Correlation of Magnetic Properties with the Local Features of the Electronic and Crystal Structure in the $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ Intermetallide: XAFS Data Analysis

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The rearrangement of the local environment of cerium has been examined using extended X-ray absorption fine structure spectroscopy above the K -Ce absorption edge for various manganese contents and temperatures in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ intermetallics ($x = 0, 1, 2$). The valence state of cerium has been studied simultaneously by X-ray absorption near-edge structure spectroscopy above the L_3 -Ce absorption under the same conditions. A correlation has been revealed between the changes observed in the local electronic and crystal structure of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds and the types of magnetic states in them.

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Intermetallic compounds R_2Fe_{17} (where R is a rare-earth element) have high magnetic moments and relatively low Curie temperatures. The Curie temperatures T_c increase upon insignificant partial substitution of aluminum, silicon, gallium, cobalt, and other elements for iron [1, 2], as well as upon the introduction of hydrogen, nitrogen, or carbon atoms [3]. The R_2Fe_{17} compounds thus modified can be used to manufacture strong and relatively cheap permanent magnets.

The R_2Fe_{17} intermetallides crystallize in a $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral crystal structure; at various temperatures, they exhibit both ferromagnetic and antiferromagnetic properties caused by the interaction between $3d$ atoms. In the case of the substitution of manganese for some iron atoms in R_2Fe_{17} , the Fe–Fe, Mn–Mn, and Fe–Mn $3d$ exchange interactions are decisive. These atoms have the same character of the dependence on the interatomic distance, but different critical distances at which the exchange interaction changes sign; i.e., the interaction between two iron atoms at distances smaller and larger than a critical value of 2.45 Å is antiferromagnetic and ferromagnetic, respectively [4]. The partial substitution of manganese for iron in R_2Fe_{17} (where $R = \text{Y, Pr, Nd, Gd, Tb, Er}$) induces a monotonic decrease in the Curie temperature and spontaneous magnetization.

The $\text{Ce}_2\text{Fe}_{17}$ compound is remarkable in the R_2Fe_{17} series. The volume of $\text{Ce}_2\text{Fe}_{17}$ unit cell is approximately by 4% smaller than the value extrapolated from the unit cell volumes of the other R_2Fe_{17} compounds. The substitution of manganese atoms for some iron atoms in $\text{Ce}_2\text{Fe}_{17}$ leads to unusual magnetic properties; the ground state at low temperatures is ferromagnetic, but the compound with the manganese content $x = 0.5–1.0$ is a helical antiferromagnet [5]. The non-monotonic behavior of the magnetic parameters can be caused by the features of the local crystal structure, as well as by the instability of the valence state of cerium [6]; throughout the hybridization with the iron and manganese $3d$ electrons, the cerium $4f$ level affects the magnetic state of the entire compound [7].

The aim of this work is to reveal correlations between the features of the local structure and magnetic properties of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ quasibinary intermetallics. The effect of substitution of manganese for iron on the local crystal structure of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds is examined using extended X-ray absorption fine-structure (EXAFS) spectroscopy above the K -Ce absorption edge. The valence state of a cerium ion is studied simultaneously by X-ray absorption near-edge structure (XANES) spectroscopy above the L_3 -Ce absorption edge.

The $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ samples were prepared using the high-frequency melting of the initial components

Table 1. Temperatures of magnetic phase transitions in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ [8]

x	Θ_T , K	T_N , K
0	94.4	204
1	—	198
1.7	54.6	180.6
2	80	168

in an Al_2O_3 crucible in an argon atmosphere. The resulting ingots were annealed in vacuum for three days at a temperature of 1173 K, then quenched in water. The temperature of the ferromagnet–antiferromagnet magnetic phase transition T and the Néel temperature of the antiferromagnetic ordering T_N are summarized in Table 1 [8]. X-ray absorption fine structure (XAFS) spectra were obtained at C beamline of the DORIS III storage ring (DESY, Hamburg, Germany) above the K -Ce (40443 eV) and L_3 -Ce (5723 eV) absorption edges. The energy resolution of double-crystal Si(311) monochromator was 2.5 eV at

an energy of 40 keV with a collimation slit width of 1.0 mm and 1.2 eV at an energy of 6 keV with a collimation slit width of 0.3 mm (for the Si(111) monochromator). The position of the monochromator crystal was detuned by 50% from the maximum intensity in order to minimize the higher harmonic contamination. Low-temperature measurements were carried out using a continuous flow liquid helium cryostat with a temperature instability of 1 and 0.1 K at 300 and 5 K, respectively. The extraction of $\chi(k)$ EXAFS functions from the initial X-ray absorption spectrum $\mu(E)$, as well as the Fourier analysis and the fitting of $\chi(k)$ functions, was performed using the VIPER software package [9].

Figure 1 shows the extracted EXAFS functions $\chi(k)k^2$ collected above the K -Ce absorption edge on $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ ($x = 0, 1, 2$) samples at a temperature of 8 K and the absolute values of their Fourier transforms. The first split maximum in the region $R \sim 2$ –3.5 Å of the absolute values of Fourier transform (Fig. 1b) corresponds to six coordination shells that include 3d metal atoms Fe(Mn) at four different crystallographic positions. A large contribution to this peak comes from the first shell that contains six 3d metal atoms at the crystallographic position 18f in the basal plane of the **a** and **b** vectors. The next small peak at $R \sim 3.7$ Å corresponds to one cerium atom located along the c axis with respect to the absorber atom. It is clear that the shape of the maxima changes with an increase in the Mn content. As a result, the data was obtained on the coordination shells around the Ce atom, which contain cerium and 3d-metal atoms. It was not possible to separate the Fe and Mn contributions to the experimental spectrum because of a low Mn content. Moreover, Fe and Mn, which are neighboring elements in the Periodic Table, have close phases and amplitudes of photoelectron backscattering.

The radius of a coordination shell containing one cerium atom or the distance $R_{\text{Ce-Ce}}$ between two cerium atoms along the c axis increases monotonically from 3.84–3.86 Å to 3.88–3.92 Å in various samples with a decrease in the temperature from 300 to 8 K (Fig. 2). This behavior correlates well with the temperature dependence of the lattice parameter $c(T)$ [10–12], which is represented in Fig. 3. An increase in $c(T)$ upon the cooling of the samples is due to strong spontaneous magnetostrictive strain, which is significant for R_2Fe_{17} -type alloys [13]. Magnetostrictive strains in R_2Fe_{17} begin at temperatures much higher than the magnetic ordering temperature because of the short-range magnetic order [14]. For the $\text{Ce}_2\text{Fe}_{17}$ binary alloy, a number of weak features are observed in the $R_{\text{Ce-Ce}}(T)$ dependence below the Néel temperature, in particular at $T = \Theta_T$, as well as in the $c(T)$ dependence. The $R_{\text{Ce-Ce}}(T)$ dependence for the $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ alloy is smoother and has no significant features compared to $x = 0$ (Fig. 2); the same is valid for the $c(T)$ and $a(T)$

Fig. 1. (a) K -Ce EXAFS functions $\chi(k)k^2$ at a temperature of 8 K. (b) Absolute values of their Fourier transforms.

Fig. 2. Temperature dependences of the distance $R_{\text{Ce-Ce}}$ to the nearest Ce atom in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$.

dependences of the lattice parameters of the $\text{Ce}_2\text{Fe}_{15.3}\text{Mn}_{1.7}$ alloy that is close in composition and related in magnetic structure (Fig. 3). This may be due to the related helical magnetic structure of ferromagnetic and antiferromagnetic states below and above Θ_T [11] in the $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ alloy.

The temperature dependences of the radius $R_{\text{Ce-Fe(Mn)}}$ of the first coordination shell, which contains $3d$ -metal atoms, are in qualitative correlation with the lattice parameters $a(T)$ (Fig. 3) for the alloys under investigation (Fig. 4). The $R_{\text{Ce-Fe}}(T)$ dependence for the $\text{Ce}_2\text{Fe}_{17}$ binary alloy has a minimum at 77 K that corresponds to a sharp jump of $a(T)$ at $T \sim 90$ K inherent in this alloy. Upon cooling below and heating above this temperature, the radius $R_{\text{Ce-Fe}}(T)$ increases similarly to the $a(T)$ dependence. The radius $R_{\text{Ce-Fe(Mn)}}(T)$ in $x = 1, 2$ alloys decreases upon cooling similar to $a(T)$, which also corresponds to the shape of the $a(T)$ dependence for the $\text{Ce}_2\text{Fe}_{15.3}\text{Mn}_{1.7}$ alloy with a close structure (Fig. 3). Note that the radius $R_{\text{Ce-Fe(Mn)}}(T)$ of the first coordination shell has a small component along the c axis. For this reason, the deformation along the c axis also affects the temperature dependence $R_{\text{Ce-Fe(Mn)}}(T)$.

The temperature dependences of the $R_{\text{Ce-Fe(Mn)}}(T)$ distance are more sensitive to the magnetic transitions in R_2Fe_{17} -type alloys than the $R_{\text{Ce-Ce}}(T)$ distance. The reason is that the $R_{\text{Ce-Fe(Mn)}}$ distance characterizes the approach of $3d$ metal atoms inside a coordination shell, which enhance the negative $3d$ - $3d$ exchange interactions and weaken the positive $3d$ - $3d$ exchange interactions. The resulting $R_{\text{Ce-Fe(Mn)}}(T)$ and $R_{\text{Ce-Ce}}(T)$ dependences and the data on the crystal structure parameters of alloys [10–12] made it possible to calculate the temperature dependence of the distance between $3d$ metal atoms that form the first coordination shell (crystallographic position 18f)

Fig. 3. Temperature dependences of the lattice parameters $a(T)$ and $c(T)$ in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ [10–12].

(Fig. 5). The figure shows that the interatomic distance of 2.45 Å [4] is overcome in both $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ below 100 K, which corresponds to the ferromagnetic ordering region in these alloys. The distance between the $3d$ metal atoms in the $\text{Ce}_2\text{Fe}_{16}\text{Mn}$ alloy at low temperature is close to but does not achieve 2.45 Å. The precision magnetic measurements on the $\text{Ce}_2\text{Fe}_{16}\text{Mn}$ single crystal sample indicate the possible existence of clusters with a noncollinear magnetic structure at liquid helium temperatures [8]. In particular, a noticeable increase in the magnetization

Fig. 4. Temperature dependences of the radius $R_{\text{Ce-Fe(Mn)}}(T)$ of the first coordination shell around Ce atom, containing six $3d$ -metal atoms in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ samples.

Fig. 5. Temperature dependences of the distance between $3d$ -metal atoms in the basal plane of the vectors **a** and **b** (crystallographic position $18f$).

for the sample cooled in the magnetic field begins below 25 K in the temperature dependence (see Fig. 8c in [8]). The $\text{Ce}_2\text{Fe}_{16}\text{Mn}$ alloy at low temperatures may be close to the ferromagnetic state, which is implemented in the neighbor compound $\text{Ce}_2\text{Fe}_{15.7}\text{Mn}_{1.3}$ [8].

The temperature dependences of Debye–Waller factors $\sigma^2(T)$ for coordination shells around the cerium atom were also obtained during the EXAFS analysis and processed in the framework of the Einstein harmonic model. As a result, the Einstein temperatures Θ_E , which characterize the rigidity of the bonds, and the static Debye–Waller factors σ_s^2 , which characterize the local static disorder (Table 2), were obtained. It is clear that the bond between cerium and $3d$ metal atom in the first coordination shell ($18f$ position) is more rigid and less static disordered than the Ce–Ce bond.

The normalized experimental L_3 -Ce XANES spectra of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ samples ($x = 0, 1, 2$) measured at a temperature of 8 K are shown in Fig. 6. The absorption peaks (the so-called white lines) are split because of the intermediate-valence state of cerium. Two maxima corresponding to different valence states of cerium are well resolved. At the same amplitude of the Ce^{4+} component, the amplitude of the Ce^{3+} component depends on Mn content. A similar picture is observed at other temperatures. The extraction of components corresponding to different cerium valences and evaluation of their contributions to the experimental L_3 -Ce XANES spectrum were performed using the conventional decomposition of a complex spectrum into the combination of Lorentz and arc tangent functions with the constrained widths and energy positions [15]. Figure 6 exemplifies the decomposition of the $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ spectrum at $T = 8$ K in the $x = 2$ plot.

Fig. 6. L_3 -Ce XANES spectra of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ samples at a temperature of 8 K. The Ce^{3+} and Ce^{4+} contributions are shown, the spectrum of the $x = 2$ sample is fitted using the analytical functions.

Figure 7 shows the temperature dependences of the cerium valence for three studied samples ($x = 0, 1, 2$). It can be seen that the valence is almost independent of the temperature, but depends on the Mn content. The cerium valence in $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ is maximal among the other samples, which qualitatively correlates with the smallest distance $R_{\text{Ce-Fe(Mn)}}$ (Fig. 4) and, therefore, the maximum possible $4f$ – $3d$ hybridization at low temperatures. The strong outer shell hybridization of cerium and $3d$ metal atoms is a possible cause of the helical ferromagnetic state in the alloy with $x = 2$, in contrast to the collinear ferromagnet with $x = 0$, where this hybridization is weaker according to a smaller

Fig. 7. Temperature dependences of the cerium valence in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ samples.

Table 2. Einstein temperatures and static Debye–Waller factors for the coordination shells around the Ce atom in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$

Bond	Θ_E , K	σ_s^2 , Å ²
$\text{Ce}_2\text{Fe}_{17}$		
Ce–Fe(18f)	190	0.4×10^{-3}
Ce–Ce	146	1.6×10^{-3}
$\text{Ce}_2\text{Fe}_{16}\text{Mn}$		
Ce–Fe(Mn)(18f)	204	0.4×10^{-3}
Ce–Ce	144	1.2×10^{-3}
$\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$		
Ce–Fe(Mn)(18f)	190	0.1×10^{-3}
Ce–Ce	168	1.5×10^{-3}

cerium valence. The difference between cerium valences in the $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{16}\text{Mn}$ samples is very small (within the error); however, it actually exists as can be seen in Fig. 6. To summarize, the cerium valences in all three samples ($x = 0, 1, 2$) are different and, furthermore, are larger in ferromagnets ($x = 0, 2$) than in antiferromagnets ($x = 1$). The closeness of cerium valence in the $x = 0$ alloy to the valence in the $x = 1$ alloy indicates the proximity of its magnetic state to ferromagnetic, which correlates with the temperature dependence of the distance between 3d metal atoms (Fig. 5).

Thus, the substitution of manganese for iron leads to changes in the local crystal and electronic structure of $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ compounds. Here, the local Ce–Fe(Mn) interatomic distances correlate with magnetic ordering both overall for the entire sample and, possibly, local in clusters with the short-range magnetic order. The sensitivity of these local distances to spontaneous magnetic transformations in $\text{Ce}_2\text{Fe}_{17-x}\text{Mn}_x$ alloys is higher than sensitivity of lattice parameters and local Ce–Ce distances. It has been revealed that the distance between iron atoms in $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{15}\text{Mn}_2$ alloys at low temperature exceeds a critical value of 2.45 Å, which leads to the ferromagnetic ordering of the system. In all alloys, cerium is in intermediate valence state, which is independent of the temperature but depends on the Mn content. The

cerium valence in ferromagnets ($x = 0, 2$) is larger than that in the antiferromagnet with $x = 1$.

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