

YBa_{1-x}Sr_xCuFeO₅ layered perovskites: An attempt to explore the magnetic order beyond the paramagnetic-collinear-spiral triple point

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Layered perovskites of general formula AA'CuFeO₅ are characterized by the presence of spiral magnetic phases whose ordering temperatures T_{spiral} can be tuned far beyond room temperature by introducing modest amounts of Cu/Fe chemical disorder in the crystal structure. This rare property makes these materials prominent candidates to host multiferroicity and magnetoelectric coupling at temperatures suitable for applications. Moreover, it has been proposed that the highest T_{spiral} value that can be reached in this structural family (~ 400 K) corresponds to a paramagnetic-collinear-spiral triple point with potential to show exotic physics. Since generating high amounts of Cu/Fe disorder is experimentally difficult, the phase diagram region beyond the triple point has been barely explored. To fill this gap we investigate here eleven YBa_{1-x}Sr_xCuFeO₅ solid solutions ($0 \leq x \leq 1$), where we replace Ba with Sr with the aim of enhancing the impact of the experimentally available Cu/Fe disorder. Using a combination of bulk magnetization measurements, synchrotron x-ray and neutron powder diffraction we show that the spiral state with $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$ is destabilized beyond a critical Sr content, being replaced by a fully antiferromagnetic state with ordering temperature $T_{\text{coll2}} \geq T_{\text{spiral}}$ and propagation vector $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$. Interestingly, both T_{spiral} and T_{coll2} increase with x with comparable rates. This suggests a common, disorder-driven origin for both magnetic phases, consistent with theoretical predictions.

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I. INTRODUCTION

Magnetoelectric multiferroics, materials with coupled magnetic and ferroelectric orders [1–3], have attracted significant attention during the last years owing to their potential for applications in spintronics and low-power data storage technologies [4]. Among them, frustrated magnets with ordered magnetic spiral phases that spontaneously break inversion symmetry [5–7] have received particular attention due to their capability to induce ferroelectricity [8–11]. In these materials, the common origin of both orders guarantees a substantial coupling between them, which is highly desirable for applications. However, spiral magnetic orders are often the signature of competing magnetic interactions, and in this case, their

ordering temperatures T_{spiral} are limited by the energy scale of the weakest magnetic coupling. With very few exceptions [12,13], this results in low T_{spiral} values (typically < 100 K), greatly restricting their fields of application. Recently, investigations on Cu/Fe-based layered perovskites uncovered an unexpected knob to control the stability range of a magnetic spiral: chemical disorder. The positive impact of this variable in the spiral ordering temperature was first demonstrated for YBaCuFeO₅ [14], a simple tetragonal material whose crystal structure is shown in Fig. 1 [15,16]. This layered perovskite contains two pseudocubic ABO₃ units due to the ordering of the A-cations Y³⁺ and Ba²⁺ along the *c* crystal axis. This results in a tetragonal unit cell $a_c \times a_c \times c$ ($c \simeq 2a_c$), where a_c denotes the pseudocubic perovskite lattice parameter. Cu²⁺ and Fe³⁺ occupy the B positions, which form layers of apex-linked bipyramids due to the existence of 1/6 of oxygen vacancies in the Y layers. Contrarily to the A cations, Cu²⁺ and Fe³⁺ present important amounts of preparation-dependent disorder [14,16–24]. This is evidenced by the variable Cu/Fe occupations n_{Cu} and n_{Fe} of the square-pyramidal sites reported in diffraction studies, which represent respectively the probabilities of having a given pyramid occupied by Cu²⁺ and Fe³⁺ ($n_{\text{Cu}} = n_{\text{Fe}} = 50\%$ in the case of maximal intermixing). This chemical disorder is illustrated in Fig. 1 by the splitting

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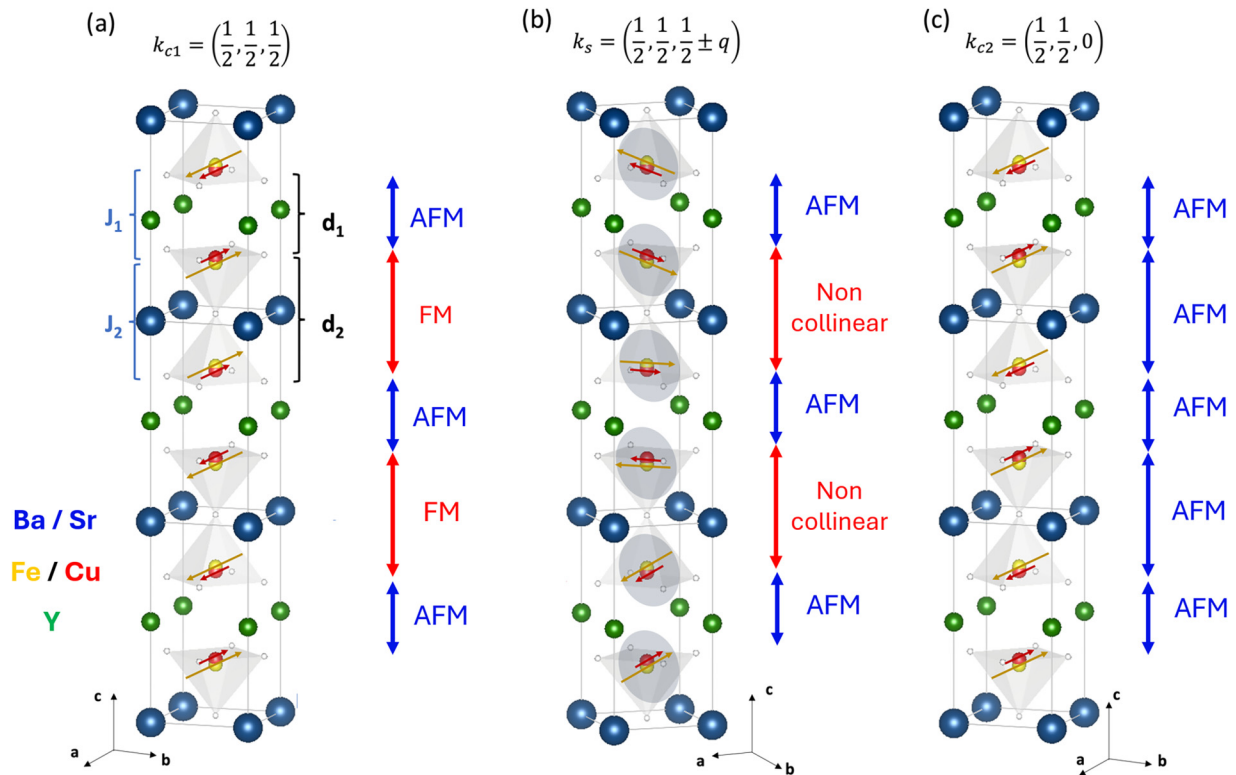


FIG. 1. The three magnetic structures observed in the $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ series. (a) Collinear with $\mathbf{k}_{c1} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. (b) Inclined circular spiral with $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$. (c) Collinear structure with propagation vector $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$. Oxygen atoms are depicted as little white spheres, and grey lines delimit the crystallographic unit cell. Red and yellow arrows denote Cu^{2+} and Fe^{3+} magnetic moments, respectively. The interatomic distances d_1 , d_2 and magnetic couplings J_1 , J_2 mentioned in the text are also indicated. For clarity, only a quarter of the magnetic unit cells is shown. As indicated by the k_x and k_y components of the propagation vectors, the magnetic moments are aligned antiferromagnetically along the **a** and **b** crystal axes in the three magnetic structures.

of the B-cation position in the pyramids, where the slightly different Cu and Fe z coordinates also reflect the different electronic configurations of Fe^{3+} ($t_{2g}^3 e_g^2$) and Cu^{2+} ($t_{2g}^6 e_g^3$). Fe^{3+} , with one electron per $3d$ orbital, prefers to reside at the center of the pyramids and establish five similar Fe-O interatomic distances. In contrast, the Jahn-Teller ion Cu^{2+} shows a strong tendency to form shorter in-plane and longer apical Cu-O bonds that relieve the double orbital degeneracy of the single e_g hole [19,25–27].

YBaCuFeO_5 displays long-range antiferromagnetic (AFM) order up to elevated temperatures, and undergoes two phase transitions [19]. At high temperature, the magnetic structure is collinear (henceforth “coll,” Fig. 1(a) [19]), but it transforms into an inclined spiral at lower temperatures (Fig. 1(b) [16,28]). Remarkably, the setup of the spiral phase can be increased from ~ 150 to ~ 400 K upon a modest enhancement in the degree of Cu/Fe intermixing [14,17]. Since this parameter has the opposite impact on the collinear ordering temperature, the two transitions eventually meet by continuously increasing the degree of Cu/Fe intermixing. According to previous studies this happens at $T_{\text{coll}} = T_{\text{spiral}} \sim 400$ K [17,18], giving rise to a paramagnetic-collinear-spiral triple point. These studies also suggest that the spiral is destabilized by further increasing the degree of Cu/Fe disorder, in which case the triple point would define the highest T_{spiral} value that can be achieved in

YBaCuFeO_5 [17,18]. Giving the scarcity of materials with magnetic spirals stable far beyond room temperature (RT), clarifying this issue is highly desirable. However, generating the disorder amounts needed to access the region beyond the triple point has been technically challenging and so far unsuccessful.

Here, we investigate this region using an alternative route aimed to enhance the impact of the maximal disorder accessible to our experimental setup. As shown in our previous study [18], the degree of magnetic frustration—and hence T_{spiral} —can be also enhanced by increasing the magnetic coupling J_2 between the B cations occupying the bipyramidal units of the crystal structure [Fig. 1(a)], an effect that adds up to that of disorder. To reach this goal we partially replace Ba^{2+} with Sr^{2+} , an isovalent cation with smaller ionic radius that reduces the size d_2 of the bipyramids [Fig. 1(a)], effectively increasing J_2 . Using an improved synthetic route aimed to create samples with similar Fe/Cu disorder and increasingly growing J_2 values we successfully prepared the full $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ solid solution ($0 \leq x \leq 1$), extending the range of our previous study ($0 \leq x \leq 0.5$) [18] and earlier publications [29–31]. We use here a combination of bulk SQUID magnetometry, neutron and synchrotron x-ray powder diffraction, that we employ to investigate the evolution of the crystal structures and the stability of the different magnetic phases. Our analysis, summarized in the schematic phase diagram of Fig. 2, confirms the existence of the triple point reported in previous

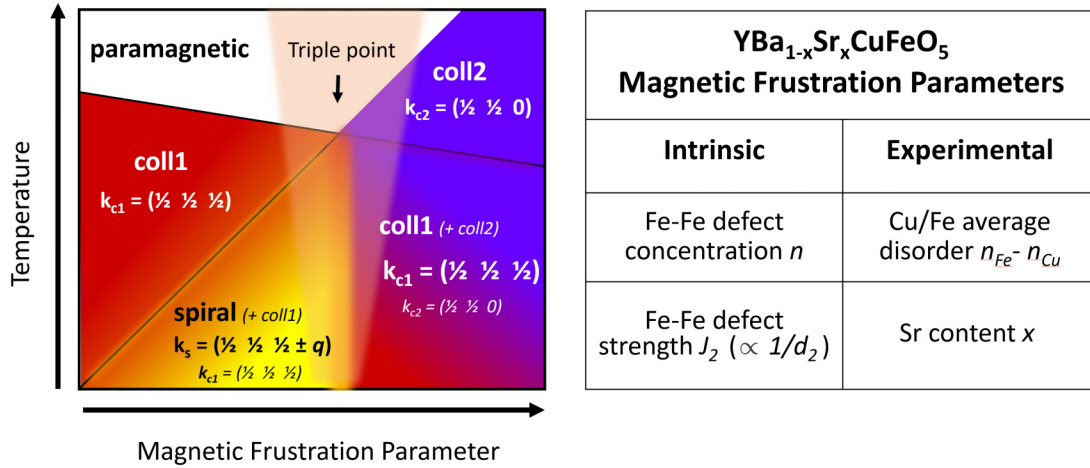


FIG. 2. Schematic phase diagram of YBa_{1-x}Sr_xCuFeO₅ layered perovskites, as inferred from the present study. The size of the magnetic propagation vector characters in the phase coexistence regions identifies the majority (large) and minority (small) magnetic phases. The approximate region affected by short-range magnetic correlations is indicated by a blurred-contour orange triangle around the triple point.

studies [17,18], which in our samples is reached for $x \sim 0.8$. It also reveals a progressive loss of the long-range character of the spiral by approaching this composition (blurred-contour region in Fig. 2), and confirms its full disappearance for higher x values. Interestingly, the spiral is replaced by a new, distinct collinear AFM phase [henceforth “coll2,” Fig. 1(c)], whose ordering temperature T_{coll2} increases with x at a rate $\partial T_{\text{coll2}}/\partial x$ comparable to that of T_{spiral} in the $x < 0.8$ region. These observations suggest a common origin for the spiral and coll2 phases, that we discuss within the framework of the random exchanges model recently proposed by Scaramucci and coworkers [32,33].

II. EXPERIMENTAL METHODS

A. Material synthesis

The eleven YBa_{1-x}Sr_xCuFeO₅ polycrystalline samples used in this study ($0 \leq x \leq 1$ in steps of 0.1) were prepared by solid state reaction. Some of these compositions have been already synthesized in the past [18,29–31], but the conditions employed in previous studies did not allow to stabilize materials with high Sr contents ($x \geq 0.5$) as a single phase. Here we follow an improved, two-step methodology where the synthesis is preceded by a thermal stability investigation of each individual composition using simultaneous thermal analysis (STA) by means of thermogravimetry and differential thermal analysis (TGA-DTA). This technique allows to explore the impact of the heating rate and annealing atmosphere in the solid state synthesis process. Moreover, when combined with powder x-ray diffraction, it enables a fast, precise determination of the minimal temperature needed for a material’s formation, as well as its thermal stability range upon heating.

As precursors we employed high-purity Y₂O₃ (99.99%, (REO)-STREM CHEMICALS, previously pre-annealed at 950°C for 10h), BaCO₃ (Puratronic, 99.997%, Metal basis, Alfa Aesar), SrCO₃ (Puratronic, 99.994%, Metal basis, Alfa Aesar), CuO₂ (Puratronic, 99.995%, Metal basis, Alfa Aesar), and Fe₂O₃ (Puratronic, 99.998%, Metal basis, Alfa Aesar). For each compound, about 10 g of precursors were weighted and mixed in stoichiometric amounts. Small portions of the

precursor mixtures ($\simeq 200$ mg) were loaded in alumina holders and subject to thermal analysis (TA) measurements on a NET-ZSCH 449C Simultaneous Thermal Analyzer (STA). Mass loss and DTA curves were subsequently measured between room temperature (RT) and 1400°C in artificial air gas flow using a heating rate of 2.5°C/min. Additional curves were obtained stopping the measurements at intermediate temperatures in order to investigate the nature of the different stable crystalline phases. The phase composition of the obtained products was assessed from the analysis of the x-ray powder diffraction (XRPD) patterns measured using a Bruker D8 Advance powder diffractometer (Cu K α).

Figure 3(a) shows three representative TG curves corresponding to the starting, middle and end members of the family YBaCuFeO₅ ($x = 0$), YBa_{0.5}Sr_{0.5}CuFeO₅ ($x = 0.5$), and YSrCuFeO₅ ($x = 1$). The curves reveal a continuous mass loss upon heating followed by one or multiple plateaus, whose fine structure is shown in more detail in Fig. 3(b) together with the curves of the remaining samples. For the Sr-free material YBaCuFeO₅, we observe a single, broad plateau starting at $T_{\text{start}} \simeq 920^\circ\text{C}$ and ending at $T_{\text{end}} \simeq 1200^\circ\text{C}$ that we define here as the temperatures where an inflection point is found in the derivative of the TG curves. According to XRPD, T_{start} and T_{end} correspond to the phase formation and melting temperatures. They delimit thus the stability region of the YBaCuFeO₅ layered perovskite structure [Fig. 3(c)]. Upon replacement of barium with strontium, steps of increasing height appear in the original plateau, suggesting the formation of other stable phases. This was confirmed by XRPD, which revealed a strong decrease of the layered perovskite stability region by increasing the Sr content [from $\simeq 280^\circ$ to $\simeq 60^\circ$, see Fig. 3(c)].

According to previous studies [14,16–22], the degree of Cu/Fe disorder in the structure is controlled by two main variables: the annealing temperature, and the cooling rate of the last annealing. To obtain large amounts of disorder (and hence T_{spiral} values), these two variables should thus be as high as possible. In the case of the YBa_{1-x}Sr_xCuFeO₅ solid solutions, where we were aiming to introduce similar Cu/Fe disorder amounts, the reduced stability range of the Sr-rich

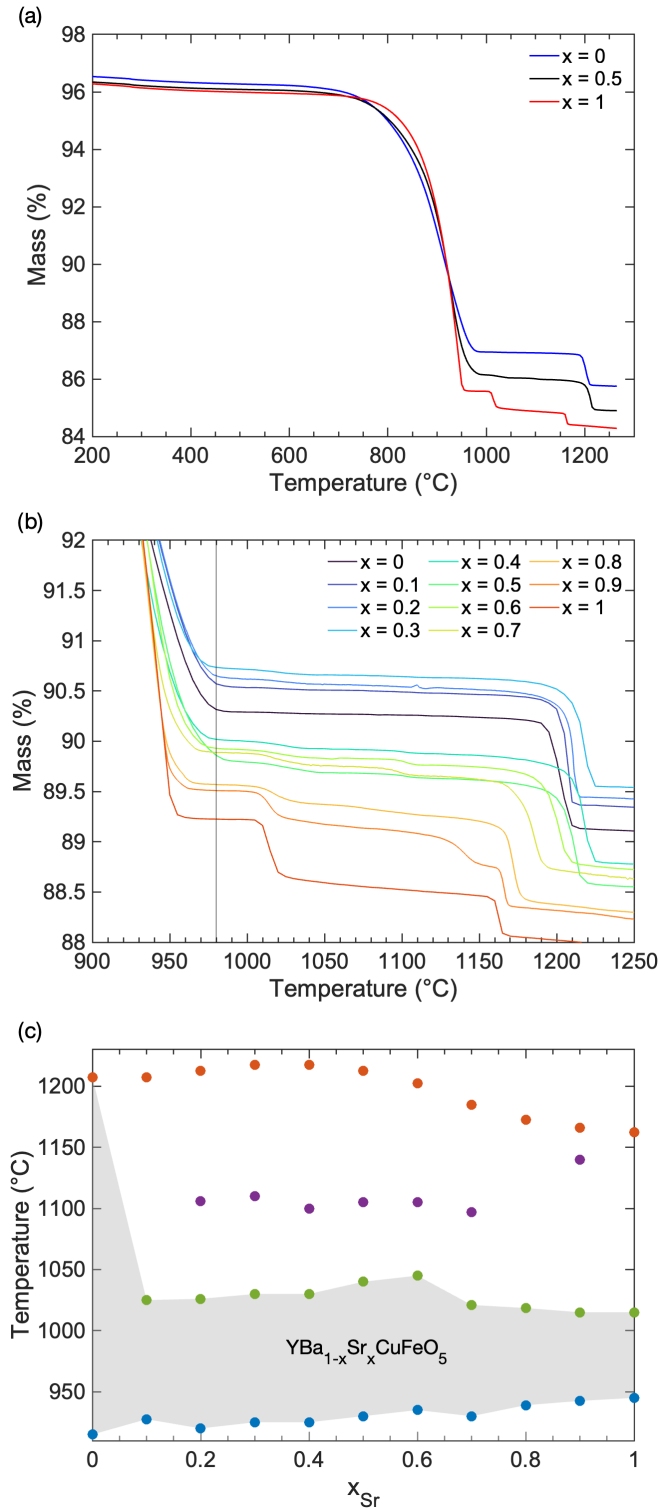


FIG. 3. (a) TG curves of the $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ samples with $x = 0, 0.5$, and 1 . (b) Detail of the plateau region for the eleven compositions investigated in this study. The black vertical line is a guide for the eye, highlighting the chosen synthesis temperature. (c) Evolution of the layered perovskite stability region for increasing Sr content. The blue and orange markers indicate respectively the beginning of the phase formation and the phase melting. Green and purple markers indicate the formation of other, competing crystalline phases. All points correspond to inflection points in the TG curves.

compounds limits considerably the choice of the annealing temperature. After some preliminary tests we chose an annealing temperature of 980°C [vertical line in Fig. 3(b)]. This value was substantially lower than that employed in our previous study (1150°C , [18]), but was a good compromise allowing to minimize the amount of impurities while still creating a fair degree of Cu/Fe disorder.

For the elaboration of the final materials, the weighted and mixed precursors were pressed into pellets, sintered in air at 980°C for 48 h, and cooled down in the oven to RT. The mixing, pelletizing and sintering process was repeated seven times, with XRPD patterns recorded after every cycle in order to keep track of the samples purity through the cyclic process. After the last annealing all samples were quenched into liquid nitrogen in order to maximize their Cu/Fe disorder. Small (50–60 mg) pieces of the final pellets were kept solid for their use in magnetization measurements, and the rest were pulverized for neutron and synchrotron x-ray powder diffraction experiments. XRPD analysis indicated that all the obtained materials were very well crystallized, and most of them ($0 < x \leq 0.9$) contained only minor amounts of $\text{Y}_2\text{Cu}_2\text{O}_5$ (see Ref. [34] Table I and Figs. 1–11). In the case of the end member of the series ($x = 1$), where the impurity content is more important, we observe also the signature of $\text{Y}_2\text{SrCuFeO}_{6.5}$ and CuO .

B. Magnetometry

The presence of magnetic order in the $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ samples was first assessed using a superconducting quantum interference magnetometer equipped with oven (MPMS XL, Quantum Design). DC magnetization (M) measurements as a function of temperature were carried out under an external magnetic field $H = 0.5$ T by heating after cooling the samples in zero field. For the low temperature range ($10\text{ K} \leq T \leq 400\text{ K}$), the samples were mounted in transparent drinking straws, whose contribution to the total magnetization was negligible. For measurements at higher temperatures ($300\text{ K} \leq T \leq 500\text{ K}$) they were wrapped in Al foil and mounted as described in Ref. [35]. The contribution of the Al and the oven insert was measured separately in the same conditions and subtracted from the data. The magnetic susceptibility $\chi = M/H$ was subsequently calculated for all samples.

C. Neutron and synchrotron x-ray diffraction

The nature and thermal stability of the different magnetically ordered phases was further investigated using neutron powder diffraction (NPD). All measurements were performed on the high-intensity powder diffractometer D1B located at the Institut Laue-Langevin, Grenoble (France), [36] equipped with a multidetector with $2\theta_{\text{max}} = 128^\circ$ and $2\theta_{\text{step}} = 0.1^\circ$. The powdered samples were introduced in vanadium cans ($D = 0.6\text{ cm}$, $H = 5\text{ cm}$), mounted in a cryofurnace, and cooled down to 2 K . NPD patterns were then recorded up to about 500 K by heating at a constant rate of 1.5 K/min using a wavelength $\lambda = 2.52\text{ \AA}$ [pyrolytic graphite, PG (002)]. The acquisition time of a single pattern was typically 3 minutes, and the background from the cryofurnace was minimized using an oscillating radial collimator. Patterns with

higher statistics were measured at 2 and 300 K, and employed for detailed magnetic structure refinements. Additional high statistics patterns were recorded at the same temperatures using a shorter wavelength [Ge (311), $\lambda = 1.28$ Å]. The wavelengths and zero offsets were determined using a Na₂Ca₃Al₂F₁₄ (NAC) reference powder sample.

The evolution on the crystal structure was further investigated using synchrotron x-ray powder diffraction (SXPD). The measurements were conducted at the Swiss Light Source (SLS) of the Paul Scherrer Institute in Villigen, Switzerland [37]. Room temperature diffraction patterns of all samples were measured on the Materials Science beamline ($\lambda = 0.496$ Å, $2\theta_{\max} = 75^\circ$, $2\theta_{\text{step}} = 0.0036^\circ$). The powder samples were finely ground, loaded in borosilicate glass capillaries ($D = 0.1$ mm, $0.32 \leq \mu R \leq 0.37$) and measured in transmission mode with a rotation speed of ~ 2 Hz using a Mythen II 1D multistrip detector (Dectris). The primary beam was vertically focused and slitted to about 300×4000 μm^2 . The wavelength and zero offset were determined using a LaB₆ reference powder sample (NIST SRM 660a).

All powder diffraction data (neutron and synchrotron x-ray) were analyzed using the Rietveld method, as implemented in the FULLPROF suite package [38]. The pictures of the crystal and magnetic structures were done using the VESTA software [39].

III. STATE-OF-THE-ART MAGNETIC FRUSTRATION MECHANISM

In insulating oxides that are not geometrically frustrated—such as YBaCuFeO₅—spiral magnetic order usually arises from the competition between nearest-neighbor J and next-nearest-neighbor superexchange interactions J' [40,41]. Since the onset of the spiral order is controlled by the energy scale of the weakest magnetic couplings J' (typically much smaller than J in insulators), this leads naturally to low T_{spiral} values. In this context both, the existence of spiral magnetic order in YBaCuFeO₅ at temperatures far beyond 300 K and the positive impact of the Cu/Fe disorder in the spiral stability are unexpected observations, and suggest that a different, nonconventional mechanism should be at the origin of the magnetic frustration in this material.

A rationalization of these observations was recently proposed in two theoretical papers by Scaramucci and co workers [32,33]. Using density functional theory (DFT) calculations these authors first demonstrated the strong preference of the bipyramidal units for hosting Cu-Fe pairs, which to be consistent with the reported variability of the Cu and Fe occupations, should be disordered in the structure [16]. They also employed this technique to calculate the nearest-neighbor (NN) magnetic exchanges in the **ab** plane (J_{ab}) and along the **c** crystal axis (J_1, J_2) for different Cu/Fe distributions [Fig. 1(a)]. The calculations revealed that the only ferromagnetic (FM) NN exchange is J_2 , the Cu-Fe coupling within the bipyramids, whereas J_1 and J_{ab} are AFM independently of the Cu/Fe distribution. Another important result was that the in-plane couplings are much stronger than those along **c** in absolute value, signaling this crystal axis as the weakest direction in terms of magnetic exchanges. The magnetic structure expected from the calculated NN exchanges, shown in Fig. 1(a),

is described by the propagation vector $\mathbf{k}_{c1} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and is indeed experimentally observed, but only at high temperatures ($T_{\text{spiral}} < T < T_{\text{coll1}}$) [14,16,17,19,42–44].

For temperatures $T < T_{\text{spiral}}$, the propagation vector changes to $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$ and the high temperature collinear magnetic order transforms into an inclined circular spiral incommensurate with the crystal lattice along the **c** crystal axis (Fig. 1(b), Refs. [14,16–18,44]). In a first attempt to rationalize, these observations Scaramucci and co workers first considered the impact of next-nearest-neighbor J_{NNN} magnetic couplings along this direction as possible source of magnetic frustration. However, the values calculated using DFT were either too small or had the wrong sign to stabilize a spiral [16].

As alternative, these authors investigated the impact of introducing a few, randomly distributed Fe-Fe ‘defects’ in the bipyramids normally occupied by Cu-Fe pairs, accompanied by the same amount of Cu-Cu defects to keep the electric neutrality [Fig. 4(b)]. According to their DFT calculations, such defects are energetically very expensive. However, the presence of small amounts cannot be disregarded in real samples, in particular in those with large amounts of Cu/Fe disorder. Since the $J_{\text{Cu-Cu}}$ exchange is extremely weak (< 0.2 meV), introducing a few Cu-Cu defects does not perturb appreciably the underlying collinear order. In contrast, the $J_{\text{Fe-Fe}}$ coupling between the two Fe³⁺ moments in a Fe-Fe defect is AFM ($\simeq -100$ meV) and much stronger than the weakly FM $J_{\text{Cu-Fe}}$ coupling ($\simeq +2.7$ meV). A tiny amount of dilute, randomly distributed defects (2% to 6% of the bipyramids occupied by Fe-Fe pairs) constitutes thus a strong perturbation of the collinear order in the vicinity of these defects. As shown in Refs. [32,33], such a perturbation does not turn the collinear order into a spin glass. Instead, it stabilizes a spiral where the collinearity is lost exclusively within the bipyramidal units, and where both, T_{spiral} and the parameter q related with the spiral periodicity are proportional to the Fe-Fe defect concentration. This mechanism is schematically shown in [Fig. 4(b)].

Scaramucci and coworkers do not address in detail what will happen when the number of Fe-Fe defects becomes too important, and/or when their strength is enhanced beyond a certain limit. However, previous experimental works [17,18] point towards an abrupt suppression of the spiral order, a possibility also considered as likely within the framework of the random magnetic exchanges model [33]. The spiral suppression would thus happen when the weak FM Cu-Fe bonds will no longer be able to compete with the strong AFM Fe-Fe defects, leading to the suppression of the magnetic frustration. The resulting magnetic structure coll2, shown in Fig. 1(c), is described by the magnetic propagation vector $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$, and at variance with the high temperature coll1 phase, has only AFM nearest-neighbor couplings [Fig. 4(c)].

To date, most of the predictions of the random exchange model show an excellent agreement with the available experimental data. This provides strong support to one of its main premises—the appearance of small but growing amounts of Fe-Fe defects by increasing the degree of average Cu/Fe disorder, very difficult to probe experimentally. Moreover, it rationalizes the positive correlation between T_{spiral} and the

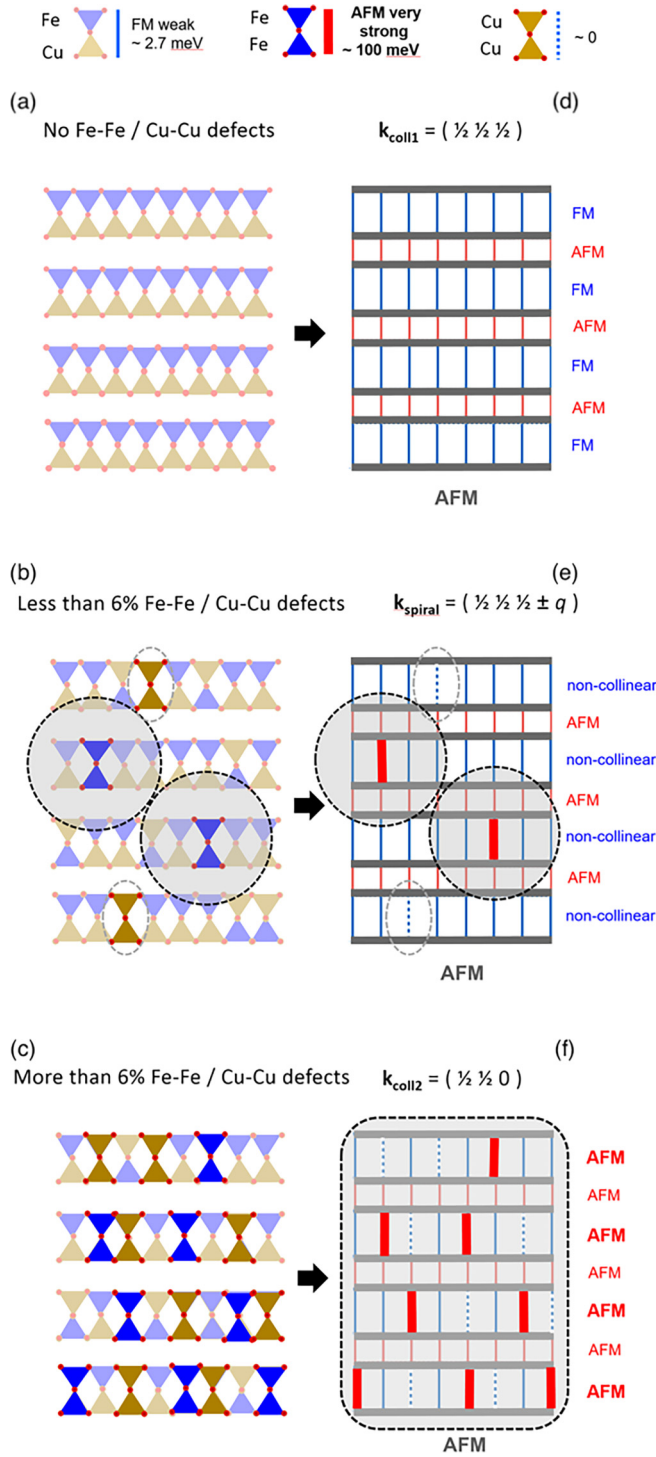


FIG. 4. Schematic representation of the random exchanges frustration model illustrating the impact of increasing amounts of Cu/Fe disorder on the YBaCuFeO₅ magnetic order. (a) Perfect Cu/Fe order. (b) Medium Cu/Fe disorder with a small amount of Fe-Fe and Cu-Cu defects. (c) Sizable Cu/Fe disorder with a large amount of Fe-Fe and Cu-Cu defects. [(d)–(f)] Representation of (a)–(c) in terms of magnetic bonds together with the resulting $\mathbf{k}$ vectors. Thinner bonds represent weak AFM or FM couplings, while thicker bonds indicate strong AFM couplings. Grey shaded areas indicate the regions where the Cu-Fe spins lose their FM alignment. In (b) and (e), the cross-talking of these regions gives rise to a spiral. In (c) and (f), the large number of strongly AFM Fe-Fe defects suppresses the

d_1/d_2 ratio observed experimentally [14,17,18], where d_2 is the bipyramid size and d_1 is the separation between the bipyramid slabs [Fig. 1(a)]. As mentioned in the introduction, creating large amounts of Fe-Fe defects is experimentally challenging. This rule provides thus the possibility of exploiting the inverse correlation between exchange constants and interatomic distances for enhancing the impact of a $J_{\text{Fe-Fe}}$ defect (and hence T_{spiral}) by increasing the d_1/d_2 ratio.

IV. EVOLUTION OF THE CRYSTAL STRUCTURE

Two space groups (SG) have been employed in the past to describe the crystal structure: $P4/mmm$ and $P4mm$, both with one unit formula per unit cell ($Z = 1$) [19,45]. $P4/mmm$ is centrosymmetric, has a mirror plane $\perp \mathbf{c}$ that contains the Y^{3+} cations, and its use implies that Cu and Fe are equally distributed within the pyramids ($n_{\text{Cu}} = n_{\text{Fe}} = 50\%$). In noncentrosymmetric $P4mm$, the mirror plane is lost and the Cu/Fe occupations can be refined, allowing to accommodate asymmetric Cu/Fe distributions ($n_{\text{Cu}} \neq n_{\text{Fe}}$). Although it was a long-standing polemic in the past around the actual SG [15,19,45], the most recent studies indicate that the Cu/Fe distribution is in general asymmetric, signaling $P4mm$ as the best suited SG for describing the crystal structure [14,16–18,20–22]. Note that the $P4/mmm$ constraints can also be reproduced with $P4mm$ as a particular case. Disentangling both scenarios requires nevertheless high resolution powder diffraction data, either neutron or synchrotron x-ray, the Cu/Fe contrast being quite similar for both types of radiation.

Here, we employed $P4mm$ and synchrotron XRPD data recorded at RT to access the Cu/Fe distributions of our eleven $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ samples. The Cu/Fe disorder was described by splitting the atomic position $(1/2, 1/2, z)$ inside the two pyramids of the unit cell (Fig. 1). The obtained results, that will be presented in the next sections, confirm the presence of asymmetric Cu/Fe distributions in nearly all samples ($n_{\text{Cu}} \neq n_{\text{Fe}}$). They also reveal important degrees of Cu/Fe intermixing, far from a full Cu/Fe order scenario with $n_{\text{Cu}} = 100\%$ and $n_{\text{Fe}} = 0$ (or $n_{\text{Cu}} = 0$ and $n_{\text{Fe}} = 100\%$). It is worth mentioning that the Rietveld fits are not sensitive to occupational correlations. The Cu/Fe disorder of our samples is thus assumed to be random, and the refined n_{Cu} and n_{Fe} values represent average values over the full sample volume.

Isotropic Debye-Waller factors were used for all atomic positions, a choice motivated by the presence of one A-site (Ba/Sr at 1a) and two B-sites (Cu/Fe, both at 2h) with chemical disorder. The z positions of the basal oxygen sites O2 and O2' were fitted separately, but their mean-square displacements (MSD) were restricted to be identical. For Cu^{2+} and Fe^{3+} , the MSD's were also constrained to have the same value. In contrast, the z coordinates of the positions that these cations can occupy in the two pyramids of the unit cell were constrained as $z(\text{Cu}1) + z(\text{Cu}2) = 1$ and $z'(\text{Fe}1) + z'(\text{Fe}2) = 1$, respectively. Plots of the Rietveld fits together

← magnetic frustration and the magnetic order becomes purely AFM. The J values are from Ref. [32].

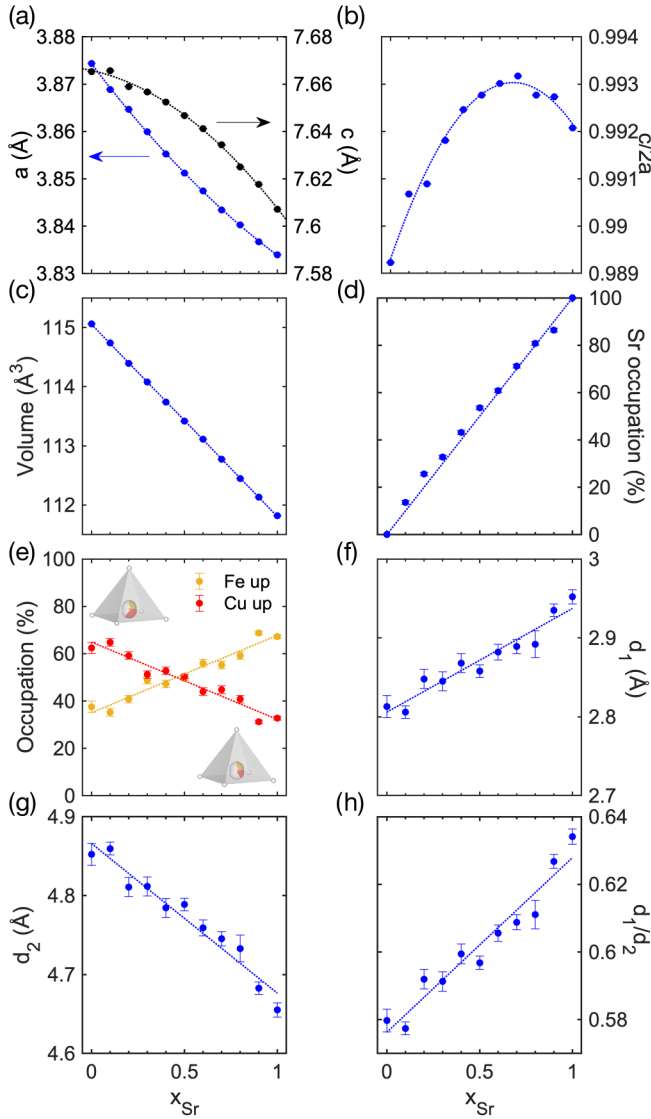


FIG. 5. Evolution of the crystal structure with the Sr content x . (a) Lattice parameters a and c . (b) $c/2a$ ratio. (c) Unit cell volume. (d) Refined Sr occupation as a function of nominal Sr content. (e) Cu/Fe occupation of the split B sites within the upper pyramid of the unit cell together with representations of the Cu/Fe occupation for the $x = 0$ (top left) and $x = 1$ (bottom right) compositions. (f) d_1 . (g) d_2 . (h) d_1/d_2 ratio. The dotted lines are guides to the eye.

with a summary of the obtained results are shown in the Ref. [34] (Figs. 1–11 and Tables II–IV).

A. Lattice parameters

Figure 5(a) shows the modification of the lattice parameters a and c upon replacement of Ba with Sr. As expected, both decrease with the Sr content x . However, their evolution along the series differs from the linear increase expected from Vegard's law [46] observed in other structurally related perovskites [47]. This deviation is better appreciated in Fig. 5(b), showing the changes in the tetragonal distortion $c/2a$ of the pseudocubic unit cell with x where $c/2a = 1$ corresponds to a layered perovskite containing two perfectly cubic perovskite

units. We note that $c/2a$ takes values smaller than one for all samples, indicating a tensile distortion that decreases with x for low Sr contents. Interestingly, this tendency is reversed beyond $x \approx 0.7$, where $c/2a$ decreases with x . The behavior contrasts with that of the unit cell volume V [Fig. 5(c)], which contracts in a perfectly linear way with the Sr content.

B. Ba/Sr and Cu/Fe distribution

To rationalize these observations, we examined the evolution of several structural parameters along the series, and compared them with the behavior of $c/2a$. We inspected first the refined Sr and Ba fractions, and found them to agree very well with their nominal values for all samples (Fig. 5(d), and Ref. [34] Tables II–IV). Moreover, we could not find any evidence for long-range Ba/Sr order (see Ref. [34], Fig. 12), even for the samples with rational Sr contents (such as $x = 1/2$), a priori more prone to Ba/Sr ordered patterns [48]. Also, we did not find any signature of (Ba/Sr)/Y intermixing, observed in layered perovskites when the ionic radii of the A cations that occupy the two ordered A sites becomes increasingly similar [22]. An homogeneous Ba/Sr distribution (that we assume to be random in our Rietveld fits) provides thus a good description of the experimental data, even if the presence of short-range correlations between the Ba and Sr site occupations cannot be completely disregarded.

Next, we examined the evolution of the Cu/Fe occupations n_{Cu} and n_{Fe} of the square-pyramidal sites, shown in Fig. 5(e) for the upper pyramid of the crystal unit cell (for the lower pyramid n_{Cu} and n_{Fe} are just reversed). As mentioned in the introduction, we aimed at similar Cu/Fe occupations for all samples. However, we found that n_{Cu} and n_{Fe} are linear functions of the Sr content x . We also note that the maximal Cu/Fe intermixing is observed for the compositions with x close to 0.5, where $n_{\text{Cu}} \approx n_{\text{Fe}} \approx 50\%$. For the remaining samples we observe a tendency towards a more ordered Cu/Fe distribution, with larger differences between the Cu and Fe occupations of a given pyramid by approaching the two end members of the series ($x = 0$ and 1). Our analysis also reveals an unexpected trend, namely, the reversal of the Cu/Fe majority occupation by moving along the series. As shown in Fig. 5(d), the probabilities of finding Cu and Fe in the upper pyramid of YBaCuFeO₅ are $\approx 60\%$ and 40% , respectively (and vice versa in the lower pyramid). Interestingly, these probabilities are $\approx 33\%$ and 67% for YSrCuFeO₅. We note also that, for this material, the higher average Fe content of the upper pyramid is consistent with its shorter height [$2.325(5)$ Å], to be compared with the height of the lower pyramid [$2.348(5)$ Å], with a higher average Cu content.

Another interesting observation is that the reversal of the Cu/Fe majority occupation starts quite close to $x = 0.7$, the Sr concentration where the $c/2a$ evolution with x changes tendency. The reasons behind the Cu/Fe occupation reversal with growing Sr contents are presently unclear, but may be related by the different stability of the FeO₅-CuO₅ bipyramidal dimers in presence of Ba²⁺ and Sr²⁺. These A cations are indeed located between the FeO₅ and CuO₅ pyramids, and have an impact on its size. DFT calculations for the two end members of the series, out of the scope of this work, will be necessary to settle whether this is or not the case.

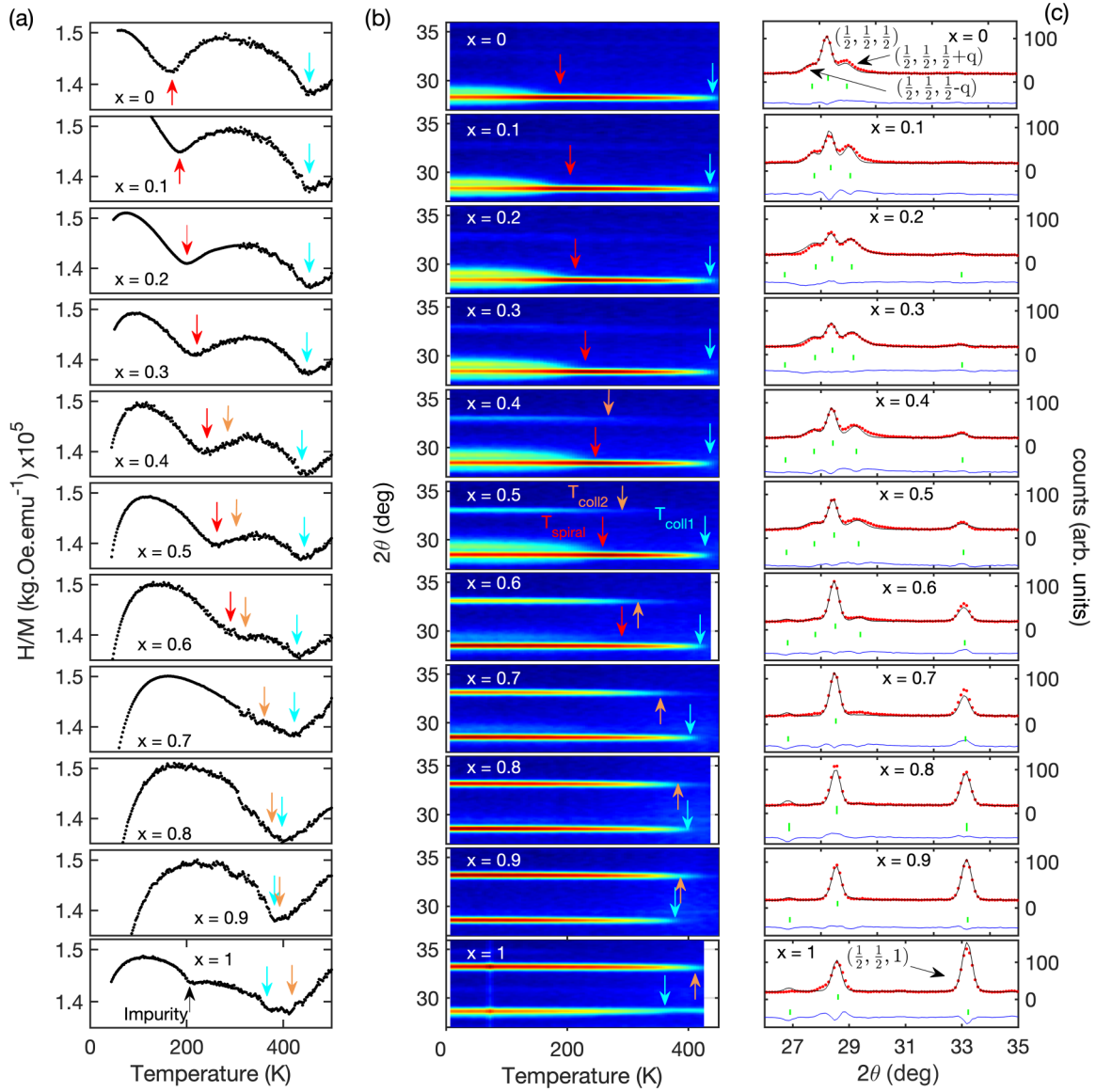


FIG. 6. (a) Temperature dependence of the inverse magnetic susceptibility. (b) Contour plots of a selected region in the neutron powder diffraction patterns showing the thermal evolution of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$, and $(\frac{1}{2}, \frac{1}{2}, 1)$ magnetic reflections related to the coll1, spiral, and coll2 phases, respectively. (c) Detail of the diffraction patterns measured at 2 K. Blue, red, and orange vertical arrows indicate the T_{coll1} , T_{spiral} , and T_{coll2} temperatures defined in the text.

C. Interatomic distances d_1 and d_2

As mentioned in the previous section, the bipyramid size d_1 and the separation between the bipyramid layers d_2 control the strength of the exchange couplings along the c axis. Moreover, their ratio d_1/d_2 has been found to correlate positively with T_{spiral} and inversely with T_{coll1} [14]. Figures 5(f) and 5(g) show the evolution of d_1 and d_2 for the full $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ series as a function of Sr content. As expected, d_2 decreases linearly with x . In contrast, d_1 increases, albeit to a slightly slower rate. This leads to an increase of d_1/d_2 upon replacing Ba with Sr [Fig. 5(h)], that we expect to result in the simultaneous increase of T_{spiral} and the decrease of T_{coll1} . We also note that, contrarily to the $c/2a$ ratio and the Cu/Fe occupation, the evolution of d_1/d_2 with x is approximately linear and does not display any noticeable anomaly.

V. EVOLUTION OF THE MAGNETIC ORDER

A. Magnetic ordering temperatures

Figure 6(a) shows the inverse magnetic susceptibility of the eleven $\text{YBa}_{1-x}\text{Sr}_x\text{CuFeO}_5$ samples. The measurements revealed the presence of (at least) two transitions in all samples at temperatures that we define here as those corresponding to minima in the $\chi^{-1}(T)$ curves. The presence of magnetic transitions was subsequently confirmed by the thermal evolution of the NPD data (Fig. 6(b) and see Ref. [34] Figs. 13–19), which also allowed a precise assignment of the anomalies observed in the $\chi^{-1}(T)$ curves.

For the samples with $0 \leq x \leq 0.6$, a comparison between the two sets of data identifies the high temperature anomalies [blue arrows in Figs. 6(a) and 6(b)] as the ordering temperatures of the coll1 phase described by the propagation vector

$\mathbf{k}_{c1} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. It also assigns the low temperature anomalies [red arrows in Figs. 6(a) and 6(b)] to the ordering temperatures of the spiral phase, which coincide with a maximum in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection and with the simultaneous appearance of the incommensurate satellites described by the propagation vector $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$ [Fig. 7(a)]. The evolution of the coll1 and spiral ordering temperatures, shown in Fig. 8 and illustrated in Ref. [34] Figs. 14–19, reveals a decrease of T_{coll1} with x , whereas T_{spiral} displays the opposite trend, in excellent agreement with the behavior inferred from the changes in d_1 , d_2 , and the d_1/d_2 ratio upon replacement of Ba with Sr [Figs. 5(e)–5(g)].

Contrarily to the behavior observed in the samples with the same compositions prepared at higher temperatures [18], the intensity of the reflections associated to the coll1 phase do not vanish completely below T_{spiral} (Fig. 6(c) and Ref. [34] Fig. 13). This phase coexistence, particularly pronounced in early works [19], can be rationalized within the framework of the random exchanges model as arising from a Fe-Fe defect distribution that does not fit the model premises [32,33]. Due to the low annealing temperatures employed in this study, these defects are presumably absent or too diluted in certain sample regions, leading to the preservation of the high temperature collinear phase in these areas down to the lowest temperatures.

We focus now in the samples with $0.7 \leq x \leq 1$, where the temperature dependence of the NPD patterns is substantially different. Starting with the coll1 phase, we note that its associated reflection $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is present for all compositions. Moreover, both the setup temperature T_{coll1} and the intensity of that reflection pursue the trend observed in the samples with lower Sr contents, decreasing continuously with x (Figs. 6(b), 7(a), 8, and Ref. [34] Figs. 14–19).

The behavior of the reflections associated to the spiral phase follows a completely different pattern. As shown in Fig. 6(b), the incommensurate satellites become extremely broad, leading to the suppression of the maximum in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection's temperature dependence that was signaling the setup of the long-range spiral order in the Sr-poor samples [Fig. 7(a)]. The low temperature minimum in the $\chi^{-1}(T)$ curves becomes also shallow, consistent with the evolution of the incommensurate satellites. These observations strongly suggest the absence of long-range spiral order for $x = 0.7$ and 0.8 (see Ref. [34] Fig. 13), where the spiral would survive in the form of short-range magnetic correlations. For these samples, the statistics of our data do not allow a precise determination neither of $\mathbf{k}_s$, nor the temperature where the magnetic correlations disappear. Interestingly, for $x = 0.8$ (the last Sr content where the signature of these correlations is still visible) the ordering temperature of the coll1 phase is close to 400 K. Since this temperature coincides with the triple point reported in previous studies (Fig. 8, [17,18]), our observations suggest that the magnetic spiral cannot survive beyond 400 K, neither as long-range ordered phase nor in the form of short-range correlations.

The progressive disappearance of the long-range spiral order is accompanied by the simultaneous stabilization of the coll2 phase with $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$ (see Ref. [34] Fig. 13). This is illustrated by the rise of the $(\frac{1}{2}, \frac{1}{2}, 1)$ reflection, barely visible

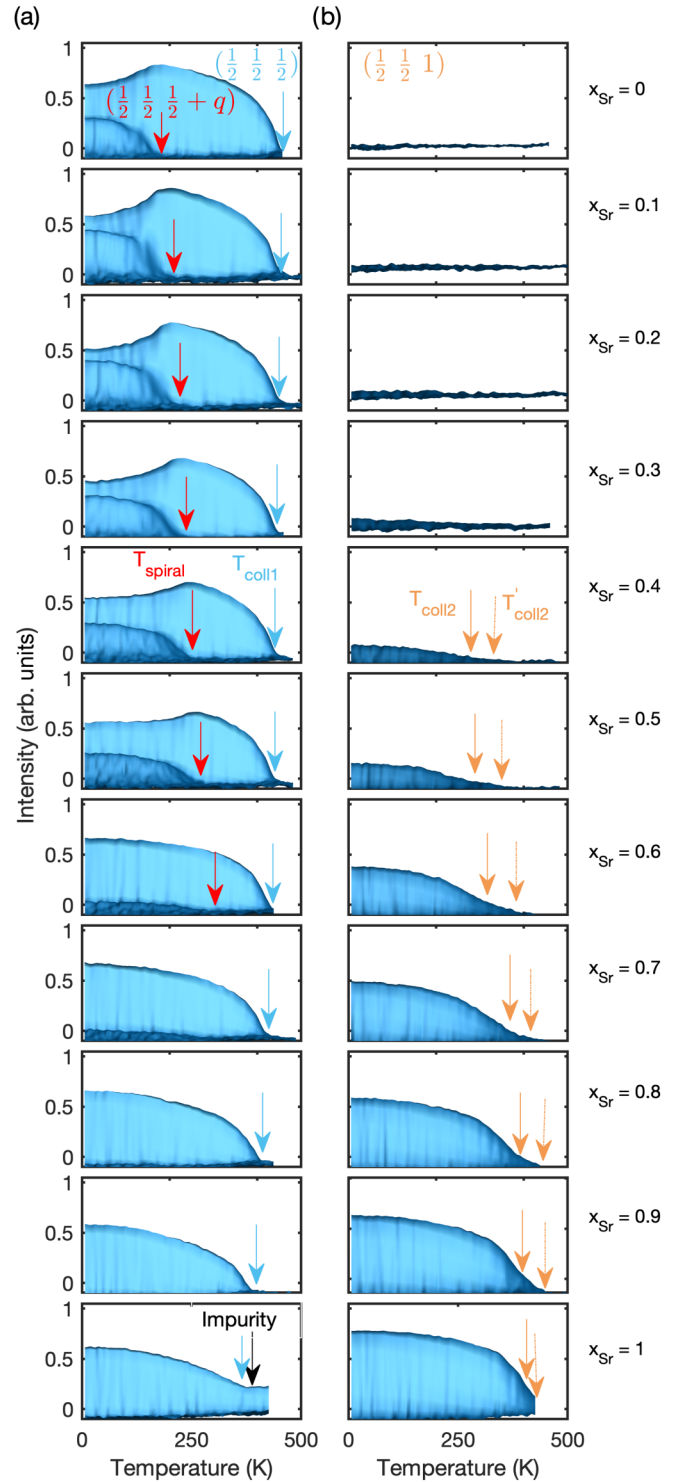


FIG. 7. Thermal evolution of the magnetic reflections of the coll1, spiral, and coll2 phases illustrating their different temperature dependencies in the vicinity of $x = 0.5$. (a) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + q)$. (b) $(\frac{1}{2}, \frac{1}{2}, 1)$. Blue, red and orange vertical arrows indicate the T_{coll1} , T_{spiral} , T_{coll2} , and T'_{coll2} temperatures defined in the text. For a given composition, the magnetic intensities in (a) and (b) are shown on the same vertical scale.

for the samples with smaller Sr concentrations [Fig. 7(b)]. We note also that the decay of this reflection is different from than of coll1 reflection $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. As shown in Fig. 7(b), the

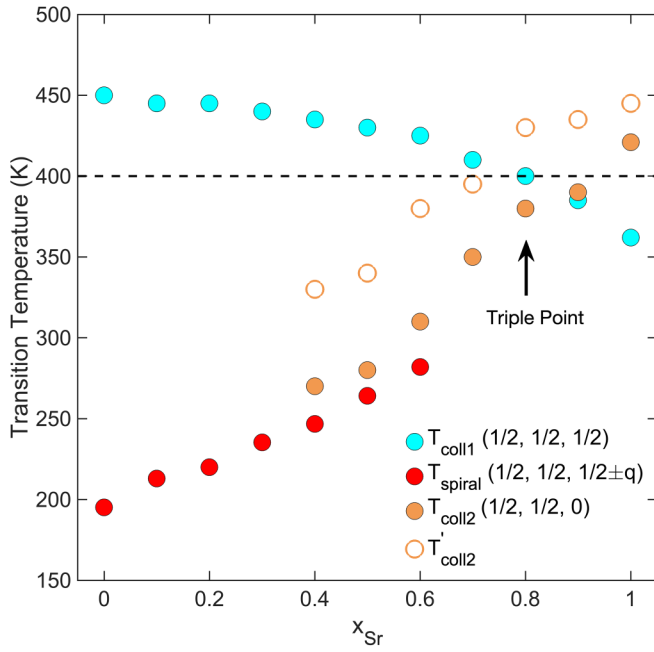


FIG. 8. Evolution of the magnetic ordering temperatures T_{coll1} , T_{spiral} , and T_{coll2} together with the setup of the coll2 magnetic correlations T'_{coll2} as a function of the strontium content. The horizontal dashed line indicates the latest estimation of the temperature associated to the paramagnetic-coll1-spiral triple point [23], and the black vertical arrow the Sr content where this point is reached in our samples.

$(\frac{1}{2}, \frac{1}{2}, 1)$ intensity decreases relatively fast for $x = 1$, but this decay becomes increasingly slow by decreasing the Sr content. Moreover, it displays a curvature change at temperatures T_{coll2} , substantially lower than the onset temperature T'_{coll2} (full and dashed arrows, respectively). A detailed analysis of the critical exponents and correlation lengths is out of the scope of this work and will be addressed separately. However, the observation of additional broadening in the region between T_{coll2} and T'_{coll2} suggests the presence of short-range magnetic correlations between these two temperatures.

Assuming that fully long-range coll2 magnetic order is realized only below T_{coll2} , we have plotted the evolution of this temperature with the Sr content together with that of T'_{coll2} , T_{coll1} and T_{spiral} . The results, shown in Fig. 8, reveal three interesting findings. Firstly, T_{spiral} and T_{coll2} nearly coincide in the spiral-coll2 crossover region ($x = 0.4, 0.5, 0.6$). Secondly, both temperatures increase with x at similar rates, i.e., $\partial T_{\text{coll2}}/\partial x \simeq \partial T_{\text{spiral}}/\partial x$. Thirdly, the $T_{\text{coll1}}(x)$ and $T_{\text{coll2}}(x)$ lines cross exactly at $T_{\text{coll1}} = T_{\text{coll2}} \sim 400$ K, i.e., the temperature of the paramagnetic-coll1-spiral triple point reported in previous studies. These observations strongly suggest a common origin for the spiral and coll2 phases, a scenario also supported by the evolution of T_{spiral} and T_{coll2} with the d_1/d_2 ratio. As shown in Fig. 9, both temperatures are linear functions of d_1/d_2 and increase with this variable at comparable rates.

By looking at Fig. 8, a question arises: if according to previous experimental studies the coll2 phase is only stable beyond a critical Fe-Fe defect concentration of $x \simeq 6\%$, why

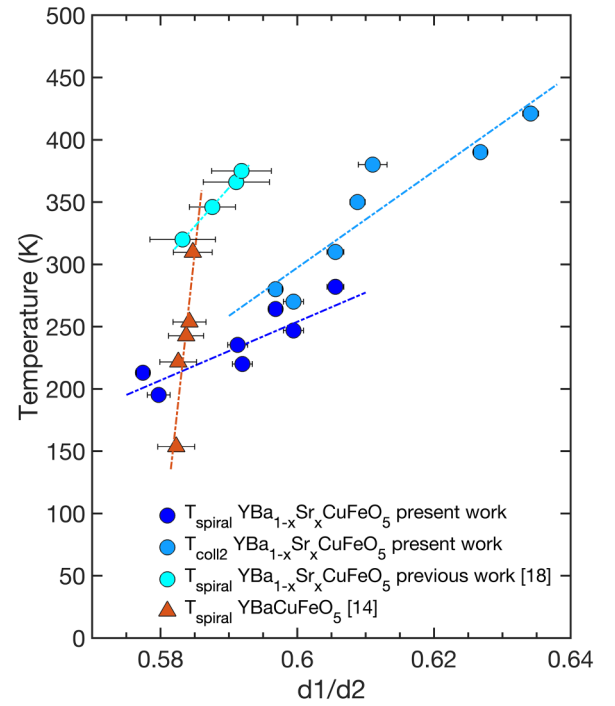


FIG. 9. Evolution of the spiral and coll2 transition temperature as a function of the d_1/d_2 ratio. The figure includes present and previously reported data. Dark blue points represent the data reported in the work with samples from $x = 0$ to 0.5, while the light blue points correspond to the transition temperatures for the second collinear phase with $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$.

is it observed in the samples with $x = 0.4, 0.5$, and 0.6 , where the simultaneous presence of the long-range spiral phase suggests defect concentrations between 3% and 4% [33]? Simultaneously, we can also wonder why for $x = 0.7$ and 0.8 the coll2 phase shows long-range order whereas the spiral phase is only present in form of short-range correlations. Again, we believe that the reason may be an inhomogeneous Cu/Fe distribution caused by the low annealing temperature, which may include Fe-rich (and Cu-rich regions) with respectively higher/lower concentrations of Fe-Fe defects. The impact of these inhomogeneities in the stability of the different magnetic phases is difficult to evaluate without a precise knowledge of the local Cu/Fe distribution, in particular close to the triple point, where the energy scale of the coll1, spiral and coll2 phases became comparable to that of the paramagnetic state. The approximate region expected to be affected by the existence of short-range magnetic correlations, either of critical origin and/or due to an inhomogeneous Fe-Fe defect concentration is schematically shown in Fig. 2.

B. Magnetic structures

After uncovering the stability of the different magnetic phases upon replacement of Ba with Sr, we address now the changes in the periodicity of the spiral phase, directly related with the incommensurate modulation parameter q of the magnetic propagation vector $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$. According to the predictions of the random exchanges frustration model [32,33], T_{spiral} should be directly proportional to the

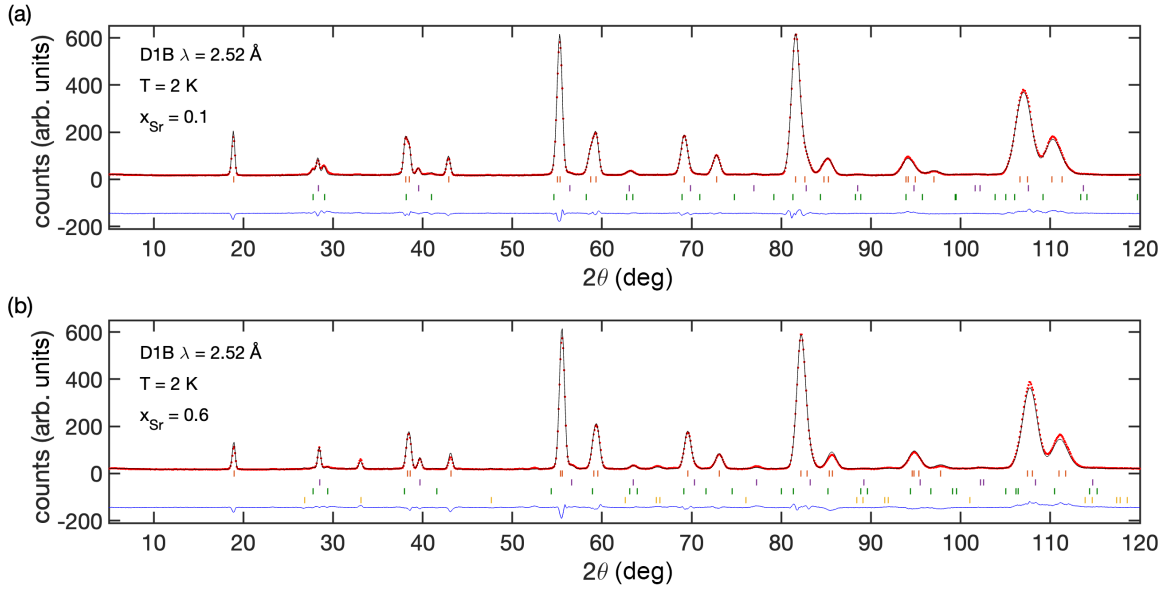


FIG. 10. Neutron diffraction patterns of the YBa_{1-x}Sr_xCuFeO₅ samples with $x_{\text{Sr}} = 0.1$ (a) and 0.6 (b) measured on D1B at 2 K. Red markers: experimental data. Black lines: Rietveld fits. The vertical ticks indicate the positions of the Bragg reflections of the different phases. Upper row: crystal structure. Second, third and fourth rows: magnetic structures of the coll1, spiral and coll2 phases described by the propagation vectors $\mathbf{k}_{c1} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $\mathbf{k}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm q)$ and $\mathbf{k}_{c2} = (\frac{1}{2}, \frac{1}{2}, 0)$.

ground state value of this parameter q_G . Here, we extracted this information from the fits of the NPD patterns at 2 K, that were conducted for all the samples (Fig. 6(c) and Ref. [34] Figs. 20–30). Representative examples of such fits for the samples with long range spiral ($x \leq 0.5$) and coll2 order ($x > 0.5$) are shown in Fig. 10.

The magnetic structures, shown in Fig. 1, were described according to the models reported in [16] (coll1, spiral) and [24] (coll2). The three magnetic phases were described using the crystallographic unit cell and the magnetic propagation vector formalism, as implemented in the Rietveld software FULLPROF SUITE [38]. The magnetic moments of all phases were described using polar coordinates, more convenient because they offer the possibility of establishing constraints between the modulus and inclination of the moments of the different phases. For the spiral phase, we employed the real-space parametrization described in [38], more intuitive than the usual description in terms of Fourier coefficients. Because of the inherent limitation of the unpolarized NPD technique, the Rietveld fits could not be performed without introducing restrictions between the refined parameters, as discussed in Refs. [16,17]. These restrictions, consistent with those employed in our previous works, and also in more recent studies, were the following. (a) The spiral envelop is assumed to be circular. (b) At all temperatures, the ratio between the Fe and Cu magnetic moments is restricted to be identical to their free ion, spin-only values (5:1). (c) For a given sample at a given temperature, the inclination angles φ_G of the Cu and Fe magnetic moments with respect to the **ab** plane are assumed to be identical. The results of the fits are summarized in Table V [34].

In the temperature regions where two (or more) magnetic phases coexist, the fraction of each phase is unknown. The refinements were thus performed by constraining the scale

factors of all phases (crystallographic and magnetic) to take identical values. This choice implicitly assumes that every magnetic phase occupies the full sample volume. This is obviously not true, and had an impact of the absolute value of the refined Fe and Cu magnetic moments, whose ordered, ground state values would be *a priori* expected to be similar for all phases, and for all samples. Our choice had in contrast little impact on the refined inclination angles φ_G , which depend on the relative values of the integrated intensities of each phase.

As shown in Fig. 11(a), the Cu/Fe moments refined for each magnetic phase at 2 K change significantly with x , somehow reflecting the evolution of the phase fractions with the Sr content. In contrast, the inclination angles were found to be very similar for all the phases present in a given sample, and were constrained to have the same values in the final stages of the fits. The evolution of the refined φ_G value at 2 K with the Sr content, shown in Fig. 11(b), indicates that the cycloidal component of the spiral increases smoothly with x (and hence with T_{spiral}), as reported in previous studies on powder samples containing exclusively Cu and Fe in the B sites [16–18,23]. We note also that the magnetic moments of the coll2 phase preserve this trend, approaching continuously the **c** crystal axis for increasing Sr contents. This finding reinforces the scenario of a common, disorder-based origin of both phases

The evolution of T_{spiral} as a function of the refined q_G values, shown in Fig. 12, reveals a nearly linear relationship that crosses the origin with a slope very similar to that reported for other Cu-Fe layered perovskite families [16–18]. According to Scaramucci and co-workers [32,33], the slope of the $T_{\text{spiral}}(q_G)$ line depends of the values of the three NN exchange constants J_1 , J_2 and J_{ab} , as well as on $J_{\text{Fe-Fe}}$. The observation of a nearly common slope with very low dispersion for AA'CuFeO₅ samples with different A-cations and different degrees of Cu/Fe disorder is thus a remarkable observation.

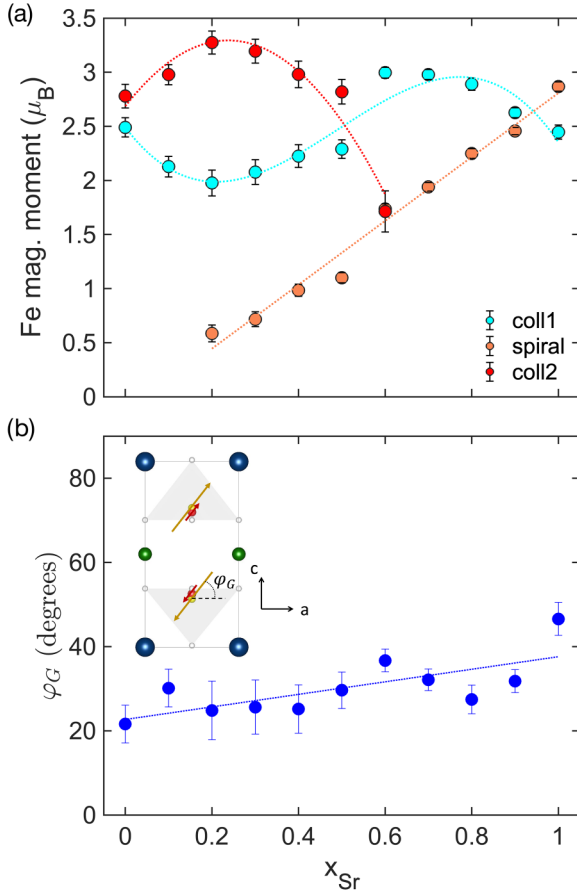


FIG. 11. (a) Evolution of the Fe magnetic moment at 2 K with the Sr content x_{Sr} for the three magnetic phases, refined as detailed in the text. (b) Inclination angle φ_G of the magnetic moments as a function of x_{Sr} , also at 2 K. The angle definition is shown in the inset. Dotted lines are guides for the eye.

Overall, it suggests that this law is robust under the variation of the NN exchanges expected from the different Cu-O and Fe-O interatomic distances reported for these materials, a non-trivial statement owing to the important differences between them. In any case, the fact that our samples follow this law suggest that the random exchanges frustration model is a good framework to describe the origin and the evolution of the magnetic frustration in the $YBa_{1-x}Sr_xCuFeO_5$ series.

VI. DISCUSSION

The aim of this study was to investigate the region beyond the paramagnetic-collinear-spiral triple point observed in Cu/Fe-based layered perovskites upon introduction of small concentration of strongly frustrating AFM Fe-Fe defects in the bipyramidal units occupied majoritarily by weakly FM Cu-Fe pairs. Being aware of the experimental difficulties linked to the generation of large defect concentrations, we attempted an alternative route for accessing the phase diagram region beyond the triple point. We thus synthesized the $YBa_{1-x}Sr_xCuFeO_5$ solid solutions ($0 \leq x \leq 1$), where we progressively replaced Ba with Sr with the aim of enhancing the strength of the experimentally available Fe-Fe bonds. We also intended to maximize their number by increasing the

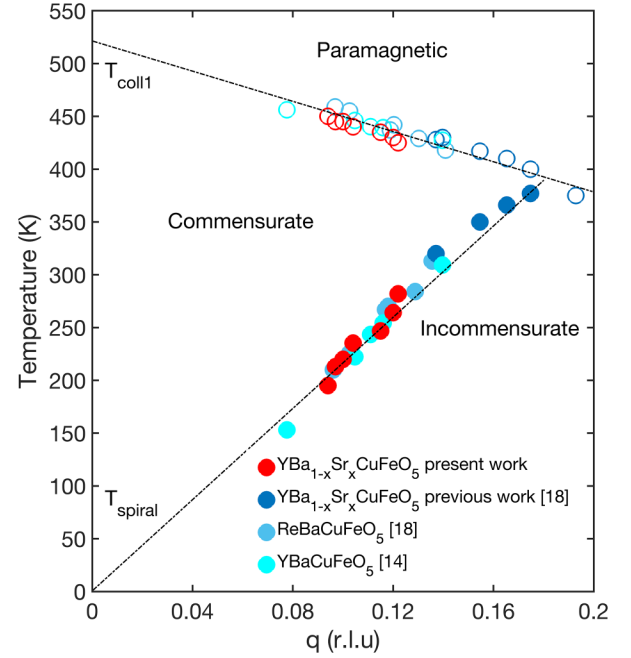


FIG. 12. T_{coll1} and T_{spiral} magnetic transition temperatures versus q_G for Cu/Fe based layered perovskites. Only samples with long-range spiral order are displayed. Red points represent the data reported in this study for the samples with $0 \leq x \leq 0.5$. Filled markers stand for the commensurate to incommensurate transition whereas the empty ones depict the paramagnetic to commensurate transition.

degree of Cu/Fe intermixing, that we assumed to be correlated with the fraction of Fe-Fe frustrating defects. For this purpose we quenched our samples in liquid nitrogen after the last annealing, a strategy successfully employed in the past for other layered perovskite families [14,17,18]. This approach was only partially successful due to difficulties associated to the synthesis procedure, that we wanted identical for all samples. This turned out to be possible, but only by employing a low synthesis temperature, a necessary compromise between the generation of large amounts of Cu/Fe disorder and the obtention of phase pure samples.

Although we quenched all samples into liquid nitrogen from the same annealing temperature, the degree of Cu/Fe average disorder was not the same for all of them. The maximal intermixing was obtained for the compositions with x close to 0.5, where $n_{Cu} \simeq n_{Fe} \simeq 50\%$. For the remaining samples we observed a tendency towards a more ordered Cu/Fe distribution by approaching the two end members of the series ($x = 0$ and 1), where the difference between the Cu and Fe occupations $\|n_{Cu} - n_{Fe}\|$ was close to 20% [Fig. 5(e)]. These values are comparable to those reported in our previous study [18] for $YBa_{1-x}Sr_xCuFeO_5$ samples with $x \leq 0.4$. However, the spiral ordering temperatures reported in the present investigation are between 100 and 150 K lower (cyan and dark blue markers in Fig. 9, respectively). As an example, the T_{spiral} value of the $x = 0.4$ presented in this study (250 K) is far below the 375 K reported for the sample with the same Sr content and nearly identical average Cu/Fe disorder in Ref. [18]. Since this last sample was quenched from a much higher

temperature (1150 °C instead of 980 °C), we conclude that identical average Cu/Fe occupations for samples with the same chemical composition may have different amounts and/or different spacial distributions of Fe-Fe defects (the two parameters controlling the T_{spiral} value according to Refs. [32,33]). Given the difficulties for accessing experimentally these two variables, the average Cu/Fe occupations n_{Cu} and n_{Fe} extracted from high resolution powder diffraction data remain a useful guidance as long as their absolute values are compared for samples prepared in similar conditions. The empirical laws linking these occupations with T_{spiral} proposed in some previous studies [17] seem thus not to be of general application (even for samples of the same composition) as n_{Cu} and n_{Fe} are values averaged over the full sample volume that do not encode the details of the Fe-Fe defect distribution.

In contrast with the relationship between T_{spiral} and the Cu/Fe occupations, Scaramucci and co-workers predict a universal linear law linking T_{spiral} and the ground state magnetic modulation vector q_G . We show in this study that our samples with $0 \leq x \leq 0.6$ nicely follow this law (Fig. 12). The evolution of T_{spiral} is more difficult to follow for higher Sr contents, where the low synthesis temperature employed in this study reduces the Fe-Fe defect concentration and prevents the available defects to be distributed homogeneously. As a result, the width of the magnetic reflections associated to the spiral phase increases dramatically by approaching the triple point. Although broadened incommensurate satellites can still be observed for $x = 0.7$, they are clearly absent for higher Sr contents ($x = 0.8, 0.9, 1$). This suggests that the spiral survives up to $x \approx 0.8$, most probably in the form of short range magnetic correlations. Interestingly, the T_{coll1} value of this composition is ~ 400 K (Fig. 8), a temperature that nicely coincides with the $T_{\text{spiral}}-T_{\text{coll1}}$ crossing reported in previous studies (Fig. 8).

Besides providing further support to the universality of the T_{spiral} versus q_G linear law, our study provides also experimental evidence supporting another theoretical prediction, namely, the common, disorder-based origin of the spiral and coll2 phases [33]. As shown in Fig. 8, the $\partial T_{\text{spiral}}/\partial x$ and $\partial T_{\text{coll2}}/\partial x$ rates are both positive and of comparable magnitude. Moreover, the magnetic moment inclination angle φ_G increases continuously with the Sr content and does not show any appreciable discontinuity at the spiral-coll2 boundary [Fig. 11(b)]. Altogether, these observations are consistent with the predicted replacement of the spiral by the coll2 phase beyond the $T_{\text{spiral}}-T_{\text{coll1}}$ crossing [33], even if an extended phase coexistence region across this point is observed in our samples as a consequence of the inhomogeneous Fe-Fe defect concentration (Fig. 2).

Before coming to the conclusion, we propose here some alternative approaches for exploring the magnetic phase diagram beyond the crossing of the T_{spiral} and T_{coll1} lines. Besides increasing the amount and/or strength of the Fe-Fe defects, the main empirical strategy for the design of materials with layered perovskite structure and high T_{spiral} values is to replace Y^{3+} , Ba^{2+} , Cu^{2+} , and/or Fe^{3+} by isovalent cations leading to an increase of the d_1/d_2 ratio [14,16]. However, it is worth stressing that any chemical substitution should also try to preserve the signs of the NN magnetic exchanges J_1 , J_2 , J_{ab} ,

and J_{imp} and their relative strengths in order to fit within the premises of the random exchanges frustration model.

In this context, isovalent B-site substitutions look a priori less promising. Although a successful attempt to reach the triple point using this strategy has been reported recently [24], the NN magnetic couplings can change substantially depending on the electronic configuration of the chosen cations. This can lead to an scenario that does not fit anymore the theory premises, even if low substitution levels of Cu^{2+} by divalent cations with smaller atonic radii can decrease the bipyramid size d_2 and eventually compensate the presence of new, non-favorable exchange couplings. This situation could be realized in the bulk magnetization study of Ref. [49], where the partial replacement of Cu with Mn, Ni, and Zn suggest a $T_{\text{spiral}}-T_{\text{coll1}}$ crossing close of 400 K for the three solid solutions.

In spite of the synthetic difficulties reported in our study, A-site substitutions appear a priori more promising that isovalent B-site substitutions because the magnetic couplings between A cations are usually smaller than those between the B cations. As a consequence, A cations act usually as spacers even if they are magnetic, their main impact on T_{spiral} being through the J_1 , J_2 , J_{ab} , and J_{imp} dependence with the interatomic distances. A nice example of this strategy is the replacement of Y^{3+} with trivalent lanthanides, successfully applied to $R = \text{Lu}$ to Dy in Ref. [18]. The increasingly larger R^{3+} ionic radii leads to growing d_1/d_2 ratios that result in a simultaneous T_{spiral} increase, with a maximal T_{spiral} value close to 300 K. If this trend is preserved, completing the 4f series (Tb to La) could eventually led to a $T_{\text{spiral}}-T_{\text{coll1}}$ crossing. A drawback of these lanthanide cations, whose ionic radii increase continuously from Tb to La, is that they allow the incorporation of extra oxygen in the R layers. Moreover, the amount of extra oxygen increases with the R^{3+} ionic radius [22,50]. The investigation of these materials will thus require the removal of interstitial oxygen in order to guarantee a perfect RBaCuFeO_5 stoichiometry.

VII. CONCLUSIONS

As final remark, we would like to say that the results reported in this study are particularly relevant on the light of the random exchanges model developed by Scaramucci and co-workers. Besides providing novel experimental information supporting one of its not-yet demonstrated predictions, namely, the common origin of the spiral and coll2 magnetic phases, they further validate the universal relationship between T_{spiral} and q_G . This novel, disorder-based frustration mechanism emerges thus as an efficient tool for the design of spiral magnets with ordering temperatures high enough to display magnetoelectric properties at temperatures compatible with real-life applications.

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- [1] P. Curie, Sur la symétrie dans les phénomènes physiques, symétrie d'un champ électrique et d'un champ magnétique, *J. Phys. Theor. Appl.* **3**, 393 (1894).
 - [2] M. Fiebig, Revival of the magnetoelectric effect, *J. Phys. D* **38**, R123 (2005).
 - [3] N. A. Spaldin and M. Fiebig, The renaissance of magnetoelectric multiferroics, *Science* **309**, 391 (2005).
 - [4] N. A. Spaldin, Multiferroics beyond electric-field control of magnetism, *Proc. Roy. Soc. A* **476**, 20190542 (2020).
 - [5] T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, Ferroelectricity and giant magnetocapacitance in perovskite rare-earth manganites, *Phys. Rev. Lett.* **92**, 257201 (2004).
 - [6] H. Katsura, N. Nagaosa, and A. V. Balatsky, Spin current and magnetoelectric effect in noncollinear magnets, *Phys. Rev. Lett.* **95**, 057205 (2005).
 - [7] S.-W. Cheong and M. Mostovoy, Multiferroics: A magnetic twist for ferroelectricity, *Nat. Mater.* **6**, 13 (2007).
 - [8] O. Heyer, N. Hollmann, I. Klassen, S. Jodlauk, L. Bohatý, P. Becker, J. A. Mydosh, T. Lorenz, and D. Khomskii, A new multiferroic material: MnWO_4 , *J. Phys.: Condens. Matter* **18**, L471 (2006).
 - [9] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Magnetic control of ferroelectric polarization, *Nature (London)* **426**, 55 (2003).
 - [10] M. Mostovoy, Ferroelectricity in spiral magnets, *Phys. Rev. Lett.* **96**, 067601 (2006).
 - [11] A. Tiwari, S. Kumawat, S. Rayaprol, and A. Dixit, Neutron diffraction studies on temperature driven crystallographic anisotropy in FeVO_4 multiferroic: Evidence of strong magnetostructural correlations, *AIP Conf. Proc.* **2115**, 030526 (2019).
 - [12] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, Cupric oxide as an induced-multiferroic with high- T_c , *Nat. Mater.* **7**, 291 (2008).
 - [13] G. Giovannetti, S. Kumar, A. Stroppa, J. van den Brink, S. Picozzi, and J. Lorenzana, High- T_c ferroelectricity emerging from magnetic degeneracy in cupric oxide, *Phys. Rev. Lett.* **106**, 026401 (2011).
 - [14] M. Morin, E. Canévet, A. Raynaud, M. Bartkowiak, D. Sheptyakov, V. Ban, M. Kenzelmann, E. Pomjakushina, K. Conder, and M. Medarde, Tuning magnetic spirals beyond room temperature with chemical disorder, *Nat. Commun.* **7**, 13758 (2016).
 - [15] L. Er-Rakho, C. Michel, P. Lacorre, and B. Raveau, $\text{YBaCuFeO}_{5+\delta}$: A novel oxygen-deficient perovskite with a layer structure, *J. Solid State Chem.* **73**, 531 (1988).
 - [16] M. Morin, A. Scaramucci, M. Bartkowiak, E. Pomjakushina, G. Deng, D. Sheptyakov, L. Keller, J. Rodriguez-Carvajal, N. A. Spaldin, M. Kenzelmann, K. Conder, and M. Medarde, Incommensurate magnetic structure, Fe/Cu chemical disorder, and magnetic interactions in the high-temperature multiferroic YBaCuFeO_5 , *Phys. Rev. B* **91**, 064408 (2015).
 - [17] A. Romaguera, X. Zhang, O. Fabelo, F. Fauth, J. Blasco, and J. L. García-Muñoz, Helimagnets by disorder: Its role on the high-temperature magnetic spiral in the YBaCuFeO_5 perovskite, *Phys. Rev. Res.* **4**, 043188 (2022).
 - [18] T. Shang, E. Canévet, M. Morin, D. Sheptyakov, M. T. Fernández-Díaz, E. Pomjakushina, and M. Medarde, Design of magnetic spirals in layered perovskites: Extending the stability range far beyond room temperature, *Sci. Adv.* **4**, eaau6386 (2018).
 - [19] V. Caignaert, I. Mirebeau, F. Bourée, N. Nguyen, A. Ducouret, J. M. Grenèche, and B. Raveau, Crystal and magnetic structure of YBaCuFeO_5 , *J. Solid State Chem.* **114**, 24 (1995).
 - [20] X. Zhang, A. Romaguera, O. F., F. Fauth, J. Herrero-Martín, and J. L. García-Muñoz, Tuning the tilting of the spiral plane by Mn doping in YBaCuFeO_5 multiferroic, *Acta Mater.* **206**, 116608 (2021).
 - [21] X. Zhang, A. Romaguera, F. Sandiumenge, O. Fabelo, J. Blasco, J. Herrero-Martin, and J. L. Garcia-Munoz, Magnetic properties of a highly ordered single crystal of the layered perovskite $\text{YBaCuFe}_{0.95}\text{Mn}_{0.05}\text{O}_5$, *J. Magn. Magn. Mater.* **551**, 169165 (2022).
 - [22] E. Marelli, J. Lyu, M. Morin, M. Leménager, T. Shang, N. Yüzbaşı, D. Aegerter, J. Huang, N. Daffé, A. Clark, D. Sheptyakov, T. Graule, M. Nachtegaal, E. Pomjakushina, T. J. Schmidt, M. Krack, M. Fabbri, and M. Medarde, Cobalt-free layered perovskites $\text{RBaCuFeO}_{5+\delta}$ ($\text{R} = 4f$ lanthanide) as electrocatalysts for the oxygen evolution reaction, *ESS Catal.* **2**, 335 (2024).
 - [23] A. Romaguera and M. Medarde, Room temperature magnetoelectric magnetic spirals by design, *Front. Mater.* **11**, 1448765 (2024).
 - [24] X. Zhang, A. Romaguera, O. Fabelo, F. Fauth, J. Herrero-Martin, and J. L. García-Muñoz, Pushing magnetic spirals beyond room temperature by reducing the uniaxial pyramidal elongation in layered Cu/Fe perovskites, *Phys. Rev. Res.* **6**, 033081 (2024).
 - [25] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Structure of the 100 K superconductor $\text{Ba}_2\text{YCu}_3\text{O}_7$ between (5÷300) K by neutron powder diffraction, *Europhys. Lett.* **3**, 1301 (1987).
 - [26] C. Meyer, F. Hartmann-Boutron, Y. Gros, and P. Strobel, Mössbauer study of $\text{YBaCuFeO}_{5+\delta}$: Site assignments of the metallic ions, *Solid State Commun.* **76**, 163 (1990).
 - [27] Q. Huang, P. Karen, V. L. Karen, A. Kjekshus, J. W. Lynn, A. D. Mighell, N. Rosov, and A. Santoro, Neutron-powder-diffraction study of the nuclear and magnetic structures of $\text{YBa}_2\text{Fe}_3\text{O}_8$ at room temperature, *Phys. Rev. B* **45**, 9611 (1992).
 - [28] J. Lyu, M. Morin, T. Shang, M. T. Fernández-Díaz, and M. Medarde, Weak ferromagnetism linked to the high-temperature spiral phase of YBaCuFeO_5 , *Phys. Rev. Res.* **4**, 023008 (2022).

- [29] S. Lal, S. K. Upadhyay, K. Mukherjee, and C. S. Yadav, Evolution of magnetic and dielectric properties in Sr-substituted high-temperature multiferroic YBaCuFeO₅, *Europhys. Lett.* **117**, 67006 (2017).
- [30] S. Lal, K. Mukherjee, and C. Yadav, Low temperature magnetic and x-ray diffraction studies of YBa_{1-x}Sr_xCuFeO₅ ($x = 0, 0.5$), *Phys. B: Condens. Matter* **570**, 191 (2019).
- [31] S. Lal, K. Mukherjee, and C. S. Yadav, Thermal conductivity of multiferroic material YBa_{1-x}Sr_xCuFeO₅ ($x = 0, 0.25, 0.5$), *AIP Conf. Proc.* **2005**, 050001 (2018).
- [32] A. Scaramucci, H. Shinaoka, M. V. Mostovoy, M. Müller, C. Mudry, M. Troyer, and N. A. Spaldin, Multiferroic magnetic spirals induced by random magnetic exchanges, *Phys. Rev. X* **8**, 011005 (2018).
- [33] A. Scaramucci, H. Shinaoka, M. V. Mostovoy, R. Lin, C. Mudry, and M. Müller, Spiral order from orientationally correlated random bonds in classical xy models, *Phys. Rev. Res.* **2**, 013273 (2020).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.110.235156> for detailed tables of crystallographic and magnetic structures, x-ray and neutron diffraction patterns together with the associated Rietveld refinements, extracted evolution of the magnetic structures as a function of temperature and composition.
- [35] J. Sesé, J. Bartolomé, and C. Rillo, Disposable sample holder for high temperature measurements in MPMS superconducting quantum interference device magnetometers, *Rev. Sci. Instrum.* **78**, 046101 (2007).
- [36] High intensity two-axis powder diffractometer, d1b, institute Laue-Langevin—<https://www.ill.eu/users/instruments/instruments-list/d1b/description/instrument-layout/>.
- [37] P. R. Willmott, D. Meister, S. J. Leake, M. Lange, A. Bergamaschi, M. Böge, M. Calvi, C. Cancellieri, N. Casati, A. Cervellino, Q. Chen, C. David, U. Flechsig, F. Gozzo, B. Henrich, S. Jäggi-Spielmann, B. Jakob, I. Kalichava, P. Karvinen, J. Krempasky *et al.*, The materials science beamline upgrade at the swiss light source, *J Synchrotron Radiat* **20**, 667 (2013).
- [38] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Phys. B: Condens. Matter* **192**, 55 (1993).
- [39] K. Momma and F. Izumi, *VESTA3* for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Cryst.* **44**, 1272 (2011).
- [40] J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, Cambridge, 2010).
- [41] S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, Oxford, 2001).
- [42] A. W. Mombrú, C. Christides, A. Lappas, K. Prassides, M. Pissas, C. Mitros, and D. Niarchos, Magnetic structure of the oxygen-deficient perovskite YBaCuFeO_{5+ δ} , *Inorg. Chem.* **33**, 1255 (1994).
- [43] M. Ruiz-Aragón, E. Morán, U. Amador, J. Martínez, N. Andersen, and H. Ehrenberg, Low-temperature magnetic structure of YBaCuFeO₅ and the effect of partial substitution of yttrium by calcium, *Phys. Rev. B* **58**, 6291 (1998).
- [44] Y.-C. Lai, C.-H. Du, C.-H. Lai, Y.-H. Liang, C.-W. Wang, K. C. Rule, H.-C. Wu, H.-D. Yang, W.-T. Chen, G. J. Shu, and F.-C. Chou, Magnetic ordering and dielectric relaxation in the double perovskite YBaCuFeO₅, *J. Phys.: Condens. Matter* **29**, 145801 (2017).
- [45] Y. K. Atanassova, V. N. Popov, G. G. Bogachev, M. N. Iliev, C. Mitros, V. Psycharis, and M. Pissas, Raman- and infrared-active phonons in YBaCuFeO₅: Experiment and lattice dynamics, *Phys. Rev. B* **47**, 15201 (1993).
- [46] L. Vegard, Die konstitution der mischkristalle und die raumfüllung der atome, *Z. Phys.* **5**, 17 (1921).
- [47] M. Guillaume, P. Allenspach, W. Henggeler, J. Mesot, B. Roessli, U. Staub, P. Fischer, A. Furrer, and V. Trounov, A systematic low-temperature neutron diffraction study of the RBa₂Cu₃O_x (R=yttrium and rare earths; $x=6$ and 7) compounds, *J. Phys.: Condens. Matter* **6**, 7963 (1994).
- [48] S. Streule, A. Podlesnyak, J. Mesot, M. Medarde, K. Conder, E. Pomjakushina, E. Mitberg, and V. Kozhevnikov, Effect of oxygen ordering on the structural and magnetic properties of the layered perovskites PrBaCo₂O_{5+ δ} , *J. Phys.: Condens. Matter* **17**, 3317 (2005).
- [49] Y. Yasui, S. Kihara, K. Ikeda, and T. Banshodani, Doping effect on magnetic properties of high-temperature multiferroic compound YBaCuFeO₅, *AIP Adv.* **14**, 015328 (2024).
- [50] A. Klyndyuk and E. Chizhova, Properties of RBaCuFeO_{5+ δ} (R = Y, La, Pr, Nd, Sm-Lu), *Inorg. Mater.* **42**, 550 (2006).