XPS spectra, electronic structure, and magnetic properties of RFe$_5$Al$_7$ intermetallics

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ABSTRACT

The results of X-ray photoelectron spectroscopy measurements (core levels and valence bands) of RFe$_5$Al$_7$ (R = Lu, Tm, Er, Ho, Dy, Tb, Gd) single crystals are presented in comparison with the results of bulk magnetization studies and electronic structure calculations. It is shown that the increase of the Curie temperature in RFe$_5$Al$_7$ from Tm to Gd is associated with an increase of the indirect R $4f$ − Fe $3d$ exchange interaction at the expense of the multiplicity $2S + 1$ (statistical weight) in the ground state $^{2S+1}L_J$ of R^{3+} ions. The nonmonotonic behavior of the ferrimagnetic compensation temperature, T_{comp}, as well as the values of the spontaneous magnetic moment, M_s, and formation energy, E_{form}, of the $4f^n$ levels in R metals in a series from ErFe$_5$Al$_7$ to GdFe$_5$Al$_7$ are explained by the difference in the quantum numbers L, J and S of the ground state of R^{3+} ions, leading to a maximum value of T_{comp}, M_s and E_{form} for the Dy-containing compound. The electronic structure of Gd/LuFe$_5$Al$_7$ is calculated using the GGA+U approach, on the basis of which the physical mechanism and relative strength of the interatomic R-Fe and Al-Fe interactions are considered, and also the difference in the magnetic moments of iron atoms in different structural positions is explained.

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1. Introduction

Magnetic behavior of intermetallic compounds based on the transition $3d$ (T) and $4f$ (R) elements results from the interplay between the itinerant magnetism of the T sublattice and the localized magnetism of the R sublattice [1–3]. Their intrinsic magnetic properties can be understood in terms of exchange interactions and magnetocrystalline anisotropy [4]. The exchange interactions are of the Heisenberg type and take place between all unpaired spins in the $3d$-$4f$ system. The magnetic anisotropy originates largely from the R sublattice through the single-ion mechanism, although the T sublattice displays some anisotropy as well. In a given compound, the R - T intersublattice exchange interaction pulls out the R magnetic moment to a high magnetic ordering temperature, up to several hundred Kelvin, determined primarily by the T sublattice, and transfers the large magnetic anisotropy from the R to the T sublattice.

Ternary R(Fe,M)$_{12}$ intermetallic compounds with a tetragonal crystal structure of ThMn$_{12}$ type (space group $I4/mmm$) came into focus as materials interesting from both, technological and fundamental perspectives (see Ref. [5] for a review). On the one hand, some of them display a combination of large magnetic anisotropy, high saturation magnetization, and high magnetic ordering temperature and are therefore considered to be potential candidates for materials for permanent magnets. On the other hand, the complexity of interactions intrinsic to these materials leads to many different ground states and intricate magnetic behavior [6,7].

RFe$_5$Al$_7$ with heavy rare-earth elements are particularly interesting systems for fundamental studies due to the presence of competitive exchange and anisotropy interactions. In their crystal structure, the R atoms reside in the $2a$ site (Fig. 1). The Fe and Al atoms occupy the $8f$ and $8i$ sites, respectively. The remaining Fe atoms share the $8j$ site with Al [8–10].

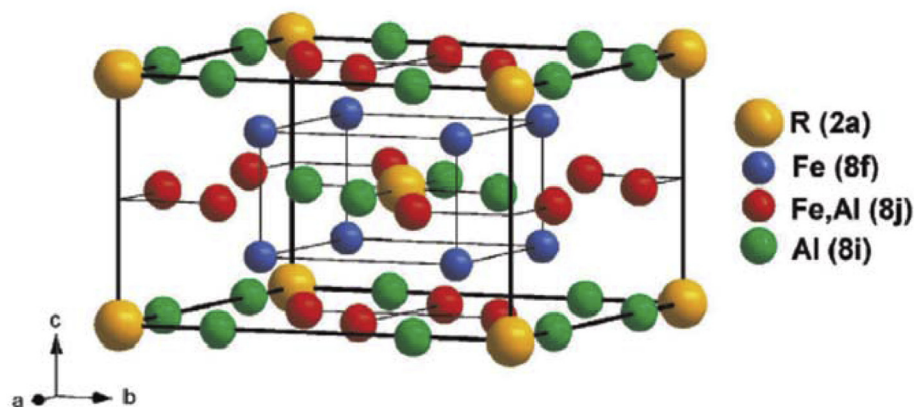The RFe$_5$Al$_7$ compounds with magnetic heavy rare-earth

Fig. 1. Crystal structure of RFe_5Al_7.

elements are ferrimagnets [8,9]. Ferromagnetic ordering within the Fe sublattice is stabilized by the $3d$-$4f$ exchange interaction since $LuFe_5Al_7$ with nonmagnetic Lu is an antiferromagnet. Although the whole Fe sublattice displays an easy-plane anisotropy, the Fe atoms residing in the $8f$ and $8j$ sites make opposite contributions to it [11]. The Tb, Dy, Ho, and Er sublattices also exhibit anisotropy of the easy-plane type [12]. By contrast, the Tm sublattice shows a uni-axial anisotropy that competes with the planar anisotropy of the Fe sublattice in $TmFe_5Al_7$ [12]. Due to the difference in the tempera-ture dependences of the magnetic moments of sublattices, magnetization compensation is observed in these compounds at a temperature T_{comp} (except those with $R - $ Gd and Tm). Magneti-zation and ultrasound studies showed rich physics of RFe_5Al_7 due to numerous spontaneous and field-induced magnetic phase transi-tions [13–17].

Although RFe_5Al_7 have been intensively studied in the past, a microscopic picture of the interaction between the R and T sub-lattices is still lacking. In the present work, we undertake X-ray photoelectron spectroscopy (XPS) and electronic structure calcu-lations to elucidate the main mechanisms responsible for the for-mation of magnetic properties of the RFe_5Al_7 compounds with different heavy rare-earth elements. The results are compared with the bulk magnetization measurements of RFe_5Al_7 single crystals. Our findings shed light on the individual atomic contributions to the magnetic properties and make it possible to explain consis-tently their variation throughout the whole RFe_5Al_7 family of compounds.

2. Experimental

Single crystals of RFe_5Al_7 with $R =$ Gd, Tb, Dy, Ho, Er and Tm were grown by a modified Czochralski method in a tri-arc furnace from a stoichiometric mixture of the pure elements (99.9% R, 99.98% Fe and 99.999% Al) on a rotating water cooled copper cru-cible under protective Ar atmosphere. A standard powder X-ray diffraction analysis showed that all crystals contain a single phase based on the $ThMn_{12}$-type structure. The lattice parameters are given in Table 1. The single crystal quality was checked using back-scattered X-ray Laue diffraction.

X-ray photoelectron spectroscopy core-level and valence band measurements were made using a PHI 5000 Versa Probe XPS spectrometer (ULVAC Physical Electronics, USA) based on a classic X-ray optic scheme with a hemispherical quartz monochromator and an energy analyzer working in the range of binding energies from 0 to 1500 eV. The apparatus uses electrostatic focusing and magnetic screening to achieve an energy resolution of $\Delta E \leq 0.5$ eV.

Table 1
Lattice parameters of RFe_5Al_7 compounds.

RFe_5Al_7	a (nm)	c (nm)	c/a	V (nm^3)
Gd	0.8711	0.5045	0.5792	0.3828
Tb	0.8703	0.5044	0.5796	0.3820
Dy	0.8689	0.5042	0.5803	0.3807
Ho	0.8678	0.5038	0.5805	0.3794
Er	0.8671	0.5037	0.5809	0.3787
Tm	0.8658	0.5032	0.5812	0.3772
Lu	0.8647	0.5031	0.5818	0.3762

Pumping of analytical chamber was carried out using an ion pump providing residual pressure better than 10^{-7} Pa. The surface of the samples was cleaned by Ar+ ion etching ($V = 2$ keV) for 2 min. Dual channel neutralization was used to compensate local surface charge generated during the measurement. The XPS spectra were recorded using Al Kα X-ray emission (1486.6 eV); the spot size was 200 μm, and the X-ray power load delivered to the sample was less than 50 W. Typical signal-to-noise ratios were greater than 10000:3. The XPS survey spectra (Fig. 2) show an efficiency of the surface cleaning demonstrating a low content of oxygen and car-bon. The high energy resolved XPS Fe $2p$ spectra (Fig. 3) also demonstrate the absence of contribution of Fe oxides and a close similarity with Fe metal.

3. Results and discussion

3.1. X-ray photoelectron spectra and analysis of the ground states of R^{3+} free ions and magnetic properties of RFe_5Al_7 compounds

XPS valence band (VB) spectra of RFe_5Al_7 compounds are shown in Figs. 4–5. For comparison, XPS VB spectra of pure rare-earth metals taken from Ref. [18] are also presented. The XPS spectra of the RFe_5Al_7 compounds indicate that in the low-energy region they are dominated by the contribution of the rare-earth $4f$- and $5p$-states. At the Fermi level, the contribution to the density of states is found to be dominated by the Fe $3d$- and R $5d$-states. According to Ref. [19], the intense contributions from rare-earth $4f$-states are related to the $4f$ final state multiplets. The peaks corresponding to the final state multiplets are slightly shifted with respect to those of pure rare-earth metals, which is probably due to the chemical shift connected with different chemical environment in the compounds. These data suggest that the rare-earth ions keep the 3+ valence in these compounds.

The Curie temperature, T_C, of RFe_5Al_7 ferrimagnets increases in the series from Tm to Gd, in accordance with the multiplicity