Inhomogeneous Magnetic State of Ce₂Fe₁₇
Evidenced by Mössbauer Spectroscopy

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Abstract—A comparative analysis of the magnetic properties and Mössbauer spectra of two Ce₂Fe₁₇ samples prepared by different methods and demonstrating different magnetic behavior is carried out. A model for processing the spectra is proposed, which gives a good description of the Mössbauer spectra of samples in different magnetic states by a superposition of eight subspectra. It is shown that in the samples in the ferromagnetic state there are regions with antiferromagnetic ordering at the local level. The relative fractions of iron atoms in these regions differs for different samples and increases when approaching the temperature of the transition from the ferromagnetic to the antiferromagnetic state.

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INTRODUCTION

The interest in the study of magnetic properties of the intermetallic compound Ce₂Fe₁₇ is due to the unique position that this compound occupies in a set of intermetallic compounds of R₂Fe₁₇ type, where R is the rare earth atom. For atoms R with a partially filled f-electron shell, a collinear ferrimagnetic structure is realized in R₂Fe₁₇ compounds with parallel orientation in the case of light R or antiparallel (heavy R) orientation of the magnetic moments of the R and Fe sublattices [1]. In Ce₂Fe₁₇ at low temperature, as a result of the competition between ferro- and antiferromagnetic interactions, the type of magnetic ordering proves to be sensitive to the application of external pressure [2, 3], doping [4] and even to the method of preparation of the alloy [5]. The presence of spontaneous and field-induced magnetic phase transitions [6], as well as the structural transition [7], makes Ce₂Fe₁₇ an attractive object for the study of magnetothermal [8, 9], magnetoresistive [10] and magnetovolume effects [11], and microwave shielding [12]. A possible cause of the abnormal behavior of Ce₂Fe₁₇ is the mixed valence state of the Ce atom [13] and its small atomic radius, which causes a decrease in the volume of the unit cell in comparison with other compounds R₂Fe₁₇.

Ce₂Fe₁₇ crystallizes into a rhombohedral structure of the Th₂Zn₁₇ type (spatial group of the symmetry R₃₅m). In the lattice, Ce atoms occupy positions 6c, and Fe atoms take four positions—6c, 9d, 18f, 18h. Magnetic measurements carried out in different scientific groups often yield conflicting results. Thus, in [14], from the measurements of the magnetic characteristics and Mössbauer spectra, the transition temperatures from the ferromagnetic state to the antiferromagnetic state \( T_C \sim 70 \) K and from the antiferromagnetic state to the paramagnetic state \( T_N \sim 270 \) K were determined. In early neutron diffraction experiments [11], evidence was found for a planar noncollinear fan structure below \( T_C = 90 \) K with a fan opening angle of about 40° at a temperature of 4.2 K. It was also found that in the range between \( T_C \) and \( T_N = 225 \) K the structure is described as a helicoidal antiferromagnet. In further works [10, 15, 16], the values of temperature \( T_N \) in the range 205–225 K were also obtained, but according to these works the antiferromagnetic state is preserved up to the temperature of liquid helium. In this case, the transition temperature between different the helicoidal states \( T_t = 125 \) K was additionally determined. At the same time, the ferromagnetic low-temperature ordering with \( T_C \) values in the range from 20 to 120 K was established by different authors both by magnetic measurements [17, 18] and by neutron diffraction studies [3]. The authors [5] grew two single-crystal Ce₂Fe₁₇ samples with the ground ferrimagnetic and modified helicoidal spin states. According to the magnetic and neutron measurements, in the first case, the collinear ferromagnetic structure was retained in the sample up to 90 K, and between 90 K and 210 K there was a simple helicoidal structure. For...
the sample with the ground antiferromagnetic state, no evidence of the presence of a ferromagnetic order was observed up to 5 K, and at \( T_1 = 125 \) K with increasing temperature, the transition from the modified to a simple helicoidal state occurred.

To determine the dependence of the magnetic state on the crystal structure, X-ray and neutron diffraction experiments were carried out in [19] on a series of samples obtained by different methods and processed at different temperature regimes. It was concluded that the main changes in the magnetic state are associated with the changes in the volume of the unit cell and the lattice parameters. As the reasons for the observed differences, the variants of deviation of the crystal structure from the ideal are discussed, as well as the mixed valence state of the Ce atom. At the same time, the authors of [16], in explaining the magnetic behavior of Ce\(_2\)Fe\(_{17}\) on the basis of the theory of itinerant-electron magnetism, involve the competition between the anti-ferromagnetic and ferromagnetic modes without emphasis on intermediate valence. The high sensitivity of the magnetic state, which is related to electronic properties, to small changes in local volumes is emphasized.

Studies of the properties of Ce\(_2\)Fe\(_{17}\) at the local level using the Mössbauer effect were carried out in a number of works. However, even in their appearance, the spectra presented in different works [14, 20–23] differ significantly, apparently due to the different magnetic states of the samples. Attempts to quantify the spectra in these works were not very successful, because of the complexity of the spectra and the proposed mathematical models for processing. Despite the fact that none of the works presents in the Figs. difference spectra, the misfit between the experimental spectra and their description can be observed visually.

The fitting of the Mössbauer spectra of compounds \( R_2 \)Fe\(_{17}\) with the anisotropy of the “easy-plane” type, as well as with noncollinear magnetic structures, is very difficult. The basis for all models was the account for the dipole contribution to the hyperfine fields in accordance with the calculations carried out for Y\(_2\)Fe\(_{17}\) [24]. It is found that for the compounds with anisotropy of the “easy-plane” type, due to the mismatch of the direction of magnetization and the direction of the electric field gradient, the spectral contributions from Fe atoms in nonequivalent structural positions \( 9d, 18f, 18h \) are split into two with the ratio of intensities \( 2 : 1 \) if the direction of the magnetization coincides with one of the main crystallographic axes in the plane. In this case, the fitting of the spectra with 7 subspectra is conducted. In [25], the analysis of Mössbauer spectra was performed on the basis of construction of the probability distributions of hyperfine fields restored from the spectra under the assumption of a linear correlation of isomer and quadrupole shifts with a hyperfine field. However, such an approximation does not make it possible to unambiguously characterize the sort of atoms in the first coordination shell of the probe Fe atom and the symmetry of its neighborhood.

Previously, we [26] successfully employed a method for processing the spectra of materials with complex magnetic structure using the so-called two-core probability distributions of hyperfine fields. The method of constructing such distributions is described in detail in [27]. This approach allows us to restore two distributions of hyperfine parameters, each of which is characterized by its linear correlation and refers to a certain structural component. Thus, it was possible to separate contributions from the antiferromagnetic and ferromagnetic components of the structure, which have quadrupole shifts of different sign. It turned out that the states, which were described as a single-phase in magnetic relation on the basis of magnetometric and morphological methods, contained regions of both magnetic phases. In this work, in order to clarify the nature of magnetic phase transitions in the Ce\(_2\)Fe\(_{17}\) compound, the analysis of the results of the Mössbauer spectra using a superposition of a set of subspectra is carried out on the example of two samples obtained by different methods and possessing different magnetic properties.

1. SAMPLES AND EXPERIMENTAL PROCEDURE

The alloys for the study were smelted from chemically pure components in an argon atmosphere in an induction furnace in a semi-gravitational copper crucible (sample 1) and in a crucible made of Al\(_2\)O\(_3\) (sample 2). To achieve the equilibrium state, the ingots were annealed at a temperature of 1000°C for 8 h (sample 1) and 300 h (sample 2). According to X-ray phase analysis, in both samples the main phase had a Th\(_2\)Zn\(_{17}\) structure, and the amount of foreign phases did not exceed 3%. The lattice parameters of the main phase in the sample 1 were: \( a = 849.0 \) pm, \( c = 1240.8 \) pm. The sample 2 was characterized by slightly increased values of parameters: \( a = 849.5 \) pm, \( c = 1241.5 \) pm.

Magnetization measurements of samples were carried out using a SQUID magnetometer MPM S5 XL (Quantum Design Inc.) in the temperature range 2–250 K. The Mössbauer measurements were carried out on a commercial spectrometer Wissel (Germany) operating in a constant acceleration mode. The source was Co–57 with the activity of 35 mCi in the matrix Rh (RITVERTs CJSC, St. Petersburg). The samples were a powder of fine grinding, evenly spread and fixed on a sticky tape. For measurements at low temperatures, the samples were clamped between two thin beryllium foils and fixed on a cold finger of a helium continuous-flow cryostat CFICEV-MOSS, ICE Oxford, UK. The Mössbauer spectra were obtained at different temperatures in the range from 4.2 to 300 K. The temperature of the sample was maintained with an accuracy of...
±0.2 K using a temperature controller 32B, CryoCan, USA. Calibration of the velocity scale was performed on the spectrum of α-Fe and iron oxide α-Fe$_2$O$_3$; the isomer shift values were determined relative to the center of gravity of the α-Fe spectrum. Mathematical processing of the spectra was performed using the software package Spectr Relax [28].

2. EXPERIMENTAL RESULTS AND DISCUSSION

The temperature dependences of the magnetization in the field $H = 50$ Oe for the two samples studied are presented in Fig. 1. The curves are close in shape to the temperature dependences of the susceptibility of samples 1 and 4 presented in [19]. In the ground state, both samples have spontaneous magnetization. At the same time, the sequence of phase transformations occurring on increasing temperature varies significantly. The sample 1 begins to transition to the antiferromagnetic state already at a temperature $T_C = 22$ K. Small anomalies in the temperature dependence of magnetization at $T_{t1} = 75$ K and $T_{t2} = 109$ K indicate magnetic phase transitions between different helical states. A significantly higher transition temperature from ferromagnetic to antiferromagnetic state $T_C = 94$ K is observed in the sample 2. The transition temperatures to the paramagnetic state $T_N$ for both samples are close.

The lower $T_C$ magnitude for a sample with smaller lattice parameters corresponds qualitatively to the previously established $T_C$ decrease when applying hydrostatic pressure [2, 3]. However, there is a significant discrepancy in the quantitative estimates. Indeed, according to [3], Ce$_2$Fe$_{17}$ at low temperature is characterized by the volume compressibility coefficient $\kappa = -V^{-1}(dV/dP) = 2.4$ Mbar$^{-1}$. The difference in the volume of unit cells of samples 1 and 2 is $dV/V = -1.56 \times 10^{-3}$, which corresponds to the effective external pressure of 0.65 kbar. Given that the effect of pressure on the transition temperature is characterized by the value $dT_C/dP = -24$ K/kbar [3], the difference between samples in the unit cell volumes gives a contribution to the change of $T_C$ of only about 15 K, which is significantly less than the experimentally observed difference 72 K. Hence, the main difference in the $T_C$ values of different samples is related to other factors: vacancies, lattice defects, dopant, and substitutional atoms.

On the basis of the temperature dependences of the magnetization, the temperatures for measurement of nuclear gamma-resonance spectra were chosen. At 300 K, both samples are in the paramagnetic state, and at 175 K,—in the antiferromagnetic state. At a temperature of 4.2 K, the samples are characterized by ferromagnetic ordering with approximately the same magnetic moment. At 80 K, the sample 2 remains in the ferromagnetic state, while in the sample 1 the helical antiferromagnetic ordering is already realized.

The Mössbauer spectra of samples 1 and 2 measured at 300 K (in the paramagnetic state) are completely identical in the hyperfine parameters which allows us to assume the identity of the crystal structures of both samples. The spectrum of sample 2 as an example is given in Fig. 2. The fitting of the spectra indicates the presence of four doublets corresponding to the nonequivalent positions of iron atoms in the crystal lattice; the inhomogeneity of the crystal lattice leads to a small broadening of the subspectra: the width of the lines is 0.32 mm/s, compared to the width of the line of pure α-Fe 0.23 mm/s obtained at calibration.
The Mössbauer spectra measured at temperatures 4.2, 80, and 175 K are shown in Fig. 3. The superposition of pairs of spectra from two samples allows one to qualitatively assess the differences in their structure. The spectra measured at 175 K are almost identical in shape, although slightly different in width. At the same time, according to the results of magnetic measurements, both samples are in the same antiferromagnetic state. However, the spectra measured at 80 K differ significantly in the shape and intensity ratio of individual lines. Taking into account that at this temperature the samples are in different magnetic states, it can be concluded that the Mössbauer spectroscopy method is sensitive to a change in the magnetic state in Ce$_2$Fe$_{17}$. A small decrease in the spectrum width for the antiferromagnetic state is understandable taking into account the examples available in the literature of reducing the mean hyperfine field at the transition from the ferromagnetic to the antiferromagnetic state (see, for example, [25]). The significant difference in the relative intensities of the individual lines of the spectra indicates a difference in the mutual orientation of the magnetic moments in the samples. The spectra also show a large difference in the intensities and shape of the individual lines at the temperature 4.2 K, although both samples are in a ferromagnetic state. The widths
of the spectra coincide, and even the intensities of separately resolved outer lines coincide that, as was shown in previous studies [24], relate to the Fe atoms at positions 6c.

To describe the observed changes, we fitted the spectra with partial spectral contributions. At the first stage, we assumed that the magnetic state of both samples at 4.2 K and sample 2 at 80 K was close to the collinear ferromagnetic with the orientation of magnetization along one of the main crystallographic directions. Then the Mössbauer spectrum can be fitted with 7 subspectra (6c, 9d6, 9d3, 18f12, 18f6, 18h12, 18h6), as it was done in previous works [20, 23]. Here and further, the letter numbering corresponds to the nonequivalent iron positions, and the lower index indicates the multiplicity of the corresponding position in the unit cell. The sequence of subspectra is given in the order of decreasing the magnitude of their hyperfine field [24]. In this case, we have imposed bonds not only on the relative intensities of the contributions, but also on the isomer shifts, which should be equal for each pair of subspectra corresponding to individual types of positions. Besides, based on the preliminary analysis of the spectra by constructing two-core distributions of hyperfine fields, we found that the signs of the quadrupole shifts for each pair of subspectra are different. The possible deviation of the magnetic structure from the collinear (fan or helicoidal distribution of magnetic moments of iron atoms) was taken into account via broadening the lines describing the partial contributions. This broadening for all positions, except dumbbell position 6c, was taken the same. However, this model failed to provide a satisfactory fitting of the experimental spectrum. The difference spectrum showed the presence of an additional contribution with a smaller value of the hyperfine field (Fig. 4b). The description of the spectrum for this subspectrum was the least satisfactory in the proposed model.

The sequence of subspectra is given in the order of decreasing the magnitude of their hyperfine field [24]. To describe the spectra in the antiferromagnetic state with a simple helicoidal magnetic structure at 175 K, we used four unsplit broadened subspectra corresponding to four crystallographically nonequivalent types of Fe atomic positions as the main contributions. At the same time, considering that the change in the direction of the magnetic moments of Fe atoms from plane to plane is the same for all types of positions, we assigned the same width to these spectral contributions. It was equal to 0.6 and 0.7 mm/s for the samples 2 and 1, respectively. Nevertheless, the difference spectrum showed that for the spectra measured at 175 K, there is one additional contribution with the magnitude of the hyperfine field $H \sim 60–70$ kOe and the intensity of 5.1 and 7.4% for the samples 2 and 1, respectively. This contribution, as the additional 8th subspectrum in the fitting of the spectra in the ferromagnetic state, cannot be associated with a separate nonequivalent position of Fe atoms.

The values of hyperfine fields of individual spectral contributions for both samples at temperatures 4.2, 80, and 175 K obtained from the Mössbauer spectra are presented in Fig. 5. For greater clarity, the points corresponding to the values of hyperfine field of subspectra of each spectrum are connected with line. It is seen that the values of hyperfine fields in the spectra measured at $T = 4.2$ K are practically the same. The values of hyperfine fields for subspectra at $T = 80$ K exhibit the same behavior as in 4.2 K, but their magnitudes are slightly lower. An interesting fact is that, despite the difference in the magnetic state, the values of the hyperfine fields for subspectra obtained from the spectra of the samples at 80 K are also virtually identical. The magnitude of the hyperfine field of the additional contribution to the spectra for both samples varies slightly with temperature changes from 4.2 to 80 K, which is certainly an important result.
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Fig. 4. Description of Mössbauer spectra of the sample 1 (a, b, c) and the sample 2 (d, e, f) at different temperatures. The bold solid of line shows the subspectrum with the smallest value of the hyperfine field.

At a temperature of 175 K in the helicoidal antiferromagnet state, the values of hyperfine fields for 4 subspectra corresponding to different crystallographic positions of iron are substantially decreased, but the relative change of $H_{\text{eff}}$ on passing between subspectra for each sample does not qualitatively change in com-
parison with the low-temperature behavior. At the same time, a sharp decrease in the hyperfine field for the additional subspectrum takes place (in Fig. 5 it is indicated as the eighth one). Given that the intensity of this additional contribution also decreases sharply, it can be concluded that the mechanism of its occurrence is fundamentally different from the nature of other contributions in the spectrum.

Previously, using high-energy X-ray diffraction, superstructure reflections associated with doubling the unit cell parameter along the c axis were detected at temperature below $T_c = 118$ K for the Ce$_2$Fe$_{17}$ sample with the antiferromagnetic ground state, the spatial symmetry group $R\bar{3}m$ being preserved [7]. The structural phase transition is the transition of the second order associated with the displacement of individual atoms in the lattice, and can be due to the following reasons. The iron atoms in the position 18f form hexagonal layers. In the center of the hexagon either a Ce atom or a pair (“dumbbell”) of Fe atoms at the position 6c are placed. In the top and bottom hexagonal layers, iron atoms in the positions 9d and 18h are located. Due to the alternation of Ce atoms and the “dumbbell” Fe pair, the atomic plane with hexagons of Fe ions at the positions 9d and 18h may be slightly corrugated, and hexagons themselves are slightly expanded or contracted, if the Ce ion or “dumbbell” Fe pair, respectively, are located opposite to them in the neighboring atomic plane [29]. Due to the corrugation of the atomic plane with the positions 18h and 9d, the interatomic Fe-Fe distances may change locally. A change in the Fe-Fe distances can cause a local change in the exchange interaction sign due to the Fe-Fe distances in $R_3$Fe$_{17}$ are close to the critical value for the change of this sign. As a result, local regions with a type of magnetic ordering different from that realized in the sample as a whole can be formed near the positions 18h and 9d [7].

In the framework of the proposed model we assume that the existence in the spectra of an additional contribution with a smaller hyperfine field than for the main structure can be associated with local distortions of the structure and the formation of regions with an antiferromagnetic order. A confirmation of the fact that these regions are nuclei of the antiferromagnetic structure is the dynamics of the change in the intensity of the subspectra as temperature changes. In both samples, in the ferromagnetic state near the temperature $T_C$ of the transition to the antiferromagnetic phase ($T_C = 22$ K for sample 1 and $T_C = 94$ K for sample 2), a close number of iron atoms is observed (30% and 20%), which determine the parameters of this additional subspectrum. Apparently, the local antiferromagnetic order is easily destroyed by the magnetic field, and, therefore, it does not manifest itself in measurements of the magnetization in a magnetic field.

The proposed approach makes it possible to explain two additional effects observed in the experiment. The hyperfine field for the 8th additional subspectrum decreases sharply, as does its intensity at 175 K, as can be seen in Fig. 5. This may be due to the disappearance of structural distortions with an increase in temperature, which occurs gradually through a second-order phase transition [7]. The external pressure, on the contrary, should strengthen interatomic interactions, stabilize structural distortions of the lattice and, at the same time, enhance antiferromagnetic interactions. Indeed, as shown in [30], for the sample with the antiferromagnetic ground state, the temperature of the beginning of the structural transition $T_i$ increases by more than 40 K with an increase in pressure from 0 to 1.2 GPa, and the critical field of the metamagnetic transition increases from 1 to 15 T.

The coexistence of two types of magnetic structures at the local level has already been demonstrated in [26], where such a model for compounds with a cubic structure of the type NaZn$_{13}$ was explained by the presence in the structure of regions with a symmetry changed within the coherent coupling. In those regions that underwent compression, the distances between the atoms locally became less than the critical value for antiferromagnetism and there was a reorientation of the magnetic moments. In contrast to [26], where the structure was described using icosahedrons with close to cubic symmetry of the local environment, in Ce$_2$Fe$_{17}$ there are four types of positions for atoms with magnetic moments lying in the plane. Due to the peculiarities of low-temperature structural distortion of the lattice, the discovered additional contribution can be associated with the splitting of the positions 18f to 18f and 18g [7] or the position 18h [29]. The paper [20] has already attempted to explain the pres-
ence or absence of a clearly resolved line between the 5th and 6th lines in the spectra, which is demonstrated in the works of different authors, by the difference between the orientation of the magnetic moment of atoms at the position $18h$ along the axis $a$ ([100]) or $b$ ([120]) in the basis plane. But none of the presented works showed a line of such intensity as in the case of the sample 1 at $T = 4.2$ K in our study. In addition, the authors of [20] determined the values of the quadrupole shift for the positions $18h_{12}$ and $18h_0$ on the magnitude of $–0.7$ and $+0.4$ mm/s, and from the comparison with the results for compounds with other rare-earth atoms concluded that for this compound the easy axis in the plane is the axis $a$. However, in this work, the spectra of compounds with Ce and Dy or Gd differ significantly, although the same values of quadrupole shifts are determined for these compounds. In our fitting, despite the presence of such a pronounced line between the 5th and 6th lines in the spectra, the values of the quadrupole shift do not coincide with the data of [20]. Therefore, we can only talk about possible significant changes in the symmetry of these types of atomic configurations. A distinctive feature of atoms in them is that in their own plane there are no cerium atoms, nor “dumbbell” positions, but the neighborhood with the adjacent plane, in which the positions of cerium and “dumbbell” alternate, can lead to their local displacement relative to the plane itself.

Thus, to describe the magnetic structure of Ce$_2$Fe$_{17}$ at the local level, it is necessary to assume the coexistence of regions with different types of magnetic ordering. The amount of atoms in such regions in samples prepared by different methods and the degree of distortion of the structure may differ greatly from sample to sample, thereby affecting the transition temperature of the compound from one magnetic state to another. For a more accurate description of the properties of individual areas of a complex magnetic diagram, additional detailed temperature investigations are required.

3. CONCLUSIONS

The intermetallic compound Ce$_2$Fe$_{17}$ demonstrates an unusual sequence of magnetic phase transitions when the temperature changes. The transition temperature values and even the type of low-temperature magnetic ordering vary according to the results of different studies. In this paper we conducted the comparative analysis of the magnetic properties and the Mössbauer spectra of two Ce$_2$Fe$_{17}$ compound samples prepared by two different methods. The samples have slightly different lattice parameters and significantly different transition temperatures from ferromagnetic to antiferromagnetic state.

The Mössbauer spectra of samples measured at room temperature are almost identical. This indicates about the same state of the crystal structure and the absence of a noticeable amount of dopant atoms in the samples prepared in different ways. Quantitative estimates using the data on the effect of pressure on the temperature of magnetic phase transitions allow us to conclude that the main difference in the properties of the samples is not caused by the difference in their lattice parameters, rather the presence of structural defects, vacancies, etc.

An analysis of the Mössbauer spectra in a magnetically ordered state is performed taking into account the available structural information on the nonequivalent positions of iron in the lattice. It was found that for an adequate fitting of the Mössbauer spectra of both samples at different temperatures in different magnetic state, it is necessary to consider a superposition of eight subspectra. In the model proposed to describe the spectra, it is shown that in ferromagnetic samples at the local level there are regions with antiferromagnetic ordering. The relative number of iron atoms in such areas varies for different samples and is strongly dependent on temperature, increasing when approaching the transition temperature from ferromagnetic to antiferromagnetic state. The presence of local regions with different types of magnetic ordering may be due to the structural phase transition of the second order, as a result of which the iron atoms at the positions $18h$ and $9d$ undergo local displacements when the temperature decreases.

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REFERENCES


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