Half metallic Co$_2$TiGe—a theoretical and experimental investigation

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ABSTRACT

Using first principle calculations the electronic structure and magnetic properties of the half metallic Co$_2$TiGe was investigated. The electronic structure calculations were performed using two different parameterization schemes. The band gap obtained in the minority spin state using LDA scheme in TB-LMTO method was smaller than that obtained using GGA scheme in FP-LAPW method. To explore the half metallic property experimentally bulk Co$_2$TiGe was synthesized by arc melting under argon atmosphere. The magnetic moment per formula unit determined from saturation magnetization at 2 K was 1.9 μ_B, which was close to the theoretically calculated value of 2 μ_B. A detailed analysis of the low temperature transport and magnetotransport properties exhibit characteristic features of half metals such as $T^{9/2}$ dependence of low temperature resistivity, negligible temperature dependence of resistivity below 20 K and a cross over from positive to negative MR around 100 K.

1. Introduction

Spintronics has attracted great interest among researchers because of the potential to simultaneously tune both charge and spin in solid state materials that may lead to the development of novel multifunctional devices [1]. To achieve high spin injection efficiency in magnetic multilayer structures, which are the basic building blocks of spintronic devices, materials with high spin polarization is required [2,3]. Half metallic ferromagnets that have 100% spin polarized charge carriers are the ideal choice for spin injection electrodes. These are materials with a band gap in one spin channel and over lapping bands in the other spin channel. In 1983, during a computational study of magnetic compounds, de Groot et al. [4] discovered half metallicity in half Heusler alloy NiMnSb. Whereas Kübler et al. [5], observed the exclusion of minority spin states at the Fermi level indicating the observation of half metallicity in full Heusler alloys. Since then there have been many reports in literature predicting the possibility of realizing half metallic characteristics in many new materials through ab-initio calculations [6]. Among these the Heusler alloys are found to be attractive as they have high Curie temperature and their structure is closer to some wide band gap semiconductors.

These are ternary intermetallic compounds with the generic formula X$_2$YZ where X and Y are transition metals and Z is a sp valent element. They crystallize in cubic L2$_1$ structure in the space group Fm-3m with X atoms occupying positions A (1/4 1/4 1/4), C (3/4 3/4 3/4), Y atoms at B (0 0 0) and Z atoms at D (1/2 1/2 1/2).

Cobalt based full Heusler alloys have high Curie temperature and high magnetic moments and hence found to be attractive for spintronic device applications. They also have the peculiar property of linear dependence of magnetic moment and Curie temperature on the number of valence electrons in the system [7–9]. Recently Shan et al. [10], have reported the observation of nearly 90% polarization in a cobalt based Heusler alloy at room temperature.

Co$_2$TiX (X=Si, Ge, Sn, etc.,) is predicted to be a half metallic system [11] and there are theoretical and experimental reports exploring their structural and magnetic properties [12–18]. There is an experimental report on half metallic properties of Co$_2$TiSn [19] and a recent report on Co$_2$TiX in which the X-ray magnetic circular dichroism (XMCD) studies showed that the series was found to be nearly half metallic [20].

The electronic structure calculation performed by us on the compounds Co$_2$TiX (Si, Ge and Sn) revealed that other than Co$_2$TiGe only Co$_2$TiSi is half metallic (using both TB-LMTO and FP-LAPW methods). However Co$_2$TiSi exhibit a large compositional disorder and hence we have carried out experimental investigations only on Co$_2$TiGe.

In this report we have compared the results obtained using two different parameterization schemes i.e., LDA using TB-LMTO method and GGA using FP-LAPW implemented in wien2k code. The material was synthesized and probed experimentally to determine the half metallic characteristics. A detailed analysis of the low temperature transport and magnetotransport properties was performed in which features characteristic for half metals were observed.

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2. Computational methodology

The spin polarized electronic structure calculations were performed for the Heusler alloy Co_2TiGe using tight bind-linear muffin tin orbital (TB-LMTO) method [21] and full potential-linear augmented plane wave (FP-LAPW) as implemented in WIEN2k code [22] within the density functional formalism and the results are compared.

von-Barth and Hedin [23] parameterization scheme has been used for exchange correlation potential within the local density approximation (LDA) for TB-LMTO method. In LDA atomic sphere approximation has been used. In this approximation, the crystal is divided into space filling spheres centered on each of the atomic site. Combined correction terms are also included, which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere to minimize the errors in the LMTO method. The Wigner–Seitz sphere is chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electronegativity criteria. The tetrahedron method of the Brillouin zone (k space) integration has been used to calculate partial and total DOS. E and k convergence are also checked.

For FP-LAPW the exchange correlation potential is chosen in the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof parameterization scheme [24]. In this method, a basis set is obtained by dividing the unit cell into non-overlapping atomic spheres and an interstitial region. Inside the atomic sphere, a linear combination of radial function times the spherical harmonic is used and in the interstitial region a plane wave expansion is augmented by an atomic like function in each atomic sphere. A grid of 500 k points was employed and tetrahedral method has been employed for the k space integration [25]. The Wigner–Seitz radii for Co, Ti and Ge are fixed as 2.3, 2.1 and 2.3 a.u., respectively. The values of $K_{max} \times R_{max} = 7.0$ and $l_{max} = 10$ are kept constant throughout the calculations. The energy convergence criteria are set to 10^{-4} Ry with respect to Brillouin zone integration and so the charge convergence criteria.

The calculations were performed for Co_2TiGe with the space group Fm-3m. The experimental value of lattice parameter 11.02 a.u. [12] has been used for the calculation with positions Co (1/4 1/4 1/4), Ti (0 0 0) and Ge (1/2 1/2 1/2).

The equilibrium lattice parameter was calculated in both the methods by compressing and expanding the lattice and then fitted to the Birch equation of state [26]. The spin polarized electronic band structures and density of states (DOS) were plotted for Co_2TiGe using both the methods.

The magnetic moment per formula unit for the alloys of 3d elements can be determined from the number of their valence electrons using Slater–Pauling rule [27–29]. Since in Half metals, a band gap appears in the minority spin states, Slater–Pauling rule will be fulfilled firmly and they will have integer value of magnetic moment [7,8]. Hence the integer value of magnetic moment is not a direct evidence for half metallicity, but it indirectly shows that the Fermi level falls in the gap resulting in half metallicity. This rule can be used to find the magnetic moment of full Heusler alloys using the formula $N_v - 24$ where N_v = total number of s, p valence electrons of main group element and s, d electrons of transition elements. The magnetic moment calculated using Slater–Pauling rule for Co_2TiGe was found to be 2 μ_B [30].

3. Results and discussion

The equilibrium lattice constant was calculated by minimizing the total energy (Fig. 1). The equilibrium value of lattice parameter is close to the experimentally reported value using
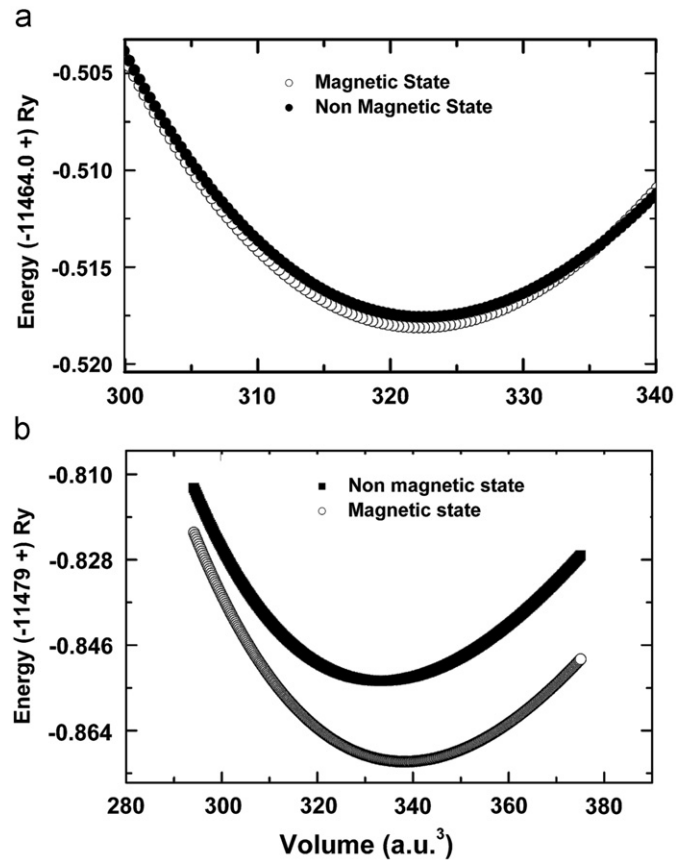

Fig. 1. Energy vs. volume for Co_2TiGe using (a) TB-LMTO method (LDA scheme) and (b) FP-LAPW method (GGA scheme).

GGA parameterization scheme whereas it is less than the experimental value when LDA scheme is used as expected. This also shows that the variation in lattice parameter with temperature is small because the calculations are performed at absolute zero whereas the lattice parameters are measured experimentally at room temperature. The bulk modulus and equilibrium lattice constant are tabulated in Table 1.

In LMTO method at equilibrium lattice parameter Co_2TiGe was not found to be half metallic. The magnetic moment per formula unit was just 1.05 μ_B as against the 2 μ_B calculated from Slater–Pauling rule. Half metallicity was observed under large volume expansion with a band gap of 0.1 eV in the minority spin band and an integer value of magnetic moment/f.u. i.e., 2 μ_B.

In LAPW method Co_2TiGe was found to be half metallic at its equilibrium value of lattice parameter itself with a band gap of 0.6 eV in the spin down channel and magnetic moment/f.u. 2 μ_B. This is because the density gradients are accounted for in the GGA scheme and hence better agreement with the experiments when compared with the LDA scheme. The spin polarized density of states plot using TB-LMTO method is shown in Fig. 2. The band structures of Co_2TiGe using LDA and GGA schemes are shown in Figs. 3–5.

A direct band gap appears for the spin down state in the spin polarized band structure (Figs. 3 and 5). There is no much difference in the band structures of the spin up and spin down channels except that a splitting of bands occurs in the spin down channel giving rise to a band gap.

In the spin down band structure, the band gap appears by the shifting of 's' and 'd' orbitals at the Γ point above the Fermi level. These bands were touching the 'p' orbitals below the Fermi level in spin up band structure. This direct band gap appears between