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First-principles study of electronic and magnetic properties of $TlNiO_3$

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ABSTRACT

First-principles calculations on the electronic and magnetic properties of $TlNiO_3$ reveal that the antiferromagnetic structure with the insulating ground state is more stable than other possible configurations in the monoclinic structure. The band gap of the antiferromagnetic insulating ground state is predicted to be 0.18 eV. The spin magnetic moments of Ni(1) and Ni(2) ions are about ± 1.62 and $\pm 0.92\mu_B$, respectively. The differing chemical environments between the two Ni positions as well as charge disproportionation effect result in unequal magnetic moments for adjacent Ni atoms in the monoclinic $TlNiO_3$.

1. Introduction

The metal–insulator (MI) transition in perovskite $ANiO_3$ (A=rare earth or yttrium) associated with charge disproportionation (CD) and spin transition has been studied extensively by application of pressure, temperature and substitution in recent years [1–8]. The magnetic and electric properties of the $ANiO_3$ family depend on the crystallographic distortion due to different sizes of A ions. $LaNiO_3$ shows metallic character with a Pauli paramagnetism, whereas $YNiO_3$ and $LuNiO_3$ show Curie–Weiss paramagnetism with antiferromagnetic order below a T_N [9]. MI transition phenomena, recently discovered in this system, are also strongly correlated with the structural distortions [10–13].

Up to now, most researches, however, have been performed on the series of the nickelates based on rare earth and yttrium ion. A new perovskite $TlNiO_3$ in which A is not rare earth has been prepared under high pressure–high temperature conditions using belttype apparatus [14,15]. The results show that the Ni in $TlNiO_3$ is in the trivalent state in the orthorhombic phase (space group Pbnm) at high temperature, and in a CD state in the monoclinic phase (space group P21/n) at low temperature, where the structure contains two crystallographically independent Ni positions (Ni(1) and Ni(2)). The Pbnm structure is with a single site for Ni cations, the (NiO_6) octahedra exhibit average $\langle$Ni–O$\rangle$ distance close to 1.971 Å. The monoclinic structure consists of an expanded (Ni_1O_6), ($\langle$Ni(1)–O$\rangle$=2.032 Å) and contracted (Ni_2O_6) octahedral, ($\langle$Ni(2)–O$\rangle$=1.907 Å) [14]. The measurements of temperature dependence of magnetic susceptibility indicate that $TlNiO_3$ underlines an antiferromagnetic (AFM) behavior with T_N=100 K [16]. However, to the best of our knowledge, there are no theoretical calculations about magnetic properties of $TlNiO_3$ so far. In this paper, we study the electronic and magnetic properties of $TlNiO_3$ by the full-potential linear augmented plane wave plus local orbital method. Note that the crystal structure of $TlNiO_3$ is the monoclinic perovskite with the space group of P21/n in this study [14].

2. Computational method

All the calculations are performed with WIEN2K package [17] by using full-potential linear augmented plane wave plus local orbital (FP-LAPW+LO) method with density-functional theory. We have used the LSDA+U method [18] which combines one calculation scheme local spin density approximation (LSDA) and Hubbard model approaches to deal with this species with strong Coulomb correlation. The muffin-tin sphere radii are $R_{i\{mt\}}$=2.2, 1.9 and 1.7 au for Tl, Ni and O atoms, respectively. Spherical harmonics with a maximum angular quantum number of 10 is used to expand the charge, potential and wave function in the muffin-tin sphere. The cut off parameter is $R_{mt}K_{max}$=7.0. We use 50 K points in the Brillouin zone. Under these optimized parameters, the calculations are well converged. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit, $\int|\rho_n-\rho_{n-1}|dr$ between input charge density is less than 0.0001.

3. Results and discussion

The spin-polarized calculations suggest that AFM ordering is the most stable phase in the monoclinic structure.

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The ferromagnetic (FM) phase is 0.14 eV higher in energy than that of AFM state. In the LSDA+U calculations, a Hubbard-like term U_{eff} was added to the effective potential, where we define the $U_{\text{eff}}=U-J$ ($J=0$). The choice of $J=0$ is common practice in literature. In order to minimize uncertainty in the calculated results, we have fixed the value of $U=7.0$ eV. It was assumed that the choice of $U=7.0$ eV could well describe the strong correction effect of Ni 3d [19,20].

Fig. 1 shows the total density of states (DOS) of $TlNiO_3$ with PM, FM and AFM ($U=7.0$ eV) orderings in the monoclinic phase with space group of P21/n. It is noticed that the PM and FM phases just provide useful references to understand the spin-polarized electronic structures in this study. The large DOS at the Fermi level suggests that PM phase is metallic and unstable by the usual Stoner argument [21] and a low-energy structure could be achieved by allowing spin polarization and structural distortion. The FM ordering shows the half-metal property with only a complete spin polarization of electrons at the Fermi energy level. As shown in Figs. 1(b) and (c), the main difference between the band structures of AFM and FM orderings is that there is indeed a band gap about 0.18 eV due to the AFM interactions.

In order to explore the dependence of magnetic properties on the correction potential parameter, the other values of U are also tested. The results suggest that spin magnetic moments of Ni(1) and Ni(2) ions in AFM ordering are related with correction potential parameter: ± 0.93 and $\pm 0.14\mu_B$ ($U=0$ eV), ± 1.24 and $\pm 0.36\mu_B$ ($U=3.0$ eV), ± 1.45 and $\pm 0.76\mu_B$ ($U=5.0$ eV), ± 1.62 and $\pm 0.92\mu_B$ ($U=7.0$ eV), ± 1.67 and $\pm 1.28\mu_B$ ($U=9.0$ eV). It is found that the magnetic moment increases with the increment of the U below 6 eV, but slightly changes from 7 to 9 eV. However, the energy gap does not change drastically with the increase of U due to the small gap value.

To understand the behavior of spin polarization of $TlNiO_3$ in the monoclinic phase, we present the total and orbital-resolved DOS of O 2p, Ni(1) and Ni(2) 3d for $TlNiO_3$ in the AFM ordering in Fig. 2. The features in the vicinity of Fermi level have dominant contributions from O 2p electronic states with small but finite intensities from the Ni 3d states. The energy position of Ni 3d overlaps with those of O 2p states, indicating the occurrence of the hybridization between O 2p and Ni 3d orbitals. The corresponding contour map of the charge–density distributions of $TlNiO_3$ (Fig. 3) also shows the strong hybridization effects of O–Ni states. It is obvious that the DOS near Fermi level are different between Ni(1) and Ni(2) ions in the monoclinic structure, as shown in Figs. 2(b) and (c), which reveals the differing chemical environments of the two Ni(1) and Ni(2) sites. The spin magnetic moments of Ni(1) and Ni(2) ions are about ± 1.62 and $\pm 0.92\mu_B$, respectively, which may be concomitant with the charge disproportionation effect. The charge density is different between Ni(1) and Ni(2) ions in the monoclinic $TNiO_3$, as shown in Fig. 3, which indicates that there is a charge disproportionation between Ni(1) and Ni(2) ions. Calculation shows that there is a higher electron density in Ni(1) than in Ni(2).

To have a further insight into the electronic structure and magnetic properties of $TlNiO_3$, the total and orbital-resolved DOS of Ni(1) and Ni(2) 3d states in the AFM ordering by the LSDA

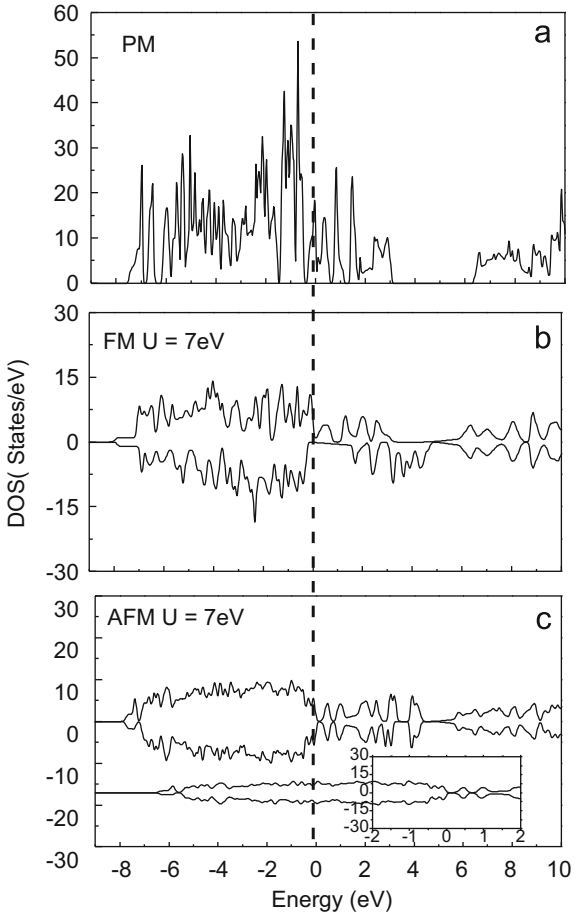

Fig.1. Calculated total densities of states (DOS) of the paramagnetic (PM), ferromagnetic (FM ,$U=7.0$ eV), and antiferromagnetic (AFM, $U=7.0$ eV) structures of $TlNiO_3$, respectively, by LSDA. The zero energy is set at Fermi level (denoted by the vertical dashed line). The inset of (c) is a blow up near Fermi level.

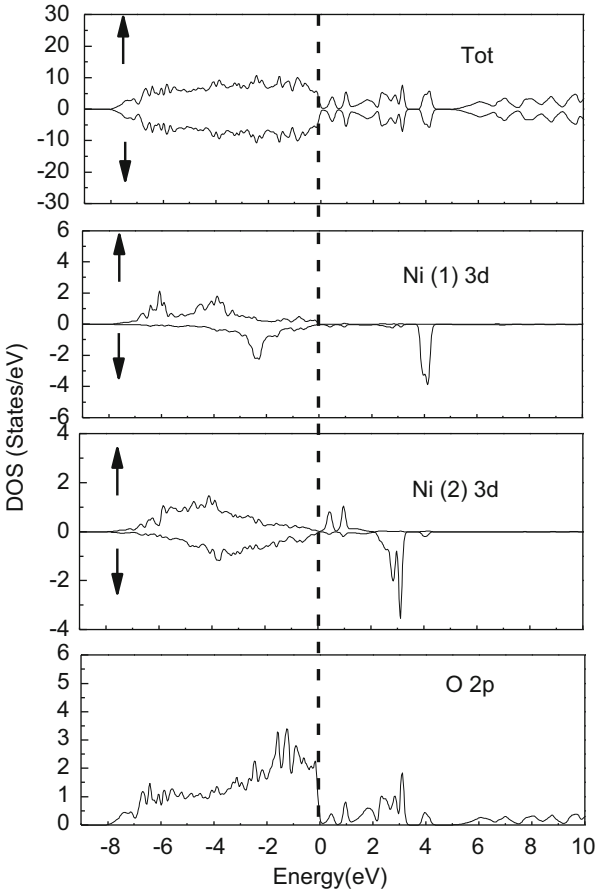

Fig. 2. Total and partial DOS of AFM structure of $TlNiO_3$ obtained in LSDA+U ($U=7.0$ eV) calculations. The Fermi level is denoted by the vertical dashed line. Arrows correspond to spin-up and down spin projections.