การศึกษาโครงสร้างอิเล็กทรอนิกส์ของ ${\bf Bi}_2 {\bf Te}_3$ ด้วยวิธีดีวีเอกซ์อัลฟา Studies on the electronic structures of ${\bf Bi}_2 {\bf Te}_3$ by the DV-X α method

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บทคัดย่อ

โครงสร้างอิเล็กทรอนิกส์ของบิสมัทเทลลูไรด์ (Bi₂Te₃) ศึกษาโดยวิธีดีวีเอกซ์อัลฟาบนพื้นฐานการคำนวณแบบ จำลองฮาร์ทรีฟ็อกซ์ที่ใช้เมตริกซ์แฮร์มิโทเนียนและสมการเพื่อหาการช้อนกันเชิงจำนวนจริงจากผลรวมของบริเวณที่ สุ่มเลือกโดยสร้างคลัสเตอร์ Bi₂Te₁₃ จากเลขกลุ่มปริภูมิ 166 (R-3m) แลตทิซพารามิเตอร์ a เท่ากับ 4.395 อังสตรอม และ c เท่ากับ 30.44 อังสตรอมพันธะโควาเลนต์พบได้ระหว่างอะตอม Bi-Te และพันธะไอออนิกพบได้ระหว่าง เลเยอร์ Te-Te และ Bi-Bi ออร์บิทัลของโมเลกุลประกอบด้วย Te4d, Te5s, Te5p, Bi5d, Bi6s และ Bi6p ระดับ พลังงานแสดงออร์บิทัลของโมเลกุลที่อิเล็กตรอนเต็มและอิเล็กตรอนไม่เต็มซึ่งพบว่าช่องว่างพลังงานระหว่างออร์บิทัล ทั้งสองมีค่าประมาณ 0.15 อิเล็กตรอนโวลต์และพลังงานเฟอร์มิพิจารณาจากความหนาแน่นสถานะรวมสูงสุดซึ่งมีค่า ประมาณ -0.2 อิเล็กตรอนโวลต์

Abstract

Electronic structures of Bismuth telluride $(Bi_2 Te_3)$ has been studied by the DV-X α method. In this method based on the self-consistent Hartree-Fock-Slater model, the matrix elements of Hamiltonian and overlap integrals in the secular equation are evaluated by the weight sums of integrand values at the discrete sampling points, instead of conventional integration procedure. The cluster model is $Bi_8 Te_{13}$, created by basis data as space group number 166 (R-3m), the lattice parameter, a and c are 4.395 and 30.44 , respectively. The cluster was appropriated to the electronic structure. The interatomic distances in the cluster were shown bonding type as covalent and ionic bond between the Bi-Te and Te-Te, Bi-Bi layers, respectively. The cluster was shown molecular orbitals are Te4d, Te5s, Te5p, Bi5d, Bi6s, and Bi6p. The energy levels demonstrated occupied and unoccupied molecular orbitals indicated that energy gap (E_g) of narrow gap as around 0.15 eV. The density of states was evaluated to Fermi energy (E_F) on the highest peak of curve as around -0.2 eV

คำสำคัญ: โครงสร้างอิเล็กทรอนิกส์ บิสมัทเทลลูไรด์ วิธีดีวีเอกซ์อัลฟา โมเดลคลัสเตอร์

Keywords: Electronic structure, bismuth telluride, DV-XQ method, cluster model

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1. Introduction

The bismuth telluride (Bi Te) is based on materials are widely used for thermoelectric devices at around room temperature (Yang et al., 2005) and mostly attention for thermoelectric cooling such as CPU cooler for computer and industry of small refrigerator in cars. The crystal structure of bismuth telluride (Bi Te) is rhombohedral structure, which belonged to R-3m (No. 166) space group (Larson et al., 2002). Employing these crystallographic data, Mishra has studied the electronic structure of Bi Te by the density-functional theory with the spin-orbit interaction included. The electron states in the gap region and the chemical bonding are shown the energy gap between valence band and conduction band as around 0.11 eV and the structure consists of quintuple layers stacked on top of one another (Mishra et al., 1996).

The paper presented the Bi_2Te_3 has been performed on the basis of Bi_8Te_{13} cluster as shown in Figure 1, the electronic structure of Bi_2Te_3 is examined by the DV-X α method (Adachi et al., 1978). The bond order and the net charge are evaluated by Mulliken's population analysis (Tanabe et al., 1978). The DV-X α method, which based on self-consistent field, averaged as weight sums of integrand values at discrete sample points, instead of conventional integration procedure (Slater, 1976).

2. Computational details

The DV-X α method is a molecular orbital calculating method, assuming the Hartree-Fock-Slater (HFS) approximation (Averill, 1973). The

way to calculation is sat on cluster model method (Monma et al., 2006). The Bi₂Te₃ has been the crystallographic data as shown in Table 1. In this calculation, the exchange-correlation between electrons, V_{xc} , is given by;

$$V_{xc} = -3\alpha \left[\frac{3}{8\pi}\rho(r)\right]^{\frac{1}{3}}$$
(1)

where ρ (r) is the local density of electrons at position r, the parameter α is fixed at 0.7 and the self-consistent charge approximation is used in this calculation (Lindgren et al., 1971). The matrix elements of Hamiltonian and the overlap integrals are calculated by a random sampling method. The molecular orbitals are constructed by a linear combination of numerically generated atomic orbitals (LCAO). The atomic orbitals used in this calculation are 4d, 5s and 5p for Te and atomic orbitals of Bi are 5d, 6s and 6p. For the energy level and density of state are using the overlapping Gaussian functions, the bond order between atoms and ionicities of each atom in the cluster are estimated according to the Mulliken's population analysis. This method had created cluster model of Bi₂Te₃, Bi₈Te₁₃ which calculated energy level by sum of orbital energy. Then the results of this method seem to closely experimental measurement. The energy gap was evaluated by distance between lowest valence energy and highest conduction energy calculated by the cluster. The Fermi energy of cluster is determined by highest density of states in the energy level of the cluster.

Cluster of	Bi ₂ Te ₃
Space group	R-3m
Space group number	166
Structure type	Rhombohedral
Lattice parameter ()	
a	4.395
b	4.395
с	30.440

 Table 1
 The crystallographic data of Bi Te

3. Results and discussion

The cluster is $\operatorname{Bi}_8\operatorname{Te}_{13}$ designed by the DV-X α method. The $\operatorname{Bi}_8\operatorname{Te}_{13}$ cluster has been the bonding of Bi-Bi and Te-Te, two Bi layers and three Te layers are stacked along z-axis as shown in Figure 1. The structural feature is very importance for the description of the chemical bonding. The distance in nearly layers of Te-Bi atoms are around 1.816 , indicate the covalence bonding corresponding to covalence radius of Bi atoms and Te atoms of references as around 1.361 and 1.169 (Winter, 1994). The bond length of Te-Te inner

layer is 4.395 , considerately longer than the bond length of Bi-Te as 1.816 , which suggests that different types of bonding exist in each case. The bond length between Te atoms in neighboring layer is much larger as 3.395 . It is the large spacing between the Te atoms that is responsible for the ready cleavage of the Bi₂Te₃ crystal along the z axis (Kagarakis, 1978).

The atomic orbitals are consisting of 4d, 5s and 5p for Te and atomic orbitals for Bi are 5d, 6s and 6p as shown in Figure 2. The energy levels and the atomic orbital coefficients are corresponding to the molecular orbitals of the Bi₈Te₁₃ cluster. The molecular orbital is constructed from the atomic orbitals of Te4d, Te5s, Bi5d, Bi6s and Bi6p, respectively. The fractional parts of the Bi molecular orbitals are smaller than Te molecular orbitals. Figure 2, the energy gap was determined by the gap between occupied molecular orbital (dash lines) and unoccupied molecular orbitals (full lines) in the calculated the energy level, indicate the valence band and conduction band, 0.15 eV mostly agreement with the experimental data (Greanya et al., 2000).



Figure 1. The $Bi_8 Te_{13}$ cluster with Te layers in the middle and both of upper and lower of cluster





Figure 2. Energy level of Bi₈Te₁₃ cluster was demonstrated Te4d, Te5s, Te5p, Bi5d, and Bi6p molecular orbitals



Figure 3. The density of state of $\text{Bi}_{8} \text{Te}_{13}$ cluster was highest on Te5p orbital as around -0.2 eV indicated that n-type conductivity

The density of state (DOS) of Bi₈Te₁₃ cluster was showed peak near Fermi energy (E_{r}) as around -0.2 eV as shown in Figure 2, indicate the Fermi energy of this cluster. The Bi6p state is mostly below E_{r} and Te5p state is mostly above E_{r} agreement with experimental data. The energy levels are corresponding to density of state in molecular orbital. The relationship of energy level and density of state is shown in Figure 2 and Figure 3. Figure 2, the Te5p molecular orbital is highest appeared (dash lines) corresponded to highest peak of Te6p molecular orbital in Figure 3. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are indicated that the energy gap in this cluster. The LUMO is higher than Fermi energy mostly agreement with the experimental data (Kittel, 2005).

4. Conclusions

The electronic structure of $Bi_{2}Te_{3}$ has been the energy level, density of state, energy gap and Fermi energy, there is calculated by the $Bi_{8}Te_{13}$ cluster. The energy gap is 0.15 eV determined by the energy levels of the cluster, it mostly agree with experimental data. The Fermi energy is around -0.2 eV determined by Density of state of the cluster agree with the experimental data. These results indicated that the DV-XC method with numerical basis sets has been proved to be very efficient for calculations electronic structures of $Bi_{9}Te_{3}$.

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