

## Mössbauer study of $\text{Ce}_2\text{Fe}_{17}$ compound in different magnetic states

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### ABSTRACT

Mössbauer spectra of two samples of the  $\text{Ce}_2\text{Fe}_{17}$  compound have been analyzed and hyperfine parameters, compared. The samples were subjected to different preparation techniques and display different magnetic properties. It is established that to well fit the Mössbauer spectra of these samples, an appropriate model should be used that takes into account an additional subspectrum differing in hyperfine parameters from the subspectra employed in conventional models. It is shown that in the ferromagnetic state, the samples contain local regions with an antiferromagnetic order, the volume fraction of which, being different for two samples, increases on approaching the temperature of ferro-to-antiferromagnet transition.

### 1. Introduction

$\text{Ce}_2\text{Fe}_{17}$  compounds possess magnetic properties that essentially differ from those characteristic of the whole series of  $\text{R}_2\text{Fe}_{17}$  intermetallics (here R is a rare earth atom). It is known that in the  $\text{R}_2\text{Fe}_{17}$  compounds containing R atoms with a partially filled *f*-electron shell there is realized a collinear ferrimagnetic structure with the parallel or antiparallel orientation of magnetic moments in the R and Fe sublattices for light and heavy R atoms, respectively [1]. In  $\text{Ce}_2\text{Fe}_{17}$ , at low temperature, there takes place a competition of ferro- and antiferromagnetic interactions, and the type of magnetic ordering turns out sensitive to external actions such as pressure [2,3], alloying [4], and the very method of alloy production [5]. Owing to the occurrence of spontaneous and induced magnetic phase transitions [6], as well as structural transition [7],  $\text{Ce}_2\text{Fe}_{17}$  is an attractive object for many researches into magnetothermal [8], magnetoelastic [9,10], and magnetovolume effects [11,12]. The anomalous behavior of properties of  $\text{Ce}_2\text{Fe}_{17}$  can be traceable in particular to a mixed valence state of atom Ce [13], which results in its small atomic radius and, correspondingly, anomalously small unit-cell volume compared to other  $\text{R}_2\text{Fe}_{17}$  compounds.

$\text{Ce}_2\text{Fe}_{17}$  crystallizes into a rhombohedral structure of the  $\text{Th}_2\text{Zn}_{17}$  type (space symmetry group  $R\bar{3}m$ ). In the crystal lattice, Ce atoms occupy sites 6c, whereas Fe atoms are distributed over four sites - 6c, 9d, 18f, 18h. Results of magnetic measurements carried out in different researches are frequently contradictory. Thus, in one of the earliest

works [11], it was stated that  $\text{Ce}_2\text{Fe}_{17}$  has a noncollinear planar fan structure below  $T_C = 90$  K and helical antiferromagnetic structure in the temperature range between  $T_C$  and  $T_N = 225$  K. In Ref. [14], based on the measured magnetic characteristics, the temperature of ferro-to-antiferromagnet transition was determined as  $T_C \sim 70$  K, and of antiferro-to-paramagnet transition, as  $T_N \sim 270$  K. Later, it was proved by different techniques that it is the collinear ferromagnetic state that is characteristic of  $\text{Ce}_2\text{Fe}_{17}$  at low temperatures and the low-temperature ferromagnetic ordering for different samples occurs at different  $T_C$  values from 20 to 120 K [3,4,15,16]. At the same time, in works [9,10,17] it was established that the antiferromagnetic state is retained up to the liquid-helium temperature. Additionally, the temperature of transition between different helical states was determined as  $T_t = 125$  K.

To clarify the interrelation between the magnetic state and crystal lattice, in Ref. [18], X-ray and neutron diffraction experiments were performed on a series of samples produced by different techniques and treated by different temperature routines. A conclusion was made that the main changes in the magnetic state are related to changes in the unit-cell volume and lattice parameters. The possible reasons for the observed differences were supposed to be deviation of the crystal structure from ideal and mixed valence state of Ce atom. At the same time, the authors of [9], when explaining the magnetic behavior of  $\text{Ce}_2\text{Fe}_{17}$  in the frame of the theory of itinerant magnetism, place emphasis on the competition between antiferromagnetic and ferromagnetic modes, paying no attention to intermediate valence. Moreover, they underlined the high sensitivity of magnetic state and the related

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electronic properties to small changes in local volumes.

Investigation of local properties of  $\text{Ce}_2\text{Fe}_{17}$  by means of Mössbauer spectroscopy was a subject-matter of different works. However, in the very appearance, the spectra shown in Refs. [14,19–22] essentially differ, which is likely to be traceable to various magnetic states of the samples. Trials to quantitatively describe the spectra in these works failed because of both the complexity of the spectra proper and poor mathematical models proposed for fitting. Although, in none of the figures in these works, the difference between experimental points and calculation lines is graphically shown, the misfits are clearly seen.

Undoubtedly, an analytical procedure for processing Mössbauer spectra of the  $\text{R}_2\text{Fe}_{17}$  compounds with the “easy-plane” anisotropy and noncollinear magnetic structures is very intricate. Basically, all the models account for the dipole contribution to hyperfine fields in accordance with the calculations made for  $\text{Y}_2\text{Fe}_{17}$  in Ref. [23]. It is established that for compounds with the “easy-plane” anisotropy, because of divergence of the axes of easy magnetization and principal axes of electrical-field gradient, partial subspectra from the nonequivalent structural positions 9d, 18f, 18h are split into two with the intensity ratio 2:1 if the magnetization direction coincides with one of the main crystallographic in-plane axes. In this case, the spectrum is fitted with 7 subspectra. In Ref. [24], the analysis of Mössbauer spectra was fulfilled via restoration from the spectra of distributions of probability density of hyperfine fields under assumption of a linear correlation of isomer shift and quadrupole shift with hyperfine field. However, such an approach fails to unambiguously characterize the symmetry of neighborhood and the sort of neighboring atoms in the first coordination shell of Fe probe. Earlier [25], we successfully applied the algorithm of description of Mössbauer spectra for material with a complex magnetic structure with the use of so-called two-core distributions of hyperfine field probabilities. This method of reconstructing such distributions is described in detail in Ref. [26]. It allows simultaneously restoring two distributions of hyperfine parameters, each of which is characterized by an independent linear correlation featuring a certain structure component. In this way, it became possible to separate the contributions from the antiferromagnetic and ferromagnetic structure components with the quadrupole shifts of opposite sign. As discovered, in the states which, based on magnetic measurements and morphological characterization, were considered magnetically single-phase, contributions from both magnetic phases were present.

In the work presented, aiming at ascertainment of the nature of magnetic phase transition, Mössbauer spectra of two samples of the  $\text{Ce}_2\text{Fe}_{17}$  compound, which were produced by different techniques and possess different magnetic properties, were analyzed based on the result of fitting of the spectra with a number of subspectra.

## 2. Experimental

Intermetallic compounds for investigations were melted from chemically pure elements in induction furnace in argon atmosphere. Two samples different in excess of Ce with respect to the stoichiometry were melted by semi-levitation method (samples 1 and 2). The ingots were turned over and remelted trice to improve the homogeneity. The third sample with an excess of the rare earth metal was melted in  $\text{Al}_2\text{O}_3$  crucible (sample 3). The results of our preliminary tests showed up that upon semi-levitation melting, the weight loss of the ingot melted from the  $\text{Ce}_2\text{Fe}_{17}$  charge 10 g in weight makes up  $\sim 10$  mg (0.44 wt% of Ce). Also, in trials on melting in an  $\text{Al}_2\text{O}_3$  crucible, we found that the best way to melt the single-phase sample is to charge 10 wt% Ce in excess with respect to the cerium weight, thus compensating for the interaction of Ce with the crucible material. Based on these results, when melting samples 1 and 3 we chose the Ce excesses corresponding to the melting mode, 0.44 and 10 wt%, respectively. In the case of sample 2, we employed the semi-levitation method, but introduced 10 wt% of the excess rare earth element, as in the melting mode in the  $\text{Al}_2\text{O}_3$  crucible. The duration of annealing for equilibrium state at a temperature of

1000°C was experimentally determined for each melting mode and weight of the as-cast ingot, namely, 8h (samples 1 and 2) and 300h (sample 3).

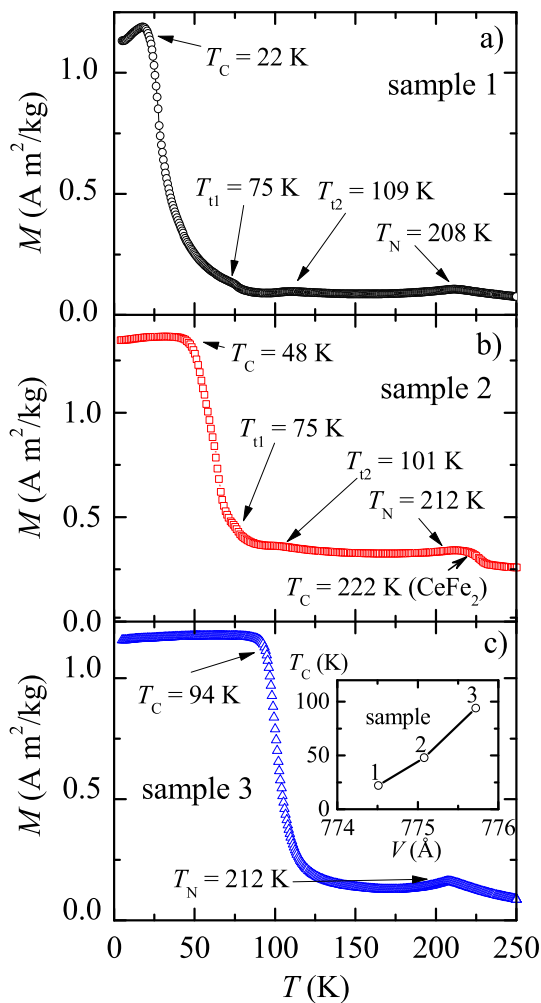
The X-ray phase analysis showed that in all samples, the main phase possesses a crystal structure of the  $\text{Th}_2\text{Zn}_{17}$  type and the amount of foreign phases does not exceed 3%. In samples 1 and 3, the impurity phase is  $\alpha\text{-Fe}$ , whereas sample 2 contains small amount of the cubic phase  $\text{CeFe}_2$ . The lattice parameters of the main phase are  $a = 8.4897(7)$  Å,  $c = 12.4083(10)$  Å for sample 1,  $a = 8.4923(7)$  Å,  $c = 12.4099(11)$  Å for sample 2 and  $a = 8.4949(8)$  Å,  $c = 12.4154(11)$  Å for sample 3. Our X-ray diffraction patterns do not allow us to find difference in the chemical composition of the alloys. However, as shown in Ref. [18], the compositions of the alloys prepared by different techniques can vary from  $\text{Ce}_2\text{Fe}_{16.7}$  to  $\text{Ce}_2\text{Fe}_{17.3}$ .

The magnetization of the samples was measured on a SQUID magnetometer MPMS5 XL (Quantum Design Inc.) in the temperature range of 2–250 K.  $^{57}\text{Fe}$  Mössbauer measurements were carried out on a commercial spectrometer Wissel (Germany), which operates in the mode of constant acceleration. The source was Co-57 in rhodium matrix 35 mCi in activity. Samples were prepared from fine powders with the density of 5 mg of Fe per  $\text{cm}^2$  uniformly distributed over substrates. For low-temperature measurements, the samples were clamped between thin beryllium foils (free of iron impurity) and mounted on a cold finger of a helium continuous-flow cryostat CFICEV-MOSS, ICE Oxford, UK. Mössbauer spectra were measured at temperatures from 4.2 to 300 K. The temperature of the sample was kept with an accuracy of  $\pm 0.2$  K with the use of temperature controller 32B, Cryo-Con, USA. The velocity scale calibration was performed on the spectrum of pure iron and of iron oxide  $\alpha\text{-Fe}_2\text{O}_3$ , isomer shift was determined relative to the gravity center of the  $\alpha\text{-Fe}$  spectrum. Mathematical processing of the spectra was performed with the help of program SpectrRelax [27].

## 3. Results

Fig. 1 shows the temperature dependences of the magnetization measured in a field of 4 kA/m. In the ground state, all three samples possess a spontaneous magnetization. At the same time, on increasing temperature, several phase transformations occur the sequence of which essentially differs among the samples. In sample 1, the ferro-to-antiferromagnet transition takes place already at  $T_C = 22$  K (Fig. 1a). Slight anomalies in the temperature dependence of the magnetization at  $T_{i1} = 75$  K and  $T_{i2} = 109$  K testify to magnetic phase transitions between different helical states. In sample 2, the magnetization changes similarly, though the value of  $T_C$  is remarkably higher (Fig. 1b). An essentially higher temperature of transition from the ferro- to antiferromagnetic state,  $T_C = 94$  K, is characteristic of sample 3 (Fig. 1c). The temperatures of transition to the paramagnetic state  $T_N$  for all samples turn out close.

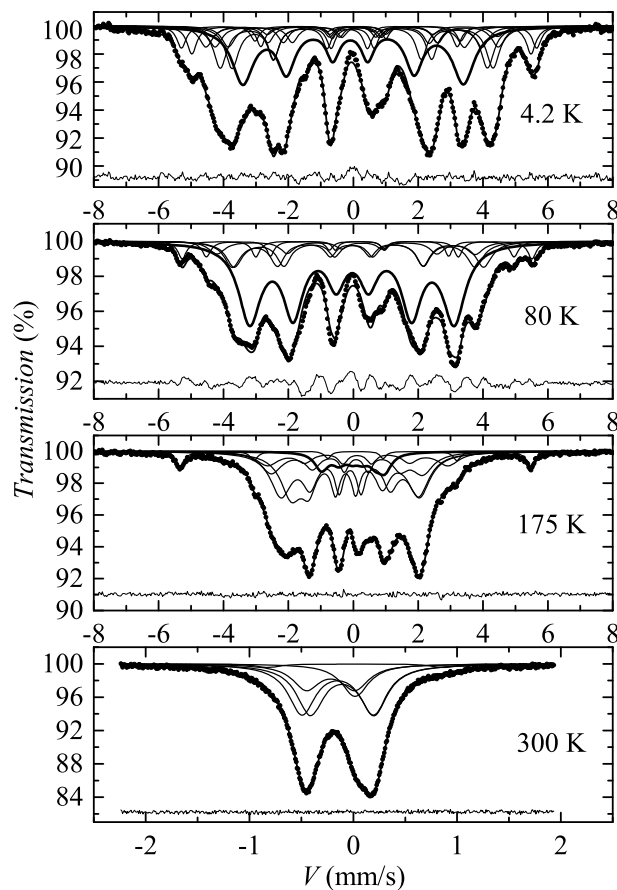
As is seen from inset in Fig. 1c, there is a well-pronounced correlation between the unit-cell volume and the temperature of ferro-to-antiferromagnet transition. A higher  $T_C$  for the sample with the largest lattice parameters qualitatively agree with the earlier observed decrease of  $T_C$  under hydrostatic pressure [2,3]. However, quantitative estimates largely fall apart. Actually, according to [3],  $\text{Ce}_2\text{Fe}_{17}$  is characterized by the coefficient of compressibility  $\kappa = -V^{-1}(dV/dP) = 2.4$  Mbar $^{-1}$  at low temperatures. If to take the difference in the unit-cell volume, for example, for samples 1 and 3, it makes up  $\Delta V/V = -1.74 \cdot 10^{-3}$ , which corresponds to an effective external pressure of 0.725 kbar. Taking into account that the effect of pressure on the transition temperature is characterized by the value  $dT_C/dP = -24$  K/kbar [3], the contribution of this difference to the changes of  $T_C$  is estimated about 17.5 K solely. This figure is by far less than the experimentally observed difference of 72 K between samples 1 and 3. Hence, the main difference in the values of  $T_C$  of different samples has to be connected with other factors: the presence of vacancies, lattice defects, interstitial and substitution impurity atoms.



**Fig. 1.** Temperature dependences of magnetization for three samples of  $\text{Ce}_2\text{Fe}_{17}$  compound measured in a magnetic field of 4 kA/m. Inset shows temperature of ferro-antiferromagnet transition versus unit-cell volume.

Based on the above temperature dependences of the magnetization, temperatures for Mössbauer experiments, 4.2, 80, 175, and 300 K, were chosen. Since sample 2 contains a small amount of impurity  $\text{CeFe}_2$ , whose Curie temperature is close to the Neel temperature of the main phase  $\text{Ce}_2\text{Fe}_{17}$ , it was not employed in the experiments. At 4.2 K, both sample 1 and sample 3 are characterized by ferromagnetic order with approximately equal magnetic moments. At 80 K, sample 3 remains in the ferromagnetic state, whereas in sample 1, a helical antiferromagnetic order is already realized. At 175 K, samples 1 and 3 are in antiferromagnetic state and at 300 K, in paramagnetic state.

Fig. 2 shows Mössbauer spectra measured on sample 1 at different temperatures. First, we processed the spectrum for the ferromagnetic state ( $T = 4.2$  K). Since at this temperature the compound is a collinear ferromagnet with the alignment of magnetic moments with one of the main crystallographic axes [3], we fitted the spectrum with 7 subspectra describing 7 magnetically nonequivalent positions of Fe atoms in the crystal lattice,  $6c$ ,  $9d_6$ ,  $9d_3$ ,  $18f_{12}$ ,  $18f_6$ ,  $18h_{12}$ ,  $18h_6$  (the subscript denotes the multiplicity of a site in the unit cell). The sequence of subspectra is given in the order of decreasing hyperfine fields, according to [19]. The intensities of the subspectra are related with the site occupancies. When processing the spectra, we ascribed different signs to quadrupole shifts in each pair of subspectra ( $9d_6 - 9d_3$ ,  $18f_{12} - 18f_6$ ,  $18h_{12} - 18h_6$ ), using a priori information gained from the preliminarily constructing the two-core distributions of hyperfine fields. The line half-widths (hereinafter, the half-width of the 1st and 6th lines



**Fig. 2.**  $^{57}\text{Fe}$  Mossbauer spectra of sample 1 measured at different temperatures. Points – experiment, envelopes – fitting results, bottom thin lines – difference between experiment and fitting.

of the Zeeman sextet is meant) were assigned equal for all subspectra except for that characterizing Fe atoms in the dumbbell position  $6c$ , since the magnetic moments of atoms at this site are aligned with the  $c$  axis [23]. It should be mentioned that for sample 1, we employed an additional subspectrum corresponding to a small amount of impurity  $\alpha$ -Fe. The presence of this impurity is well visualized in the spectra of sample 1 measured at other temperatures, in which the high-field subspectrum of iron is spaced apart. In what follows, we omit it in discussion.

Within such an approach we failed to correctly process the experimental spectrum for sample 1 at  $T = 4.2$  K; in the difference spectrum there were present features in small fields, which testified to the presence of extra contributions to the spectrum. Note that earlier in Ref. [24], a sample of the  $\text{Ce}_2\text{Fe}_{17}$  compound produced by levitation melting was investigated by NMR method and an additional low-field peak in the spin-echo spectrum was not given an explanation either. In view of this, an additional subspectrum with an independent half-width was introduced in the model, and we, judging by the smooth difference spectrum, can state a good fitting of the spectrum at  $T = 4.2$  K.

The above described model with the additional subspectrum was applied to processing of the spectra for sample 3 in ferromagnetic state ( $T = 4.2, 80$  K), which are shown in Fig. 3. In Figs. 2 and 3, the additional contribution is shown by bold line.

To treat the spectrum of a helical antiferromagnet is quite difficult, as in the helical magnetic structure, directions of magnetic moments located at sites  $9d$ ,  $18f$ , and  $18h$  change from layer to layer, thus forming ensemble of a large number of directions in plane (001) (unlike the only direction in the case of collinear ferromagnet). This should result in the necessity to employ in the model a great number of

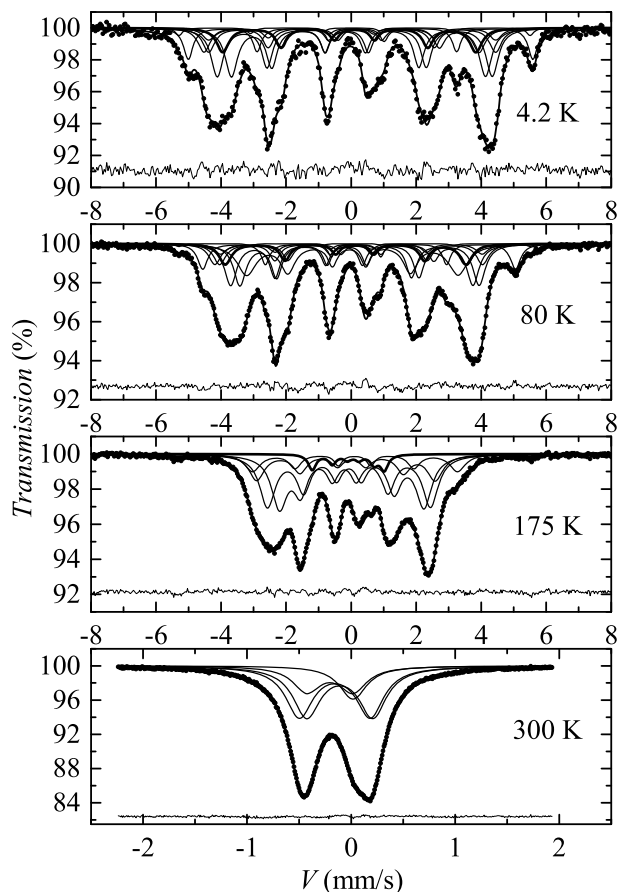


Fig. 3.  $^{57}\text{Fe}$  Mossbauer spectra of sample 3 measured at different temperatures. Points – experiment, envelopes – fitting results, bottom thin lines – difference between experiment and fitting.

contributions; all the more so that the account for the dipole interaction would lead to splitting the subspectra into two or three each. However, the processing of the thus increased number of parameters varied is hardly possible. Therefore, we fitted the spectra of the  $\text{Ce}_2\text{Fe}_{17}$  compound in the helical states with four subspectra with enlarged half-widths, thus allowing for the sets of different states of Fe at each crystallographically nonequivalent site.

Assuming that changes in the direction of Fe magnetic moments from plane to plane occur in the same way for all sites except for 6c, which differs by the type of local ordering from 9d, 18f, 18h sites, we equaled the half-widths of the latter three subspectra. However, to properly treat the spectra, we had to again introduce additional contribution with a low hyperfine field and independent parameters, as it was done for the ferromagnetic state. The results of fitting of the spectra taken on both samples at 175 K were thus improved essentially; yet, the fitting of the spectrum for sample 1 at  $T = 80$  K was not at its best. The latter result can be explained by a complicated many-phase magnetic structure, as it follows from the results of magnetic measurements (Fig. 1).

It should be underlined that the additional contribution introduced in fitting of the spectra for both ferromagnetic and helical anti-ferromagnetic states cannot be ascribed to a particular crystallographically nonequivalent position, as all partial contributions are already taken into account.

As for the spectra of samples 1 and 3 measured at  $T = 300$  K (in paramagnetic state), they are well fitted with four subspectra, with no additional subspectrum required. The half-widths of all the subspectra are equal and make up  $\sim 0.32$  mm/c for both samples. The hyperfine parameters of these subspectra are given in Fig. 4; the error in the

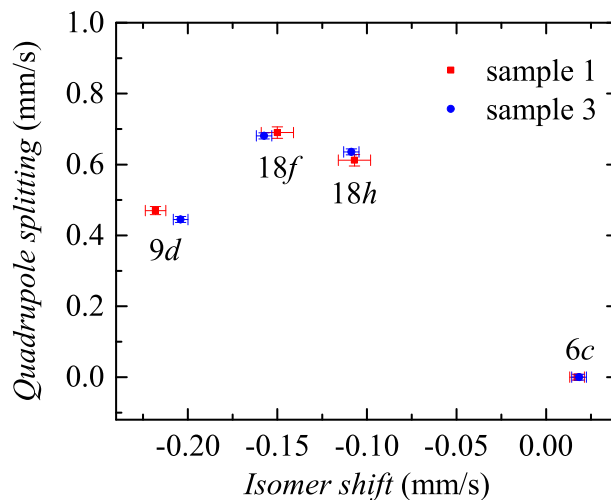


Fig. 4. Quadrupole splitting vs isomer shift taken from the results of fitting of the spectra measured at 300 K for both samples.

determination of isomer shift and quadrupole splitting arises mainly due to the spectrum discretization. As is seen from the Fig. 4, the hyperfine parameters for both samples are virtually equal, which purports that in the paramagnetic state, the samples are crystallographically identical and do not contain in the main phase a meaningful amount of impurity atoms whose presence was supposed in Refs. [9,22]. Hence, the difference in the  $^{57}\text{Fe}$  Mössbauer spectra of the samples in the magnetic states is accounted for by the high sensitivity of the hyperfine interaction parameters to changes in the type of magnetic ordering.

Table 1 presents the values of isomer shift  $\delta$  and quadrupole shift  $\Delta E_Q$  obtained from fitting the spectra measured at 4.2 K. The hyperfine interactions parameters are seen to slightly change in comparison with the data obtained at 300 K. The isomer shifts increase and virtually coincide for two samples. Besides, the values of isomer shift for positions 18f and 18h turned out equal within the error of measurement, which purports that there may exist, along with temperature, another factor affecting the electronic structure of Fe atoms, say,  $s$ - $d$ - $f$ -electron exchange between Ce and Fe atoms. However, this question is impossible to answer based on the results of the present work. As for the quadrupole shifts, this parameter obtained for the subspectrum related to atoms in position 6c becomes nonzero unlike the case of room temperature. At the same time, the quadrupole shifts of the subspectra ascribed to Fe atoms in positions 9d, 18f, 18h decrease more significantly than in positions 18f and 18h and even next to vanish. However, it should be noted that these values are determined with a high error since the subspectra are of comparatively low intensity, and, when solving a many-parameter problem of fitting the spectra, an uncertainty in the determination of the exact positions of such subspectra does arise.

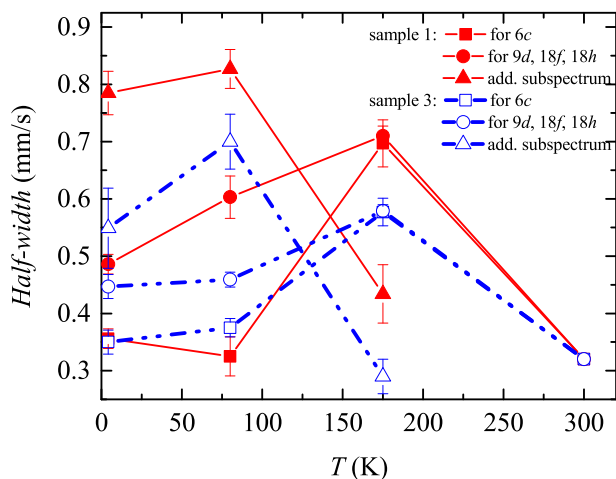
To analyze the changes in the magnetic state of two samples with temperature, we compared the temperature behavior of the half-width of different partial contributions. The results of fitting at different temperatures are shown in Fig. 5 where, for better visualization, lines connecting points that correspond to an individual spectrum are drawn.

As is seen from the Fig. 5, with increasing temperature to 175 K, the half-width of the lines in the subspectra corresponding to iron atoms in positions 9d, 18f, 18h grows, which is expedient within the model suggested for the description of the spectra for helical anti-ferromagnetic states of the samples. The line widening is traceable to the scattering of magnetic moments both in plane and from plane to plane. At the same time, in the spectra of both samples measured at 4.2 and 80 K, the half-width of the line corresponding to Fe atoms in the dumbbell position 6c is close to that determined for the paramagnetic state. This fact indicates that at low temperatures, magnetic ordering does not bring about any additional scattering of magnetic moments at



**Table 1**  
Isomer  $\delta$  and quadrupole  $\Delta E_Q$  shifts for different subspectra obtained on fitting the spectra measured at the temperature 4.2 K.

Subspectrum	Sample 1		Sample 3	
	$\delta$ , mm/s	$\Delta E_Q$ , mm/s	$\delta$ , mm/s	$\Delta E_Q$ , mm/s
6c	$0.224 \pm 0.009$	$0.048 \pm 0.007$	$0.219 \pm 0.009$	$0.098 \pm 0.009$
9d <sub>6</sub>	$-0.024 \pm 0.010$	$-0.040 \pm 0.043$	$-0.024 \pm 0.016$	$-0.070 \pm 0.028$
9d <sub>3</sub>	$-0.024 \pm 0.010$	$0.116 \pm 0.104$	$-0.024 \pm 0.016$	$0.054 \pm 0.089$
18f <sub>12</sub>	$0.030 \pm 0.006$	$0.152 \pm 0.009$	$0.017 \pm 0.011$	$0.312 \pm 0.024$
18f <sub>6</sub>	$0.030 \pm 0.006$	$-0.346 \pm 0.014$	$0.017 \pm 0.011$	$-0.470 \pm 0.021$
18h <sub>12</sub>	$0.020 \pm 0.006$	$0.384 \pm 0.007$	$0.014 \pm 0.007$	$0.396 \pm 0.008$
18h <sub>6</sub>	$0.020 \pm 0.006$	$-0.432 \pm 0.014$	$0.014 \pm 0.007$	$-0.310 \pm 0.024$
addition	$-0.063 \pm 0.016$	$0.032 \pm 0.015$	$-0.093 \pm 0.027$	$0.002 \pm 0.025$

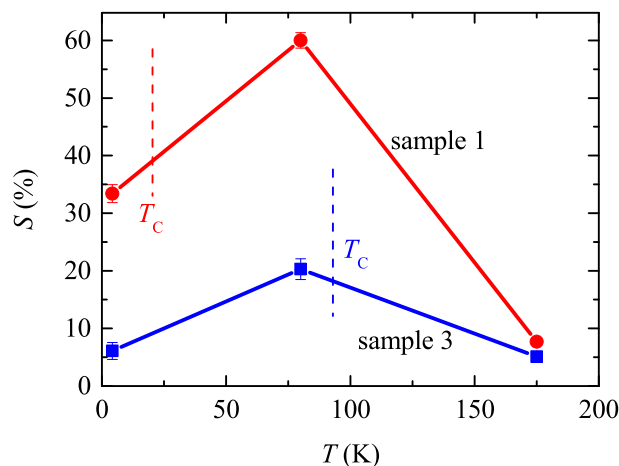


**Fig. 5.** Temperature dependences of half-width of resonance lines for different  $^{57}\text{Fe}$  subspectra. Solid lines – sample 1, dash-dot lines – sample 3.

these sites. However, this value noticeably increases on coming to  $T = 175$  K and we can suppose a tangible deviation of the magnetic moments from the c axis in the helical antiferromagnets. The half-width of the additional spectral lines is quite large already at  $T = 4.2$  K, 0.78 and 0.55 mm/c for the samples 1 and 3, respectively. These values are likely to reflect the fact that there is a superposition of a number of contributions rather than the one assigned to a particular magnetic order, but to discern these contributions is beyond the capacity of the experiment performed. At  $T = 80$  K, this parameter reaches its maximum for both samples, 0.83 and 0.7 mm/c, respectively, and at  $T = 175$  K, the half-width sharply decreases and becomes equal to 0.43 and 0.3 mm/c for the samples 1 and 3, respectively.

Besides, the relative intensity of this spectrum,  $S$ , also changes with temperature and, correspondingly, magnetic state of the samples. Fig. 6 presents the  $S(T)$  dependences for both samples, which are essentially different. Whereas at  $T = 4.2$  K, the relative intensity of this subspectrum for sample 1 amounts to more than 35%, in the spectrum of sample 3 it is small and equal to  $\sim 5\%$ . At  $T = 80$  K, in the spectrum of sample 1 this contribution is most intense and makes up  $\sim 60\%$ , whereas in the spectrum of sample 3, only 20%. On increasing temperature to 175 K, the relative intensity of this contribution sharply diminishes to about 7 and 5% for samples 1 and 3, respectively, and completely vanishes in the spectra for the paramagnetic state.

Fig. 7 demonstrates the values of hyperfine fields of all spectral contributions versus temperature for both samples (the errors in the determination of hyperfine fields are of the size of symbols on the graphs). As in the ferromagnetic samples, because of dipole contribution, atoms in positions 9d, 18f, and 18h present two subspectra each, their mean values are plotted. It is seen that the graphs run qualitatively the same course, though the spectra differ even in their appearance and, at 80 K, the magnetic ordering in the samples is different. It is worth



**Fig. 6.** Temperature dependences of relative intensity of additional subspectrum for both samples.

noting that with increasing temperature from 4.2 to 80 K, the hyperfine field of the additional contribution changes insignificantly for both samples, whereas, on raising temperature to  $T = 175$  K, sharply drops (almost three times), with the other values of hyperfine fields decreasing by a factor of  $\sim 1.5$ . Such behavior of the hyperfine parameters of this contribution indicates that it originates from the regions essentially different from the main state of the sample bulk.

#### 4. Discussion

Earlier, single-crystal and powder samples of the  $\text{Ce}_2\text{Fe}_{17}$  compound in the ground antiferromagnetic state were studied using high-energy X-ray diffraction, which revealed a second-order structural phase transition at  $T_t = 118$  K. Upon this transition, individual atoms in the crystal lattice shift from their positions by diffusionless mechanism, thus doubling the lattice parameter along the hexagonal c-axis, with the symmetry space group  $R\bar{3}m$  being retained [7].

Of interest is the model of crystal structure for  $\text{Ce}_2\text{Fe}_{17}$  proposed in Ref. [28]. In one type of layers, atoms of Fe occupy positions 18f that form equilateral hexagons in the center of which there are Ce atoms or dumbbell pair of Fe atoms in position 6c. Between such layers, there are pure iron layers in which atoms form two types of hexagons – mixed, containing positions 9d and 18h and those containing positions 18h only. Because of alternation of Ce atoms and dumbbell Fe atoms, the planes with positions 9d and 18h become slightly corrugated and the hexagons proper, three-dimensional rather than two dimensional. Moreover, the hexagons constituted by atoms in positions 18h only are equilateral, whereas the mixed hexagons are slightly contracted because of a somewhat smaller distance between positions 18h and 9d compared to the distance 18h–18h [28]. The corrugation of the atomic plane containing positions 18h and 9d results in local changes in the

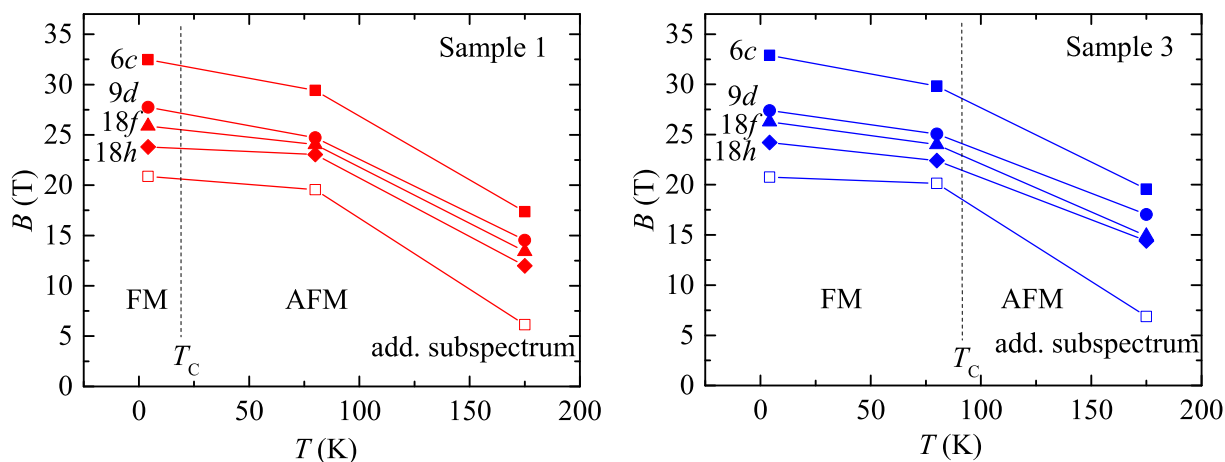


Fig. 7. Temperature dependences of hyperfine fields of partial contributions.

distance between nearest Fe atoms, which, in turn, can lead to a local sign reversion of the exchange interactions, since the interatomic spacings Fe-Fe in the compound  $\text{Ce}_2\text{Fe}_{17}$  are close to a critical one. In other words, positions 18h and 9d can find themselves in the regions with a local magnetic order unlike the order realized over the bulk [7].

Note that the authors of [25], using Mössbauer spectroscopy, showed up the possibility of coexistence on a local level of different types of magnetic ordering in the compound  $\text{LaFe}_{13}$  doped with Al and Si. In the  $\text{NaZn}_{13}$ -type structure of  $\text{LaFe}_{13}$ , Fe atoms are located in icosahedra and their local symmetry is close to the cubic. Upon substituting other atoms (Al, Si) for Fe, small changes in the symmetry result in contraction of part of icosahedra and expansion of the others, i.e., changes in the distance between neighboring Fe atoms. This in turn causes alteration of the sign of exchange interaction and reorientation of magnetic moments. The same effect is likely to take place in the compound  $\text{Ce}_2\text{Fe}_{17}$  as well.

In view of the above-said, it is reasonable to consider the discovered additional contribution in the spectra, which possesses the lowest hyperfine field and demonstrates unlike temperature behavior, to be related to Fe atoms located in the regions undergoing local structural distortions. One can say, judging by the temperature course of the relative intensity of this subspectrum (Fig. 6), that these regions are antiferromagnetically ordered; yet, the type of order can differ from the bulk. For both samples, on increasing the temperature from 4.2 K toward the temperature of ferro-antiferromagnetic transition  $T_C$  ( $T_C = 22$  K for sample 1 and  $T_C = 94$  K for sample 3), the relative intensity of this contribution grows, which purports the increase in the number of iron atoms in these regions. The absence in the temperature dependence of the magnetization (Fig. 1), measured in external field, of any peculiarities, which can evidence the presence in the ground ferromagnetic state of a sample of several magnetic phases, is feasibly accounted for by the destruction of such local magnetic order under action of external magnetic field.

The validity of the approach stated is proved by the explanations that can be given to the other experimental facts observed. First, the additional contribution to the spectra disappears with increasing temperature (its hyperfine field and relative intensity sharply diminish at  $T = 175$  K for both samples under study). This fact correlates well with the disappearance of structural distortions, detected in Ref. [7], which occurs gradually on increasing temperature via the second-order transition. Second, earlier [17], it was shown that for the sample of the  $\text{Ce}_2\text{Fe}_{17}$  compound with the ground antiferromagnetic state, the temperature of the onset of structural transition  $T_i$  from the low-temperature antiferromagnetic phase to the high-temperature one increases by more than 40 K with increasing pressure from 0 to 1.2 GPa. In addition, it was found that the critical field of the metamagnetic transition to the ferromagnetic state induced by external field at  $T = 4.2$  K grows from 1

to 15 T with the same increase in pressure. Such an enhancement of antiferromagnetic interactions in  $\text{Ce}_2\text{Fe}_{17}$  under external pressure proves the statement that it is the lattice distortions and the decrease in the interatomic spacings that stabilize antiferromagnetic ordering.

Based on the data of earlier works on the lattice distortions in  $\text{Ce}_2\text{Fe}_{17}$  at low temperatures, we can assign the additional contribution to the splitting of either position 18f into 18f and 18g [7] or position 18h [28]. The results of our work point to the latter supposition as the hyperfine field of this subspectrum is closer to the value for the subspectrum related to Fe atoms in position 18h.

## 5. Conclusions

Intermetallic compound  $\text{Ce}_2\text{Fe}_{17}$  demonstrates an unusual magnetic behavior, as in different researches, essentially various results are reported on the number of phase transitions with temperature, the transitions temperatures proper, and even the type of magnetic ordering. Based on the data of our magnetic measurements, we performed Mössbauer experiments on two samples of the  $\text{Ce}_2\text{Fe}_{17}$ , compounds produced by different techniques. Magnetic characterization of the samples is different, though X-ray data on the lattice parameters are quite close. Quantitative estimates made using the literature data on the influence of pressure on the temperatures of magnetic transitions allows a conclusion to be made that the difference in magnetic properties of the samples under study is not connected with the difference in the lattice parameters only.

Mössbauer spectra were analyzed based on the available information on nonequivalent positions of Fe atoms in the crystal lattice of  $\text{Ce}_2\text{Fe}_{17}$  and type of magnetic ordering at different temperatures. When processing the experimental spectra, a model was proposed within which fitting of the spectra for magnetically ordered states was performed with an additional subspectrum compared to the subspectra employed in conventional models. The relative intensity of this contribution changes with temperature and depends on the state of samples. The spectra for the samples in the paramagnetic state are completely alike, which testifies to the crystallographically identical states of Fe atoms and to the absence of any meaningful amount of impurities in the main phase of the samples produced by different techniques.

When analyzing the results, it is shown that the additional subspectrum introduced into the fitting is traceable to the existence on a local level of regions with an antiferromagnetic ordering unlike that characterizing the bulk of the samples. The presence of such local regions can be accounted for by the second-order structural phase transition discovered earlier, upon which slight structural distortion occurs within one group of space symmetry and, with decreasing temperature, Fe atoms shift from their positions. The fraction of such regions in the samples produced by different techniques and, consequently, degree of

structural distortions strongly vary from sample to sample, which can affect the temperatures of transition from one magnetic state to another. To describe the properties of the intermetallic compound  $\text{Ce}_2\text{Fe}_{17}$  in more detail and construct more complete magnetic phase diagram, additional temperature studies are needed.

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### References

- [1] I.S. Tereshina, S.A. Nikitin, K.P. Skokov, T. Palewski, V.V. Zubenko, I.V. Telegina, V.N. Verbitsky, A.A. Salamova, *J. Alloy. Comp.* 350 (2003) 264–270.
- [2] I. Medvedeva, Z. Arnold, A. Kuchin, J. Kamarad, *J. Appl. Phys.* 86 (1999) 6295–6300.
- [3] O. Prohnenko, C. Ritter, Z. Arnold, O. Isnard, J. Kamarad, A. Pirogov, A. Teplykh, A. Kuchin, *J. Appl. Phys.* 92 (2002) 385–391.
- [4] A.G. Kuchin, V.I. Khrabrov, A.S. Ermolenko, E.V. Belozerov, G.M. Makarova, *Phys. Met. Metallogr.* 90 (2) (2000) 123–127.
- [5] Y. Makihara, Y. Uwatoko, H. Matsuoka, M. Kosaka, H. Fucuda, H. Fujii, *J. Magn. Magn Mater.* 272–276 (2004) 551–552.
- [6] F. Ishikawa, T. Goto, H. Fujii, *Physica B* 329–333 (2003) 657–658.
- [7] A. Kreyssig, S. Chang, Y. Janssen, J.W. Kim, S. Nandi, J.Q. Yan, L. Tan, R.J. McQueeney, P.C. Canfield, A.I. Goldman, *Phys. Rev. B* 76 (2007) 054421-1-8.
- [8] W. Iwasieczko, A.G. Kuchin, *J. Alloy. Comp.* 563 (2013) 130–134.
- [9] Y. Janssen, S. Chang, A. Kreyssig, A. Kracher, Y. Mozharivskiy, S. Misra, P.C. Canfield, *Phys. Rev. B* 76 (2007) 054420-1-17.
- [10] Y. Janssen, H. Fujii, T. Ekino, K. Izawa, T. Suzuki, T. Fujita, F.R. de Boer, *Phys. Rev. B* 56 (1997) 13716–13719.
- [11] D. Givord, R. Lemaire, *IEEE Trans. Magn. Mag.* 10 (2) (1974) 109–113.
- [12] A.V. Andreev, A. Lindbaum, *J. Alloy. Comp.* 297 (2000) 43–45.
- [13] J.M.D. Coey, J.E.M. Allan, A.A. Minakov, Yu.V. Bugaslavsky, *J. Appl. Phys.* 73 (1993) 5430–5432.
- [14] K.H.J. Buschow, J.S. van Wieringen, *Phys. Status solidi* 42 (1970) 231–239.
- [15] A.G. Kuchin, A.S. Ermolenko, V.I. Khrabrov, *Phys. Met. Metallogr.* 86 (3) (1998) 276–280.
- [16] Yu.G. Chukalkin, A.E. Teplykh, A.G. Kuchin, *Phys. Met. Metallogr.* 106 (6) (2008) 566–576.
- [17] K. Koyama, H. Fujii, T. Goto, H. Fukuda, Y. Janssen, *Physica B* 294–295 (2001) 168–171.
- [18] R.A. Teplykh, A.N. Pirogov, A.G. Kuchin, A.E. Teplykh, *Physica B* 350 (2004) 99–102.
- [19] Bo-Ping Hu, Hong-Shuo Li, Hong Sun, J.M.D. Coey, *J. Phys. Condens. Matter* 3 (1991) 3983–3995.
- [20] D.P. Middleton, S.R. Mishra, J. Long Gary, O.A. Pringle, Z. Hu, W. Yelon, F. Grandjean, K.H.J. Buschow, *J. Appl. Phys.* 78 (1995) 5568–5576.
- [21] S.R. Mishra, J. Long Gary, O.A. Pringle, D.P. Middleton, Z. Hu, W. Yelon, F. Grandjean, K.H.J. Buschow, *J. Appl. Phys.* 79 (1996) 3145–3155.
- [22] D. Hautot, J. Long Gary, F. Grandjean, O. Isnard, *Phys. Rev. B* 62 (2000) 11731–11741.
- [23] W. Steiner, R. Haferl, *Phys. Status Solidi (a)* 42 (1977) 739–750.
- [24] V.V. Serikov, V.I. Voronin, N.M. Kleinerman, A.G. Kuchin, *Phys. Met. Metallogr.* 94 (2) (2002) 170–176.
- [25] A.V. Vershinin, V.V. Serikov, N.M. Kleinerman, V.S. Gaviko, N.V. Mushnikov, *J. Alloy. Comp.* 621 (2015) 274–282.
- [26] V.S. Rusakov, *Mössbauer Spectroscopy of Locally Inhomogeneous Systems*, Almaty, (2000) (in Russian).
- [27] M.E. Matsnev, V.S. Rusakov, *AIP Conf. Proc.* vol. 1489, 2012, pp. 178–185.
- [28] A.V. Lukoyanov, Yu.V. Knyazev, Yu.I. Kuz'min, A.G. Kuchin, *Eur. Phys. J. B* 90 (2017) 243-1-7.