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Magnetic states of $MgCo_2$ and $CaCo_2$ with the cubic and hexagonal Laves phase structures

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Abstract

Electronic structures of $MgCo_2$ and $CaCo_2$ in the cubic C15-type and hexagonal C14-type Laves phases are calculated in a self-consistent LMTO-ASA method, including the correction of the GGA, for the paramagnetic, ferromagnetic and antiferromagnetic states. By the comparison of calculated total energies, the ground states of $MgCo_2$ and $CaCo_2$ are shown to be ferromagnetic in the C14-type structure and in the C15-type one, respectively, being consistent with the observed results. A good agreement between the calculated and observed values of lattice constant and magnetic moment is obtained for $MgCo_2$, but the agreement between them is not so good for $CaCo_2$.

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Keywords: Magnetic state; $MgCo_2$; $CaCo_2$; Laves phase structure; Electronic structure

1. Introduction

Most of Laves phase Co-compounds ACo_2 form a cubic C15-type lattice structure with a transition-metal element A = Sc, Ti, Y, Zr, Nb, Lu, Hf and Ta. The ground state of these compounds is paramagnetic [1]. Some of them, YCo_2 and $LuCo_2$, are known to be strongly exchange-enhanced paramagnets and to exhibit a metamagnetic transition from the paramagnetic state to the ferromagnetic one by external magnetic fields at low temperature [2].

With divalent atoms Mg and Ca, Co atom may also form the Laves phase structure. Buschow [3,4] found that $MgCo_2$ with a hexagonal C14-type Laves phase structure is a ferromagnet with the magnetic moment 1.3 μ_B per Co atom and the Curie temperature 321 K. The isoelectronic compound $CaCo_2$, on the other hand, has recently been synthesized at high pressure 8 GPa [5]. This compound forms the C15-type structure and the ground state is ferromagnetic; the magnetic moment is 1.75 μ_B per Co atom and the Curie temperature is 528 K. $MgCo_2$ and $CaCo_2$ are ferromagnetic with relatively large magnetic moment, while the compounds ACo_2 with the transition-metal elements are non-magnetic as mentioned above. First-principle band calculations based on the local-spin-density functional formalism have been carried out for $CaCo_2$ [5,6], but the calculated result of the Co moment is smaller than the observed one. For $MgCo_2$, no band calculation has been carried out so far.

In this paper, the electronic structures of $MgCo_2$ and $CaCo_2$ are calculated by the linear muffin-tin orbital method (LMTO) with the atomic sphere approximation (ASA) for the C14-type Laves phase structure in the paramagnetic, ferromagnetic, and antiferromagnetic states and for the C15-type structure in the paramagnetic and ferromagnetic states. By the comparison of these calculated total energies, the most stable lattice structure and magnetic state for $MgCo_2$ and $CaCo_2$ are discussed.

2. Calculated results

The first-principle band structure calculations for $MgCo_2$ and $CaCo_2$ are carried out by the LMTO method with the

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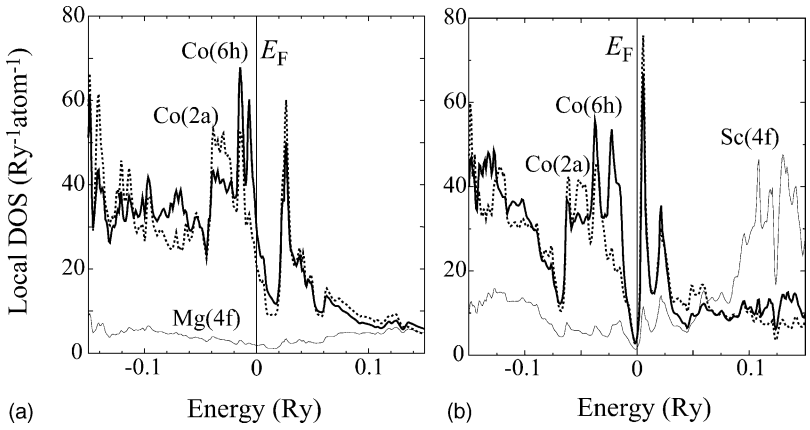

Fig. 1. Local DOS curves of $MgCo_2$ (a) and fictitious compound $ScCo_2$ (b) with the C14-type structure (bold solid and dotted curves are local DOS of Co atoms at 6h and 2a sites, and thin curve is that of Mg/Sc atom at 4f site. The Fermi level E_F is at $E = 0$.

ASA. A non-local exchange-correlation potential, so-called the generalized gradient approximation (GGA) [7], is used in this paper. All relativistic effects are included except the spin-orbit interaction. The self-consistent calculations are carried out at 133 inequivalent *k*-points in the irreducible 1/24 Brillouin zone for the C14-type lattice structure and 120 inequivalent *k*-points in the irreducible 1/48 Brillouin zone for the C15-type one. The basis set with angular momentum is taken up to $l_{max} = 3$. The ratio between atomic spheres of Mg/Ca and Co used in ASA is taken as $(3/2)^{1/2}$ for both lattice structures, which is determined by the touching rigid spheres of atoms. The *c*/*a* ratio of the lattice parameters in the C14-type structure is kept to an ideal ratio $(8/3)^{1/2}$.

In Fig. 1(a) the local density-of states (DOS) curves for $MgCo_2$ in the non-magnetic state with the C14-type structure at the observed lattice constant [3]. The local DOS curves for Co atoms at 6h and 2a sites in the C14-type structure are shown by the bold solid and dotted curves. The local DOS curve of Mg atom at 4f site is shown by thin curve. The Fermi level E_F lies at the high portion of the local DOS of Co. Then, the ferromagnetic state is stabilized in $MgCo_2$ with the C14-type structure. For the C15-type structure, E_F lies at a sharp peak of the local DOS of Co, being similar to the case of $CaCo_2$ [6]. The shape of local DOS of Co for the C15-type structure is similar to that of YCo_2. However, the position of E_F for YCo_2 lies beyond the sharp peak. The shift of E_F comes from the different hybridization between the d-states of Mg/Y and Co, as shown in the case of $CaCo_2$ [6]. For the case of C14-type structure also, the hybridization between the d-states of Mg and Co plays an important role in the position of E_F. To see this fact, the local DOS curves are calculated for fictitious compound $ScCo_2$ with C14-type structure and the same lattice constant as that for $MgCo_2$, which are shown in Fig. 1(b). The high local DOS of Sc around the energy $E = 0.1$ Ry is constructed mainly by the d-states of Sc. As the energy levels of d-states of Sc come close to the levels of d-states of Co, then the d–d hybridization becomes strong, compared with that in $MgCo_2$. This fact means that local DOS's of Co at 2a and 6h sites become low (by the mixing) and the position of E_F shifts towards higher energy side than that for $MgCo_2$ so that the number of electrons on Co atoms does not change.

Fig. 2 shows the calculated total energies of $MgCo_2$ as a function of the volume per formula unit (one Mg and two Co). The energies for the paramagnetic, ferromagnetic and antiferromagnetic states in C14-type structure are denoted by C14(P), C14(F) and C14(AF), respectively. Here, the antiferromagnetic spin structure is assumed to be a $TiFe_2$-type collinear one. The energies for the paramagnetic and ferromagnetic states in C15-type structure are denoted by C15(P) and C15(F). The minimum energy is obtained for the ferromagnetic state at the observed volume V_{exp} [3] for C14-type structure. The total energy for the antiferromagnetic state in C14-type structure is found to be higher than that in the ferromagnetic state. The present result supports the result derived from the NMR measurements [4] that the discontinuity of the magnetization observed in $MgCo_2$ is not due to the antiferromagnetic-to-ferromagnetic transition.

The calculated local moments of Co and Mg atoms in $MgCo_2$ for the ferromagnetic and antiferromagnetic states

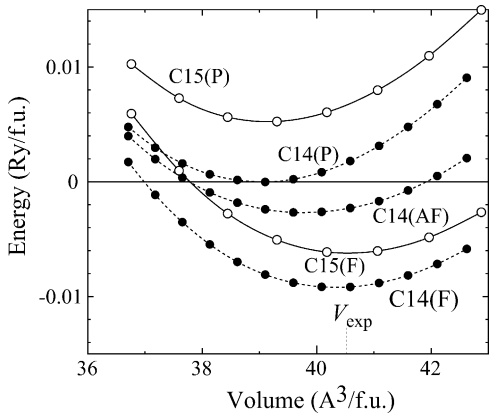

Fig. 2. Total energies of $MgCo_2$ with C15-type and C14-type structures. The curves denoted by (P), (F) and (AF) are those in the non-magnetic, ferromagnetic and antiferromagnetic states.

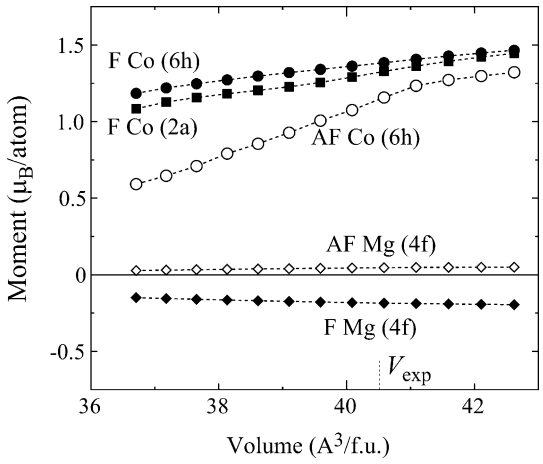

Fig. 3. Calculated local moments of Co atoms on 6h and 2a sites and Mg at 4f site in $MgCo_2$ with C14-type structure. The sublattice moments of Co and Mg in the antiferromagnetic state are shown by AF Co and AF Mg.

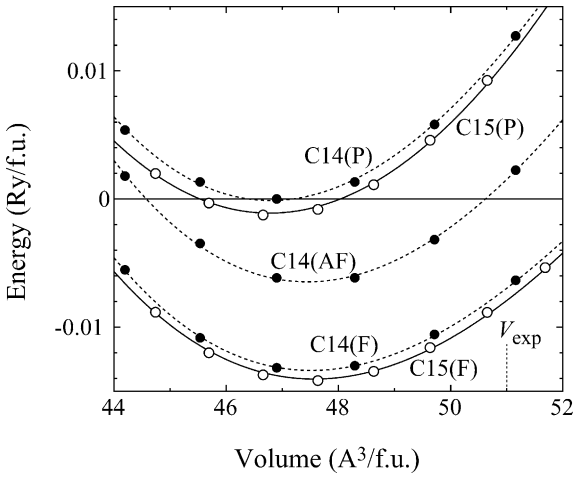

Fig. 5. Total energies of $CaCo_2$ with C15-type and C14-type structures. The curves denoted by (P), (F) and (AF) are those in the non-magnetic, ferromagnetic and antiferromagnetic states.

are shown in Fig. 3 as a function of the volume per formula unit. At V_{exp}, the local moments of Co at the 6h and 2a sites are 1.32 and 1.23 μ_B. A small and negative induced moment -0.17 μ_B is found on the Mg atom in the ferromagnetic state. The calculated results of the lattice constant and the magnetic moment are in a good agreement with the observed one [3,4] and also with the recent NMR measurements [8]. For antiferromagnetic state, the sublattice moments on Co atom at 6h site and Mg atom at 4f site are obtained to be 1.16 and 0.05 μ_B, respectively, at V_{exp}. The Co atom at the 2a site has no moment in the antiferromagnetic state. The calculated local moments of Co and Mg for C15-type structure are shown in Fig. 4.

Fig. 5 denotes the calculated total energies of $CaCo_2$ with C14-type and C15-type structures for the non-magnetic, ferromagnetic and antiferromagnetic states. The ground state is obtained to be the ferromagnetic state in C15-type structure. The minimum energy for the ferromagnetic state in C15-type structure is found to be a little lower than that in C14-type one. Then the C15-type structure is stabilized in $CaCo_2$, being consistent with experiment [5]. However, the observed value of the volume per formula unit V_{exp} is rather larger than the theoretical one.

The local moments of Co and Ca in $CaCo_2$ with C15-type and C14-type structures are shown in Figs. 6 and 7 as a function of the volume per formula unit. In C15-type structure, calculated local moments on Co and Ca at the theoretical volume, where the calculated total energy becomes minimum, are 1.40 and -0.29 μ_B, respectively. Those values at V_{exp} are 1.49 and -0.32 μ_B, which are close to the previously calculated one [5]. However, the observed magnetic moment under magnetic field 0.9 T is rather large, 3.5 μ_B per formula unit, i.e., 1.75 μ_B per Co atom, at 4.2 K. Recent magnetization measurements [8] show somewhat smaller moment 3.1 μ_B per formula unit in $CaCo_2$, being still larger than the calculated result.

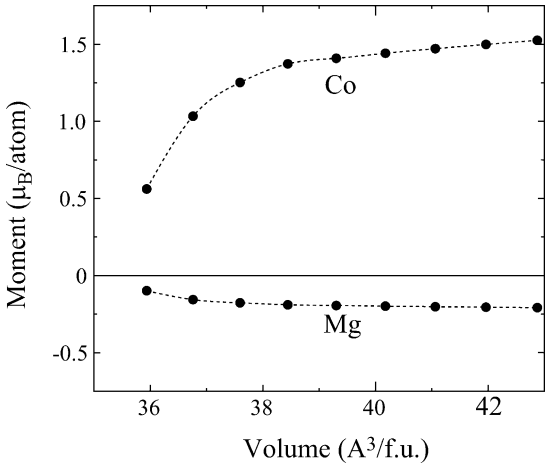

Fig. 4. Local moments of Co and Mg in $MgCo_2$ with C15-type structure.

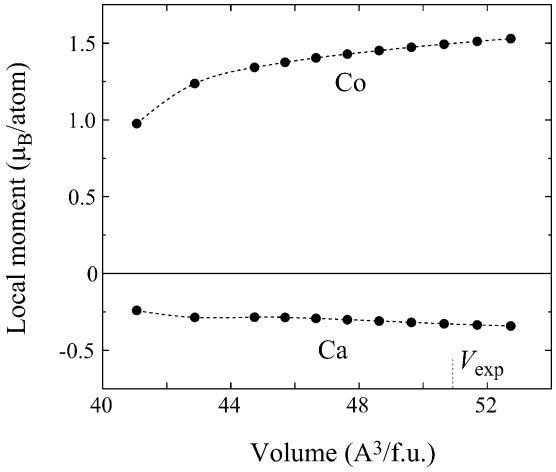

Fig. 6. Local moments of Co and Ca in $CaCo_2$ with C15-type structure.

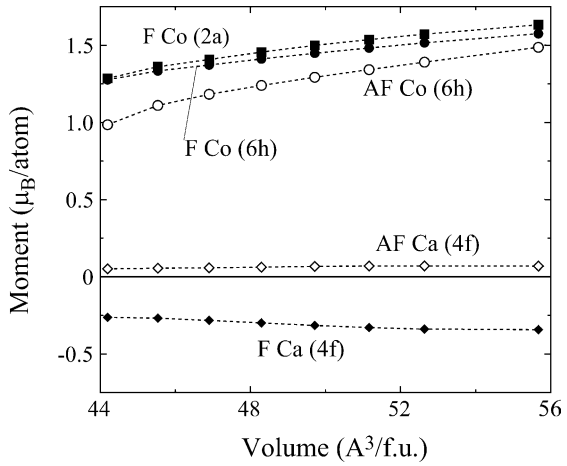

Fig. 7. Calculated local moments of Co atoms on 6h and 2a sites and Ca at 4f site in $CaCo_2$ with C14-type structure. The sublattice moments of Co and Ca in the antiferromagnetic state are shown by AF Co and AF Ca.

3. Conclusion and discussion

In this paper, the ground states of $MgCo_2$ and $CaCo_2$ are discussed by calculating their electronic structures. By comparing the total energies calculated for C15-type and C14-type Laves phase structures, the ground states of $MgCo_2$ and $CaCo_2$ are found to be ferromagnetic in the C14-type and C15-type structures, respectively. The difference between the energies in the two structures for $CaCo_2$ is very small. This result might be related to the experimental fact that $CaCo_2$ is synthesized only under high pressure [5].

The calculated total energy for $MgCo_2$ in the ferromagnetic state is shown to be minimum at the observed lattice constant [3]. The calculated local moment of $MgCo_2$ is also shown to be close to the observed one [3,4]. Therefore, the present band calculation, including the GGA correction, is found to be reliable for the present system. However, the theoretical lattice constant estimated from the minimum point of the total energy for $CaCo_2$ is rather smaller than the observed one. Moreover, the calculated magnetic moment of $CaCo_2$ is also smaller than the observed value. The discrepancies for $CaCo_2$ may be attributed to the off-stoichiometry of the Ca and Co composition, as pointed out in [8].

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