

DENSITY FUNCTIONAL CALCULATION OF THE CRYSTAL FIELD INTERACTION IN RARE EARTH INTERMETALLIC COMPOUNDS*

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(Received July 10, 2002)

We present a theoretical investigation of electronic properties and $4f$ -excitation spectra on several rare earth RX_2 compounds. Both compounds with a transition metal ($X = \text{Co}$), carrying an induced magnetic moments, and with essentially non-magnetic simple metals ($X = \text{Al}$) are considered. The calculations are based on a combination of density functional (DF) and crystal field model theories. The Kohn–Sham equations of DF theory were solved using local spin density approximation (LSDA) but we also tested the influence of the generalized gradient approximation (GGA).

PACS numbers: 71.15.Mb, 71.70.Ch, 75.50.-y

1. Introduction

The rare-earth (R) transition metal or p -metal Laves phase compounds present interesting examples of phenomena which can occur in systems combining both itinerant and localized magnetic moments [1]. In this paper we focus our attention on the Co-based $R\text{Co}_2$ and Al-based $R\text{Al}_2$ Laves phase compounds ($R = \text{Y}, \text{Nd}, \text{Ho}, \text{Er}$). In contrast to the isostructural $R\text{Ni}_2$, $R\text{Al}_2$ and $R\text{Fe}_2$ compounds, in which the $3d$ -electron subsystem is either non-magnetic ($R\text{Ni}_2$), not occupied ($R\text{Al}_2$), or bears a stable magnetic moment ($R\text{Fe}_2$), in the $R\text{Co}_2$ compounds the hybridized itinerant $3d$ - $5d$ electron

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

subsystem ($3d$ - $4d$ in the case of YCo_2) shows to some extent an intermediate behavior. The YCo_2 and LuCo_2 compounds exhibit exchange enhanced Pauli paramagnetism and a metamagnetic transition (field-induced magnetic phase transition from the paramagnetic to the ferrimagnetic state under an external magnetic field exceeding 69 T and 74 T for YCo_2 and LuCo_2 , respectively) [1]. In the RCo_2 compounds with magnetic R ions, in the ordered state the effective internal field may exceed the critical field necessary to induce the metamagnetic transition in the $3d$ -electron subsystem. The respective magnetic phase transitions at Curie temperature T_C are of first order in RCo_2 with $\text{R} = \text{Dy}$, Ho and Er , and of second order in the others [1,2]. In the case of RAl_2 compounds the magnetic properties originate from the localized R-moments which are coupled by indirect exchange interaction via the conduction electron subsystem ($\text{R-}5d$, $\text{R-}6s$, $\text{Al-}3s$, $\text{Al-}3p$ electron states). Thus, the RAl_2 system can serve as a model system to test various theoretical approaches [3].

The electronic structure of RCo_2 intermetallics can be described as a combination of a relatively narrow $\text{Co-}3d$ band with a wider $\text{R-}5d$ band which is higher in energy. The hybridization of the more than half filled $\text{Co-}3d$ band with the almost empty $\text{R-}5d$ band can result in an antiferromagnetic coupling if magnetic ordering is established. In this work, the electronic structure of RCo_2 and RAl_2 was studied in the framework of density functional theory (DFT). Thus, the calculations include also the nearly-free electron states like $\text{Co-}4s$, $4p$, $\text{Al-}3s$, $3p$ and $\text{R-}6s$, $6p$ to establish a realistic description of the electronic structure. The strongly correlated $\text{R-}4f$ -states do not contribute to the chemical bonding in the considered systems due to strong intra-atomic correlations which overcome the small hybridization with the valence states. This behavior is conveniently modeled by the “open-core” approach [4,5].

2. Theoretical method

We have applied both local spin density approximation (LSDA) and generalized gradient approximation (GGA) [6] for the treatment of the exchange and correlation effects. In the present study we used two different computational methods, namely (*i*) general potential linearized augmented plane wave (LAPW) [7] and (*ii*) fully relativistic optimized linear combination of atomic orbitals (OLCAO) [8], to solve the effective single particle Kohn–Sham equations. In all our calculations we used lattice parameter values $a = a_{\text{exp}}$ (see [1], p. 371 for RCo_2 ; [3], p. 391 for RAl_2).

To simulate localized $4f$ -states in the framework of the LAPW method we switched off the hybridization of the $4f$ -states with all other valence states and treated the neodymium (holmium, erbium) $4f$ -states in the spherical part of the crystal potential as atomic-like core states. An integer occupa-

tion with 3 (10, 11) electrons was fixed for the Nd (Ho, Er) 4*f*-states. In the case of OLCAO method the 4*f*-states were treated using the self-interaction corrected (SIC) LSDA approach that accounts for the first Hund's rule couplings among the 4*f* electrons within the atom [9]. This scheme provides deeper 4*f*-levels and more localized 4*f* densities than non-spin-polarized SIC-LSDA. It improves, as was demonstrated for the compounds PrPd₂X₃ and NdPd₂X₃ (*X* = Al, Ga), the agreement between calculated and experimental crystal field splitting of the localized 4*f*-states [9]. Other computational details of presented DFT calculations for RX₂ compounds are similar to our calculations on YCo₂ [10].

3. Results and discussion

The interaction with the crystal field (CF) produced by the neighboring core charges and the anisotropic valence electronic charge density is the strongest perturbation of the localized atomic-like 4*f*-states of trivalent R ions in RX₂ compounds. In the cubic symmetry the corresponding CF Hamiltonian can be written as $H_{CF} = \beta \cdot (A_4^0 \langle r^4 \rangle (O_4^0 + 5O_4^4) + \gamma \cdot (A_6^0 \langle r^6 \rangle (O_6^0 - 21O_6^4))$ where O_l^m are the Stevens equivalent operators and β and γ are the reduced matrix elements [11].

To calculate $A_l^m \langle r^l \rangle$ we use a first principles method based on the DFT [5, 9]. Within this method the electronic structure and the corresponding distribution of the ground state charge density is obtained using the LAPW method. The CF parameters $A_l^m \langle r^l \rangle$ originating from the aspherical part of the total single particle DFT potential in the crystal can be obtained from $A_l^m \langle r^l \rangle \propto \int |R_{4f}(r)|^2 V_l^m(r) r^2 dr$ where $V_l^m(r)$ are the components of the total (Coulomb and exchange-correlation) potential. To obtain the radial wave function R_{4f} of the localized 4*f* electrons of the R³⁺ ion we used a SIC wave function (OLCAO method). The following CF parameters were obtained for NdCo₂: $A_4^0 \langle r^4 \rangle = 93$ K and $A_6^0 \langle r^6 \rangle = -17$ K; HoCo₂: $A_4^0 \langle r^4 \rangle = 43$ K and $A_6^0 \langle r^6 \rangle = -3.6$ K; ErCo₂: $A_4^0 \langle r^4 \rangle = 42$ K and $A_6^0 \langle r^6 \rangle = -3.4$ K. The values have the same sign and similar magnitude as the experimental CF parameters (see Tab. 1 of [11]). Fig. 1 shows the CF splitting of the ground state multiplets for R = Nd, Ho and Er obtained from diagonalization of the CF Hamiltonian using CF parameters from our DFT approach. Comparing our CF splittings with those derived from the final analysis of the INS spectra [11], one can see that our total CF splittings for R = Ho and Er are generally comparable with those from [11]. In the case of RAl₂ the calculated CF parameters have again the same sign (positive $A_4^0 \langle r^4 \rangle$ and negative $A_6^0 \langle r^6 \rangle$) and similar magnitude as the experimental CF parameters [3].

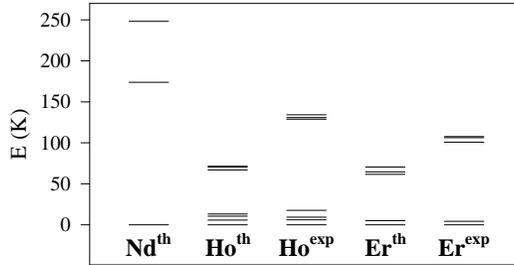


Fig. 1. The CF splitting of the Hund ground state multiplets of Nd, Ho and Er calculated using LSDA-SIC CF parameters (label th) and experimental CF parameters (label exp) from [11].

In summary we calculated the CF interaction for RX_2 using first principles DFT method. We demonstrated that our approach can be used to estimate quantitatively the CF parameters. The theoretical CF energies are in fair agreement with the experimental ones. The work on other RX_2 systems is in progress.

The work was supported by GACR (Pr. 202/00/1602 and 202/02/0739), the research program MSM113200002, GAUK (Pr. 145/2000/B FYZ) and Deutsche Forschungsgemeinschaft, SFB 463, TP B11.

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