Electronic structure, magnetism and spin fluctuations in the superconducting weak ferromagnet Y₄Co₃

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Results of the first principles study on the electronic structure and magnetism of the superconducting weak ferromagnet Y₄Co₃, are presented. Using the full potential Korringa-Kohn-Rostoker (FP-KKR) method, densities of states, dispersion curves and magnetic moments were calculated for quasi-ordered structural model of the compound in the framework of the local density approximation. Spin-polarized KKR calculations confirm that weak ferromagnetic properties of Y₄Co₃ can be attributed to only one cobalt atom located on (2b) site in the unit cell, while other twenty Co and Y atoms acts as a diamagnetic environment. Moreover, the magnetic Co atoms form a quasi-one-dimensional chains along z direction. The magnitude of Co(2b) magnetic moment (0.55 µB) markedly overestimates the experimental value (0.23 µB), which suggests the importance of spin fluctuations in this system. Calculated distribution of spin magnetization in the unit cell provides a background for discussion of ferromagnetism and superconductivity in Y₄Co₃. Finally, the effect of pressure on magnetism is discussed and compared with experimental data, also supporting weak ferromagnetic behaviors in the system.

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I. INTRODUCTION

Unusual properties of Y₄Co₃, that is the coexistence of superconductivity and ferromagnetism, were observed 30 years ago. The superconducting and ferromagnetic critical temperatures are about \( T_s \sim 2.5 \) K and \( T_C \sim 4.5 \) K, respectively. After this finding, the system was intensively studied using different techniques, since it was the first example where superconductivity coexisted with weak itinerant ferromagnetism, with both phenomena driven most likely by the d-band electrons. To our best knowledge, Y₄Co₃ is up to now a unique compound containing transition-metal elements only, where coexistence of ferromagnetism and superconductivity occurs, since other systems always contain f-like elements, e.g. UGe₂ (Ref. 2), URhGe (Ref. 3), UCoGe (Ref. 4) or recently discovered P-doped EuFe₂As₂ (Ref. 5). Moreover, Y₄Co₃ was likely the first example, where superconductivity occurred below a transition to ferromagnetism, with both phenomena coexisted at least in the range between 1 K and 2.5 K (6, 7). This was another difference to previously known magnetic superconductors e.g. ErRh$_3$B$_4$ or HoMo$_6$S$_8$ (see, Refs. 8–10), where magnetism appeared below \( T_s \), suppressing superconductivity.

Although Y₄Co₃ has been known since 1980, the first principles study on its magnetism (e.g. calculations of magnetic moments) has not been presented until now. We have found two papers reporting electronic structure of this system from ab initio calculations. Interesting discussion of electronic structure of related compound Y₅Co₇ based on non-spin-polarized computations can be found in Ref. 11 (for connections between Y₄Co₃ and Y₅Co₇, see below). More recent paper, Ref. 12, briefly reports electronic structure calculations for Y₄Co₃, also in non-magnetic state.

Noteworthy, one may notice a renewed interest on this system due to very recent experimental investigations.

In this paper the results of band structure calculations

![Image](image-url)

FIG. 1: (Color online) (a) Unit cell of Y₄Co₃ used in the calculations. The edges of the unit cell, i.e. (2b) sites, are occupied by cobalt or vacancy (in red), on average every second position is occupied by cobalt, called here Co(3). Atomic positions are presented in Table I. (b) The body of the unit cell is formed by the trigonal prisms of Y(1) (yellow), Y(2) (green), Co(1) (violet) and Co(2) (blue), the black lines and labels denotes atoms in the \( z = 0.75 \) plane, while white denotes \( z = 0.25 \) plane. (c) The in-plane triangles of Y(1) atoms form channels along z direction, surrounding the Co(3) atoms chains.
A. Review of the experimental data

In this section we summarize shortly crystal structure and magnetism data, available for $\text{Y}_4\text{Co}_3$. For a more complete review, see e.g. Refs. 16,17. The crystal structure of the Y-Co system near 1:1.3 stoichiometry is rather complex, and was originally described in the hexagonal unit cell of the $\text{Ho}_4\text{Co}_3$ type,6,7,15 (Fig. 1). Unit cell can take 22 atoms, being distributed over three inequivalent Co sites and two inequivalent Y sites. All positions are gathered in Table I. As the unit cell includes three formula units, for the Y-Co stoichiometry equals to 4:3, the Co(2b) sites are half-filled (50%) and the number of atoms in the unit cell is equal to 21. Thus, in this crystallographic model, $\text{Y}_4\text{Co}_3$ can not be regarded as an ordered compound, but as a disordered alloy with (2b) sites occupied randomly by cobalt (Co atom on (2b) site will be called Co(3)) and vacancies (Vac). Thus, the crystal cell of this alloy better corresponds to the formula $\text{Y}_{12}\text{Co}_{8+x}$, with $x = 0.50$ than to the formula $\text{Y}_4\text{Co}_3$, suggesting an ordered system. The unit cell (Fig. 1) consists of the separated Co/Vac chains forming the cell edges and the Y(1)-(Y(2)-Co(1)-Co(2)) trinodal prisms filling most of the unit cell. The partial occupation of the Co(3) site is likely connected with a short distance between the neighboring (2b) positions (~2 Å).

In 80-ties, after revealing the coexistence of ferromagnetism and superconductivity in $\text{Y}_4\text{Co}_3$, the $\text{Ho}_4\text{Co}_3$-type unit cell appeared to be only an approximation for the real structure of the system. There was a debate whether this system should be called $\text{Y}_9\text{Co}_7$ (instead of $\text{Y}_4\text{Co}_3$), since it was found that $\text{Y}_9\text{Co}_7$ (richer in cobalt) exhibited better superconducting properties (~0.5 K higher $T_c$) than $\text{Y}_4\text{Co}_3$. It was even suggested, that $\text{Y}_4\text{Co}_3$ as a single phase compound might not exist. Employing the initial notation, the 9:7 stoichiometry compound corresponds to $\text{Y}_{12}\text{Co}_{8+x}$, but one should bear in mind that for $\text{Y}_9\text{Co}_7$ an ordered model of structure was suggested with the unit cell tripled along the c-axis. In such a superstructure, the Co(3) atoms positions are adapted in such way to make the Y-Co system perfectly ordered for 9:7 composition (100% filling of all sites, see e.g. Refs. 11,15 for details). The resulting crystal structure exhibits reduced symmetry, trigonal instead of hexagonal. However, the ordered model of the superstructure was not confirmed by X-ray measurements on single crystal samples. Moreover, it was also reported that the Co(3) atoms did not occupy the fixed lattice positions, and were rather arranged in chains with undetermined period. Thus, the basic unit cell shown in Fig. 1 can be treated as the best established and simplest approximation of the real structure both for $\text{Y}_4\text{Co}_3$ and $\text{Y}_9\text{Co}_7$, as far as the Co(3) atoms location is concerned. The $\text{Y}_{12}\text{Co}_{8+x}$ model represents the $\text{Y}_4\text{Co}_3$ and $\text{Y}_9\text{Co}_7$ compounds, when the Co(3) concentration reaches the values of $x = 0.50$ and $x = 0.66$, respectively. However, the question on the real unit cell of $\text{Y}_4\text{Co}_3$ and $\text{Y}_9\text{Co}_7$ and whether they describe the same crystal structure with various Co contents, is still open.

In the present work, the basic unit cell, presented in Fig. 1 with $x = 0.50$ was employed to account for the $\text{Y}_4\text{Co}_3$ case. This crystal model has allowed us to use the full potential Korringa-Kohn-Rostoker code adapted to electronic structure calculations of ordered compounds (see, Section 11).

As far as the superconducting properties are concerned, it is generally believed, that superconductivity in $\text{Y}_4\text{Co}_3$ has a singlet-like character and probably mediated by the electron-phonon interactions. The system exhibits all the characteristic features of conventional superconductors (see Refs. 6,17 and references therein), e.g. perfect diamagnetic Meissner state, the specific heat jump at $T_c$ correlated with drop in resistivity and susceptibility. More puzzling seems the type of its magnetism. The system shows e.g. a modified Curie-Weiss behavior, with susceptibility maximum and a hysteresis loop in the magnetization measurements interpreted as fingerprints of a ferromagnetic state. There are different values of magnetization reported in literature. For the 4:3 composition one can find $M = 0.045 \mu_B$/f.u. measured for $\text{Y}_4\text{Co}_{3.03}$ samples and extrapolated to $T = 0$K or $M \sim 0.03 \mu_B$/f.u. $\text{Y}_4\text{Co}_3$ at 1.24 K. Note, that these values are not exact, firstly diamagnetism induced by superconductivity below 2.5 K does not allow to accurately measure bulk magnetization, and secondly it is difficult to measure magnetization in weak ferromagnetic system.

From the NMR measurement it was found that

| Atom (1) site | coordinates | $x/y$ |
|--------------|-------------|-------|
| Y(1) (6h)    | $(x, y, z) = (0, 0, 0)$, $(y, x, z) = (x, 0, 0)$ | 0.7543 0.9791 |
| Y(2) (6h)    | as above | 0.1360 0.5150 |
| Co(1) (6h)   | as above | 0.4415 0.1578 |
| Co(2) (2d)   | $(x, y, z) = (x, 0, 0)$, $(x, y, z) = (x, 0, 0)$ | – – |
| Co(3) (2b)   | $(0, 0, 0)$, $(0, 0, 0)$, $(0, 0, 0)$ | – – |

In our calculations (2b) positions are split into (1a) $(0, 0, 0)$ and (1b) $(0, 0, 0)$, being occupied by Co and vacancy, respectively (see text).
there were three inequivalent Co sites in $Y_4Co_3$, but magnetism was attributed only to the cobalt atoms on (2b) site. The estimated magnetic moment was $\mu_{Co(3)} = 0.23 \mu_B$, and important spin fluctuations were observed. Actually, there are no other experimental papers on determination of the Co(3) magnetic moment, thus our theoretical result is compared to this value. Most of the experimental results concerning magnetism of the Y-Co system were interpreted in the framework of the spin-fluctuation theory of the weak itinerant ferromagnetism showing characteristic features as e.g. the zero-field magnetization $M(T)^2 \propto T^{4/3}$ (Ref. 17) or resistivity $\rho \propto T^2$ (Ref. 17). However, more exotic models without long-range ferromagnetic ordering were also considered, i.e. basing on the $\mu$SR measurements the magnetic state of $Y_9Co_7$ was called ‘crypto-itinerant ferromagnet’, some hybrid magnetic and superconducting state was suggested while short range order was discussed elsewhere.

On the whole, magnetic properties of the Y-Co system near 4:3 or 9:7 stoichiometry were found to be similar and weakly dependent on Y:Co composition (comparing to superconducting behaviors), maybe except for increasing magnetization with increasing Co content. All these data allow to suppose that general conclusions deduced from the first principles calculations for $Y_4Co_3$ should also be maintained for $Y_9Co_7$ (e.g. we may expect similar local magnetic moments). Also, some experimental results available only for $Y_9Co_7$ (e.g. effect of pressure on magnetism), should provide reliable comparison with theoretical results obtained for the quasi-ordered model of $Y_4Co_3$.

To summarize this short review, the commonly accepted phenomenological model of the coexistence of superconductivity and magnetism in $Y_4Co_3$ / $Y_9Co_7$ system is as follows: there is an itinerant weak ferromagnetic state below $T_C$ with the Co(3) sublattice responsible for magnetism, combined with superconductivity below $T_s$, being mostly attributed to the Y-Co triangular prisms inside the unit cell. Both physical phenomena visibly compete (e.g. external pressure suppresses magnetism and enhance superconductivity) but their coexistence is possible due to some spatial ‘separation’ of atom sublattices responsible for different phenomena. However, this separation cannot be treated in the strict sense, since the Ginzburg-Landau coherence length was estimated to be as large as 300 $\AA$ (roughly thirty times larger than the unit cell size). One can tentatively imagine this uncommon state as a ‘superconducting sea’ with the Co(3) ‘magnetic islands’ embedded. The question on the existence of the ‘magnetic islands’ and whether Co(3) moments are ordered in $Y_4Co_3$ has not been yet addressed to first principles calculations. Hence, the KKR results presented here may help to enlighten this problem.

II. COMPUTATIONAL DETAILS

Electronic structure calculations were performed using the full potential Korringa-Kohn-Rostoker (FP-KKR) technique based on the Green function multiple scattering theory. In our implementation of the FP-KKR method, the unit cell is divided into the set of generalized Voronoi polyhedrons arbitrary formed around inequivalent sites, that completely fill the Wigner-Seitz cell. The crystal potential has been constructed in the framework of the local spin density approximation (LSDA), using Perdew-Wang formula for the exchange-correlation part. All results were carefully checked for the k-point number convergence, using more than 100 points in the irreducible part of Brillouin zone for the tetrahedron integration method. The results of FP-KKR semi-relativistic calculations are presented, with the fully relativistic treatment of core electron energy levels.

In this work, the ordered model of the hexagonal cell (Fig. 1) was used in the electronic structure calculations. To take into account the partial filling of the Co(2b) site in $Y_4Co_3$ in KKR method, we employed a ‘quasi-disordered’ structure, i.e. the (2b) position was split into two non-equivalent sites, (1a) and (1b). The (1a), i.e. (0,0,0) position, was occupied by Co atom (Co(3)) and (1b), (0,0, $\frac{1}{2}$) site, by a vacancy (Vac), i.e. an empty sphere with $Z = 0$. This structural modification resulted in the lowering of the hexagonal cell symmetry from space group P63/m (No. 173) to P-3 (No. 147), with reduction of symmetry operations from 12 to 6. As above-mentioned, this model admits to consider the $Y_4Co_3$ composition only. It was verified by additional calculations that the KKR results remain unchanged when the positions of Co(3) and Vac were exchanged (cobalt on (1b) site and empty spheres on (1a) site), as one expects from equivalence of both sites in the proper space group.

![FIG. 2: (Color online) Total and site-decomposed densities of electronic states in $Y_4Co_3$ (per unit cell, i.e. three formula units), from non-spin-polarized calculations.](image-url)
III. RESULTS AND DISCUSSION

A. Non spin-polarized electronic structure

The discussion of electronic structure of Y₄Co₃ is started from analysis of general features in non spin-polarized case. The total and site-decomposed electronic densities of states (DOS) are presented in Fig. 2. Due to the large number of atoms in the unit cell and in consequence various interatomic distances, the DOS has a complex shape. The Fermi level ($E_F$) is located in the DOS valley, which can tentatively support the chemical stability of this system. The valence band region is formed from the strongly hybridized atomic states of Co (3d, 4s) and Y (4d, 5s), with important $s-p$ and $s-d$ charge transfers. The Y-4p states constitute semi-core level, located about -1.5 Ry below the Fermi level (not shown). Generally, the body of the electronic structure is dominated by contributions from the Y(1)-Y(2)-Co(1)-Co(2) block, which form the triangular prisms inside the unit cell (Fig. 1). Nominally, the major contribution to DOS comes from six Co(1) atoms, due to the highest number of valence electrons (54 $e^{-}$) given to the bands. The single Co(3) atom, building the separated cobalt chains, roughly governs the position of the Fermi level due to DOS significantly different from other atoms (a high $d$-like peak below $E_F$), what enables the Co(3) to play important role in ground state properties of Y₄Co₃.

To have a deeper insight into influence of each atom on electronic structure, the site-decomposed DOS are plotted for inequivalent sites (Fig. 3 and Fig. 4). The most striking DOS feature of Y₄Co₃ is that except for Co(3), the Fermi level is systematically placed in the local DOS valleys, resulting in relatively low total DOS. The calculated small DOSs at $E_F$ per atom (see, Table II) would rather not suggest a transition to ferromagnetic state. In contrast to other atoms, Co(3) exhibits apparently different DOS, due to a large $d$-like peak found just below the Fermi level ($E_F$ is placed on the decreasing DOS slope). This feature yields the highest DOS value (per atom) for Co(3) in comparison to other contributions (Table II). Actually, the value $n(E_F)$ $\approx$ 10 Ry⁻¹ is too small to satisfy the Stoner criterion, since the calculated Stoner parameter for Co(3) atom $S$ is too small to satisfy the Stoner criterion, since the calculated Stoner parameter for Co(3) atom

| Atom | $n(E_F)$ | $n_d(E_F)$ | $S$ |
|------|---------|-----------|-----|
| Y(1) | 3.62    | 2.50      | 0.15|
| Y(2) | 4.85    | 3.37      | 0.19|
| Co(1)| 7.71    | 5.79      | 0.43|
| Co(2)| 8.00    | 6.86      | 0.48|
| Co(3)| 10.31   | 8.19      | 0.61|
| Vac  | 1.73    | 0.47      |     |

$N(E_F) = 250$ Ry⁻¹ per unit cell

TABLE II: Electronic properties of Y₄Co₃. Values of DOS $n(E_F)$ are given in (Ry⁻¹/spin), magnetic moments $\mu$ in ($\mu_B$), $S$ stands for the Stoner parameter.

The single Co(3) atom, building the separated cobalt chains, roughly governs the position of the Fermi level due to DOS significantly different from other atoms (a high $d$-like peak below $E_F$), what enables the Co(3) to play important role in ground state properties of Y₄Co₃. However, the presence of large and narrow DOS peak in the vicin-
ity of \( E_F \) causes that the simple Stoner criterion of ferromagnetism onset should be taken with care and accurate spin-polarized calculations may determine the preferred ground state.

### B. Ferromagnetism

Indeed, the spin-polarized calculations do not confirm the non-magnetic state deduced from the Stoner criterion. Figure 5 presents the spin-polarized DOS shape of \( Y_4Co_3 \). At first glance, the differences between the non spin-polarized (Fig. 2) and spin-polarized (Fig. 5) total DOSs are hardly visible, since spin-up and spin-down DOS functions are very similar. However, the spin-polarized KKR calculations finally resulted in stable, ferromagnetic ground state. The partial, site-decomposed DOSs (Fig. 5) show that only the Co(3) atom exhibits polarization in DOS shape, as depicted in Fig. 5 being confirmed by appearance of local magnetic moment (Table I). The Co(3) magnetic moment of about \( \mu_{Co_3} = 0.55 \mu_B \) decides in favor of magnetism in \( Y_4Co_3 \), since the remaining atoms possess small magnetic moments (\( \leq 0.02 \mu_B \)). Such a small DOS polarizations seen on other atoms should be rather considered as a response to magnetic field of Co(3) atom, than an intrinsic local magnetic moments. The total magnetization \( M_{tot} = 0.38 \mu_B/unit\ cell \) yields \( M \simeq 0.13 \mu_B \) per \( Y_4Co_3 \) formula unit. \( M_{tot} \) is lower than \( \mu_{Co_3} \) due to the overall 'diamagnetic' response of the Y-Co triangular prisms, generating about -0.1 \( \mu_B \). The comparison with the experimental values is discussed in Section III D.

The specific character of the \( Y_4Co_3 \) electronic structure can be observed in the electron dispersion curves, shown in the Fig. 6. In the \( \Gamma - M - K - \Gamma \) triangle no band crosses the Fermi level for both spin directions, and this behavior holds for any direction in the \( k_z = 0 \) plane, as was checked by extensive calculations along randomly chosen directions. Similar result was earlier observed from non spin-polarized calculations. The ferromagnetic state leads mainly to the slight shift of dispersion curves and some changes in details. Since, the \( Y_4Co_3 \) system is predicted to possess an energy band gap in the \( k_z = 0 \) plane, it would be interesting to verify it (likely detectable on the ARUPS spectra, but due to lack of single crystals there are no such results available). The vanishing Fermi surface in the \( k_z = 0 \) plane is presumably responsible for the DOS valley formed around \( E_F \) (Fig. 3). In the \( \Gamma - A \) direction (along the \( k_z \) axis), almost linear and strongly dispersive bands cross \( E_F \), while in the \( A - L - H - A \) triangle, which is just a shift of the \( \Gamma - M - K - \Gamma \) triangle to the Brillouin zone top, bands crossing \( E_F \) become flat, which mostly gives rise to metallic-like properties of \( Y_4Co_3 \).

On the whole, the important result from presented spin-polarized KKR calculations, concerns the fact that there is no need to search for unconventional mechanism to explain magnetism in \( Y_4Co_3 \) system. The energetically unfavorable DOS peak just below \( E_F \) (Fig. 1) on the single Co(3) atom, seems to be the reason of turning the system into the ferromagnetic state. In magnetic state, the spin-up peak is not seen near \( E_F \), while in the spin-down DOS the peak is smaller and is expelled above \( E_F \). In Ref. 11, devoted to the electronic structure and magnetism of \( Y_3Co_7 \), authors suggested two models of magnetism of this system, called A and B. Briefly, in the model A magnetism was attributed to the excess Co atoms on Y(1) and Y(2) sites, while in the model B the magnetism came from itinerant electrons of Co on (2b) sites. Authors did not definitely conclude, which model was valid, but the model A was said to be the most probable, and the 'perfect \( Y_3Co_7 \) crystal' was expected to be paramagnetic. From our results we see, that itinerant ferromagnetism is an intrinsic property of \( Y_4Co_3 \) system. Hence, additional defects as the excess Co atoms on Y sites are not necessary to give rise ferromagnetism, even if instead of long range order in real material short range order appears, as suggested e.g. in Ref. 26. Similar behavior is expected to be valid for \( Y_5Co_7 \), since as we mentioned in Introduction, experimentally the magnetic properties of the Y-Co system do not change much between \( Y_4Co_3 \) and \( Y_5Co_7 \).

To look closer on the magnetism of the Co(3) atom we can calculate the spin dependence of \( d \) orbital occupation (actually, the diagonal elements of occupation matrix calculated using imaginary part of Green’s function, defined as \( \langle l_m \mid -\frac{1}{\pi} \text{Im} G[l_m m_n] \rangle \)). The Co(3) (2b) site, being surrounded by Y(1) triangles in \( z = \pm \frac{1}{4} \) planes, has a trigonal, \( C_{3i} \) symmetry. Thus, there are two degenerated \( E_g \) doublets, \( \{d_{xy},d_{xz},d_{yz}\} \) and \( \{d_{yz},d_{xz}\} \) with occupation for both doublets approximately equal to 0.81e\(_{\uparrow}\) and 0.19e\(_{\downarrow}\).
The magnetic structure, a feature which was announced for
Thus, the Co(3) atoms form a quasi-one-dimensional
arrangement of Co(3) atoms in chains, lying in channels
producing magnetic moments on the Co(1) and Co(2) atoms
is the main source of magnetism in this compound. The
directional character of this orbital favors the simple ferromagnetic ordering of magnetic moments along the z-axis.

The fact that the magnetic moments are ‘localized’ only on Co(3) atoms can be well visualized on the spin magnetization contour maps, presented in Figs. 7 and 8. The spin magnetization is calculated as a difference between the spin-up and spin-down electron densities. The magnetic moments resides on the Co(3) corner atoms, while the rest of the presented xz plane has magnetization close to zero (Fig. 8). The shape of magnetization around the Co(3) atom in the xz plane (Fig. 7a) confirms that the 3dz orbital plays the major role in constitution of magnetic state. The xy cross-sections well reflect the local symmetry of the magnetization, which should be trigonal (C3v). Interestingly, in the z = 0 plane we may have an impression of cylindrical symmetry (Fig. 8b), due to the equally distanced Y(1) triangles (z = ±1), each rotated by 60°. But, when we move off the z = 0 plane, the triangle symmetry occurs (Fig. 8c).

Magnetism in Y$_4$Co$_3$ appears to be unusual. There is only one ‘magnetic atom’ in the complex unit cell, and twenty other atoms form diamagnetically polarized background. The reason why other Co atoms are non-magnetic is understood from non spin-polarized partial DOS, where only Co(3) atom exhibits unstable DOS function due to the pronounced peak near $E_F$, while for Co(1) and Co(2) $E_F$ is located in the DOS minimum. Inducing magnetic moments on the Co(1) and Co(2) atoms would make the system energetically unfavorable.

Another peculiarity of this crystal structure is the arrangement of Co(3) atoms in chains, lying in channels formed by the octahedras of Y(1) atoms (see, Fig 11). Thus, the Co(3) atoms form a quasi-one-dimensional magnetic structure, a feature which was announced for this system\textsuperscript{20, 23} but not explored in the past. This low-dimensionality rises the question if the long-range ferromagnetic order can occur here, as the Mermin-Wagner theorem\textsuperscript{36} predicts the lack of long-range magnetic order within a Heisenberg model with short-range interactions in one dimension. This of course does not completely rule out the presence of magnetic ordering for the three dimensional structures with quasi-one-dimensional chains, but the properties of such systems are affected by the low-dimensional character. Recently, the quasi-one-dimensional ferromagnetism was investigated in some cobalt-based systems, like monoatomic Co chains on Pt substrate\textsuperscript{27} or Co oxides, like BaCoO$_3$ or Ca$_3$Co$_2$O$_6$ (see, e.g. Refs. 38–40). It is interesting to underline some structural similarities between Y$_4$Co$_3$ and aforementioned Co oxides. The Co(3) chains surrounded by Y(1) triangles, forming octahedras in z-direction, are similar to CoO$_6$ octahedras in oxides family. In both cases, the chains are running along c axis of the hexagonal cell. The geometrical difference is that in Y$_4$Co$_3$ the intra- and inter-chain Co-Co distances are about twice as large as in the oxides. The large interchain distance in Y$_4$Co$_3$ (11.5 Å) rather excludes the importance of interchain magnetic interaction, which is of great importance in oxides, and leads to two-dimensional antiferromagnetic effects.\textsuperscript{20} This quasi-one-dimensional character of magnetism in Y$_4$Co$_3$ makes this system even more interesting and opens new areas for future investigation.

C. Ferromagnetism vs. superconductivity

The fact that most of the unit cell volume of Y$_4$Co$_3$ has negligible magnetization, allows to draw some qualitative conclusions on the possibility of coexistence of ferromagnetism and superconductivity. For example, in the xz cross-section of the unit cell, presented in the Fig. 8, about 90% of the area has magnetization lower than 10$^{-3}$ $\mu_B/a_B^2$. For the whole unit cell, only 1.3 % of the volume has magnetization higher than 10$^{-3}$ $\mu_B/a_B^2$. Roughly speaking, if the electron density inside the unit cell has negligible polarization, in principle it can not disturb forming singlet Cooper pairs. Certainly, the Cooper
pairing acts in momentum space, so we should generally verify whether there are \((k_\uparrow, -k_\downarrow)\) electrons near the Fermi level. Since the \((k, -k)\) degeneracy is ensured by the centrosymmetry of the unit cell, we should look for the \((k_\uparrow, k_\downarrow)\) states. From the band structure plot e.g. in the \(\Gamma - A\) direction we observe three bands crossing \(E_F\). Two of these bands are almost the same for both spin-directions and they are crossing \(E_F\) in points: \(k_\uparrow = (0, 0, 0.2308)\frac{2\pi}{c}, k_\downarrow = (0, 0, 0.2307)\frac{2\pi}{c}\) and \(k_\uparrow = (0, 0, 0.3422)\frac{2\pi}{c}, k_\downarrow = (0, 0, 0.3410)\frac{2\pi}{c}\). These bands are mostly of the Co(1) and Y(2) character. So, one concludes that in principle there are electrons in the Y-Co trigonal prisms, which can form Cooper pairs and lead to singlet superconductivity. But more quantitative analysis of electron-phonon coupling is required to assess whether the BCS type superconductivity can appear in Y\(_4\)Co\(_3\).

Nevertheless, our results and conclusions may support the model of coexistence of weak ferromagnetism and superconductivity in Y\(_4\)Co\(_3\), with the ferromagnetism carried by chains of Co(3) atoms, screened by superconducting trigonal prisms of Y(1)-Co(1)-Y(2)-Co(2). Interestingly, this picture is qualitatively similar to the vortex lattice in type-II superconductors, since in both cases we have superconducting sample penetrated by the magnetic field lines, forming hexagonal lattice.

**D. Spin fluctuations**

The calculated value of Y\(_4\)Co\(_3\) magnetization \((0.13 \mu_B/(f.u.))\), if compared to the measured \(M = 0.045 \mu_B/(f.u.)\) is about 2.5 times overestimated. Similarly, comparing the calculated Co(3) magnetic moment \(\mu_{Co3} = 0.55 \mu_B\) with the NMR estimation\(^{22}\) \(\mu_{Co3} = 0.23 \mu_B\) we get 2.5 times overestimation. This shows, that Y\(_4\)Co\(_3\) can be a rare example of weak ferromagnetic system, where LDA tends to overestimate the tendency to magnetism, and suggests that it may be near the ferromagnetic quantum critical point.\(^{41}\) The well-known similar examples are: ZrZn\(_2\) Sc\(_3\)In and Ni\(_3\)Al/Ni\(_3\)Ga (see, e.g. Refs. \(^{42}43\)), where due to strong spin fluctuations appearing in real samples, measured magnetic moments are much smaller than LDA (or GGA) values. Thus, our KKR-LDA results strongly support the classification of Y\(_4\)Co\(_3\) as a weak itinerant ferromagnet with spin fluctuation effects, as already suggested, basing on the analysis of experimental results.\(^{47}\) In Y\(_4\)Co\(_3\), overestimation of magnetic moment is a little smaller, comparing to aforementioned cases, since in hexagonal Sc\(_3\)In LDA magnetic moment \(\mu_{Sc} \approx 0.35 \mu_B\) is about 7 times higher than experimental one,\(^{42}\) while the factor about 3 is established in ZrZn\(_2\) (Ref. \(^{42}\)) and Ni\(_3\)Al (Ref. \(^{43}\)). This suggests that the spin fluctuations in Y\(_4\)Co\(_3\) should be comparably weaker. The spin fluctuations strength parameter \(\lambda_\delta\), which can be treated as the analog of the electron-phonon coupling constant \(\lambda_{ph}\), can be extracted from the electronic specific heat coefficient \(\gamma\). The experimental value lies in the range of \(\gamma \approx 3.1 - 3.4 \text{ mJ/(mol at. K}^2\). Using the KKR-LDA value of total DOS at Fermi level (spin-polarized case), \(N(E_F) = 229 \text{ Ry}^{-1}\) we get \(\gamma_{\text{LDA}} = 1.89 \text{ mJ/mol at. K}^2\). Assuming that the band value is renormalized by the electron-phonon as well as the electron-paramagnon interaction (spin
fluctuations), the formula $\gamma = \gamma_{\text{LDA}}(1 + \lambda_{ph} + \lambda_{sf})$, gives $\lambda_{ph} + \lambda_{sf} = 0.6 - 0.8$. This allows to safely put the upper limit $\lambda_{ph} + \lambda_{sf} < 1$. It is possible to have independent estimation of $\lambda_{ph}$ and $\lambda_{sf}$ if one admits that superconductivity is driven by phonons and the McMillan formula\textsuperscript{38} can be applied here. We use the experimental value of $T_s$ and the renormalized McMillan formula to take into account the spin fluctuations\textsuperscript{21} (see, also Ref. 50 and references therein)

$$T_c = \frac{\Theta_D}{1.45} \exp\left\{ -\frac{1.04(1 + \lambda_{\text{eff}})}{\lambda_{\text{eff}} - \mu^* (1 + 0.62\lambda_{\text{eff}})} \right\},$$

with the renormalization:

$$\lambda_{\text{eff}} = \lambda_{ph}/(1 + \lambda_{sf})$$

$$\mu^* = (\mu^* + \lambda_{sf})/(1 + \lambda_{sf}).$$

The experimental Debye temperature is $\Theta_D \approx 215$ K\textsuperscript{66}. Noteworthy, the strong renormalization of Coulomb pseudopotential parameter $\mu^*$ restricts the possible range of $\lambda_{sf}$, e.g. we can get $T_c \approx 2.5$ K for $\lambda_{sf} = 0.1$, $\lambda_{ph} = 0.7$ and $\mu^* = 0.08$ (yielding $\mu_{\text{eff}} = 0.164$ and $\lambda_{ph} + \lambda_{sf} = 0.8$) or for $\lambda_{sf} = 0.15$, $\lambda_{ph} = 0.85$ ($\mu_{\text{eff}}^* = 0.20$ and $\lambda_{ph} + \lambda_{sf} = 1.0$). Thus, we can estimate the electron-paramagnon interaction parameter to be of the order of $\lambda_{sf} \sim 0.1$, but rather not higher than 0.2. This qualitative discussion shows that the spin fluctuations are likely present in $Y_4Co_3$, but they are not as strong as e.g. in Sc$_3$In, where $\lambda_{sf} > 1$ can be deduced from the specific heat measurements in the magnetic field\textsuperscript{21,22}. Noteworthy, similar measurements, i.e. the influence of high magnetic field on the electronic specific heat, would be very helpful to study the presence and strength of spin fluctuations in $Y_4Co_3$.

E. Effect of pressure

The effect of pressure on the magnetic properties of $Y_4Co_3$ was also analyzed. We have performed calculations under 'quasi-hydrostatic' conditions. The $a$ and $c$ parameters were equally contracted in the range 0%-2% and all self-consistent calculations were started from the beginning. The bulk modulus, estimated under these conditions, is about $B = 75 \pm 5$ GPa, which is higher than the bulk modulus of yttrium ($\sim 40$ GPa\textsuperscript{25}) and much smaller than the corresponding value for cobalt ($\sim 200$ GPa\textsuperscript{26}). In calculations for the smaller unit cell volume, the magnetism is suppressed and the magnetic moment decreases rapidly, with the slope $\partial \mu / \partial p \approx 0.08 \mu_B/\text{GPa}$, as seen in Fig. 9. The reason for such behavior can be apparently seen from the evolution of the partial Co(3) DOS under pressure (Fig. 10). When the unit cell volume decrease, the spin-up DOS peak under $E_F$ tends to constitute, while the spin-down peak, expelled above $E_F$ in magnetic state, tends to move below $E_F$. Thus, the pressure lowers the DOS polarization and the magnetic moment, which additionally confirms that the Co(3)-DOS peak is responsible for appearance of magnetic moment on cobalt atoms on (2b) sites.

The suppression of magnetism under pressure from KKR calculations remains in agreement with the experimental trends observed in $Y_3Co_7$ (e.g. lowering of Curie temperature and magnetization\textsuperscript{19,28} for $Y_4Co_3$ there are no such results available in the literature). Extrapolation of the curve from Fig. 9 to zero magnetic moment gives the critical pressure, where magnetism completely disappears, as $p_c \approx 7$ GPa. This value can be compared with very recent measurements of $Y_3Co_7$ under pressure\textsuperscript{25} where the critical pressure was estimated to be $p_c \approx 3$ GPa. The overestimation of the critical pressure is in line with the spin fluctuations and weak ferromagnetism in this system, as revealed from our calculations. Interestingly, if the zero-pressure value of the magnetic moment the NMR experimental estimation $\mu(Co_3) \sim 0.23 \mu_B$ is accounted for, the theoretical slope $\partial \mu / \partial p \approx 0.08 \mu_B/\text{GPa}$ also predicts decrease of $\mu$ to zero for $p \approx 3$ GPa.

IV. SUMMARY AND CONCLUSIONS

The results of the FP-KKR electronic structure calculations for $Y_4Co_3$ system were presented. The ferromagnetic state obtained from spin-polarized calculations can be attributed to the single Co atom located on the (2b) site, being the only magnetic atom among 21 ones in the unit cell, and forming the quasi-one-dimensional magnetic chains. The LDA values of the magnetization ($M \approx 0.13 \mu_B/\text{f.u.}$), $Co(3)$ magnetic moment ($\mu \approx 0.55 \mu_B$) and critical pressure ($p_c \approx 7$ GPa) are overestimated comparing with experiments, which can be tentatively explained in terms of weak ferromagnetism with moderate spin fluctuations ($\lambda_{sf} \sim 0.1$). The calculated spin magnetization distribution as well as other band structure parameters, tend to the conclusion that the conventional, singlet-like superconductivity may coexist with ferromagnetism in $Y_4Co_3$, due to relatively weak magnetic moments arranged along thin chains (the
unit cell edges) on the one hand, and the presence of non-polarized electrons at the Fermi level (filling most of the unit cell) on the other hand. On the whole, the FP-KKR results confirmed that the quasi-one-dimensional magnetism is an intrinsic property of Y$_3$Co$_3$ and its coexistence with singlet superconductivity may be possible.

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55 Magnetization measured for $Y_9Co_7$ sample and extrapolated to $T = 0$ K was $M \approx 0.383$ emu/g, which referred to the 4:3 composition gives about $M = 0.10 \mu_B/(f.u. Y_4Co_3$, and is higher than in $Y_4Co_3$ likely due to higher Co(3) atoms concentration.\textsuperscript{55}