Photoemission electronic states and magnetic properties of Dy(Co$_{1-x}$Fe$_x$)$_2$

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Abstract

The valence band electronic states of Dy(Co$_{1-x}$Fe$_x$)$_2$ Laves phases with $x = 0, 0.05, 0.1, 0.7$ and 1.0 were measured by the ultraviolet photoemission spectroscopy (UPS) in room temperature. The Curie temperatures were determined from the electrical resistivity measurements and from the temperature dependence of the hyperfine fields by ^{57}Fe Mössbauer spectroscopy. The UPS spectra showed the very pronounced composition dependent emission at the Fermi energy E_F, the broad band within 0 and -4 eV binding energy interval below E_F and two strong features at about -6.5 and -9.0 eV. The spectra were compared with the band structure calculations using the full-potential linearized augmented plane waves (FLAPW) method. From the comparison we concluded that the intensities at E_F are correlated with the values of the Curie temperatures, the broad band comes entirely from different 3d Co and/or Fe states and the strong two features come entirely from 4f electrons of dysprosium.
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1. Introduction

The heavy rare earth-transition metal ferrimagnets of the RM$_2$ type are widely studied for a fundamental interest and for their practical applications [1–4]. Ferrimagnetism of the compounds is a result of the coexistence between the 4f (5d6s) and 3d magnetism. The electronic band structure of these intermetallics, and in particular that of their transition metal sublattice, is rather complex and poorly understood up to date.

It was previously found from our ^{57}Fe Mössbauer effect studies of the Dy(Mn$_{1-x}$Fe$_x$)$_2$ and Dy(Co$_{1-x}$Fe$_x$)$_2$ pseudobinaries that the ^{57}Fe magnetic hyperfine field treated as a function of the average number of 3d electrons calculated per transition metal site, resembles the Slater–Pauling plot, with a maximum value of the field for the Dy(Fe$_{0.7}$Co$_{0.3}$)$_2$ compound [5]. This Slater–Pauling dependence mainly reflects the magnetism of the transition metal sublattice. Additionally, it was found that the substitution Mn/Fe and Fe/Co in the above mentioned series also

induces a dependence of the Curie temperature on the number of 3d electrons. For the Dy(Co$_{1-x}$Fe$_x$)$_2$ series the parabola-like dependence of the Curie temperature T_C as a function of x with a maximum in the area of the Dy(Fe$_{0.8}$Co$_{0.2}$)$_2$, Dy(Fe$_{0.7}$Co$_{0.3}$)$_2$ compounds was observed and the following Curie temperatures were determined from the resistivity measurements: 670 K ($x = 1.0$), 699 K ($x = 0.95$), 714 K ($x = 0.90$), 718 K ($x = 0.8$), 692 K ($x = 0.7$), 687 K ($x = 0.6$), 682 K ($x = 0.5$), 624 K ($x = 0.45$), 523 K ($x = 0.30$), 303 K ($x = 0.2$), 293 K ($x = 0.10$), 167 K ($x = 0$) [6]. It was found that as a first approximation the Curie temperature scales linearly with the square of exchange energy splitting between the 3d majority and minority sub-bands [6]. In a more accurate approach to explain the dependence $T_C(x)$ the density of states at the Fermi level should also be considered. There is no doubt that the dependence originates from the changes in the 3d band.

We did not find in literature many experimental and theoretical results on the subject but only a few older ones [7–9]. Therefore, in the present paper we have focused our attention on the valence band (VB) structure and have undertaken the UPS study for a few compounds of the Dy(Co$_{1-x}$Fe$_x$)$_2$ series. The results have been compared with our band structure calculations

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with the full-potential linearized augmented plane waves (FLAPW) method. An attempt has been made to correlate the $T_C(x)$ dependence to the 3d band properties.

2. Experimental

The polycrystalline intermetallics Dy(Co$_{1-x}$Fe$_x$)$_2$ with $x = 0$, 0.05, 0.1, 0.3 and 1.0 (and also a few others), were synthesized by arc melting in a high purity argon atmosphere using appropriate amounts of Dy (99.9% purity), Fe and Co (all 99.99% purity) as starting materials. For the sake of homogenization the obtained small ingots were annealed in vacuum at 1200 K for 4 h and then cooled down with the furnace (cooling procedure: approximately 250 K/h). The standard X-ray powder diffraction measurements using Mo Kα radiation were performed at 300 K. The clean cubic, *Fd3m*, *MgCu$_2$*-type (C15) crystal structure was observed for all studied compounds.

The valence band (VB) spectra were detected in room temperature with the angle resolved ultraviolet photoemission spectrometer (ARUPS) equipped with the high-energy resolution analyzer of photoelectron kinetic energy AR 65 from Omicron. In fact, the UPS spectra were recorded only for the angles $\theta = 20°$ of incident ultraviolet radiation and the angle $\phi = 20°$ of out-coming electrons with respect to the surface normal because these are the polycrystalline samples and they did not depend of these angles. The energy resolution of the spectrometer was about 70 meV calibrated for the Fermi edge of Ag. The high intensity ultraviolet helium source from FOCUS of energy $h\nu = 21.2$ eV was used. Surfaces of the specimens were cleaned by heating up to 500–700 °C and annealed them *in situ* at ultra-high vacuum conditions down to the lowest pressure a few times 10^{-10} mbar. The standard procedure was used to subtract the background from secondary electrons [10]. Binding energies are related to the Fermi level ($E_F = 0$ eV) of a silver foil on which the samples were mounted to improve the electric contact with the sample holder and to decrease the charge loading of the sample surface.

3. Method of calculations

The electronic structure was calculated by *ab initio* self-consistent full-potential linearized augmented plane waves (FLAPW) method as implemented in WIEN2K code [11]. The generalized gradient approximation (GGA) in the parametrization of Perdew–Burke–Ernzerhof [12] was employed. The local density approximation (LDA + U) method was used for 4f electrons including the on site correlation energy U to settle down energy scale of Dy4f electronic states. The Brillouin zone integration was performed using a k mesh of 280k points in the irreducible Brillouin zone wedge. The core states were treated fully relativistic, while the valence states were treated within the scalar relativistic approximation. Some results of the calculations for selected compositions of the investigated compounds are presented in Fig. 1 where the sum of minority and majority partial density of states (DOS) for Fe, Co3d and Dy4f4f and 5d and the total DOS are shown for DyFe$_2$ and Dy(Co$_{0.5}$Fe$_{0.5}$)$_2$, as some selected examples. As the result of calculations the ferromagnetic coupling between Dy4f and 5d electrons and the antiferromagnetic coupling to those electrons from Fe and Co3d electrons were obtained. The spin-orbit coupling was not included into the calculations.

The density of states for Co and/or Fe atoms shows in general the five maxima between 0 and −4 eV and the Dy4f states contribute to VB entirely in the higher BE region from −4 to −8 eV with the contribution from Dy5d being negligible. Thus, the Co/Fe3d states form a broad maximum in the region between E_F to −4 eV and Dy4f states form the maxima in-between −4 and −8 eV which coincides with the measured spectra (see the next paragraph).

4. Results and their analysis

The UPS spectra of the investigated compounds are presented in Fig. 2.

The valence bands (VB) extend from the Fermi energy to the binding energy of about −12.5 eV. However, we believe that the
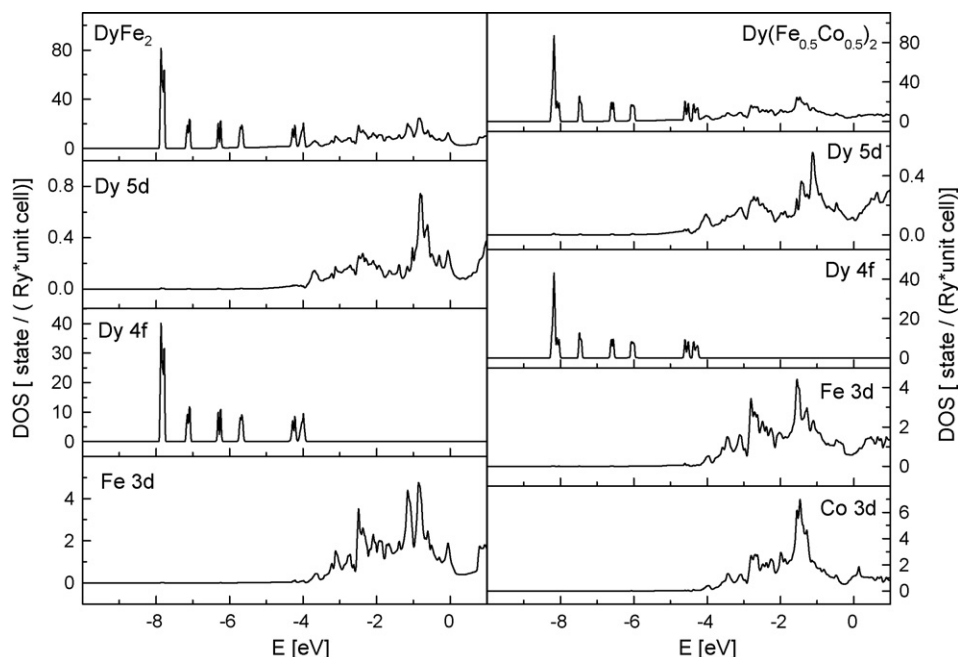

Fig. 1. The sum of minority and majority partial density of states (DOS) from constituent atoms (Fe, Co3d and Dy4f and 5d) and the total DOS for DyFe$_2$ and Dy(Co$_{0.5}$Fe$_{0.5}$)$_2$.
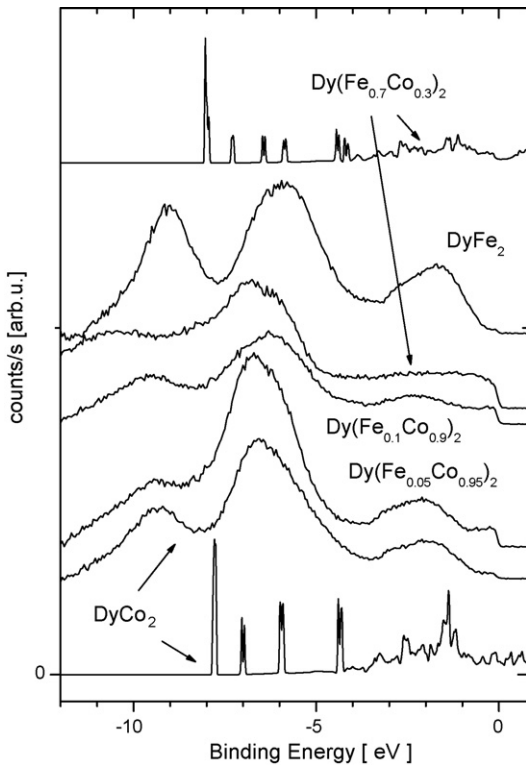
Fig. 2. The UPS valence band spectra of the given compounds together with the calculated total DOS for $DyCo_2$ (lower panel) and for $Dy(Fe_{0.7}Co_{0.3})_2$ (upper panel).

Fig. 3. The Curie temperatures T_C (full squares) and the intensities at the Fermi edge $N(E_F)$ (open circles) as a function of x-content of iron for $Dy(Co_{1-x}Fe_x)_2$. Inset shows the UPS spectra on expanded scale around the Fermi energy from which the intensities $N(E_F)$ were determined.

extension of VB is only to about -8 eV as shown our theoretical calculations in Fig. 1. The massive peak at about -9.5 may come from Dy4f electronic states (see text below), but partial contribution from some surface oxygen may not be excluded. The spectra were compared to our band density of states (DOS) calculations for $DyCo_2$ and $Dy(Fe_{0.7}Co_{0.3})_2$ in the lower and upper panels of the Fig. 2 as selected examples. As one can notice from Figs. 1 and 2 the calculated partial and total DOS are very similar instead of some details in vicinity of the Fermi energies, which cannot be reproduced very accurately from the calculations. In general, the valence band photoemission spectra of all compounds agree qualitatively with the result of the band calculations.

From the comparison one can conclude that the broad maximum at about -2 eV comes entirely from different Co- and/or Fe-3d states and the strong emission at about -6.5 eV originates entirely from the Dy4f states. For the pure heavy rare-earth metals Dy, Er and Ho the 4f states spread from about -4 eV even to about -12 eV specifically for Dy [13].

The very important observation from the UPS spectra is the rather sharp and intensive Fermi edge for the composition with $x = 0.05$, 0.1 and 0.7 in comparison to the parent compounds with $x = 0$ and 1.0. The properly calibrated to the same number of counts/s intensity in the mid-height at Fermi edge scales with the Curie temperature for all compounds with exception of $DyFe_2$. This correlation is shown in Fig. 3 together with the extended spectra in vicinity of the Fermi energy shown in the inset of Fig. 3. The exception of $DyFe_2$ from the correlation is
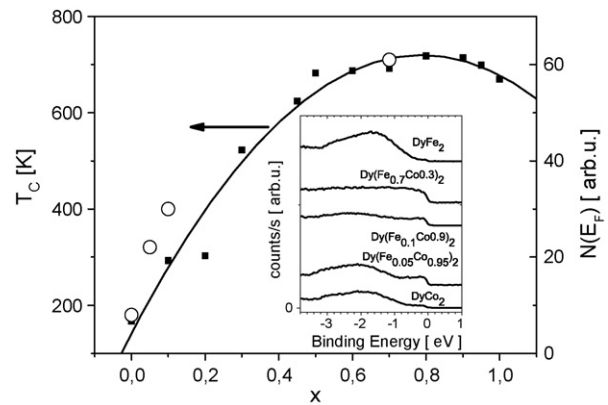
probably associated with the fact that the exchange integral of the compound is bigger and here 3d electrons are more localized than in other investigated compounds [2,3], giving rise to the increase of the Curie temperature over the simple correlation.

In fact we shall expect here the quadratic relation between T_C and $N(E_F)$ because from one side $T_C \sim \Delta E \times N(E_F)$ [2] and from the other side it was argued in our previous paper that $T_C \sim \Delta E^2$ [6], where ΔE is the exchange splitting.

The measured conductivities σ at room temperature [6] also scales with the intensities at E_F, which we believe are proportional to the relevant density of states at the Fermi energy $N(E_F)$. For example, the resitivity ratio ρ $[DyCo_2]/\rho$ $[Dy(Co_{0.9}Fe_{0.1})_2]$ is about 9 in 300 K [6] and the relevant ratio of the experimental density of states is similar but of course in inverse proportion because $\sigma \sim 1/\rho$.

Finally, to fit the energy position of measured features coming from Dy4f electronic states to their calculated DOS we had to fix the on-site correlation energy of f-electrons to $U_{ff} = 7$ eV. It means that also the correlation effects are very important in understanding the electronic, transport and magnetic properties of these compounds.

5. Summary and conclusions

We have performed UPS measurements of the polycrystalline intermetallic Laves phases $Dy(Co_{1-x}Fe_x)_2$ with $x = 0$, 0.05, 0.1, 0.3 and 1.0 in room temperature. The UPS spectra were qualitatively compared to our electronic band structure calculations by the FLAPW method and the local density approximation (LDA + U) was used for treatment of Dy4f electrons (see Figs. 1 and 2). It was argued that the states from Co and/or Fe3d electrons form the Fermi edge and the broad maximum centered at about -2 eV and that the Dy4f states with the correlation energy $U_{ff} \cong 7$ eV contribute to VB entirely in the higher BE region from -4 to -10 eV with the contribution from Dy5d being negligible.

From comparison of the Curie temperatures with the intensities at the Fermi edge as a function of x-content of iron (see

Fig. 3), the conclusion was drawn on their proportional scaling relation.

References

[1] K.N.R. Taylor, Adv. Phys. 20 (1971) 551.
[2] K.H.J. Buschow, in: E.P. Wohlfarth (Ed.), Ferromagnetic Materials, North-Holland, Amsterdam, 1980, pp. 1–299.
[3] E. Burzo, H.R. Kirchmayr, in: K.A. Geschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, North-Holland, Amsterdam, 1989, pp. 12–71.
[4] A.M. Tishin, Y.I. Spichkin, The Magnetocaloric Effect and Its Applications, Institute of Physics Publishing, Bristol, 2003.
[5] B. Gicala, J. Pszczoła, Z. Kucharski, J. Suwalski, Solid State Commun. 96 (1995) 511.
[6] P. Stoch, J. Pszczoła, P. Guzdek, J. Chmist, A. Pańta, J. Alloys Compd. 394 (2005) 116.
[7] R. Coehoorn, K.H.J. Buschow, J. Magn. Magn. Mater. 118 (1993) 175.
[8] R.F. Sabirianov, S.S. Jaswal, J. Appl. Phys. 79 (1996) 5942.
[9] J. Inoue, M. Shimizu, J. Phys. F: Met. Phys. 18 (1988) 2487–2497.
[10] S. Taugard, Surf. Sci. 216 (1989) 343.
[11] K. Schwarz, P. Blacha, Comput. Mater. Sci. 28 (2003) 259.
[12] J.P. Perdew, S. Burke, M.E. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[13] S. Hüfner, Photoelectron spectroscopy, Springer Ser. Solid-State Sci. 82 (1995) 455.