Magnetic percolation and inequivalence of Fe sites in YFe$_x$Co$_{2-x}$ ($x = 0.03$ and 1) Laves phase compounds

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Abstract YCo$_2$ compound is an exchange-enhanced Pauli paramagnet on the verge of being magnetic. Topological or chemical disorder can induce in it ferromagnetic long-range ordering. The influence of Fe substitution and quenched-in topological disorder on the magnetic properties of YFe$_{0.03}$Co$_{1.97}$ and YFeCo is studied. Structural and magnetic properties of these compounds are analyzed by means of X-ray diffraction, vibrating sample magnetometry, Mössbauer spectroscopy and AC magnetic susceptibility measurements. All samples crystallize in cubic MgCu$_2$-type phase with lattice constant changing from 7.223 Å for YCo$_2$ through 7.221 Å for YFe$_{0.03}$Co$_{1.97}$ to 7.313 Å for YFeCo. Fe atoms are responsible for stabilization of magnetic moments on Co, and mictomagnetism is observed in YFe$_{0.03}$Co$_{1.97}$ sample. Upon further substitution, as in YFeCo, long-range ordering appears. The Mössbauer spectra permitted distinction between two magnetically inequivalent Fe sites, as reported earlier for YFe$_2$.

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1 Introduction

The Y–Co system has been studied extensively in last decades. One of the most interesting is YCo$_2$ intermetallic compound, which can be described as an exchange-enhanced Pauli paramagnet. Moreover, the Stoner criterion is almost fulfilled in this compound, and even an insignificant change in band filling can result in a considerable effect on the density of states at the Fermi level [1]. This compound is on the verge of being magnetic and small perturbations, as for example, substitution of nonmagnetic Y by another element or introduced disorder can bring ferromagnetic long-range ordering [2]. The cobalt moments can be also stabilized by substituting Co with other metals, e.g., Fe [3]. There is a percolation limit for the onset of ferromagnetism which can be reached after substitution of 12 at.% of Co by iron [4]. Mictomagnetic behavior has also been observed in such systems [5]. The ^{57}Fe Mössbauer spectroscopy and macroscopic magnetic measurements have been helpful in determination of magnetic properties of Fe-substituted YCo$_2$ compounds [5]. The YCo$_2$ is a Laves phase compound, and the cubic structure is preserved for the whole range of compositions of pseudo-binary YFe$_x$Co$_{2-x}$. Hence, the proposed system is appropriate to determine not only the influence of Fe substitution but also the influence of topological and chemical disorder on magnetic properties of YFe$_x$Co$_{2-x}$. The latter condition, which is the topological and chemical disorder, can be realized by the synthesis of metastable, slightly disordered samples by the rapid quenching of the melt.

2 Experiment

The initial ingots of YFe$_x$Co$_{2-x}$ ($x = 0.03$, 1) were prepared with the use of arc furnace, by repeated melting of

required amounts of pure Y (99.9 %), Co (99.9 %) and Fe (99.9 %) in the Ar atmosphere. ^{57}Fe was used in the synthesis of the $YFe_{0.03}Co_{1.97}$ compound to ensure the appropriate amount of this Mössbauer isotope. The polycrystalline ingots were rapidly quenched in a melt spinning device on a rotating copper wheel with the surface velocity of 40 m/s. The X-ray diffraction (XRD) with Co-$K\alpha$ radiation in Bragg–Brentano geometry was used to characterize the crystalline structure of the flakes. Structural parameters were determined by the Rietveld method. Temperature dependence of magnetic susceptibility was measured by AC method using Quantum Design Physical Property Measurement System (PPMS). Magnetization versus applied field $M(H)$ curves were measured up to 8 T with vibrating sample magnetometer (option of PPMS). The same equipment was used to measure magnetization versus temperature up to 380 K. Home-built equipment based on Hartshorn bridge was utilized for thermomagnetic measurements. Conventional Mössbauer measurements were carried out in transmission geometry at room temperature for as-quenched alloys. Mössbauer measurements were performed using a conventional constant acceleration spectrometer with a ^{57}Co-in-Rh source of about 25 mCi activity. All isomer shifts were related to the metallic α-Fe standard. The Mössbauer spectra were fitted using the NORMOS program. The hyperfine parameters (the hyperfine fields, isomer shifts, quadrupole splittings and quadrupole shifts) were determined from the spectral fits.

3 Results and discussion

X-ray diffraction patterns (Fig. 1) exhibit single C15 Laves phase with $MgCu_2$-type structure (Fd-3 m space group). YCo_2 as a Laves phase binary compound is shown here as a reference and was described before in [2]. In all examined alloys there are no signs of presence of an amorphous phase. In YCo_2 and $YFe_{0.03}Co_{1.97}$, there is a negligibly small amount of C15 phase with increased lattice constant $a = 7.960$ Å (an additional small peak visible at about 44°) as reported previously in Ref. [2]. The lattice constant determined for Laves phase in YCo_2 and $YFe_{0.03}Co_{1.97}$ is nearly the same and equal to 7.223 and 7.221 Å, respectively. Upon further substitution of Co by Fe, the lattice constant increases to 7.313 Å. This expansion of unit cell is in accordance with the behavior observed for $Dy(Co_{1-x}Fe_x)_2$ [6]. Melt spinning due to its abrupt quenching is a method which generates a non-equilibrium state when compared to the typical synthesis techniques. It allows implementation of chemical and/or topological disorder, which can influence the structural properties [2]. In YCo_2, it also reduces the possibility of formation of other crystalline phases, especially magnetic YCo_3.
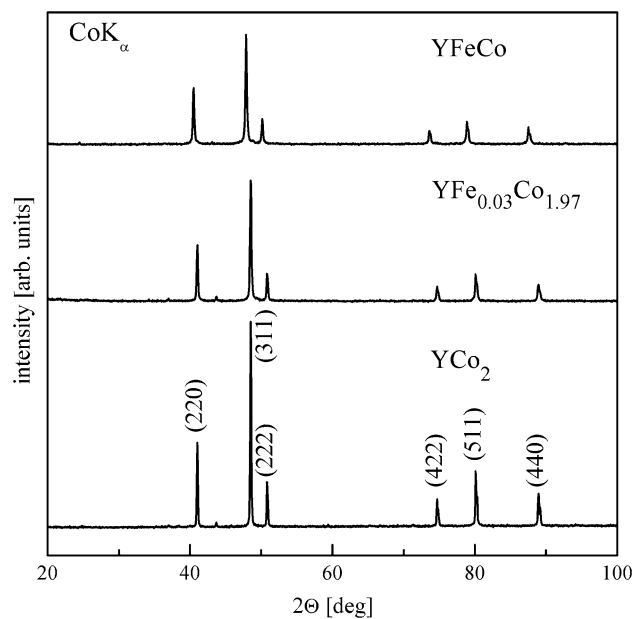

Fig. 1 X-ray diffraction patterns of as-quenched YFe_xCo_{2-x} ($x = 0$, 0.03, 1) ribbons
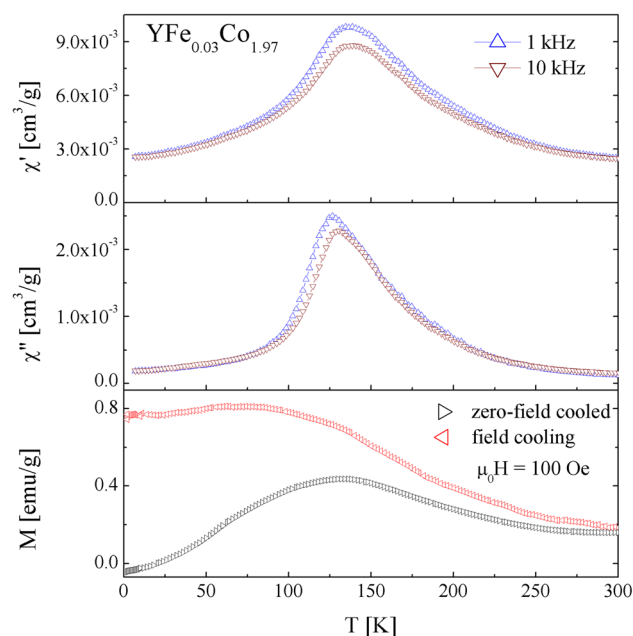

Fig. 2 Real χ' and imaginary χ'' part of AC magnetic susceptibility as a function of temperature (measured at $\omega = 1$ and 10 kHz) along with temperature dependence of magnetization M (measured at 100 Oe) for as-quenched $YFe_{0.03}Co_{1.97}$

Temperature dependences of real and imaginary part of magnetic susceptibility of $YFe_{0.03}Co_{1.97}$ are shown in Fig. 2 along with magnetization versus temperature ZFC (zero-field cooled) and FC (during cooling in magnetic field) curves. In the ZFC protocol, the sample is cooled to
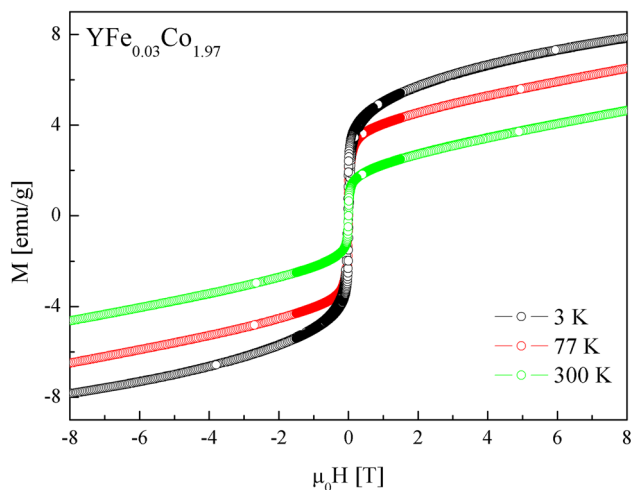
Fig. 3 Magnetization as a function of magnetic field for the $YFe_{0.03}Co_{1.97}$ measured at 3, 77 and 300 K

2 K in zero field, then the measuring field is applied and the magnetization is measured while sweeping up the temperature up to 300 K. FC curve was measured during cooling in applied field. One can observe a distinct peak with a maximum at around 130 K in the temperature dependence of susceptibility and ZFC magnetization. This feature, which is frequency dependent (in AC susceptibility measurements) along with the bifurcation of ZFC and FC curves, suggests the presence of a spin-glass [7], micto-magnetic [8] or superparamagnetic [9] state. Moreover, applied field dependence of magnetization was measured at 3, 77 and 300 K (Fig. 3). Curves are characteristic for mentioned systems with dynamical features, but any further explicit conclusions cannot be drawn.

As YCo_2 is an exchange-enhanced Pauli paramagnet, there is no magnetic ordering in this system. Upon substitution of Co by Fe atoms [5], Fe moments have been reported to be present even at the largest Co concentrations close to YCo_2 composition. Percolation limits for the onset of long-range magnetic ordering in YFe_xCo_{2-x} system differ slightly depending on the method of Curie temperature determination [T_C determined from (1) macroscopic magnetic measurements and (2) temperature of vanishing of magnetic hyperfine splitting in the Mössbauer spectra]. It has been also shown that for compositions with small Fe contents ($x < 0.12$), there is no long-range magnetic ordering, but mictomagnetic behavior was still observed. This is in accordance with the presented results as the frequency dependence of $\chi(T)$ was observed as an indication of dynamic processes in $YFe_{0.03}Co_{1.97}$. At low fields and below peak temperature, the FC magnetization should be constant with temperature for canonical spin-glass [10]. It is not the case in present investigation, as the magnetization

value is decreasing slightly at low temperatures. Moreover, peak observed in Fig. 2 is very broad and suggests the presence of magnetically ordered clusters and the dispersion of spin flipping times, characteristic of mictomagnets [8]. Co and Fe are magnetically coupled with each other in small clusters, while RKKY interaction or magnetic frustrations define the inter-cluster correlations. Positive para-magnetic Curie temperature determined from Curie–Weiss fit of high temperature $\chi^{-1}(T)$ suggests ferromagnetic interparticle interaction. There is a large difference in freezing temperatures T_f between the compounds reported earlier [5] and the sample investigated in the present study. For compounds with $x < 0.12$, T_f was determined to be below 50 K in all samples studied, with the T_f equal to about 10 K for the sample with x of about 0.05. In Fig. 2, for $YFe_{0.03}Co_{1.97}$ compound, the freezing temperature is well above 100 K. The competition between nucleation of the magnetic state and frustration of the long-range ferro-magnetic order is the source of observed mictomagnetic behavior. Clusters are made of groups of Fe atoms and host Co atoms polarized by them. YCo_2 is already on the border of being magnetically ordered, and a small amount of Fe stabilizes the Co moment [3]. In rapidly quenched ribbons, the Laves phase occupation of some structural positions is highly disordered. In such structures, the *3d* band of Co is closer to Fermi level, even causing a long-range magnetic ordering [2, 11]. This could be the reason for a large shift of freezing temperature observed in $YFe_{0.03}Co_{1.97}$. High sensitivity of the magnetic ordering to the structure and/or microstructure has been also observed in other systems, e.g., thin films, where surface magnetic ordering occurs at higher temperatures than the bulk Curie point [12, 13].

The $M(T)$ (Fig. 4) and $M(H)$ curves (inset in Fig. 4) were measured to confirm the presence of expected [5] long-range ordering in YCoFe. This alloy was investigated to show clear distinction between the system close to the percolation limit ($YFe_{0.03}Co_{1.97}$) and that with evident long-range magnetic order. Temperature dependence of magnetization is characteristic for fer-romagnetic materials and the transition temperature to paramagnetic state is equal 559 K. This value is slightly higher than 542 K determined for YFe_2 [14]. Fluctuations observed on $M(T)$ curve are not the physical effects but are connected with lower sensitivity of home-built susceptometer that was used for the measurements above 380 K. High temperature curve was rescaled to fit the low temperature data obtained on vibrating sample magnetometer. Hysteresis loops (inset of Fig. 4) for each temperature are typical of soft fer-romagnetic materials. Small magnetocrystalline anisot-ropy is characteristic of the cubic phases of the alloys such as FeCo or FeNi [15].
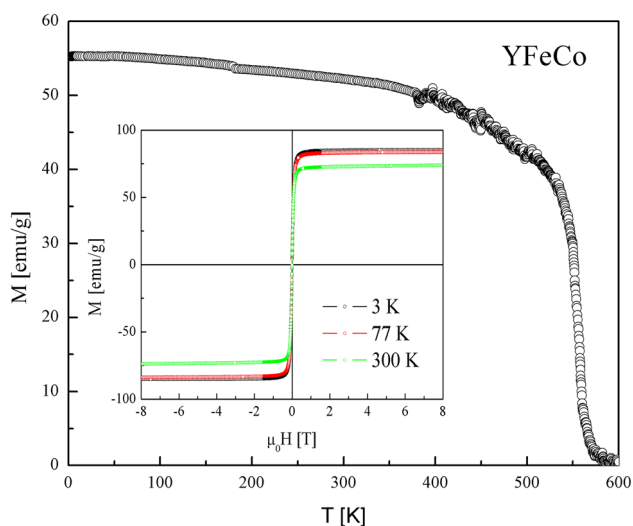
Fig. 4 Magnetization as a function of temperature measured for the YFeCo. Signal above 380 K was measured with high temperature equipment in arbitrary units and then rescaled to match the low temperature curve. Magnetization as a function of magnetic field measured at 3, 77 and 300 K for the YFeCo is shown in the *inset*

The Mössbauer spectrum (Fig. 5) of $YFe_{0.03}Co_{1.97}$ at 300 K shows pure quadrupole structure consistent with the paramagnetic state. It can be well fitted and described by one quadrupole doublet with line width $\Gamma = 0.350$ mm/s, isomer shift IS $= -0.113$ mm/s and quadrupole splitting QS $= 0.446$ mm/s. A small and negative value of IS together with the QS value indicate that Fe is in a low-spin state. The spectrum measured for YCoFe at RT exhibits a sextet, which is a typical feature of ferromagnetic order. It was fitted with two sextets with hyperfine magnetic field values equal to 21.3 and 19.5 T. The line width of the two sextets is equal to 0.395 and 0.400 mm/s, IS $= -0.092$ and -0.075 and quadrupole shift amounts to 0.078 and -0.071 for first and second spectral component, respectively. Nonzero values of quadrupole shift suggest that the cubic structure is slightly distorted (not visible in XRD measurements), while the change in sign indicates the difference in the direction between electric field gradient and hyperfine field in both distinguished Fe sites. Typically, the Mössbauer spectra of YFe_2 Laves phase below the temperature of magnetic phase transition are the superposition of spectra for two magnetically inequivalent Fe sites. One can observe two sextets with different hyperfine splitting values, although iron occupies just one crystallographically inequivalent position in the Laves phase structure. Local threefold symmetry axes of electric field gradient generate different magnetic fields due to the difference in the direction of electric field gradient axes and Fe spins [16]. Therefore, all the conclusions drawn for YFe_2 system can be adapted
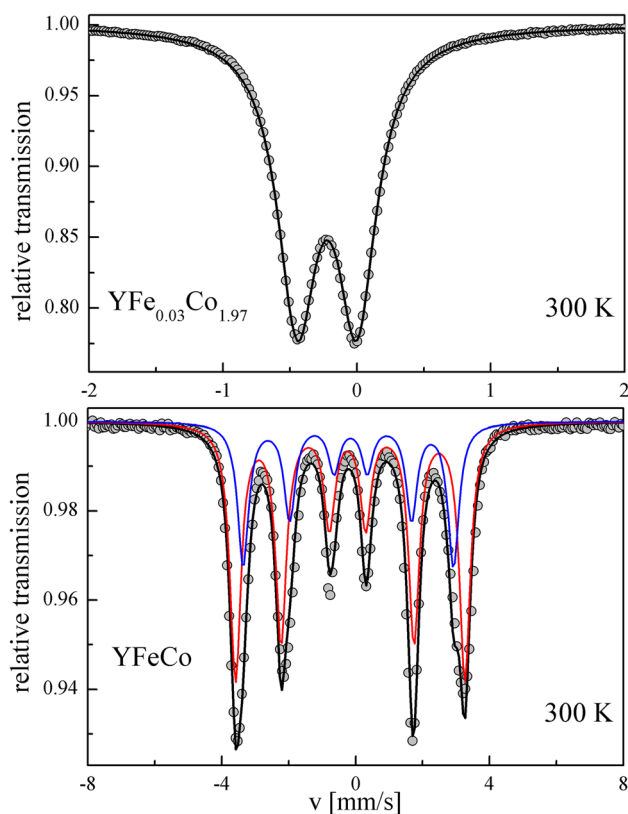

Fig. 5 Mössbauer spectra of as-quenched YFe_xCo_{2-x} ($x = 0.03$, 1) measured at 300 K

to the presented results [16]. In YFeCo, there is an additional chemical disorder on Fe/Co sites, as the occupation of this crystallographic site by Fe or Co is with a high probability stochastic. This could create other magnetically inequivalent positions, but it is not visible in Mössbauer spectrum, as just two distinct hyperfine field values were determined. The spectra were also measured in a wider range of velocities to exclude the presence of Fe_2O_3 and Fe_3O_4 oxides.

4 Conclusions

The effect of iron substitution on magnetic properties of YCo_2 with quenched-in topological and chemical disorder has been investigated. Even the smallest amount of Fe atoms causes the stabilization of magnetic moments on Co. Mictomagnetic (cluster spin-glass) behavior is observed for $YFe_{0.03}Co_{1.97}$, where Co and Fe are magnetically coupled with each other in small clusters, while RKKY interaction or magnetic frustrations define the inter-cluster correlations. Moreover, there is a significant difference in freezing temperatures T_f between the compounds reported earlier [5] and the sample investigated in the present study. It is

probably connected with chemical and topological disorder introduced by the unique method of synthesis (rapid quenching). It can be the source of differences in all magnetic characteristics between the investigated samples and those energetically closer to equilibrium. Moreover, topological disorder is confirmed also by Mössbauer spectroscopy results (nonzero values of quadrupole shift). A threshold of long-range magnetic interactions can be reached with increasing Fe content, as observed for YFeCo sample.

References

1. M. Cyrot et al., J. Phys. C **40**, 171 (1979)
2. Z. Śniadecki et al., J. Appl. Phys. **115**, 17E129 (2014)
3. E. Burzo, Solid State Commun. **25**, 525 (1978)
4. W. Steiner et al., J. Magn. Magn. Mat. **14**, 47 (1979)
5. W. Steiner et al., J. Magn. Magn. Mater. **70**, 105 (1987)
6. Z. Han et al., J. Magn. Magn. Mater. **302**, 109 (2006)
7. J.A. Mydosh, J. Magn. Magn. Mater. **157**, 606 (1996)
8. Z. Śniadecki et al., J. Appl. Phys. **109**, 123921 (2011)
9. S. Bedanta, W. Kleemann, J. Phys. D. Appl. Phys. **42**, 013001 (2009)
10. D. Kumar, A. Banerjee, J. Phys. Condens. Matter **25**, 216005 (2013)
11. M. Ghidini et al., J. Magn. Magn. Mater. **140**, 483 (1995)
12. S. Khmelevskyi et al., Phys. Rev. Lett. **94**, 146403 (2005)
13. Y. Dedkov et al., Phys. Rev. Lett. **99**, 047204 (2007)
14. K.H.J. Buschow, R.P. van Stapele, J. Appl. Phys. **41**, 4066 (1970)
15. M.E. McHenry et al., Prog. Mater Sci. **44**, 291 (1999)
16. Y. Nishihara et al., J. Phys. Soc. Jpn. **51**, 2487 (1982)