Project Title:

Atomistic modeling of the properties of MAX phase and MXenes structures from first-principles

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Introduction

The main them of my research is materials properties modelling from first- principles. My current research activities are mainly focused on structural, elastic, electronic, magnetic, topological order, and quantum transport properties of MAX phases and their two-dimensional derivative MXenes. MAX phases are a great family of layered materials, made of transition metal carbides and nitrides with chemical formula of $M_{n+1}AX_n$, where " n" =1, 2, 3, " M" is an early transition metal, " A" is an element from an A-group of elements in the periodic table, and X is either C or N. MAX phases with ceramic nature and metallic properties possess many extraordinary mechanical, physical and chemical related characteristics such as high melting point, high thermal and electrical conductivity, high bulk modulus, excellent thermal shock resistance, damage tolerance, and microscale ductility at room temperature [Prog. Solid State Chem 28, 201 (2000), Annual Review of Materials Research 39, 415 (2009), Annual Review of Materials Research 41, 195 (2011)]. Recently, there exists a growing interest in theoretical and experimental studies of MAX phases because they have been considered as new source for obtaining novel two-dimensional transition metal carbides or nitrides, so called MXenes. The MXenes are prepared experimentally from the corresponding MAX phase by exfoliation in hydrofluoric acid [ACS Nano 6, 1322 (2012), Adv. Mater. 26, 992 (2014)]. The MXenes attract great attention due to their potential applications in sensors, catalysis, energy storage and nanoelectronics [ACS Nano 6, 1322 (2012)]. Among MAX compounds, Cr_2AlC is a typical member of MAX phases which additionally has excellent high temperature oxidation resistance [J. Am. Ceram. Soc. 90, 1663 (2007), J. Appl. Phys. 99, 076109 (2006), Acta Mater. 96, 291 (2005)]. Lin et al. experimentally studied the crystal structure of Cr_2AlC. Many theoretical and experimental attempts have so far been devoted to the electrical and mechanical properties of many MAX phases. Fortunately, there is a good agreement between theoretical predicted properties and experimentsn MAX phases, except for Cr_2AlC, Cr_2GeC. For instance, theoretically the value of the density of state at Fermi level N(Ef) is estimated to be 6.65 (state/eV per unit cell), which is much larger than the corresponding values in other M_2AlC MAX phases. However, the experiment gives the lowest electrical conductivity for Cr_2AlC in comparison to other MAX phases. In addition, the theoretical values of bulk and Young' s moduli for Cr_2AlC are much higher than those reported in the experiment. Also, the calculated thermal expansion coefficient for the Cr_2GeC is 30 % higher than that obtained experimentally [J. Appl. Phys. 106, 033501 (2009), J. Appl. Phys. 105, 013543 (2009)]. In the first part of my research, I have employed density functional theory (DFT) to resolve the discrepancy between theory and experiment on family of Cr-based MAX phases. In order to consider the electron correlation effects in the localized 3d electrons of Cr atoms, I have used the DFT+U method. I have concluded that the best agreements between theoretical and experimental results are obtained at U_{eff} values less than 1.00 eV.

At the next step of my research, I have again employed the DFT+U approach to include Hubbard U interaction onto the Cr 3d electrons of two dimensional (2D) layered Cr-based MAX phases (MXenes). 2D materials, such as graphene, have great potential for applications in a next generation of electronic and spintronic devices [Nat. Mater. 6, 183 (2007), Science 353, 6298 (2016), Nat. Rev. Mater. 1 16042 (2016)]. However, a majority of 2D materials are intrinsically non-magnetic, consequently their applications in spintronics are limited [Rev. Mod. Phys. 81, 109 (2009)]. For practical applications in spintronics it is crucial to find 2D materials with room temperature ferromagnetism and 100% spin polarization. Half-metallic magnets, with a metallic nature and complete (100%) spin polarization in one spin channel and an insulating/semiconducting property in the other spin channel, are considered to be the most promising materials for spintronics. They have a theoretically infinite magnetoresistance and can be potentially used as spin filters or detectors and sensors [Rev. Mod. Phys. 80, 315 (2008)]. Nowadays, only a few 2D materials have so far been predicted to be intrinsic half-metals. Therefore, finding 2D half-metallic materials with a room temperature spin-polarization is highly important for developing the next generation devices. One of the promising materials for spintronics might be Cr-based MXenes. It has been observed that the experimentally prepared MXenes have surfaces terminated with F, OH or other atoms [ACS Appl. Mater. Inter- faces 7, 17510 (2015)]. The functionalized MXenes are thermodynamically more favorable than the pristine ones. I have used the pristine and the functionalized MXenes with different transition metals as target materials to search for any intrinsic half-metals. I have found

that the electronic and magnetic states of pristine Cr_2C and Cr_2N can be tuned by functionalization with surface groups or/and by applying Hubbard U interaction onto the Cr 3d electrons.

Research Results and Achievements

Using a set of first-principles calculations, within density functional theory (DFT) framework based on the generalized gradient approximation (GGA) for exchange-correlation functional, I have studied the structural, electronic, magnetic and elastic properties of Cr_2AX phases with different A (Al, Ge and Ga) and X (C, N and B) elements. In order to treat the electron-correlation effects properly, I have employed the GGA+U formalism to investigate various properties. In this regard, by applying Hubbard U interaction onto the Cr 3d electrons, the formation energies, lattice constants, magnetic ground states, magnetic moments, elastic parameters and electronic density of states of the Cr_2AX were examined in detail. I have shown that it is very vital to consider different initial spin configurations, i.e., nonmagnetic (NM), ferromagnetic (FM), and anti-ferromagnetic (AFM), in the GGA and GGA+U calculations to obtain the correct magnetic ground state. A schematic picture of all considered collinear AFM magnetic states as well as NM and FM states in this study has been illustrated in Fig. 1. For a FM magnetic states, all spins on Cr atoms are parallel. The double layer AFM ordering with two consecutive Cr-layers with the same spin orientation, before changing sign upon crossing an A or X are denoted by AFM[0001]$^{A}_{2}$, and AFM[0001]$^{X}_{2}$, respectively. A single layer AFM with spins changing sign for every Cr-layer is named as AFM[0001]$_1$. The in-AFM1, in-AFM2 and in-AFM3 configurations with antiparallel spins within Cr-layers are presented in Fig. 1.

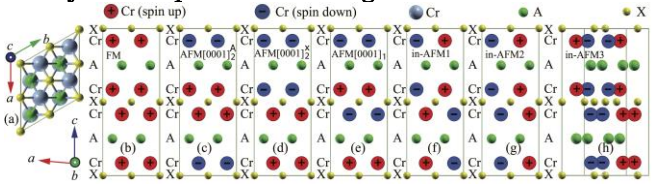

Figure 1: Schematic representations of seven initial spin configurations (I.S.C)

From our calculations, it is seen that the ground state of all Cr_2AX structures in the GGA calculations is in-plane antiferromagnetic order (in-AFM1), except for Cr_2AlB (Cr_2GaB) and Cr_2GeB that are NM (NM) and AFM[0001]$^{A}_{2}$, respectively. I have compared the computed lattice parameters (a, c, V0 and ρ), Poisson's ratio (σ), bulk (B), shear(G), and Young (E) moduli in the level of GGA and GGA+U with the available experimental data, which exist for Cr_2AlC, Cr_2GaC, Cr_2GaN and Cr_2GeC. As a typical member of Cr_2AX family, in FIG. 2 I have summarised the calculated results of the a, c, V0, ρ, σ, B, G, E, magnetic moments of Cr, Al and C atoms and final magnetic ground state at various U_{eff} values changing from 0.00 eV (equal to GGA) to 2.00 eV for Cr_2AlC MAX phase.

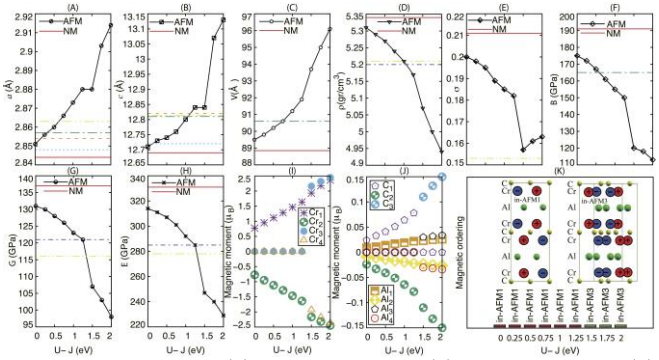

Figure 2: Our calculated (A) lattice constant; a, (B) lattice constant; c, (C) cell volume; V0, (D) mass density; ρ, (E) Poisson's ratio; σ, (F) bulk modulus; B, (G) shear modulus; G, (H) Young's modulus; E, (I) Magnetic moment per Cr, (J) Magnetic moment per C and per Al, and (K) final magnetic ordering for Cr_2AlC MAX phase.

The available experimental values taken from literatures are shown as dashed horizontal lines. As It is seen in FIG. 2 the best agreements between theoretical and experimental results are obtained at U_{eff} values less than 1.00 eV. It is noteworthy that in addition to Cr-based MAX phases, I have extended the methodology to other MAX phases (M= V, Ti, Zr, Nb and A =Al, Ge, Ga and X= C, N, B). However, it is found that they are nonmagnetic systems.

At the next step of my research, I have intensively studied the structural, electric, and magnetic properties of various pristine and functionalized MXenes with F, OH and O groups. It is found that in the MXenes, the Cr_2C, Cr_2N show very interesting magnetic properties upon different functionalization. My DFT results show that the electronic state of pristine Cr_2C changes from metal FM to half-metal FM by introducing the correlation effect onto the Cr 3d electrons (See FIG. 3).

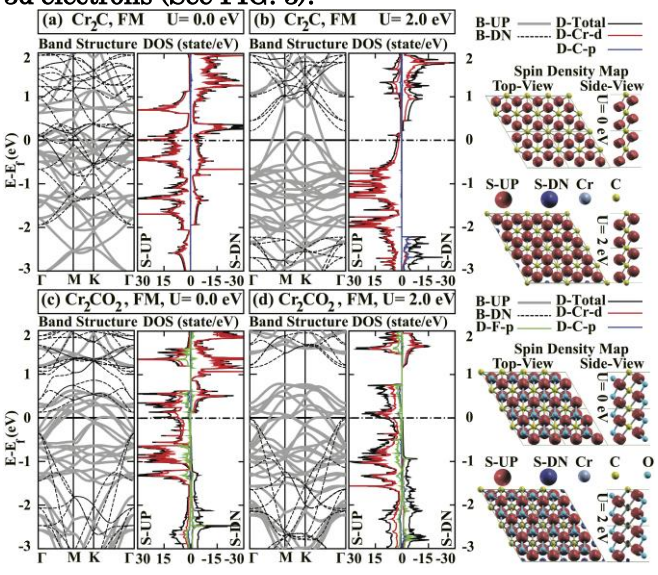

Figure 3: Calculated DFT band structure, partial and total density of states in the GGA and GGA+U [U= 2.0 eV] levels for (a, b) pristine FM Cr_2C and (c,d) functionalized FM Cr_2CO_2 .

Cr_2N has a larger number of valence electrons than Cr_2C. Hence, in contrast to Cr_2C, the ground state of Cr_2N is antiferreomagnetic as shown in FIG. 3. However, the half-metallicity appears in Cr_2N upon surface functionalizations with O. This is important because the synthesis of pristine half-metallic MXenes such as Cr_2C is difficult when the etching technique is employed. The half-metallicity in Cr_2C

upon surface functionalizations with O has been also
resulted in the both GGA and GGA+U levels.

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Publication]

Mohammad Khazaei, Vei Wang, Cem Sevik, Ahmad Ranjbar, Masao Arai, and Seiji Yunoki, "Electronic structures of iMAX phases and their two-dimensional derivatives: A family of piezoelectric materials" Phys. Rev. Materials 2, 074002 (2018).

Mohamad Khazaei, Ahmad Ranjbar, Keivan Esfarjani, Dimitri Bogdanovski, Richard Dronskowski, and Seiji Yunoki, "Insights into exfoliation possibility of MAX phases to MXenes" Phys. Chem. Chem. Phys. 20, 8579 (2018).