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Interplay between structural and magnetic properties of Lu_2Fe_{17} at high pressure

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Abstract. A crystal structure of Lu_2Fe_{17} was studied by means of neutron powder diffraction method in the pressure range up to 1.65 GPa and ambient temperature. Modification of the magnetic properties corresponding to the pressure-induced change of the crystal structure of Lu_2Fe_{17} is analysed on the basis of local moment model in the mean field approximation. The experimentally observed suppression of FM state and stabilization of the non-collinear AFM state under high pressure in Lu_2Fe_{17} can be explained qualitatively from model calculations. FM and non-collinear AFM states in Lu_2Fe_{17} are found to be nearly degenerate at ambient pressure with the estimated difference between the total energy minima of $\Delta E = 2.73$ mRyd and the application of high pressure removes this degeneracy in the favor of non-collinear AFM state.

PACS. 61.50.Ks Crystallographic aspects of phase transformations; pressure effects – 75.25.+z Spin arrangements in magnetically ordered materials – 61.12.Ld Neutron diffraction

1 Introduction

A search for the prospective materials for production of permanent magnets have attracted recently a considerable attention to rare-earth – iron intermetallic compounds. The richest in iron content R_2Fe_{17} compounds are characterized by rather low Curie temperatures (T_C) compared to that of metallic Fe, high saturation magnetization and Invar-like phenomena – significant decrease of T_C under high pressure and large positive spontaneous magnetostriction for $T < T_C$ [1,2].

The complex magnetic behavior of R_2Fe_{17} compounds is related to the interplay of the itinerant and localized character of the magnetic moments of Fe and R atoms, respectively [2,3]. A role of Fe sublattice in the formation of magnetic properties of these systems may be revealed by studies of compounds with nonmagnetic R - Y or Lu.

At ambient pressure Lu_2Fe_{17} crystallizes in the disordered variant of the hexagonal Th_2Ni_{17} – type structure (space group $P6_3/mmc$) [4,5]. Below $T_N = 270$ K Lu_2Fe_{17} exhibits a non-collinear helical antiferromagnetic (AFM) structure with a propagation vector (0, 0, τ) and $\tau \approx 0.019$ Å^{-1} [6]. At $T < T_C \approx 165$ K a fan magnetic structure parallel to the basal plane having ferromagnetic (FM) and AFM components was observed [6]. Later neutron diffraction study [7] confirmed the existence of the high temperature helical magnetic phase, but the low temperature magnetic phase was found to have a collinear FM structure.

The magnetic properties of Lu_2Fe_{17} can be substantially modified by "chemical" pressure (volume change due to partial substitution of Fe by other elements – Al, Si, etc.) or external high pressure. A partial substitution of Fe by Al or Si in Lu_2Fe_{17} leads to a suppression of the AFM phase in the favor of the FM phase and considerable increase of T_C up to 360–430 K [5,8]. In contrast to that, the application of relatively moderate external high pressure leads to a destabilization of FM phase and its complete disappearance at $P > 0.5$ GPa [7,9].

The low Curie temperatures and pronounced magnetovolume effects of pure R_2Fe_{17} systems as well as the large increase of T_C in $R_2Fe_{17-x}M_x$ systems with a partial substitution of Fe by Al, Si, Ga atoms were successfully interpreted in the framework of the spin fluctuation theory of Mohn and Wohlfarth [10]. According to this theory, the small values of the Curie temperatures in R_2Fe_{17} compounds result from the intense spin fluctuations due to the high density of states (DOS) at the Fermi level. Partial substitution of Fe for Al, Si and Ga leads to a sharp decrease of DOS at the Fermi level and increase of T_C. This theory was confirmed both experimentally [11,12] and by ab initio calculations [13,14].

Alternatively, the properties of R_2Fe_{17} compounds are often described in terms of the phenomenological local

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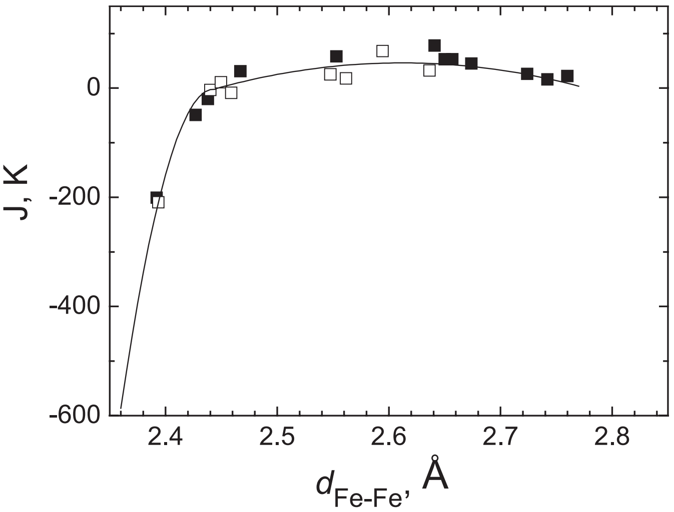

Fig. 1. The exchange coupling constant J as a function of interatomic Fe-Fe distance. Open symbols – data obtained for Y_2Fe_{17} in [15]. Solid symbols – data obtained for Sm_2Fe_{17} in [16]. The solid line represents a fit of experimental data by two second order polynomial functions, $J_1(d_{\text{Fe-Fe}} - d_0)$ for $2.36 < d_{\text{Fe-Fe}} < 2.45$ Å and $J_2(d_{\text{Fe-Fe}} - d_1)$ for $2.45 < d_{\text{Fe-Fe}} < 2.8$ Å, which have a sense of Taylor series expansion of $J(d_{\text{Fe-Fe}})$ function in the vicinity of points $d_0 = 2.39$ Å and $d_1 = 2.6$ Å.

moment model by the presence of competing positive and negative exchange interactions in Fe sublattice [6]. An exchange coupling constant J as a function of distance (Fig. 1) between different Fe sites in Y_2Fe_{17} [15] and Sm_2Fe_{17} [16] was determined from the analysis of the hyperfine fields extracted from the experimental Mössbauer data in the framework of the mean field approximation. It was found that the value of J is positive for $d_{\text{Fe-Fe}} > d_c = 2.45$ Å and negative for $d_{\text{Fe-Fe}} < d_c$.

From the point of view of the local moment model, the instability of the ferromagnetic state in Lu_2Fe_{17} under high pressure can be associated with the enhancement of the negative Fe-Fe exchange interactions due to the reduction of some interatomic Fe-Fe distances. High pressure effects on the magnetoelastic phenomena in Lu_2Fe_{17} were studied previously in the 0–1 GPa range [17]. However, pressure-induced changes of Fe-Fe interatomic distances in Lu_2Fe_{17} have not been analyzed. In order to elucidate a possible relationship between the pressure – induced changes of the structural and magnetic properties of Lu_2Fe_{17}, the crystal structure of Lu_2Fe_{17} has been investigated in the extended pressure range up to 1.65 GPa by means of neutron diffraction method.

2 Experimental

The details of the sample synthesis procedure are described in [7]. Neutron powder diffraction measurements at high external pressures up to 1.65 GPa were performed at ambient temperature with the DN-12 spectrometer [18] at the IBR-2 high-flux pulsed reactor (FLNP JINR, Dubna, Russia) using the sapphire anvil high pressure cells [19]. The sample volume was about 2 mm^3.

Several tiny ruby chips were placed at different points of the sample surface. The pressure was determined by the ruby fluorescence technique with the accuracy of 0.05 GPa at each ruby chip and the pressure value on the sample was determined by averaging of values obtained at different points. The estimated inhomogeneity of the pressure distribution on the sample surface was less than 10%.

Diffraction patterns were collected at a scattering angle $2\theta = 90°$. The spectrometer resolution at $\lambda = 2$ Å is $\Delta d/d = 0.015$. The typical data collection time at each pressure point was 15 h. Experimental data were analysed by the Rietveld method using MRIA program [20].

3 Results

Neutron diffraction patterns of Lu_2Fe_{17} measured at different pressures and ambient temperature are shown in Figure 2. They correspond to the disordered hexagonal Th_2Ni_{17} – type structure (space group $P6_3/mmc$) [4,5]. In this structure, Lu atoms occupy crystallographic sites 2b (0, 0, 1/4) and 2d (1/3, 2/3, 3/4) and Fe atoms occupy sites 4f (1/3, 2/3, z), 6g (1/2, 0, 0), 12j (x, y, 1/4), 12k (x, $2x$, z) and 4e (0, 0, z) [5]. The Fe atoms locating in sites 4f create dumbbell-like pairs along the crystallographic c-axis. The other Fe atoms in sites 12j and (6g, 12k) form alternating planes perpendicular to the c-axis. The site 2b is not fully occupied by Lu atoms and instead of the lucking Lu atoms in this position additional dumbbell-like pairs are formed by the Fe atoms in positions 4e. The occupancies of different crystallographic sites and structural parameters at different pressures determined from the Rietveld refinement of diffraction data are listed in Table 1. The obtained sample composition is $Lu_2Fe_{19.6}$. A small admixture of the α-Fe impurity was evidenced in the sample in the amount of about 5%. As it was found in [4,21], the equilibrium composition of Lu_2Fe_{17} is shifted from the ideal 2-17 to approximately 2-19 stoichiometry. The structural parameters obtained at ambient pressure agree well with [4,5].

Both a and c lattice parameters decrease linearly with a pressure increase (Fig. 3). The linear compressibility $k_i = -(1/a_{i0})(da_i/dP)_T$ along the a-axis, $k_a = 0.0027$ GPa^{-1}, is smaller than along the c-axis, $k_c = 0.0045$ GPa^{-1}. These values are comparable with those $k_a = 0.0031$ GPa^{-1} and $k_c = 0.0035$ GPa^{-1} obtained in [17]. The anisotropy of lattice compression in Lu_2Fe_{17} is more pronounced in comparison with Y_2Fe_{17} where $k_a \approx k_c$ [22], although the volume compressibilites $k_V = -(1/V_0)(dV/dP)_T$ of both compounds are nearly identical, $k_V = 0.0099$ GPa^{-1} for Lu_2Fe_{17} and $k_V = 0.0096$ for Y_2Fe_{17} [22]. The nearest-neighbor Fe-Fe distances as functions of pressure are shown in Figure 4. Most of them decrease with a pressure increase. The shortest 4f-4f dumbbell and 12k-12k distances exhibit the most pronounced reduction, 6g-12k and $12j_1$-$12j_1$ distances remain nearly constant and 4f-12k distance increases under high pressure. A similar increase of the 4f-12k distance was also found in Y_2Fe_{17} under high pressure [22].

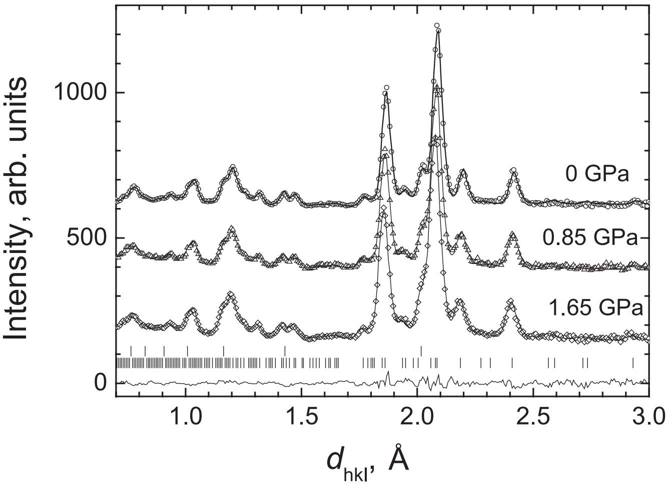

Fig. 2. Parts of neutron diffraction patterns of Lu_2Fe_{17}, measured at $P = 0$, 0.85 and 1.65 GPa and ambient temperature and processed by the Rietveld method. Experimental points, calculated profiles and difference curve (for P = 1.65 GPa, bottom) are shown. The ticks below represent calculated positions of diffraction peaks of Lu_2Fe_{17} (lower raw) and impurity of α-Fe (upper raw) which contribution was also included in calculations.

Table 1. Site occupancies and structural parameters of Lu_2Fe_{17} at different pressures. Lu atoms are located in sites 2b (0, 0, 1/4) and 2d (1/3, 2/3, 3/4). Fe atoms are located in sites 4f (1/3, 2/3, z), 6g (1/2, 0, 0), 12j (x, y, 1/4), 12k (x, $2x$, z) and 4e (0, 0, z).

P, GPa	0	0.85	1.65
a, Å	8.382(5)	8.367(5)	8.344(5)
c, Å	8.305(5)	8.264(6)	8.243(5)
Lu(2b) n	1.52(2)	-	-
Lu(2d) n	2.00(2)	-	-
Fe(4f) n	4.00(2)	-	-
z	0.106(2)	0.107(2)	0.107(2)
Fe(6g) n	6.00(2)	-	-
Fe($12j_1$)n	10.32(4)	-	-
x	0.330(3)	0.331(3)	0.330(3)
y	0.371(3)	0.370(3)	0.370(3)
Fe($12j_2$)n	1.68(4)	-	-
x	0.328(5)	0.331(5)	0.349(5)
y	0.314(5)	0.292(5)	0.300(5)
Fe(12k) n	12.00(2)	-	-
x	0.166(2)	0.163(3)	0.163(3)
z	–0.016(1)	–0.016(1)	–0.016(1)
Fe(4e) n	0.48(2)	-	-
z	0.110(5)	0.100(5)	0.107(5)
R_p, %	6.22	5.31	5.02
R_{wp}, %	5.35	5.77	5.19

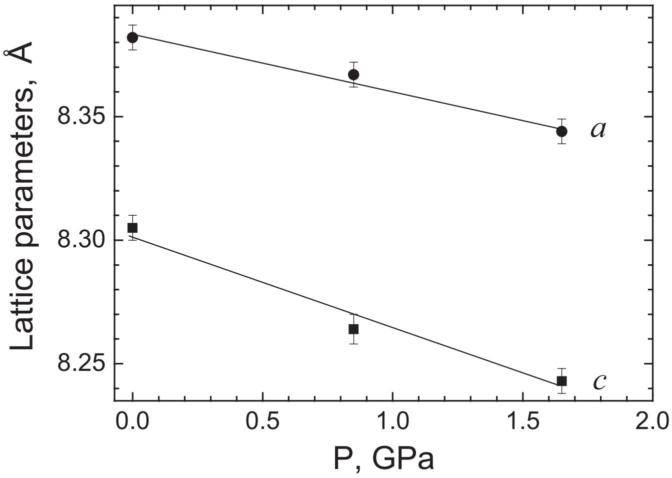

Fig. 3. Pressure dependencies of lattice parameters of Lu_2Fe_{17}. Solid lines represent linear fits to experimental data.

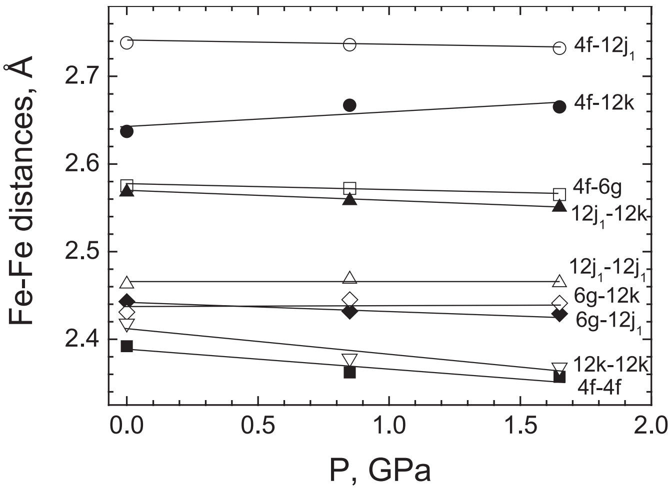

Fig. 4. The nearest-neighbor Fe-Fe distances in Lu_2Fe_{17} as functions of pressure. Solid lines represent linear fits to experimental data. The error bars are within the symbol sizes.

4 Discussion

In the mean field approximation the temperature of the transition to the ferromagnetic (T_C) or antiferromagnetic (T_N) ground state in Lu_2Fe_{17} may be expressed as

$$T_C(T_N) = \frac{2S_{\mathrm{Fe}}(S_{\mathrm{Fe}}+1)}{3} ZJ, \qquad (1)$$

where $S_{\mathrm{Fe}} = 1$ is the spin of Fe atoms, $ZJ = \sum_{i,j} n_i z_{ij} J_{ij} / \sum_i n_i$, n_i is the number of atoms of i type in the unit cell (i = 4f, 6g, $12j_1$, 12k), z_{ij} is the number of the nearest-neighbor atoms of j type around the atom of i type and J_{ij} is the exchange coupling constant between the atoms of i and j types. To simplify the calculations, we will neglect the Fe atoms located in positions $12j_2$ and 4e with small occupation numbers.

The obtained Fe-Fe distances of Lu_2Fe_{17} as functions of pressure (Fig. 4) and the known $J(d_{\text{Fe-Fe}})$

Table 2. Numbers of the nearest-neighbor atoms z_{ij} in Lu_2Fe_{17}.

z_{ij}	4f	6g	$12j_1$	12k
4f	1	3	6	3
6g	2	0	4	4
$12j_1$	2	2	2	4
12k	1	2	4	2

dependence [15,16] (Fig. 1) and its extrapolation allow to calculate the pressure behavior of the transition temperature to the magnetic ground state using equation (1), which is FM for $ZJ > 0$ and AFM for $ZJ < 0$. The used z_{ij} values are presented in Table 2. The variation of lattice parameters of Lu_2Fe_{17} does not exceed 1% in the 10–300 K temperature range [17] and the temperature dependence of Fe-Fe distances may be neglected. At ambient pressure the values $ZJ = 145$ K and $T_C = 195$ K were obtained. The calculated value of T_C is comparable with the experimental one $T_C = 165$ K [9]. At high pressure $P = 0.85$ GPa the values $ZJ = -107$ K and $T_N = 142$ K were obtained. The dominant negative contribution to the ZJ quantity comes from the shortest 4f-4f and 12k-12k distances. The change of the sign of the ZJ value means that under high pressure the AFM state becomes stable, in consistence with the experimental observation of the full suppression of the FM state in Lu_2Fe_{17} at $P > 0.5$ GPa [9]. However, the calculated value of T_N is considerably lower than the experimental one $T_N \approx 260$ K at $P = 0.85$ GPa [9]. This difference may be related to the inaccuracy of $J(d_{\text{Fe-Fe}})$ dependence extrapolation in the region $d_{\text{Fe-Fe}} < d_f$ (the shortest 4f-4f distance at ambient pressure) were J changes strongly with a slight variation of $d_{\text{Fe-Fe}}$. At higher pressures the extrapolation inaccuracy is expected to increase due to the further pressure-induced reduction of $d_{\text{Fe-Fe}}$ values, so we restricted the calculation to $P = 0.85$ GPa only. Another reason for the difference between the experimental and calculated values of T_N is that in the case of helical magnetic structures the contribution from the next nearest-neighbor exchange interactions would become important. Although in the theoretical study of the Y_2Fe_{17} compound [23] with structure and properties close to Lu_2Fe_{17} it was found that the most of the next nearest-neighbor exchange interactions are much smaller in comparison with the nearest-neighbor ones, their total contribution would be considerable.

Although the phenomenological local moment model describes qualitatively the observed suppression of the FM state in Lu_2Fe_{17} at high pressure, it cannot describe some other phenomena observed in the $R_2Fe_{17-x}M_x$ compounds, for example, the huge increase of T_C with the partial substitution of Fe by Si, Al or Ga atoms which does not correspond to relatively small change of the Fe-Fe distances [12,24,25]. Thus, the changes of the electronic structure corresponding to the relevant changes of the crystal structure and interatomic distances of R_2Fe_{17} compounds should also be considered. The average coordination number of Fe atoms in R_2Fe_{17} compounds, $Z = 10$, is close to one for the fcc γ-Fe ($Z = 12$). As it was pointed out in [23], the features of DOS of Y_2Fe_{17}, isostructural to Lu_2Fe_{17}, are similar to those of the fcc γ-Fe which is well-known for the existence of non-collinear AFM structures. Ab initio calculations have shown that the total energy minima for the FM and non-collinear AFM states in γ-Fe are rather close to each other, FM state is favorable for larger volumes and the non-collinear AFM state is stabilized with a volume decrease [26]. The similar situation occurs in Lu_2Fe_{17}. The critical unit cell volume of this compound corresponding to the disappearance of FM state at $P = 0.5$ GPa is $V_C = 502.7$ Å^3. For $V > V_C$ a low temperature FM ground state is observed, which disappears with a unit cell volume decrease for $V < V_C$.

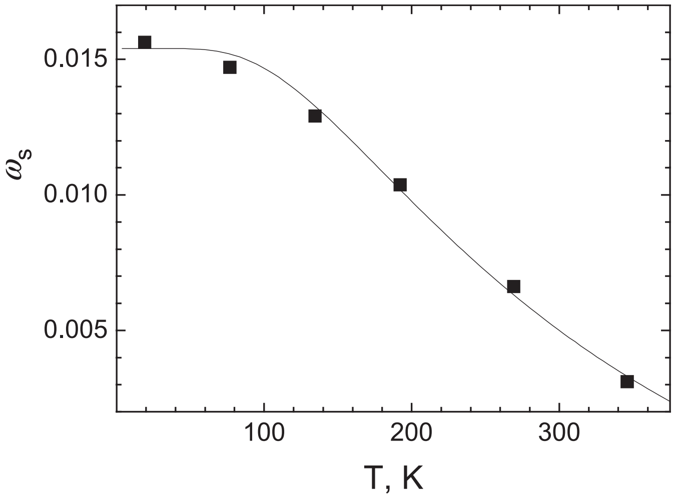

Fig. 5. Spontaneous volume magnetostriction as a function of temperature (experimental data from [27]) and its fit by equation (2).

The difference between total energy minima of the FM and non-collinear AFM states in Lu_2Fe_{17} at ambient pressure can be estimated from the spontaneous volume magnetostriction $\omega_s(T)$ data [27] applying the two levels model developed for description of Invar phenomena in Fe compounds [28,29]. In this model, the ground level is the larger volume FM state and the upper level is the lower volume AFM state which can be excited thermally. Then the temperature dependence of ω_s can be described as the Shottky-type thermal activation between two levels

$$\omega_s = \omega_{s0} - A/(1 + G\exp(\Delta E/k_BT), \tag{2}$$

where ω_{s0} and A are constants, G and ΔE are the ratio of the degeneracy and energy separation of two levels, respectively. Assuming $G = 1$ (which corresponds to equal degeneracies and zero temperature magnetic moments M_0 of both levels) from the fitting of the experimental $\omega_s(T)$ data (Fig. 5) by equation (2) one obtains $\omega_{s0} = 0.015$, $A = 0.054$ and $\Delta E = 2.73 \times 10^{-3}$ Ryd. The calculated value of ΔE is comparable with the difference between total energy minima of the FM and non-collinear AFM states in γ-Fe obtained in [26], $\Delta E \approx 1.4 \times 10^{-3}$ Ryd. The ab initio calculations are necessary to confirm this estimation. The spontaneous volume magnetostriction is strongly suppressed in Lu_2Fe_{17} under high pressure [17].

Within the described two level model, it corresponds to the reduction of the ΔE value under high pressure, prerequisite for the appearance of the AFM state with the lower unit cell volume.

5 Conclusions

In the present paper a correlation between the pressure-induced changes of the crystal structure and magnetic properties of Lu_2Fe_{17} under high pressure was analyzed using the local moment model. The calculations performed in the mean field approximation using the obtained structural data explain qualitatively the experimentally observed suppression of the FM state in the favor of noncollinear AFM state under high pressure by the increased negative contribution from 4f-4f and 12k-12k Fe exchange interactions which leads to the change of the sign of the average exchange coupling constant. However, the calculated value of T_N under high pressure is lower than the experimental one. The detailed information about the next nearest-neighbor exchange interactions and the $J(d_{\text{Fe-Fe}})$ dependence in the short $d_{\text{Fe-Fe}}$ distances region under high pressure which could be obtained from the Mössbauer experiments would be necessary for the more accurate T_N estimation for Lu_2Fe_{17}.

Both FM and AFM states in Lu_2Fe_{17} are nearly degenerate at ambient pressure with a small difference between total energy minima of 2.73 mRyd. One would expect instability of the FM ground state under high pressure in other R_2Fe_{17} compounds with a similar structure.

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