Electronic structure and magnetism of $RMn_6Sn_6$ ($R = Tb, Dy$)

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Abstract: This article reports first-principles band structure calculations for $RMn_6Sn_6$ ($R = Tb, Dy$). The calculation uses the linear muffin-tin orbitals (LMTO) method in the atomic-sphere-approximation (ASA), and yields results showing that both TbMn$_6$Sn$_6$ and DyMn$_6$Sn$_6$ are ferrimagnetic compounds with antiparallel aligned moments of $R$ and Mn atoms. In this research the 4f states of $R$ atoms are treated as localized states, i.e., the hybridization of 4f states with other valence electrons is neglected. The moments of Mn in both compounds were determined to be 2.43 $\mu_B$ and 2.38 $\mu_B$, respectively. The considerably small additional moments for Mn from the spin-orbit coupling indicates that the spin-orbit coupling is not dominated for Mn atoms. The total moments of Tb and Dy atoms are 10.28 $\mu_B$ and 11.20 $\mu_B$. All the calculation findings accorded well with experimental results.

Key words: rare earth, ab initio band structure, atomic sphere approximation

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INTRODUCTION

Malaman et al. (1988) reported the crystallographic data and magnetic properties of new ternary stannides $RMn_6Sn_6$ ($R = Sc, Y, Gd$-$Tm, Lu$). Chafik El Idrissi et al., 1991a; Chafik El Idrissi et al., 1991b; Venturini et al., 1993a; Venturini et al., 1993b; Venturini et al., 1996) All these compounds crystallize in the HfFe$_6$Ge$_6$-type structure (No. 191, P6/mmm) that can be described as built of alternate (001) layers containing $R$ and transition metal atoms, respectively. $R$ elements build hexagonal planes and transition metal atoms Kagomé nets stacked along the c-axis. As regards the transition metal and rare earth this structure is also closely related to the well-known CaCu$_5$ and ThMn$_12$-type structures. Fig. 1 shows the crystalline structure in this study.

Magnetic measurements (Venturini et al., 1991) showed that GdMn$_6$Sn$_6$, TbMn$_6$Sn$_6$, DyMn$_6$Sn$_6$ and HoMn$_6$Sn$_6$ display ferrimagnetic behavior below $T_C = 435, 423, 393$ and $376$ K, respectively. Furthermore, except for GdMn$_6$Sn$_6$, these compounds exhibit an additional transition (at $T_i = 330, 240$ and $180$ K, for Tb, Dy, and Ho, respectively) which could be related to a change in their easy axis direction. In contrast, ErMn$_6$Sn$_6$, behaves antiferromagnetically below $T_N = 352$ K and a second-order magnetic transition to a ferrimagnetic state occurs at $75$ K.
Neutron diffraction experiments on some of these compounds (Chafik El Idrissi et al., 1991) demonstrated clearly that the ferrimagnetism is caused by an anti-ferromagnetic arrangement of rare earth (R) and Mn moments. In a recent research Malaman et al. (1999) presented the neutron diffraction on magnetic structures of GdMn₆Sn₆ (at 2 K and 280 K), TbMn₆Sn₆ (above room temperature, i.e., between Tᵣ and Tₑ), DyMn₆Sn₆ (between 2 K and Tₑ) and ErMn₆Sn₆ (below 75 K).

In this work, we performed a first-principles band structure calculation on TbMn₆Sn₆ and DyMn₆Sn₆ to determine the band features near Fermi energy, and the magnetism and moments in these compounds, because in most cases the physical properties of solids are dominated by the electronic states near Fermi energy. At the same time, we intended to check the validity of our calculation efforts on special treatment of nearly localized 4f states in rare earth compounds.

**CALCULATION DETAILS**

In this work, we used a relativistic version of LMTO-ASA scheme (Andersen et al., 1976). The spin-orbital coupling (SOC) for heavy elements such as Tb and Dy was treated as a first order perturbation. We used the experimental crystalline data near 0 K in this work. Tb (6s, 6p, 5d), Dy (6s, 6p, 5d), Mn (4s, 4p, 3d), and Sn (5s, 5p) were treated as valence states where frozen-core approximation was applied to the deeply bound core levels. During self-consistent calculation, the one-center expansion of charge density and potential were expanded up to $l_{max} = 4$. The Fermi level was determined by the usual linear tetrahedron integration technique (Jepsen et al., 1971) in Brillouin zone (BZ). Furthermore, as for the exchange-correlation energy and potential, we took the form proposed by von Barth and Hedin (von Barth et al., 1972). In order to reach necessary numerical precision, we used 1326 $k$-points within the irreducible wedge of BZ (1/24 of hexagonal BZ). The numerical accuracy for charge density and total energy are $10^{-6}$ e/a.u.$^3$ and $10^{-6}$ Ryd, respectively. The convergence of energy band eigenvalues and related parameters was ensured by increasing the $k$-points in irreducible BZ.

**RESULTS AND DISCUSSION**

Figs. 2 and 3 are the plotted band structures and density of states plots for TbMn₆Sn₆ and DyMn₆Sn₆, respectively. Before we discuss our own results, we would like to mention the problem concerning the special treatment on 4f states of rare earth elements such as terbium and dysprosium. It is well known that the interaction between 4f states of individual R atoms are well screened by conduction bands due to the small effective radius of 4f electrons. In the so-called late rare earth (Gd-Yb) cases the 4f states form a narrow band without interaction with other valence electrons even though their energy levels are quite close to each other. In order to account for this observation, one usually regards the 4f states as partially occupied core states from the viewpoint of the "open core" technique as used in our previous research (Bin et al., 1986). For some ideal cases corresponding to Hund's rules, e.g., empty, half filled and fully filled 4f shell, we just needed to fix the number of 4f electrons as 0, 7 or 14 in practice. However, for the rare earth atoms with 4f shell deviating from the ideal Hund's rules (Hund, 1927) case, it is difficult to determine the number of 4f electrons constrained as core states. Usually, this difficulty could be overcome by fixing this number to the number of 4f electrons in an individual R atom. As free atoms, the valence electron configuration of Tb and Dy are $4f^85d^16s^2$ and $4f^{10}5d^06s^2$, respectively. In accordance with the above analysis, it seems that one should take the 4f electrons as 8 and 10 for Tb and Dy in calculation. This treatment caused an unphysical consequence on the position of the occupied 4f levels for DyMn₆Sn₆. If we decreased the number of constrained 4f states to 9, the computed results were satisfactory as expected. This finding indicates that one of the 4f electrons in Dy is between well-localized f states and fully itinerant valence electrons in character.

In relation to the calculation of moments, one has to sum up the components from the valence electrons and partially occupied core states. Usually the orbital part of moment from