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First-principles study on the electronic structure and transport properties of $Mn_3Cu_4Bi_4$

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ABSTRACT

Density functional calculations were used to elucidate the electronic structure and some transport properties of $Mn_3Cu_4Bi_4$. The calculations results indicate that $Mn_3Cu_4Bi_4$ compound possesses metallic character and has high carrier concentration. Moreover, $Mn_3Cu_4Bi_4$ compound is a ferromagnetic material due to the exchange interaction of Mn-3d electrons. The Boltzmann kinetic transport theory was used to calculate the Seebeck coefficient with the constant relaxation time approximation. The result shows that the thermoelectric properties of $Mn_3Cu_4Bi_4$ is isotropic and the Seebeck coefficient reaches 30.9 μV/K at 490 K when the chemical potential μ is −0.043 eV, which is higher than that of many metals. It is the first time to report the Seebeck coefficient of $Mn_3Cu_4Bi_4$.

1. Introduction

The ternary system of $Mn_3Cu_4Bi_4$ has been reported as a new class of magnetic compounds [1]. $Mn_3Cu_4Bi_4$ has large spontaneous magnetization and its Curie temperature is 183 °C. The saturation magnetic moment per formula unit for $Mn_3Cu_4Bi_4$ is 11.4 μ_B [2]. The crystal-structure information of $Mn_3Cu_4Bi_4$ has been determined by neutron diffraction using powder samples [3]. $Mn_3Cu_4Bi_4$ has cubic crystal structure with space group Fm-3m, lattice parameter: a = 1.213 nm and density 9.339 g/m^3. A unit cell of $Mn_3Cu_4Bi_4$ contains 32 Bi atoms, 32 Cu atoms and 24 Mn atoms and consists of four Cu-atom layers and four Bi–Mn-atom layers shown as in Fig. 1(A). There are four large cages (size ~0.24 × 0.24 × 0.24 nm) in one unit cell, one of the cages is at the center of the unit cell shown as in Fig. 1(B).

For predicting magnetic properties, a schematic band-structure model has been determined which is based on local-site symmetries and includes both strongly correlated and itinerant d electrons [2]. The optical and magneto-optical properties of the Mn–Cu–Bi alloy thin films have been reported in Refs. [4,5], and the results show that the maximum value of the magneto-optic figure of merit $2F/a_c$ (where F is the specific Faraday rotation and a_c is the absorption coefficient) is 1.1° at a wavelength of 632.8 nm. However, so far, few theoretical studies on the electronic structures and thermoelectric properties of $Mn_3Cu_4Bi_4$ have been reported. In this work, we calculated the geometries, electronic structure and magnetic and thermoelectric properties of $Mn_3Cu_4Bi_4$ using the density functional theory (DFT) method.

2. Computation method

Based on the generalized gradient approximation of Perdew, Burke and Ernzerhof [6,7], our density functional calculations were done by the method of plane-wave total energy pseudopotential as implemented in the CASTEP code [8,9]. This software has been applied very successfully in studying electronic structure of $CoSb_3$ [10], $Ca_3Co_2O_6$ [11] and Mg_2Si systems [12]. The valence-electron configurations for the Bi, Cu and Mn atoms were chosen as $6s^2$ $6p^3$, $3d^{10}$ $4s^1$ and $3d^5$ $4s^2$, respectively. The electronic structure was calculated by optimizing all the atoms of the crystal using ultrasoft pseudopotentials for the core electrons. The cut-off energy in plane wave expansion was 300 eV. The total energy, maximum stress, maximum force and maximum displacement were converged to less than 1×10^{-5} eV/atom, 0.05 GPa, 0.3 eV/nm and 0.0001 nm, respectively. The tolerance in the self-consistent field (SCF) calculation was set to 10^{-6} eV/atom. We used $10 \times 10 \times 10$ k-point Monkhorst–Pack mesh and used formal spin as initial value for the bulk in the calculation.

3. Results and discussion

The structure parameters for the cubic phase from experimental observations [3] are optimized using formal spin as initial value, and the resultant lattice constant (a) is 1.197 nm, which is close to the experimental value (a = 1.213 nm [3]). The error of the

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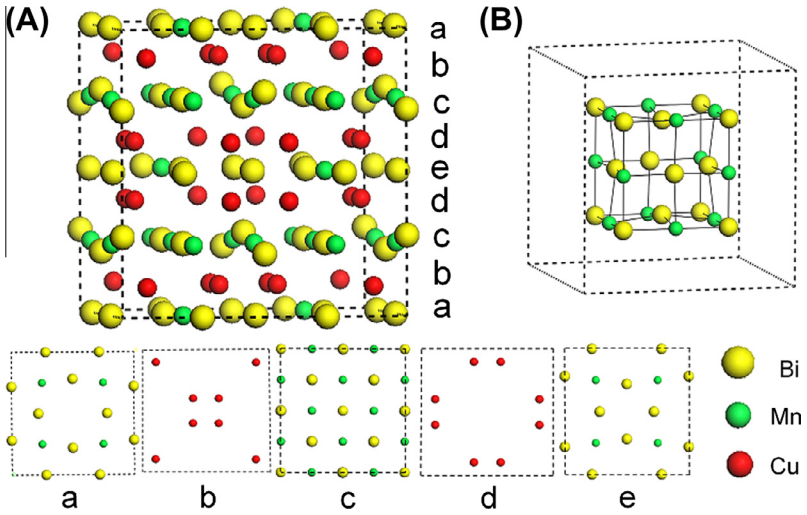

Fig. 1. Crystal structure of $Mn_3Cu_4Bi_4$. (A) The crystal structure of $Mn_3Cu_4Bi_4$ consists of four Cu-atom layers and four Bi–Mn-atom layers and (B) a large cage in the center of unit cell.

lattice constant for calculation relative to the experimental result is about 1.3%. Hence, the computational parameters selected in this paper are suitable.

The cohesive energy (E_{coh}) is calculated for studying the stability of the $Mn_3Cu_4Bi_4$ compound. The cohesive energy is known as a measure of the strength of the forces that bind atoms together in the solid state and can be calculated by the following equation [13]:

$$E_{coh} = \frac{1}{n_A + n_B + n_C}(E_{tot} - n_A E^A_{atom} - n_B E^B_{atom} - n_C E^C_{atom}) \quad (1)$$

where E_{tot} is the total energy of the compound with equilibrium lattice constant, and E^A_{atom}, E^B_{atom} and E^C_{atom} are the atomic energies of the pure constituents A, B and C in elemental state, respectively. The heat of formation of $Mn_3Cu_4Bi_4$ is −369.16 eV. Negative value means that $Mn_3Cu_4Bi_4$ phase is energetically stable.

The total densities of states (DOS) for the $Mn_3Cu_4Bi_4$ without and with spin-polarized are shown in Fig. 2(a and b) respectively. It is seen from Fig. 2 that the Fermi level across the conduct bands. The DOS and its slope near the Fermi level are large, indicating that the $Mn_3Cu_4Bi_4$ may have high Seebeck coefficient [14]. It can be seen from Fig. 2 that the curve of the total DOS for the $Mn_3Cu_4Bi_4$ with spin is very different from the one without spin. This is because that the Mn atom performs spin-polarization due to its 3d electron distribution being asymmetric, which affects the interaction of electrons and therefore changes the curve of the total DOS. Hence, the spin effect can not be neglected in the $Mn_3Cu_4Bi_4$ system.

To understand the electronic nature of the material, the decomposed partial densities of states (PDOS) of each atom were calculated and plotted in Fig. 3. It is seen from Fig. 3 that the main bonding peaks for $Mn_3Cu_4Bi_4$ compound are basically located in the energy range from −14.5 to 4.5 eV (all energies are given with respect to the Fermi energy E_F). The bonding peaks in a lower region from −14.5 to −10.8 eV are due to the Bi-6s states in the $Mn_3Cu_4Bi_4$ compound. The total DOS between −8.0 and −2.5 eV are due to Cu-3d, Mn-3d and Bi-6p states, which indicates that covalent electron orbit hybridization takes place in this energy range. The interesting region from −2.5 to 2.0 eV is dominated by Mn-3d and Bi-6p states and the most of the Mn-3d states are located at this region. The upper region from 2.5 to 4.5 eV mainly

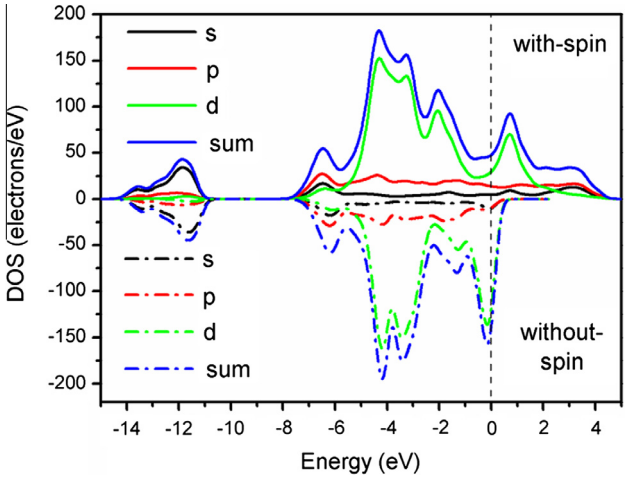

Fig. 2. The total DOS of $Mn_3Cu_4Bi_4$ with spin-polarized (positive) and without spin-polarized (negative) from the GGA calculation. The Fermi level is set to 0 eV.

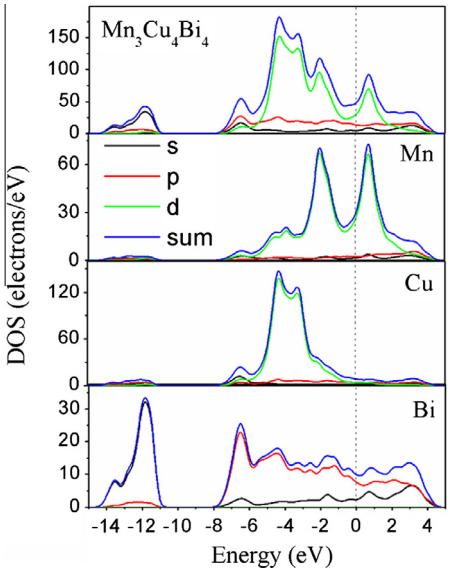

Fig. 3. The partial DOS of Mn, Cu and Bi atoms in $Mn_3Cu_4Bi_4$.