Binder, K. *A guide to Monte Carlo simulations in statistical physics*; Cambridge University Press, 2014.

(16) Newman, M.; Barkema, G. *Monte carlo methods in statistical physics chapter 1-4*; Oxford University Press: New York, USA, 1999.