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Magnetism and electronic structures of hexagonal 1:1:1 rare earth-based intermetallic compounds

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Correlations between magnetic properties and electronic structure of rare earth based intermetallics of the ZrNiAl-type crystal structure have been analysed. The analysis has been supported by results of magnetometric, neutron diffraction and photoelectron spectroscopy measurements. It has been demonstrated that structure of the valence band and crystal electric field effects are the most important factors affecting the magnetic behaviour of the discussed compounds.

Key words: *magnetic properties; electronic structure; rare earth compounds*

1. Introduction

Rare earth based intermetallics of RTX stoichiometry (R – rare earth, T – d-electron element, X – p-electron element), crystallizing with the ZrNiAl-type crystal structure exhibit a great variety of intriguing physical properties. Ce-based compounds of CeTX composition have attracted special interest due to their unusual magnetic behaviour driven mainly by hybridisation of the 4f states with the conduction bands [1–4]. Dominance of the Kondo effect over the RKKY interactions results in non-magnetic ground states in CeNiAl [5, 6], CeNiIn [3, 7], CePdIn [4], CePtIn [8] or CeRhSn [9]. Otherwise, long-range magnetically ordered phases (CeCuAl [6], CeAuIn [7]) are observed. In weakly hybridized Ce- and Nd-based ZrNiAl-type phases, the crystal field (CF) splitting of ground multiplets leads to formation of magnetic CF doublet

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ground states. An opposite situation occurs in the case of PrTX compounds, where intrinsically non-magnetic CF singlet ground state is expected. However, some Pr-based RTX compounds exhibit long-range magnetic order (as found, e.g., in PrNiAl [10, 11] and PrCuAl [12]). This is possible when energies of excited CF levels are comparable to exchange interaction energy. Apart from the CF effects, the hybridisation of Pr 4f states with T nd states may result in absence of any magnetic order (established for PrPdIn [13], PrPtSn [14], PrRhSn [9]). For compounds with heavy rare earths (Gd–Er), the magnetic order is rather common. As non-magnetic exceptions HoRhSn and ErRhSn may be given [14].

2. Crystal structure

About one third of known RTX compounds crystallize in the ZrNiAl-type structure (space group No. 189). Within this crystal structure the atoms occupy the following positions: R at 3(f) site: $(-x_R, -x_R, 0)$, $(x_R, 0, 0)$, $(0, x_R, 0)$, T at 1(a) site: (0, 0, 0) and 2(d) site: (1/3, 2/3, 1/2), (2/3, 1/3, 1/2) and X at 3(g) site: $(-x_X, -x_X, 1/2)$, $(x_X, 0, 1/2)$, $(0, x_X, 1/2)$.

This hexagonal system is very interesting as it induces topological frustration of magnetic interactions due to triangular coordination of rare earth magnetic ions lying within ab-planes. These well separated planes may be considered as quasi two-dimensional. Recently, magnetic phase diagram of the ZrNiAl lattice has been investigated by means of XY model yielding the existence at $T = 0$ of three different long-range ordered phases [15]. Another interesting feature of the ZrNiAl lattice is that, according to group symmetry analysis, not all magnetic ions must belong to the same orbit symmetry [16].

3. Magnetic properties and electronic structure

3.1 Influence of d-electron element (T)

Among the RTX compounds crystallising in the ZrNiAl-type structure the indides family has been comprehensively studied till now [17]. Within this family, RNiIn, RPdIn and RAuIn series exhibit the most interesting magnetic properties. Magnetism in these compounds seems to be mostly influenced by Ni 3d, Pd 4d and Au 5d states lying in the valence band. The authors focused on some selected Pr-based compounds, as their magnetic properties are not satisfactorily known.

The magnetic susceptibilities of PrTIn (T = Ni, Pd, Au) samples do not indicate any magnetic ordering down to low temperatures (see Fig. 1a). In Figure 1b, the valence bands of PrTIn compounds are presented. Similarly to most RNiIn compounds [18], the Ni 3d states are located just below the Fermi level (FL). The relatively high density of states (DOS) at the FL is reflected in high ordering temperatures which follow the de Gennes scaling (Fig. 2). No magnetic ordering was found for CeNiIn (Kondo lattice) and for PrNiIn. In both cases, the R 4f–Ni 3d hybridisation is the key factor to understand the non-magnetic behaviour. The Ce 4f states are located at about 2 eV below the FL, while the Pr 4f ones are at about 3 eV, and these states heavily overlap with the Ni 3d ones. The magnetic order appears in NdNiIn, where the separation between the Nd 4f and Ni 3d states is notably larger.

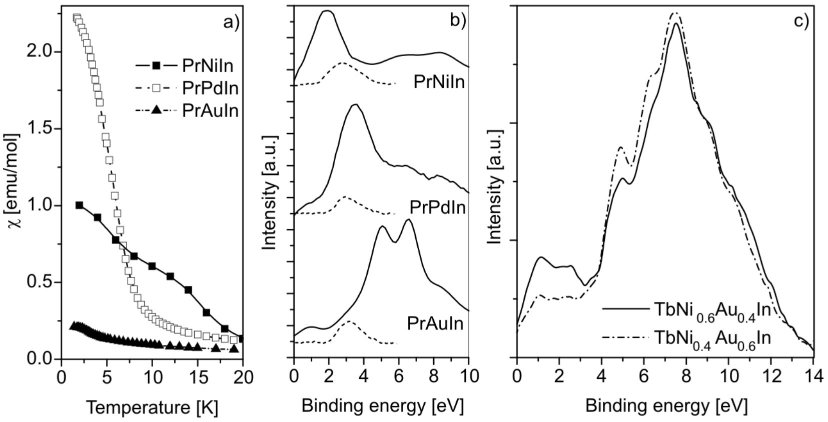

Fig. 1. Magnetic properties and valence bands structures of selected RTIn compounds: a) low temperature magnetic susceptibility of PrTIn phases, b) PrTIn valence band spectra (solid lines) with estimated contribution of Pr 4f states (dotted lines), c) influence of T element on the valence band spectra for non stoichiometric $TbNi_xAu_{1-x}In$ compounds

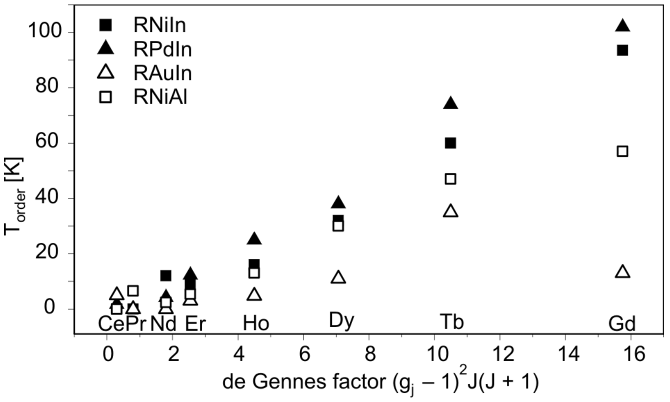

Fig. 2. De Gennes scaling for selected RTX compounds

The RPdIn family exhibits magnetic properties similar to the RNiIn series. In this case, the Pd 4d states are shifted a bit deeper below the Fermi level (~3.8 eV), however DOS at the FL is similar to the RNiIn case. Thus, the ordering temperatures of the RPdIn compounds are comparable to those of RNiIn (see Fig. 2). Overlap of the

Pd 4d states with the Pr 4f ones is larger than that with the Ce 4f or Nd 4f states (Fig. 1b). Consequently, PrPdIn does not exhibit magnetic ordering down to 1.7 K, opposite to the Ce- and Nd-based analogues [13].

The magnetic behaviour of the RAuIn family is different from the before-discussed cases. While the maximum of Au 5d states lies about 5 eV below the Fermi level, the DOS at the FL is significantly lower than that in RNiIn and RPdIn. This is clearly reflected in the valence band spectra of the $TbNi_{0.4}Au_{0.6}In$ and $TbNi_{0.6}Au_{0.4}In$ solid solutions (Fig. 1c). The ordering temperatures of the RAuIn phases are much lower than those of the Ni- or Pd-based compounds, and they do not obey the de Gennes scaling (Fig. 2). These findings indicate rather small coupling of the 4f electrons with the valence band. Thus, CeAuIn is a simple antiferromagnetic metal. For PrAuIn and NdAuIn, no magnetic ordering was observed, however the main reason for such behaviour is different in each case. In Pr-based indide, the hybridization between the Pr 4f and Au 5d states is not considered to be significant due to their large energetic separation. In turn, the magnetic susceptibility of this compound shows some kind of plateau at low temperatures, being indicative of singlet CF ground state (Fig. 1a). In contrast, the CF effect cannot be responsible for non-magnetic behaviour of NdAuIn, because of the expected Kramers doublet of CF ground state. Apparently, in this compound it is the hybridisation between the Nd 4f and Au 5d states which makes it non-magnetic. The Nd 4f states strongly overlap with the Au 5d ones, as both are located at about 5 eV below the FL. Within the RAuIn family, the TbAuIn indide exhibits the most interesting magnetic properties; for this compound an unusual sequence of magnetic transitions: paramagnet – spin-glass – antiferromagnet has been found [19].

3.2 Influence of p-electron element (X)

In order to relate magnetic properties of the RTX compounds to the kind of the p-electron element, two families of the RNiAl and RNiIn compounds can be chosen. In both series, similar ordering temperatures are observed, as the DOS at the FL originates mainly from the Ni 3d states. Moreover, similar valence band structures, i.e. similar 4f3d hybridisation strength imply that mainly the CF effects are responsible for different magnetic behaviour in these compounds.

For example, whereas PrNiIn is non-magnetic, PrNiAl exhibits antiferomagnetism below 6.5 K [10, 11]. In the latter compound, the excitation energy between the CF singlet ground state and the next CF levels is significantly lower than that in the indide. In TbNiAl and TbNiIn antiferromagnets, the ordered magnetic moments lie along the *c* axis and the *ab* plane, respectively [20, 21]. This essential difference is certainly due to CF induced anisotropy, as from the topological point of view the alignment within the *ab* plane is energetically more preferable in the case of antiferromagnetic interactions [15].

3.3 RTX based hydrides

Introducing hydrogen into the RTX compounds is considered to be equivalent to applying a negative chemical pressure. However, as electronic band structure calculations revealed, hydrogenation may suppress the DOS at the FL [22]. Recently, it was shown that the coupling between the 4f states and the conduction band considerably decreases upon hydrogenating. This effect results in the appearance of magnetic ordering in originally non-magnetic Kondo systems [23]. In the case of an RTX compound crystallizing with the ZrNiAl-type structure, expansion of the crystal unit cell is strongly anisotropic, when the stoichiometry of $R_3T_3X_3H_4$ is achieved. In contrast, for another stable composition of $R_3T_3X_3H_2$ an isotropic expansion is expected.

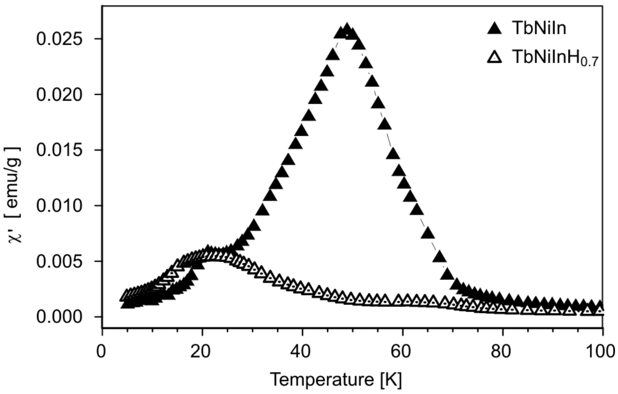

Fig. 3. AC magnetic susceptibility of TbNiIn and $TbNiInH_{0.7}$; f = 125 Hz, H_{ac} = 2 Oe

As an example of hydrogenation influence on the magnetic properties, Fig. 3 shows the behaviour of TbNiIn, hydrogenated up to the composition $TbNiInH_{0.7}$. A distinct change in the magnetic behaviour is evident, namely the kink in $\chi'(T)$ at 48 K due to the magnetic ordering in TbNiIn is almost totally suppressed after hydrogenation, and simultaneously a significant shift of the magnetic ordering temperature is observed.

4. Summary

Magnetism of the RTX intermetallics is governed by the interplay between RKKY interactions, Kondo screening (in the case of Ce- and Yb-based compounds) and crystal field effects. According to the photoemission and bulk magnetic data, the lack of magnetism in light rare earth compounds is due to hybridisation of the R 4f states with the T *n*d states. Whereas this scenario is commonly accepted for the Ce-based compounds, it seems that it may also be applicable for the Pr- and Nd-based ones. In the case of the Pr-based compounds the crystal field effects may become responsible for the absence of any magnetic ordering as well.

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