Research

**Structural, Electronic, Magnetic and Thermodynamic of the Intermetallic RMgSn (R: Er, Nd) Ternary CeScSi-Type**

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**Abstract**

Numerical Simulation using the full potential linear augmented plane wave (FPLAPW) method based on density functional theory (DFT) is applied to study intermetallic RTX. The structural, electronic and magnetic properties of the CeScSi-type ErMgSn and NdMgSn compounds have been investigated. A self-consistent calculation of the electronic structure of these compounds was performed using the LSDA and LSDA+U method, where U is the on-site Coulomb interaction correction. The structural parameters have been analysed, total and partial densities of states. The results show a metallic ferromagnetic ground state for ErMgSn and NdMgSn in LSDA+U due to the strong hybridization between f-states of the Er and Nd, the results obtained are in a good agreement with experimental and theoretical values.

**Introduction**

Structural and electronic properties and crystallographic data of the large group ternary intermetallic RTX-type compounds (R: rare earth; 3d–metals; X: p-elements) were extensively studied during the last years. The RMgX (X = Ga, In) compounds exhibit a low temperature anti-ferromagnetic order but they crystallize in the ZrNiAl-type [1–3], while the CeScSi-type compounds were found generally ferromagnetic [2, 3, 4–9]. Compounds crystallize in numerous types of structure within the CeScSi (I4/mmm), CeFeSi (P4/nmm), TiNiSi (Pnma) and ZrNiAl (P-62m) which are the most represented [9].

Recently, Manfrinetti et al. [10] have reported on new RMgSn ternary compounds which crystallize in TiNiSi (R = La–Pr, Eu), CeScSi (R = Y, Nd, Sm, Gd–Tm, Lu) and ZrNiAl (R = Yb) types of structure but, surprisingly, their magnetic behaviors have not been analyzed. This paper deals with the magnetic properties of the RMgSn series through macroscopic magnetic measurements. A number of experiments on the temperature dependence of the magnetic properties have been performed to clarify the relationship between the electronic structures for both compounds has investigated by photoelectron spectroscopy and compared with the resultant of LSDA calculation of filled energy bands [11].

In the present work, experimental results and theoretical studies of the structural and electronic properties of CeScSi-type ErMgSn and NdMgSn compounds are reported. The peculiarities of electronic densities in these compounds were analyzed on the basis of LSDA and LSDA+U calculation data of total and partial densities of electronic states.

**Keywords**: Rare-Earth Compounds; Structural; Electronic Structure; Magnetic Properties; FP-LAPW

**Application Areas**

Magnetic refrigeration allows a better theoretical yield than conventional thermodynamic systems due to the losses significant energy savings during the compression and expansion phases of...
the gas, as has been demonstrated in particular for refrigerators operating with gadolinium [15,16,17,18]. The use of solid refrigerant materials implies a low congestion, superior reliability and does not require a compressor, which is responsible for vibrations and noise. These advantages make it possible to competitive the use of magnetic refrigeration in various fields.

Metallic glasses are today used in many fields. Some metallic glasses are nevertheless, today already commercially exploited. As examples, we can mention the use of these in the manufacture of golf clubs, tennis rackets, baseball bats, but also springs for valve pistons used in the automotive industry. It is important in this type of application that the material can store and restore a maximum of energy elastic in a minimal volume.

Finally, their glossy appearance and their good hardness make them excellent materials for the manufacture of projector mirrors, or “jewelry objects” that require good quality surface and a perfect polish. We will mention, for example, their use in the manufacture of watch dials, jewelry, cell phone cases, or USB sticks.

Computational Methodology

In this section, we present the results for the Intermetallic RMgSn or ternary alloys (R: Er, Nd) Compared with other theoretical and experimental work. The calculations were performed with the WIEN2k code [1] based on the augmented plane wave method linearity in a total potential (FP-LAPW). The code is used to calculate the band structure, the density of states, the charge density and other properties. In calculating the potential for exchange and correlation we used the local density approximation (LDA). Basis functions were expanded as combinations of spherical harmonic functions inside non-overlapping spheres around the atomic sites (MT spheres) and in Fourier series in the interstitial region. The valence wave functions, inside the spheres are expanded up to lmax=8.0. Reciprocal space integration is carried out with a 500 K-points in the irreducible Brillouin zone, which is found to be sufficient to achieve convergence. The wave functions in the interstitial region were expanded in plane waves with a cutoff of kmax=8/RMT (where RMT is the average radius of the MT spheres). The muffin-tin radius RMT is based on two conditions: (i) no core charge leaks out of MT spheres and (ii) no overlapping is permitted between spheres.

The lattice constants and bulk modulus are calculated by fitting the total energy versus volume according to the Murnaghan's equation of state [12]. For the exchange correlation function, we have used the LDA as well as the LSDA+U. In this formalism; the 4f orbital (for the Nd, Er) were treated using the LSDA+U approach with the values of U= 2eV and U=4eV. Compound RMgSn crystallizes in the tetragonal symmetry, the group 14/nmm space (No. 139) same type of structure CeScSi. The indexation of the powder X-ray diagrams confirmed the space group 14/nmm for all of these compounds except Ce, and Yb. Lattice parameters are gathered in Table 1. Diffraction patterns show unambiguously that R, Sn and Mg atoms occupy 4(e) [zR ≈0.33, zSn ≈0.13] and 4(c) crystallographic positions, characteristic of the tetragonal CeScSi-type structure. All these data are in fair agreement with those previously published by Manfrinetti et al. [13].

Results and Discussions

Structural Properties

In order to obtain the equilibrium lattice constant and the bulk modulus for the tetragonal RMgSn in ferromagnetic phase (FM), we performed the structural optimization by minimizing the total energy with respect to the cell parameters and the atomic positions. ErMgSn and NdMgSn assume a tetragonal CeScSi-type the space group 14/ mmm, as illustrated in fig. 1.

The calculated total energies as a function of unit cell volume were fitted by Murnaghan's equation of state. In order to determine the network balance parameters a and c, the compressibility module B and their derived B′ for ErMgSn and NdMgSn compounds, the total energy as a function of the two variables the volume V and the ratio (c / a) are calculated and listed in table 1. To the best of our knowledge, there are no experimental or theoretical data reported for the bulk modulus and its pressure derivative for the material of interest, and hence our results are predictions. We confirm from fig. 2 that the FM configuration is the most stable one.

The value of the calculated lattice parameters (a, c) using the LDA and LDA+U show good agreement with experimental values.

<table>
<thead>
<tr>
<th>Nombre des points k</th>
<th>( R_{MT} \times K_{max} )</th>
<th>RMT (Bohr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>Mg</td>
</tr>
<tr>
<td>ErMgSn</td>
<td>500</td>
<td>8</td>
</tr>
<tr>
<td>NdMgSn</td>
<td>500</td>
<td>8</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>( a_{eq}(\text{Å}) )</th>
<th>( c_{eq}(\text{Å}) )</th>
<th>Volume of Cell [Å(^3)]</th>
<th>B'</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErMgSn</td>
<td>4.335</td>
<td>15.764</td>
<td>296.24</td>
<td>4.2164</td>
</tr>
<tr>
<td></td>
<td>4.344(^a)</td>
<td>15.740(^a)</td>
<td>296.9(^a)</td>
<td>/</td>
</tr>
<tr>
<td>NdMgSn</td>
<td>4.458</td>
<td>16.142</td>
<td>320.8</td>
<td>3.5842</td>
</tr>
<tr>
<td></td>
<td>4.472(^a)</td>
<td>16.146(^a)</td>
<td>322.9(^a)</td>
<td>/</td>
</tr>
</tbody>
</table>

\(^a\) Ref.[19] Exp.
Consequently the LDA+U method was found to be very successful when applied to systems with long-range spin and orbital order.

Electronic Band Structure and Density of States (DOS)

Equilibrium lattice parameters are used in order to calculate the band structures of tetragonal ErMgSn and NdMgSn structure CeScSi-type. The Energy band structure for majority and minority spins, calculated in the high symmetry directions of the Brillouin zone, is given in fig. 3. The zero of energy is chosen to coincide with the Fermi level. Using the LDA, we show that the band structure of ErMgSn and NdMgSn has a metallic behavior because of the polarization of Fermi level in the majority spin electrons and minority one. However, the LDA+U shows spin polarization phenomenon, because the material has a metallic behavior for majority spins, and an insulating character for the minority ones. The bottom of the conduction bands and the top of the valence bands are at the Γ point in the Brillouin zone which confirms that ErMgSn and NdMgSn compounds have a metallic character. We can deduce from these results that the U Hubbard correlation influences on the positions of the electronic states. Generally, the LDA+U give a wider band gap than LDA.

The spectra of band structures of RMgSn show three regions that characterize drivers:

The first spectrum bands to the conduction Fermi level are dominated by a mixture of the 4f states of Er and Nd. The bands that follow are the p-states of Sn for stability component RTX above which, there is the s-state of the cation (X: Sn).

To determine the densities of states TDOS total and partial PDOS, it is necessary to identify of the type of hybridization and the states that are responsible for binding. In the range of 1–4eV below EF the p- and d-contributions in N(E) are nearly identical, while the narrow intense peaks observed at 6-10eV below EF are related to s- and f- states. The strongest maxima of N↓(E) localizing in the energy range between 1 and 3eV corresponds to f↓-electrons of Er, Nd ions, as illustrated in fig. 4 and fig. 5. The structural details of curves of electron states...
density for ErMgSn the same observed in the band structure from fig. 6, but a principal features are maintained. The localization and with of $f\downarrow$-band formed by-states 4f of Er and Nd due to hybridization is very extended in energy and is characterized by high intensity.

Fig.3. Spin polarized band structures of the ErMgSn and NdMgSn, CeScSi-type using LSDA approximation.

Fig.4. Total density of States (TDOSs) and the partial (PDOSs) of the ErMgSn and NdMgSn, CeScSi-type using LSDA approximation.
Fig. 5. Total density of states (TDOSs) of the ErMgSn and NdMgSn, CeScSi-type using LSDA+U approximations.

Fig. 6. Total density of states (TDOSs) and band structures of the ErMgSn, CeScSi-type using LSDA approximation.
Magnetic Properties

We have investigated in our paper, a detailed study on the ground states properties of the of tetragonal ErMgSn and NdMgSn structure CeScSi-type. To find the spin effect on this material; we examined especially the magnetic moment in all atoms that formed our compound using LDA and LDA+U approximations. The results are resumed in table 2. The total magnetic moment which includes the contribution from the interstitial region arises from the Nd and Er ions with a small contribution of Mg sites in both approximations. For LDA+U calculations, the total magnetic moment of the compound is 11.25 μB. The value of the total magnetic moment is one of the significance of the metallic nature of this material. Magnetism in ErMgSn and NdMgSn occurs because there is an indirect exchange interaction between rare-earths and transition metal via nonmagnetic anion Sn. There are two possible exchanges, one is double-exchange and the other one is super exchange [14]. Generally, double exchange is ferromagnetic and super exchange is anti-ferromagnetic. So, we suppose that the double exchange mechanism is responsible for the ferromagnetism observed in tetragonal RMgSn. From table 2 we can deduce that, the Coulomb interaction may increase the localization of the related f and d orbital and increase the local magnetic moments in the Nd and Er sites, but decrease Sn local magnetic moment.

| Table2: Calculated Magnetic Moments (in Bohr Magneton μB) For Several Sites of the ErMgSn, NdMgSn CeScSi-type obtained with LSDA ,LSDA+U. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                | ErMgSn          | NdMgSn          |
|                                | LDA             | LDA+U(2eV)      | LDA             | LDA+U(2eV)      |
| Eg (eV)                        | 0.3812          | 0.4554          | 0.093           | 0.4551          |
| μEr,Nd                        | 3.4646          | 95              | 3.2785          |
| μMg                            | 0.0088          | 0.1199          | 0.0503          | -0.0104         |
| μSn                            | 0.1729          | 0.6316          | 0.6442          | -0.0433         |
| μintersititial                | 2.4128          | 2.8264          | 1.732           | 0.468           |
| μCell                          | 5.8141          | 11.2589         | 6.0664          | 6.9174          |

Conclusion

FPLAPW method based on density functional theory within the LDA and LDA+U exchange potential as implanted in WIEN2k is used to study the optoelectronic and magnetic responses of the tetragonal RMgSn structure CeScSi-type. The calculated total energy difference ΔE=EAFM-EMF is positive, so, our compound is stable in the FM phase via the double exchange mechanism. For LDA+U the metallic nature of ErMgSn, NdMgSn is observed. On the contrary. The important variations in the electronic properties of the material of interest, we have computed the total and partial density of states, using LDA, substantial states at EF can be observed from LDA calculations for the tetragonal ErMgSn and NdMgSn, pointing to a metallic result. Corrections that account for the strong correlation between Er, Nd 4f states can be made by using LDA+U approach. We can see that there is a visible overlap EF. In particular, the Majority Er, Nd 4f orbital are more hybridized than the minority states.

References


