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

Z. Śniadecki · M. Kopcewicz · N. Pierunek · B. Idzikowski

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Abstract

\( \text{YCo}_2 \) 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 \( \text{YFe}_{0.03}\text{Co}_{1.97} \) and \( \text{YFeCo} \) 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 \( \text{MgCu}_2 \)-type phase with lattice constant changing from 7.223 Å for \( \text{YCo}_2 \) through 7.221 Å for \( \text{YFe}_{0.03}\text{Co}_{1.97} \) to 7.313 Å for \( \text{YFeCo} \). Fe atoms are responsible for stabilization of magnetic moments on Co, and mictomagnetism is observed in \( \text{YFe}_{0.03}\text{Co}_{1.97} \) sample. Upon further substitution, as in \( \text{YFeCo} \), long-range ordering appears. The Mössbauer spectra permitted distinction between two magnetically inequivalent Fe sites, as reported earlier for \( \text{YFe}_2 \).

1 Introduction

The \( \text{Y–Co} \) system has been studied extensively in last decades. One of the most interesting is \( \text{YCo}_2 \) 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 \( ^{57}\text{Fe} \) Mössbauer spectroscopy and macroscopic magnetic measurements have been helpful in determination of magnetic properties of Fe-substituted \( \text{YCo}_2 \) compounds [5]. The \( \text{YCo}_2 \) is a Laves phase compound, and the cubic structure is preserved for the whole range of compositions \( \text{YCo}_2 \) compounds [5]. The \( \text{YCo}_2 \) is a Laves phase compound, and the cubic structure is preserved for the whole range of compositions \( \text{YCo}_2 \) compounds [5]. 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 \( \text{YFe}_x\text{Co}_{2-x} \). 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 \( \text{YFe}_x\text{Co}_{2-x} \) (\( x = 0.03, 1 \)) 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 $\alpha$-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 ($Fd\bar{3}m$ 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 $a = 7.960 \text{ Å}$ (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$_3$.

3.1 Temperature dependence of magnetic susceptibility

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], 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 YCo$_2$. 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 ferromagnetic materials and the transition temperature to paramagnetic state is equal 559 K. This value is slightly higher than 542 K determined for YFe$_3$ [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 ferromagnetic materials. Small magnetocrystalline anisotropy is characteristic of the cubic phases of the alloys such as FeCo or FeNi [15].
The Mössbauer spectrum (Fig. 5) of YFe\textsubscript{0.03}Co\textsubscript{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\textsubscript{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\textsubscript{2} system can be adapted 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\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} oxides.

### 4 Conclusions

The effect of iron substitution on magnetic properties of YCo\textsubscript{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. Micromagnetic (cluster spin-glass) behavior is observed for YFe\textsubscript{0.03}Co\textsubscript{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.

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