$Lu_2Fe_{16.5}Ru_{0.5}$金属間化合物の結晶構造と磁歪特性

Crystal Structure and Magnetoelastic Properties of $Lu_2Fe_{16.5}Ru_{0.5}$ Intermetallic Compound

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1. Introduction

The compounds R_2Fe_{17} (R = rare earth) belong to a very interesting group of magnetic materials with extremely strong magneto-volume coupling and exhibit the most of Invar-like anomalies such as an anomalous and anisotropic positive spontaneous magnetostriction and negative thermal expansion behavior in a wide temperature range [1]. The peculiar magnetic properties of the R_2Fe_{17} series are mainly determined by the Fe-Fe interatomic distances and by the number of Fe nearest neighbors, resulting in competition of positive and negative exchange interactions between the Fe atoms at four non-equivalent crystallographic sites of the rhombohedral (Th_2Zn_{17} type) and hexagonal (Th_2Ni_{17} type) crystal structures as formed for the light and heavy rare earths, respectively. The presence of dumbbell-like pairs of Fe atoms with the shortest interatomic distances d_{FeFe} and the strongest negative exchange interactions between the atoms is a special feature of R_2Fe_{17} compounds.

For the Lu_2Fe_{17} compound with the smallest non-magnetic rare earth element, the competition of exchange interactions results in appearance of two types of magnetic ordering when increasing the temperature: ferromagnetic (F) phase up to the Curie temperature T_C = 130 K and the non-collinear antiferromagnetic (AF) (helimagnetic) phase up to the Néel temperature T_N = 274 K [2]. The variation of interatomic distances in Lu_2Fe_{17} by means of changing the external (pressure) and internal (substitution, hydrogenation) conditions was found to influence drastically the magnetic properties. As it was found recently, the small substitution of Ru for Fe in $Lu_2Fe_{16.5}Ru_{0.5}$ (similar to the substitution case of Ce for Lu, in $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$, studied previously [3]) leads to stabilization of the antiferromagnetic state in the whole range of magnetic order up to the Néel temperature of 208 K [4].

Figure 1 shows the magnetization isotherms along the a and c axes for $Lu_2Fe_{16.5}Ru_{0.5}$. The same as the parent Lu_2Fe_{17}, $Lu_2Fe_{16.5}Ru_{0.5}$ compound has the easy-plane type of magnetic anisotropy with the hard c-axis magnetization direction.

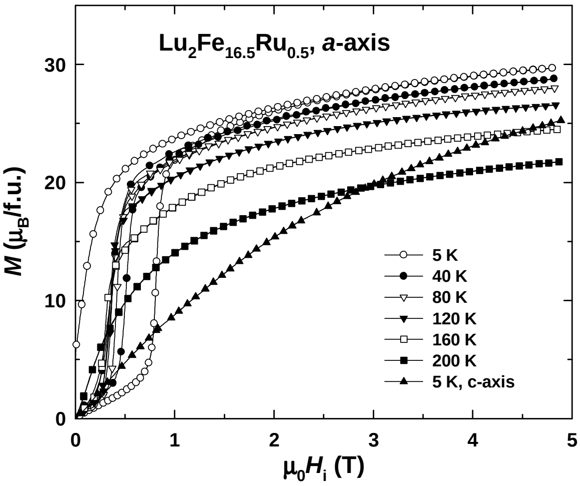

Fig. 1. Magnetization curves along the axes a (various temperatures) and c (5 K) of $Lu_2Fe_{16.5}Ru_{0.5}$ single crystal.

The magnetization process for $Lu_2Fe_{16.5}Ru_{0.5}$ consists of two stages: the metamagnetic transition from the non-collinear AF into the possible non-collinear F (so-called fan structure) in magnetic field of 0.8 T with a subsequent turn of magnetic moments into the collinear F at higher fields. In contrast to $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$, where the magnetization reaches its saturation value of 35 μ_B/f.u. (i.e. the same as the spontaneous magnetic moment in the ferromagnetic Lu_2Fe_{17}) at approx. 2 T [3], the second stage of magnetization process for $Lu_2Fe_{16.5}Ru_{0.5}$ is found to extend up to the highest applied magnetic field. The observed metamagnetic transitions are clearly of the first order and exhibit a wide hysteresis at low temperatures. As the temperature rises, the width of hysteresis gradually decreases and disappears above 120 K. As in the case of $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$ [3], both stages of the magnetization process are expected to exhibit a pronounced magnetostriction.

In the present study, we report on the crystal structure investigation by powder neutron diffraction and the comparative study of magnetostriction performed by bulk (capacitor dilatometer on a single crystal) and microscopic (X-ray powder diffraction) methods for the $Lu_2Fe_{16.5}Ru_{0.5}$ compound.

2. Experimental

The single crystal of $Lu_2Fe_{16.5}Ru_{0.5}$ was prepared by the Czochralski method in a tetra-arc furnace. The magnetic isotherms were measured in Prague in a PPMS-14 magnetometer (Quantum Design) along the principal axes of the single crystal and on an isotropic powder sample in fields up to 5 T in the 5-300 K temperature range. The longitudinal and transverse magnetostriction were measured on the $Lu_2Fe_{16.5}Ru_{0.5}$ single crystal in the PPMS-14 in Prague by the capacitor method along the *a* and *c* axes in fields applied along the *a* axis.

For the crystal structure determination, a high-resolution powder diffractometer D1A (1.909 Å wavelength) at the Institute Laue-Langevin (Grenoble, France) was employed. The diffraction patterns were refined by means of Rietveld analysis. High-field powder X-ray diffraction experiments were carried out in Sendai with CuKα radiation at 10-300 K using a Gifford-McMahon (GM) type cryocooler (helium gas closed-cycle refrigerator) and for $B \leq 5$ T using a cryocooled split-pair superconducting magnet. The diffraction data were obtained for $20° \leq 2\theta \leq 100°$ with the step of 0.01°.

The samples for X-ray and neutron diffraction were prepared from obtained single crystal both from the top and the bottom in order to exclude the possibility of different compositions within the length of the crystal and from $Lu_2Fe_{16.5}Ru_{0.5}$ polycrystalline ingots.

3. Results and discussion

a) Crystal structure of $Lu_2Fe_{16.5}Ru_{0.5}$

The X-ray Laue patterns showed good quality of the $Lu_2Fe_{16.5}Ru_{0.5}$ crystal obtained. Further, the hexagonal crystal structure of the Th_2Ni_{17} type was approved by the powder neutron diffraction for $Lu_2Fe_{16.5}Ru_{0.5}$ with the lattice parameters a = 840.6 pm and c = 830.2 pm (see Fig. 2). The refinement procedure allowed us to determine positions of atoms in the crystal lattice of $Lu_2Fe_{16.5}Ru_{0.5}$ (see Table 1). The disordered structure model with a substitution of a part of Lu atoms located along the *c* axis by Fe atoms in 4*e* positions as proposed by Givord et al. [5] has led to a satisfactory fit. The real composition of the compound was determined as $Lu_{1.78}Fe_{16.51}Ru_{0.58}$.

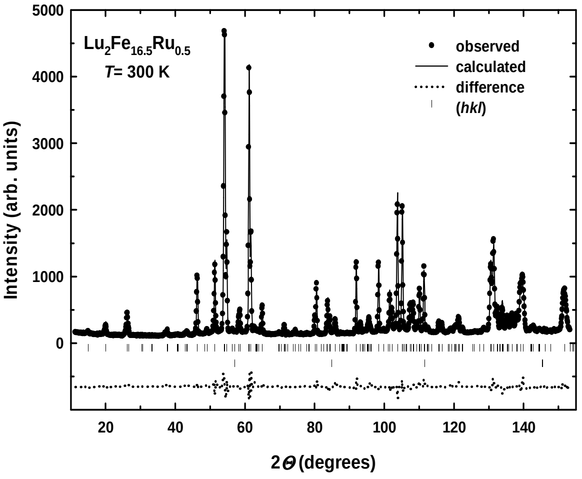

Fig. 2. Neutron powder diffraction pattern of $Lu_2Fe_{16.5}Ru_{0.5}$ compound at room temperature (D1A).

Due to the fact that Ru atomic radius is larger that of Fe, Ru atoms should not occupy the dumbbell 4*f* positions of Fe that was indeed observed during the

Table 1. Structural parameters of $Lu_2Fe_{16.5}Ru_{0.5}$ compound at room temperature from the neutron diffraction experiment.

Atom	Site	Coordinates			Occ (%)
		x	*y*	*z*	
Lu_1	2*b*	0	0	1/4	82.6
Lu_2	2*d*	1/3	2/3	3/4	100
Lu_3	2*c*	1/3	2/3	1/4	0
Fe_1	4*f*	1/3	2/3	0.106(5)	100
Ru_1	4*f*	1/3	2/3	0.106(5)	0
Fe_2	6*g*	1/2	0	0	100
Ru_2	6*g*	1/2	0	0	0
Fe_3 (1)	12*j*	0.330(2)	-0.041(1)	1/4	71.4
Ru_3 (1)	12*j*	0.330(2)	-0.041(1)	1/4	0
Fe_3 (2)	12*j*	0.294(3)	0.013(4)	1/4	8.3
Ru_3 (2)	12*j*	0.294(3)	0.013(4)	1/4	0
Fe_3 (3)	12*j*	0.315(3)	-0.032(4)	1/4	20.3
Ru_3 (3)	12*j*	0.315(3)	-0.032(4)	1/4	0
Fe_4 (1)	12*k*	0.165(3)	0.330(7)	-0.021(7)	75.6
Ru_4 (1)	12*k*	0.165(3)	0.330(7)	-0.021(7)	0
Fe_4 (2)	12*k*	0.165(3)	0.330(7)	0.000(2)	14.6
Ru_4 (2)	12*k*	0.165(3)	0.330(7)	0.000(2)	9.8
Fe_5	4*e*	0	0	0.103(9)	17.4
Ru_5	4*e*	0	0	0.103(9)	0

Conventional Rietveld Factors (%)		*R*-factors (%)	
R_{wp}	13.0	Bragg	5.9
R_{exp}	3.9	R_F	5.7

refinement procedure when the occupation factors for Ru atoms were allowed to vary at different sites. Presence of Fe dumbbells in the 4*e* sites around Lu atoms in the 2*b* position results in the induced weak distortion nearby 12*j* and 12*k* Fe sites, which both split into three and two sites, respectively. The 12*k* position splits into 12*k*(1) and 12*k*(2) sites suggesting two possible configurations of (*x*,*y*) plane and Ru atoms were found to reside only in 12*k*(2) Wyckoff positions of the crystal structure.

b) Magnetoelasticity of $Lu_2Fe_{16.5}Ru_{0.5}$

The magnetostriction of $Lu_2Fe_{16.5}Ru_{0.5}$ was measured by two independent methods. As highly sensitive and an accurate method, the capacitor dilatometer was employed for the measurement of the single-crystalline sample. The X-ray dilatometry, on the other hand has a much lower sensitivity and accuracy but is a direct method of determination the interatomic distances changes. Furthermore, possible field-induced structure changes can be observed by means of X-ray diffraction. The atomic coordinates deduced from the powder neutron diffraction experiment were used for refinement of the X-ray diffraction patterns obtained.

The field evolution of the characteristic (600) and (306) reflections at 10 K is shown in Fig. 3. With the increasing field, both lines shift towards the smaller angles 2*Θ*, indicating an expansion of the lattice upon the metamagnetic transition presented in the lower part of Fig. 3 for the random fixed powder sample of $Lu_2Fe_{16.5}Ru_{0.5}$.

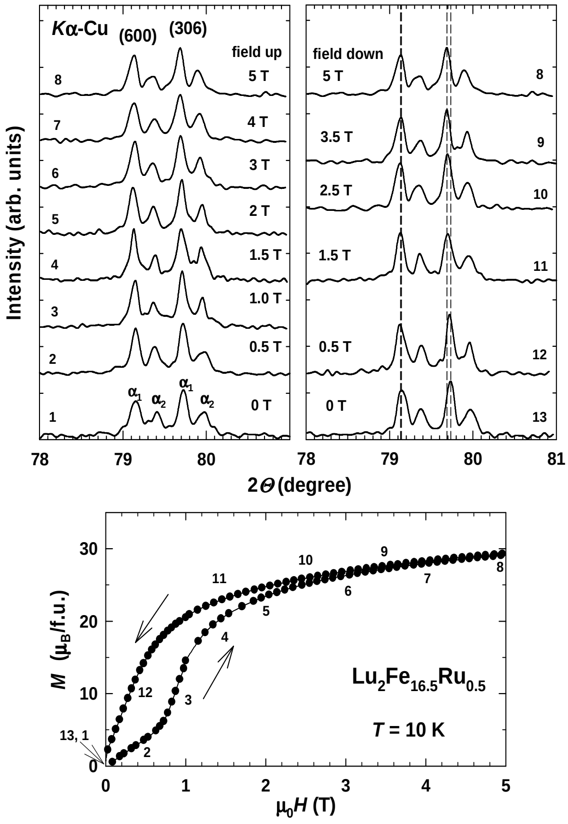

Fig. 3. Magnetization process of a fixed random powder $Lu_2Fe_{16.5}Ru_{0.5}$ sample and corresponding profiles of the (600) and (306) reflections in Cu*K*α radiation at 10 K. The numbers of profiles correspond to those on magnetization curve. The dashed lines indicate the position of the α_1-(600) and α_1-(306) reflections at 0 and 5 T.

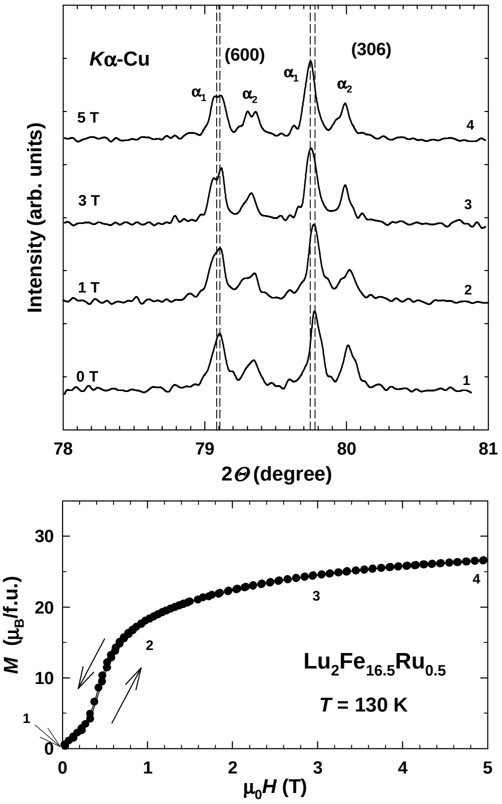

Fig. 4. The same as Fig. 3 at T = 130 K.

Surprisingly, the diffraction pattern profiles do not change the character upon the applied magnetic field and the α_1-α_2 doublet is well-resolved up to the highest available field of 5 T as seen in Fig. 3. This is in contrast to previously studied $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$ compound [3], where the α_1-α_2 doublet was well pronounced only at low and high fields whereas for the 0.5–3.5 T field interval the line profiles showed the behavior characteristic for the coexistence of two phases. The second-order magnetization process without hysteresis at 130 K does not change the line profiles as well (Fig. 4).

Fig. 5 presents the results of the bulk measurements of magnetostriction along the *a* and *c* axes in magnetic field up to 5 T applied along the easy *a*-axis at 10 K. The field-induced transition observed in magnetization curves below 1 T is also manifested in the lattice expansion both along the *c*-axis (λ_c) and in the basal plane (λ_a). The comparison of results obtained by both macro- and microscopic methods at 10 K is shown in Fig. 5. Generally speaking, since the samples are different (single- and polycrystalline), and the magnetic anisotropy at low temperatures is rather strong (see Fig. 1), one can compare the results of linear magnetostriction along the *a* and *c* axes only in fields sufficiently high so that both samples are magnetically saturated. Despite an extended second stage of the magnetization process in $Lu_2Fe_{16.5}Ru_{0.5}$, the obtained results agree well, especially if one takes into account the large error of the X-ray dilatometry (~10^{-4}).

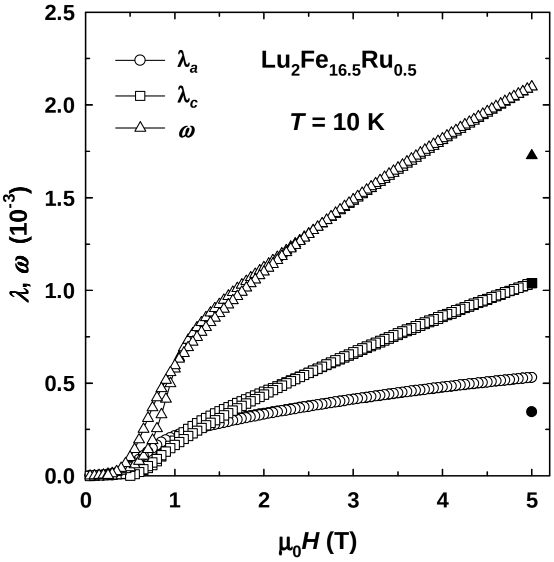

Fig. 5. The comparison of magnetostriction curves along the *a* and *c* axes of a $Lu_2Fe_{16.5}Ru_{0.5}$ single crystal measured in a field applied along the *a* axis (open symbols) with the X-ray powder diffraction results for a fixed random powder sample (filled symbols) at 10 K. $\omega = 2\lambda_a + \lambda_c$ stands for the volume magnetostriction.

Since $Lu_2Fe_{16.5}Ru_{0.5}$ possesses the easy-plane type of magnetic anisotropy, it should experience an orthorhombic magnetostrictive distortion in the magnetically ordered state (such distortion should be particularly high at the lowest temperatures). If the distortion is large enough, the magnetostriction in additional geometry - field along *a* and strain along [120] (*b*-axis in the orthorhombic notation) – has to be measured in order to determine the volume effect. The X-ray study detected no distortion suggesting the anisotropic magnetostriction responsible for the distortion to be below the experimental sensitivity. Therefore, the volume effect for $Lu_2Fe_{16.5}Ru_{0.5}$ can be determined as $\omega = 2\lambda_a + \lambda_c$. The results of $\omega(H)$ are presented in Fig. 5.

It was shown in the work by Andreev at al. [3], the linear strains and the volume effect in $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$ reach very large values after the metamagnetic transition ($\lambda_a = 1.3\times10^{-3}$, $\lambda_c = 3.4\times10^{-3}$, $\omega = 6.0\times10^{-3}$), i.e. ω is about 0.6 % at 5 T, which is comparable with the volume spontaneous magnetostriction $\omega_s = 1.5\%$ in Lu_2Fe_{17} [1]. As seen from the Fig. 5, the metamagnetic AF-F transition along the *a*-axis in $Lu_2Fe_{16.5}Ru_{0.5}$ at 10 K is accompanied by a smaller lattice expansion than that in $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$ with the magnetostrictive strains along the *a*- and *c*-axis and the volume effect at 5 T as $\lambda_a = 0.5\times10^{-3}$, $\lambda_c = 1.0\times10^{-3}$, $\omega = 2.1\times10^{-3}$, respectively. The observed difference in values qualitatively corresponds to the lower magnetic moment of the compound due to extended second stage of magnetization process.

Figure 6 shows the temperature dependence of the linear and volume magnetostriction of $Lu_2Fe_{16.5}Ru_{0.5}$ measured by the X-ray diffraction on a fixed random powder sample in 5 T. The dashed line in Fig. 6 represents the fit $\omega(T) = \omega(0)\cdot [M(T)/M(0)]^2$, where the experimental value at $T = 40$ K has been taken for $\omega(0)$ (see further explanations).

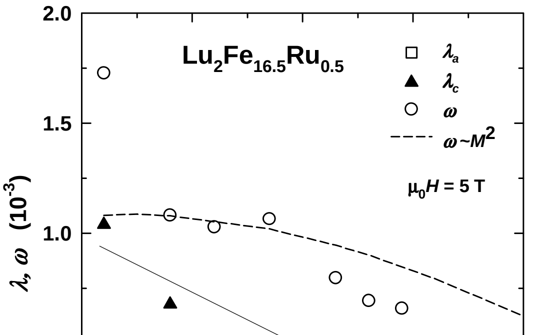

Fig. 6. Temperature dependence of the linear and volume magnetostriction of $Lu_2Fe_{16.5}Ru_{0.5}$ in 5 T, measured by the X-ray diffraction on a fixed random powder sample. The dashed line is the $\omega(T) \sim M^2(T)$ fit.

It is known that the magnetostriction is proportional to the square of magnetization [1]. However, in both $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$ and $Lu_2Fe_{16.5}Ru_{0.5}$ compounds, the dependence $\omega(T)$ decreases much faster with increasing the temperature than M^2. In $(Lu_{0.8}Ce_{0.2})_2Fe_{17}$, the slope of $\omega(T)$ was found to change in the vicinity of 150 K, which was attributed to the presence of possible AF-AF transition similar to that observed for Ce_2Fe_{17} [6]. In case of $Lu_2Fe_{16.5}Ru_{0.5}$, the strong deviation from the square-magnetization fit already occurs at lowest temperatures. Nevertheless, above $T = 40$ K the experimental points fairly correspond to $M^2(T)$ dependence.

The presence of two distinct AF phases was revealed in the work by Tereshina et al. [7] for the $Lu_2Fe_{16.5}Ru_{0.5}H_{0.4}$ hydride in the course of the high-pressure study, where the suppression of the antiferromagnetic order upon hydrogenation and subsequent total restoration of the latter under applied pressure was observed. Therefore, the parent $Lu_2Fe_{16.5}Ru_{0.5}$ compound may also possess two types of the antiferromagnetic structures with the higher value of magnetostriction below 40 K corresponding to the low-temperature AF phase, whereas an abrupt decrease of the measured magnetostrictive strains at elevated temperatures may correspond to the second, the high-temperature phase.

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