XAFS and XRD studies of local structure peculiarities in magnetic $R_2Fe_{17-x}Mn_x$ ($R = Ce, Lu$) intermetallics

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Abstract. The rearrangement of cerium and lutetium local environment in $Ce_2Fe_{17-x}Mn_x$ and $Lu_2Fe_{17-x}Mn_x$ intermetallics vs. Mn concentration and temperature was investigated by means of the extended X-ray absorption fine structure (EXAFS) spectroscopy above K-Ce absorption edge and powder X-ray diffraction. The valence state of Ce in $Ce_2Fe_{17-x}Mn_x$ was also studied by X-ray absorption near-edge structure (XANES) spectroscopy above $L_3$-Ce absorption edge. The correlation between changes in local electronic and crystal structure and the types of magnetic ordering in these compounds is discussed.

1. Introduction

$R_2Fe_{17}$ ($R$ - rare-earth element) intermetallic compounds are extensively studied due to large magnetic moments and multiple magnetic transitions [1, 2]. In compound $Ce_2Fe_{17}$ with the $Th_2Zn_{17}$-type crystal structure the partial substitution of Mn for Fe causes the origin of unusual magnetic properties: at the low temperature the basic state is ferromagnetic, but in the Mn concentration range $x = 0.5 - 1.0$ it is helical antiferromagnetic [3]. The $Lu_2Fe_{17}$ compound with related $Th_2Ni_{17}$-type structure exhibit the similar magnetic behavior as $Ce_2Fe_{17}$ being ferromagnetic at low temperature and antiferromagnetic at higher temperature [4]. However, upon Mn-doping the temperature of "ferromagnetic-antiferromagnetic" transition $\Theta_T$ in $Lu_2Fe_{17-x}Mn_x$ increases up to Néel temperature and, finally, the compounds in the range $x = 0.7 - 2$ exhibit only ferromagnetic ordering with a near constant $T_C(x)$ value [4].

It is assumed that magnetic ordering in $R_2Fe_{17}$ is dictated generally by 3$d$-atoms exchange interaction characterized by the critical distance of sign change (e.g. two Fe atoms in the distance more than 2.45 Å interact ferromagnetically [5]) and, hence, depends on the features of crystal structure. Therefore, the aim of present research was to refine the local crystal structure of $R_2Fe_{17-x}Mn_x$ ($R = Ce, Lu$) compounds with the methods of extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray diffraction (XRD), and to check if there are any correlations with magnetic ordering. Besides, the valence state of Ce ion in $Ce_2Fe_{17-x}Mn_x$ was studied by means of X-ray absorption near edge structure (XANES) spectroscopy since it might contribute into non-monotonous behavior of magnetic parameters.

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Figure 1. (a) $K$-Ce EXAFS-functions $\chi(k)k^2$ of Ce$_2$Fe$_{17-x}$Mn$_x$ at 8 K; (b) their Fourier-transformation modules

Figure 2. The temperature dependences of (a) $R_{Ce-\text{Fe}(Mn)}(T)$ interatomic distance; (b) distance between 3d-metal atoms in the position 18f of Ce$_2$Fe$_{17-x}$Mn$_x$ structure

2. Experimental

The preparation and temperatures of magnetic transitions in Ce$_2$Fe$_{17-x}$Mn$_x$ ($x = 0; 1; 2$) and Lu$_2$Fe$_{17-x}$Mn$_x$ ($x = 0; 0.2; 0.5; 0.7; 2$) samples are reported in [3, 4, 6]. The X-ray absorption spectra were collected at C beamline of DORIS III storage ring (DESY, Hamburg, Germany) above $K$-Ce (40443 eV) and $L_3$-Ce (5723 eV) absorption edges on Ce$_2$Fe$_{17-x}$Mn$_x$ and above $L_3$-Lu (9244 eV) absorption edge on Lu$_2$Fe$_{17-x}$Mn$_x$. The energy resolution of double-crystal Si (311) monochromator was about 2.5 eV at 40 keV and 1.2 eV at 6 keV (the Si (111) plate). Low-temperature measurements were carried out using a liquid helium continuous flow cryostat with a temperature control of ±1 K at 300 K and ±0.1 K at 5 K. The XRD patterns of Lu$_2$Fe$_{17-x}$Mn$_x$ were collected at B2 beamline of DORIS III using the X-ray wavelength 0.688106 Å and the closed cycle refrigerator for measurements in the 8 – 308 K temperature range.

3. Results and discussion

The EXAFS spectra of Ce$_2$Fe$_{17-x}$Mn$_x$ were collected above the high-energy $K$-Ce (40443 eV) absorption edge so that they are not limited in length by the presence of another edges and contain more information on local structure. Because of the small Mn concentration and the similarity of Fe and Mn photoelectron back scattering phases and amplitudes it was not possible to distinguish between the Fe and Mn contributions in the experimental spectrum. Fig.1 shows
the EXAFS-functions $\chi(k)^2$ of Ce$_2$Fe$_{17-x}$Mn$_x$ ($x = 0; 1; 2$) samples at 8 K and their Fourier-transformation modules (FT). The first split maximum in the $R \sim 2 - 3.5 \text{ Å}$ region of FT (fig.1(b)) corresponds to 6 coordination shells containing 3$d$-metal atoms Fe(Mn). The next small peak at $R \sim 3.7 \text{ Å}$ corresponds to one Ce atom situated along the $c$ axis relative to the absorbing atom. It is clearly seen that the shape of maxima changes with the Mn concentration.

The radius of coordination shell containing 1 cerium atom or the $R_{\text{Ce-Ce}}$ distance between two Ce atoms along the $c$ axis monotonously increases from $3.84 - 3.86$ to $3.88 - 3.92$ Å in various samples with the temperature decrease from 300 to 8 K. It correlates well with the temperature dependence of cell parameter $a(T)$ [7]. The temperature dependences of the first coordination shell radius $R_{\text{Ce-Fe(Mn)}}(T)$ containing 3$d$-metal atoms (fig.2(a)) are in qualitative agreement with the cell parameters $a(T)$ [7] for the investigated compounds. In the binary alloy Ce$_2$Fe$_{17}$ the $R_{\text{Ce-Fe}}(T)$ dependence has the minimum at 77 K corresponding to the drastic fall of the $a(T)$ at $T \sim 90$ K [7].

The $R_{\text{Ce-Fe(Mn)}}(T)$ and $R_{\text{Ce-Ce}}(T)$ dependences obtained and the crystal structure data [7] allowed us to calculate the temperature dependence of distance between the 3$d$-metal atoms forming the first coordination shell (crystallographical position 18f) (fig.2(b)). The figure shows that the critical value of 2.45 Å is exceeded in both Ce$_2$Fe$_{17}$ and Ce$_2$Fe$_{15}$Mn$_2$ at the temperature less than 100 K corresponding to the ferromagnetic ordering region in these alloys. In Ce$_2$Fe$_{18}$Mn alloy the distance between the 3$d$-metal atoms at the low temperature is close but less than 2.45 Å. It might be that this sample at low temperature is close to the ferromagnetic state which forms in the neighboring alloy Ce$_2$Fe$_{15.7}$Mn$_{1.3}$ [6] but does not reach it.

The determination of cerium valence from $L_3$-Ce XANES spectra of Ce$_2$Fe$_{17-x}$Mn$_x$ is reported elsewhere [8, 9]. The main result is that the average oxidation state of cerium does not depend on temperature, but slightly depends on Mn concentration. In all three samples $x = 0; 1; 2$ the valence of Ce is intermediate around 3.30 – 3.33, however, in ferromagnets $x = 0; 2$ its value is slightly larger, than in antiferromagnet $x = 1$.

In the Th$_2$Ni$_{17}$-type crystal structure of Lu$_2$Fe$_{17}$ intermetallics Lu atoms occupy two different crystallographical positions 2$b$ and 2$d$, which makes EXAFS analysis of Lu$_2$Fe$_{17}$-based compounds extremely complicated. Therefore, we report here only on Lu$_2$Fe$_{17-x}$Mn$_x$ study by more self-consistent method of powder X-ray diffraction. The XRD patterns of Lu$_2$Fe$_{17-x}$Mn$_x$ were processed by the Rietveld method. The temperature dependences of lattice parameters and atomic coordinates were refined, interatomic distances calculated. The results indicate...
that the pair of 3d-metal atoms in position 12j probably gives the main contribution into formation of magnetic properties, since only change of distance between this pair of atoms passes the critical value of 2.45 Å [5] at some temperature $T_{cr}$ in all samples except for $x = 2$ (Fig.3). Within the temperature range 8 – 308 K the distances between other possible pairs of Fe(Mn) atoms are always greater or less than the critical value. The obtained values of $T_{cr}$ increase monotonously with the Mn concentration and are in satisfactory agreement with the temperatures of "ferromagnetic-antiferromagnetic" transition $\Theta_f$ (Fig.4) including the $x = 0.7$ sample for which the temperatures of "ferromagnetic-antiferromagnetic" and "antiferromagnetic-paramagnetic" transitions match and Curie temperature $T_C$ appears [4].

In the Th$_2$Ni$_{17}$-type crystal structure of Lu$_2$Fe$_{17-x}$Mnx the 12j position is analogous to 18f position in the Th$_2$Zn$_{17}$-type structure of Ce$_2$Fe$_{17-x}$Mnx. The temperature and concentration behavior of distance between Fe(Mn) atoms in these positions correlates well with the change of magnetic ordering in both Ce$_2$Fe$_{17-x}$Mnx and Lu$_2$Fe$_{17-x}$Mnx. Since the magnetic phase diagrams are quite different for these systems, one can conclude that the exchange interaction between 3d-metal atoms in positions 18f/12j is determinant for the type of magnetic ordering in such compounds. The recent high pressure study of Lu$_2$Fe$_{17-x}$Mnx revealed a probable high impact of Mn atoms on the magnetic transition temperatures in addition to Fe atoms [10].

4. Conclusion
The substitution of Mn for Fe causes the changes in local crystal structure of R$_2$Fe$_{17-x}$Mnx (R = Ce, Lu) compounds. The distances between the Fe atoms in positions 12j and 18f in Ce$_2$Fe$_{17-x}$Mnx and Lu$_2$Fe$_{17-x}$Mnx alloys respectively exceed the critical value of 2.45 Å [5] exactly in the T and x regions of ferromagnetic ordering. Besides, in all Ce$_2$Fe$_{17-x}$Mnx samples the intermediate valence state of cerium was confirmed, changing with Mn concentration but independent from the temperature. In summary, the results agree with the assumption of magnetic ordering in such systems being governed by exchange interaction between the 3d-metal atoms, but leave open the possible impact of an electronic factor.

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