Progress in Physics (79)

Towards multiferroelectricity from frustrated magnetic order at room temperature

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Multiferroic materials

The first documented references about the existence of ordered magnetic moments can be traced back to ancient Greece, where the unusual properties of the mineral magnetite (Fe_3O_4) were recognized more than 2500 years ago. The discovery of spontaneously ordered electric moments took much more time and was first reported by Valasek in the Rochelle Salt ($KNaC_4H_4O_6 \cdot 4H_2O$) in the early nineteens [1]. This phenomenon was dubbed ferroelectricity due to its close similarities with ferromagnetism, in particular the presence of hysteresis under cyclic application of an external electric field.

Although the technological potential of (ferro-)magnetism and ferroelectricity was rapidly recognized after their respective discoveries, the two properties were long believed to be mutually exclusive [2]. The experimental demonstration that both types of order may not only coexist, but also be strongly coupled in the same material thus challenged the scientific community [3-4], and started a tremendous research effort at both, the fundamental and applied levels during the last decades to explore the plethora of phenomena that intertwine magnetism and electric polarization [5-8]. A variety of new materials combining both types of order - so-called multiferroics - have been reported, and novel mechanisms coupling spontaneous ferroelectric polarization to magnetic order have been identified [9].

These discoveries have raised great expectations about the possible control of magnetization with electric fields or vice versa. In most of today's hard disks, the information is stored in magnetic bits that are written with the help of magnetic-field-generating electric currents. In an ideal multiferroic, a voltage pulse could be used to induce electric polarization, and thanks to the magnetoelectric coupling, this would result in a change of magnetization. The waste heat and long switching times associated with electric currents might then be avoided. This fuels the hope that multiferroics will lead to faster, more compact and more energy-efficient data-storage technologies.

Multiferroicity from frustrated magnetic order

The number of reported materials with some degree of coupling between magnetism and ferroelectricity has enormously increased during the last decades. However, in many such materials both properties appear at different temperatures and have different origins, resulting in weak magnetoelectric effects [5-8]. Interestingly though, in a subclass of these materials ferroelectricity is directly induced by the onset of magnetic order [10]. In this case, the common origin of both orders guarantees a substantial coupling between them, which is highly desirable for applications. Among these materials, frustrated magnets with ordered magnetic spiral phases that spontaneously break inversion symmetry have received particular attention. Their capability to induce ferroelectricity was first demonstrated for $TbMnO_3$ [11-12], which develops spontaneous polarization and gigantic dielectric anomalies when the Mn^{3+} magnetic moments order, forming a cycloidal spiral below T_{spiral} = 28 K. The control of the electric polarization orientation with magnetic fields [11] and of the spiral's sense of rotation with electric fields [13] were also demonstrated. At the same time, this rose the fundamental question as to the origin of these phenomena.

Currently, the multiferroic cross-coupling in this class of materials is believed to originate from spin-orbit splitting on the magnetic ions, whose exchange drives an electric polarization when the magnetic order exhibits non-vanishing twists $S_i \times S_j$, as found in spiral patterns [9]. A spin pair at (r_i, r_j) contributes to the polarization by the double cross product $P \sim (r_i - r_j) \times (S_i \times S_j)$. This requires the spins to rotate in a plane that is not perpendicular to the spiral wavevector q_{spiral} (unlike in helicoidal spirals). Instead the spiral should have a cycloidal character. (cf. Fig. 1).
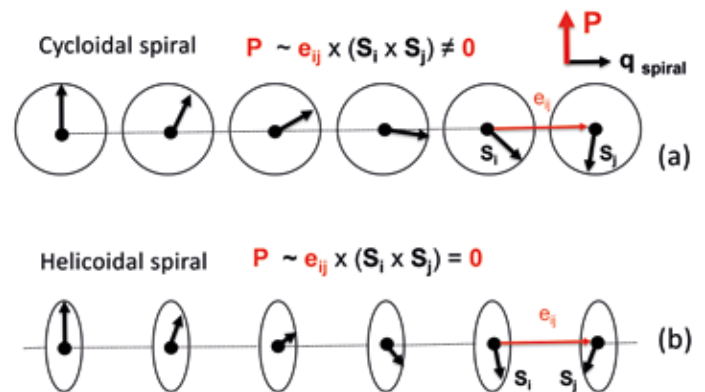

Figure 1. Cycloidal and helicoidal spirals: They differ in their ability to induce electric polarization.

In spite of their promising multifunctionalities, two handicaps have hindered the implementation of spiral multiferroics in real devices [14]. One is their low polarization values, typically far below the 1 $\mu C/cm^2$ limit considered the minimum for applications. This is a consequence of the often rather weak spin-orbit (SO) interactions, which results in modest charge displacements. The other main limitation is the very low magnetic ordering temperatures of most known spiral magnets (typically lower than 100 K) [10]. The underlying reason is that spiral order requires substantial frustration (which means that the magnetic interactions cannot all be satisfied simultaneously). In insulators, such frustration usually arises from a competition between nearest-neighbor and next-nearest neighbor magnetic interactions. The ordering temperature cannot exceed the energy scale of the latter, which, as a large-distance coupling, is very small.
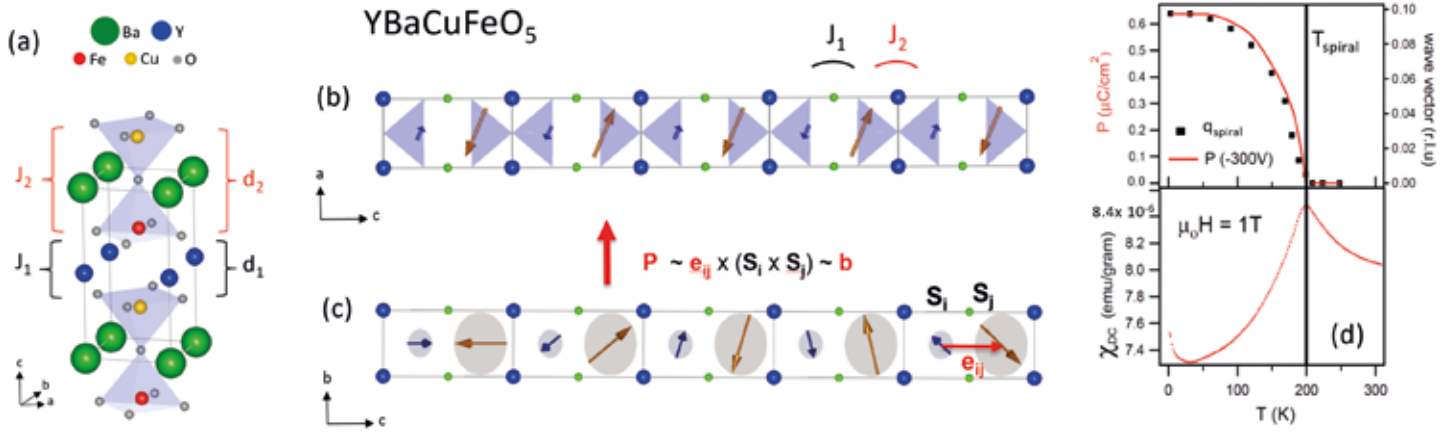
Figure 2. a) Crystal structure of YBaCuFeO₅. Usually bipyramids host a pair of Cu²⁺ and Fe³⁺, while disorder results in occasional Cu-Cu/Fe-Fe pairs. b) High temperature collinear magnetic structure. c) Low-temperature spiral magnetic structure. d) Temperature dependence of the electric polarization, the magnetic susceptibility and the magnetic wave vector of the spiral in YBaCuFeO₅ (adapted from refs [17] and [18]).

The main challenge in spiral multiferroic research is thus to identify design principles to obtain materials with magnetic spiral phases stable well above room temperature (RT), and having substantial SO coupling so as to induce large polarization.

Stabilizing magnetic spirals at RT with chemical disorder

Recently, an unexpected, but exquisite knob to control both the ordering temperature and the pitch of magnetic spirals has emerged: chemical disorder. This is indeed surprising, as disorder is usually detrimental to long-range order. The positive effect of disorder was first demonstrated in YBaCuFeO₅ (Fig 2a), where the spiral ordering temperature of this simple, tetragonal, layered perovskite increased from 154 to 310 K upon enhancing the Cu/Fe chemical disorder in the structure. The giant impact of disorder on the stability of the spiral state was both remarkable and puzzling, as it seemed at odds with traditional frustration mechanisms.

This material, whose crystal structure is shown in Fig. 2a, has been known since the late eighties, but their magnetic and ferroelectric properties have only been investigated recently [15]. Two experimental reports on this and the isostructural compounds LuBaCuFeO₅ and TmBaCuFeO₅ suggested that these three materials could display magnetism-driven ferroelectricity at unprecedentedly high temperatures covering a wide range, see Fig. 2d and [15-16]. The polarization reported was unusually large for this kind of materials, reaching 0.6 μC/cm² in powder samples (Fig. 2d). Moreover, the electric polarization could be suppressed by applying an external magnetic field, suggesting magnetoelectric coupling [15].

Intrigued by these reports, we started to investigate the full REBaCuFeO₅ family (where RE stands for a rare earth/lanthanide ion), to uncover the origin of the proposed magnetism-driven ferroeletricity [17-19]. Our detailed investigation of the reference material YBaCuFeO₅ established the existence of preparation-dependent Cu/Fe occupational disorder, and neutron powder diffraction showed that the high temperature collinear magnetic order undergoes a transition to a circular spiral of partially cycloidal character at lower temperature (see Figs. 1, 2c and [17]), compatible with the existence of spontaneous electric polarization

in the **ab** plane. The spiral manifests itself in neutron diffraction patterns by splitting the magnetic Bragg reflection (½ ½ ½) into two satellites at (½ ½ ½ ± q_{spiral}), where q_{spiral} is the wavevector of the spiral along the **c**-axis, cf. Fig. 3b [18].

To investigate the impact of Cu/Fe occupational disorder on the spiral ordering temperature T_{spiral} we used different cooling rates during the sample preparation, faster cooling resulting in more disorder. By quenching the sample from 1150 °C into liquid nitrogen we managed to double T_{spiral} and push it above room temperature, see also Fig. 3 [18].

RT spirals from random frustrating bonds

The emergence of a stable spiral phase without any obvious source of magnetic frustration, and the positive impact of increasing chemical disorder on its ordering temperature T_{spiral} was very puzzling. Motivated by this challenge, theoreticians in the Materials Theory group (ETH Zürich) and the Condensed Matter Theory group (Paul Scherrer Institut) figured out that the introduction of small amounts of Cu/Fe disorder results in dilute, randomly distributed Fe-Fe pairs in the bipyramids normally occupied by Cu-Fe pairs (Fig. 2a). They also remarked that their exchange coupling (green thick bonds in Fig. 4) is opposite in sign and much stronger than that of both, the predominant Fe-Cu pairs (red thin bonds), and the few, extremely weak Cu-Cu (blue dashed bonds) required to preserve the charge neutrality [20-21].

The strong Fe-Fe defects frustrate the collinear order prevailing in their absence. The degree of chemical disorder thus tunes the frustration in the material. The Fe-Fe coupling is so strong that it imposes a near antialignment of the two Fe spins, to which the surrounding spins adjust by forming a local canted pattern. In a fixed collinear background, assuming the spins to remain in their easy plane, there are two energetically equivalent ways for the Fe pair to cant, which constitutes a binary (Ising) degree of freedom associated to every defect. The cantings of two defects interact with each other as their respective distortions interfere. This results [20-21] in an effective dipolar interaction whose typical strength is proportional to the density of Fe-Fe defects. At a temperature T_{spiral} of this scale, the cantings of different defects start to align and establish long range order, like in a dipolar Ising ferromagnet, except that here order occurs with respect to the sense of canting at the
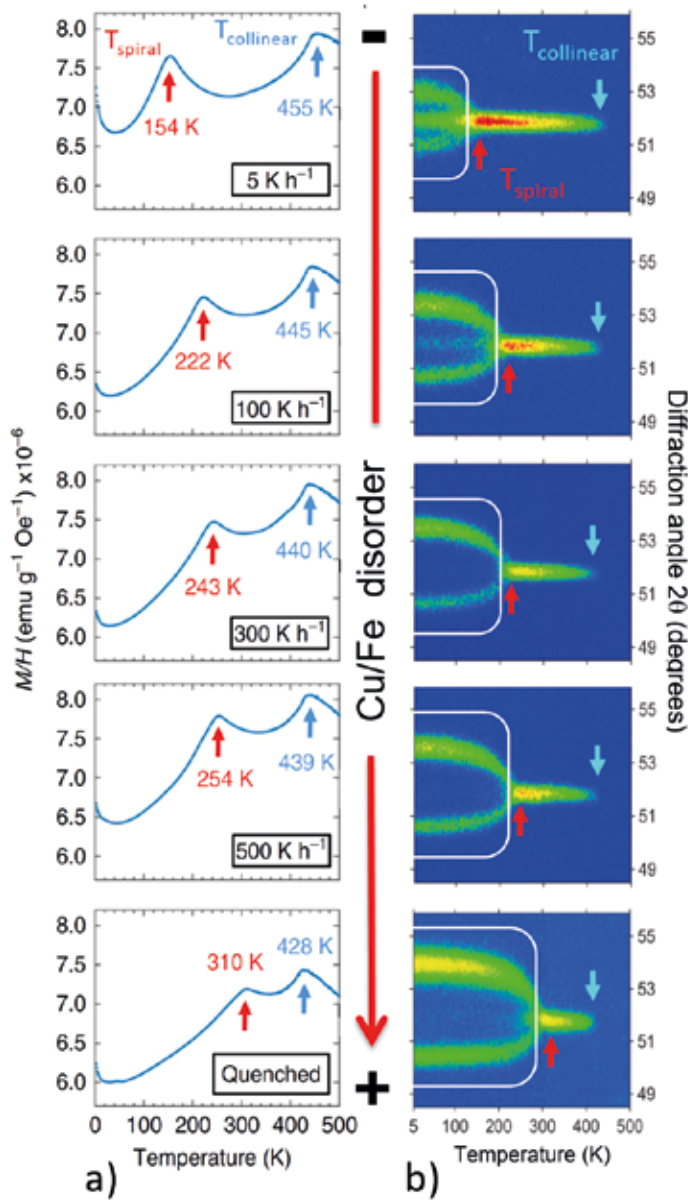
Figure 3. Evolution of the collinear and spiral ordering temperatures in YBaCuFeO$_5$ by increasing the degree of Cu/Fe chemical disorder, as manifested in magnetic susceptibility (a) and the neutron powder diffraction patterns (b), where the stability region of the spiral is indicated by the white lines. The figure highlights the increase of the spiral ordering temperature T$_{spiral}$ (red arrows) by enhancing the Cu/Fe disorder in the structure. The vertical axis in (b) corresponds to the diffraction angle 2θ [18].

that a modest density of 4 - 5 % of Fe-Fe defects suffices to obtain spirals at RT (Fig. 5b).

Note that higher q_{spiral} implies bigger spin twists ($\mathbf{S}_i \times \mathbf{S}_j$) for ($\mathbf{r}_i$ - $\mathbf{r}_j$) along the **c**-axis. Moreover, a larger defect density turns out to enhance the angle between, ($\mathbf{r}_i$ - $\mathbf{r}_j$) and ($\mathbf{S}_i \times \mathbf{S}_j$), too. Both effects increase the electric polarization associated with the formation of the magnetic spiral, which is thus expected to grow faster than linearly with defect density and may become appreciable in the samples with the most stable spirals.

Manipulating and Optimizing Multiferroicity

To gain insight into the role of various magnetic couplings, we used targeted chemical substitutions in the families YBa$_{1-x}$Sr$_x$CuFeO$_5$ and REBaCuFeO$_5$, as replacing Y^{3+} or Ba^{2+} by isovalent cations of different size allow us to tune the interatomic distances and thereby the magnetic exchanges. The obtained $T_{collinear}$ and T_{spiral} , together with those obtained by tuning the Cu/Fe disorder in YBaCuFeO$_5$, are shown in Fig. 6 [19]. This strategy enabled us to reach T_{spiral} values close to 400 K, almost 100 K higher than using Cu/Fe disorder alone, and well above RT.

These results are promising in view of potential applications. The most important effect of chemical substitution consists in modifying the inter- and intra-pyramidal spacing along the **c**-axis, denoted d_1 and d_2 in Fig. 2a, respectively. As anticipated, the smaller the ratio d_2/d_1 the higher is T_{spiral}, since a small d_2 enhances the frustrating coupling on Fe-Fe defects. This is achieved either by increasing the ionic radius of the element RE, or the Sr content, see [19] and Fig. 5c. Further, as theoretically predicted [20-21], T_{spiral} and the low temperature spiral wavevector q_{spiral} are proportional to each other, cf. Fig. 5, their ratio depending only weakly on the studied family, in good agreement with theory (Fig. 5b shows the effect of varying only the coupling J_{imp} between Fe-Fe pairs, while in reality any modification affects all couplings). Combining experimental data and theory suggests that the Sr-doped material produces the same T_{spiral} with a smaller concentration of defects, and can therefore be pushed to more stable spiral phases upon using the same annealing protocols [19-21]. Preliminary investigations suggest, however,
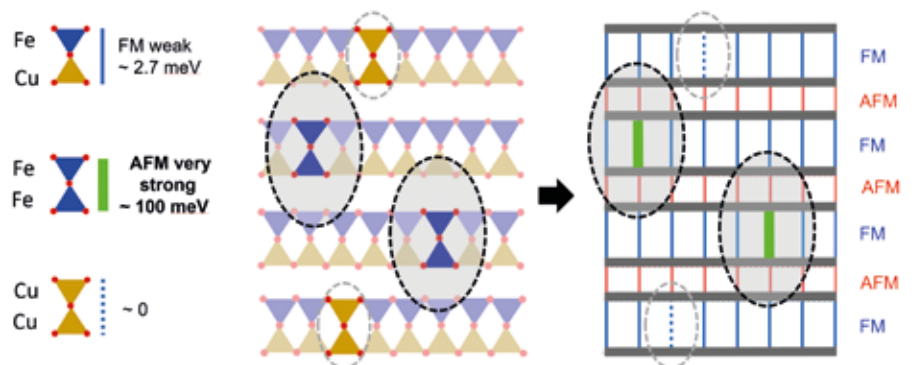
Fe-Fe pairs. Every defect canting favors the collinear background to rotate along a bit. Therefore, once all Fe-Fe pairs cant in the same sense, they collectively induce a global spiral. Rather naturally the spiral wavevector q_{spiral} is proportional to the density of the defects that drive it. Since both T_{spiral} and q_{spiral} are proportional to the defect density, their ratio will be *independent* of it. This non-trivial prediction [20-21] is indeed confirmed by the experimental data (cf. Fig. 5a) [19, 21]. Even the ratio agrees very well with the theoretical prediction based on ab initio calculations for coupling strengths and on a statistical mechanics analysis of the spiraling transition (Fig. 5b). The theory allows us to estimate the defect density of a given sample from its T_{spiral}. It turns out

Figure 4. Schematic representation of the Cu-Fe chemical disorder in YBaCuFeO$_5$. The impact of a few strong, randomly distributed AFM Fe-Fe "defects" is illustrated by the gray ellipses, which delimit the regions where the Cu-Fe spins lose their collinearity. Thinner bonds represent weak AFM or FM couplings, while thicker bonds indicate strong AFM couplings. The cross-talk of these regions eventually gives rise to a spiral. While an equal number of weakly interacting Cu-Cu "defects" is present to preserve the material's stoichiometry, they do not drive the spiral formation. The exchange constants are quoted from Scaramucci et al [20].
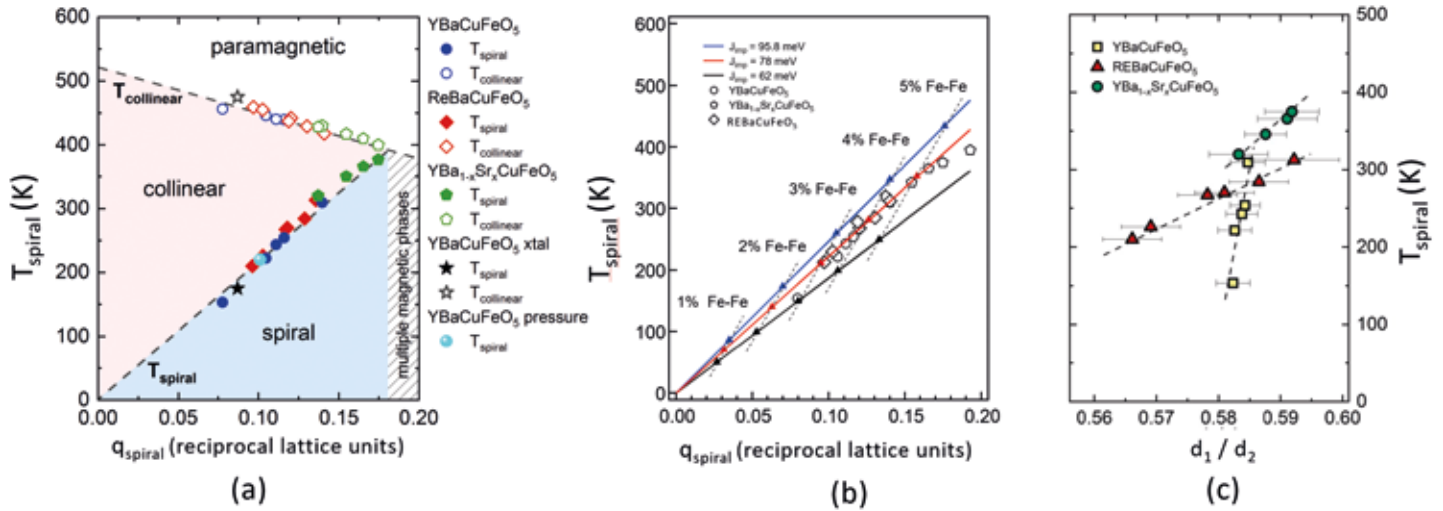
Figure 5. **a:** *Correlation between T_{spiral} and q_{spiral} in three families of AA′CuFeO$_5$ layered perovskites: YBaCuFeO$_5$ prepared with different cooling rates [18], REBaCuFeO$_5$ with RE = Lu to Dy [19], and YBa$_{1-x}$Sr$_x$CuFeO$_5$ with $0 \leq x \leq 0.4$ [19]. The $T_{collinear}$ values of all samples (open symbols) are also shown to illustrate its approach toward T_{spiral} at $q_{spiral} \sim 0.18$.* **b:** *Comparison between theory and experiment [21]. We plot the predicted slope for different values of the exchange on the strongly frustrating Fe-Fe bonds, fixing the other exchanges to the estimates in [20]. The larger the frustrating coupling and the higher the fraction of frustrating Fe-Fe bonds in the bipyramids of the perovskite, the larger the transition temperature and the spiral wave vector. Each triplet of triangular symbols joined by a dashed line corresponds to the same concentration of frustrating bonds in our theory.* **c:** *Variation of T_{spiral} with the d_1/d_2 ratio for the three main layered perovskite families investigated.*

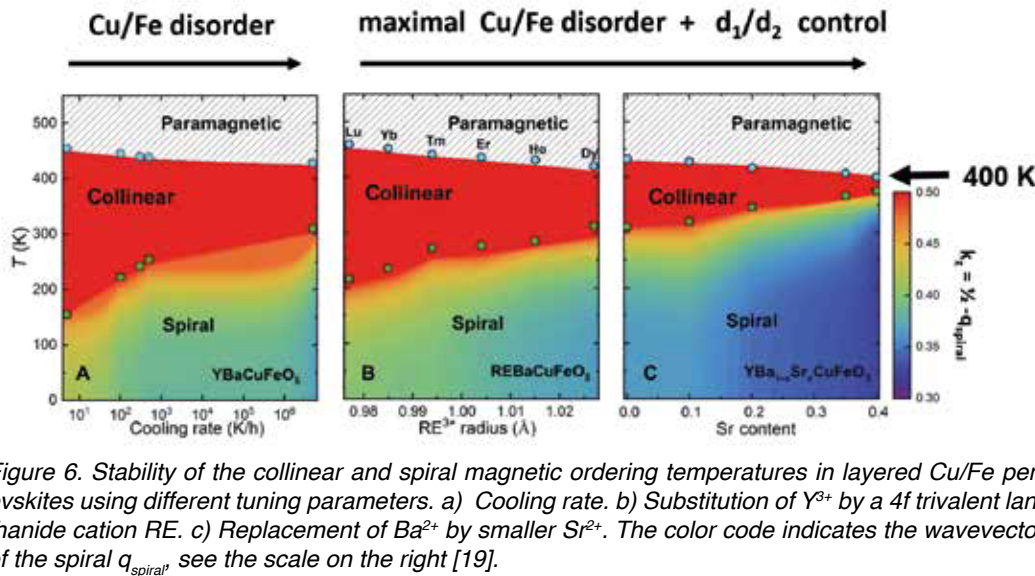*Figure 6. Stability of the collinear and spiral magnetic ordering temperatures in layered Cu/Fe perovskites using different tuning parameters. a) Cooling rate. b) Substitution of Y^{3+} by a 4f trivalent lanthanide cation RE. c) Replacement of Ba^{2+} by smaller Sr^{2+}. The color code indicates the wavevector of the spiral q_{spiral}, see the scale on the right [19].*

Note that the idea to introduce a controlled dose of frustration and thereby tune desired properties of an ordered phase may well have a broader scope than the magnetic materials discussed here. It could be realized in different types of magnets as well as in superconductors, whose pairing phase is analogous to that of XY spins. In that case frustration-driven spiraling of the phase implies a spontaneous supercurrent.

that at higher defect densities the spiral phase gives way discontinuously to a differently ordered phase, so that the spiral ordering temperature is probably limited from above by ~ 400 K in these Cu-Fe-based layered perovskites [19].

Conclusions and Outlook

In the family of layered Cu/Fe perovskites frustration is introduced through chemical disorder: the more disorder, the larger is the stability range of the resulting magnetic spiral order. The simple knob of cooling speed allows to tune the degree of frustration and adjust it such as to induce an inversion-symmetry breaking ordered state susceptible to induce ferroelectricity. These findings, revealed through a close collaboration between experimental and theory teams, suggest that chemical disorder may be a promising route for the design of other spiral magnets with magnetoelectric properties beyond room temperature, contributing to the progress towards the future use of these materials for technological applications based on the magnetoelectric effect.

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Progress in Physics (80)

Advanced Niobium-Tin superconductors for the Future Circular Collider

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The search for new physics beyond the Standard Model is driving the High Energy Physics (HEP) community to conceive novel experiments based on a highest-energy hadron collider with a centre-of-mass collision energy of 100 TeV [1]. One of the main challenges in view of this Future Circular Collider (FCC) is the development of high-field superconducting accelerator magnets. Assuming a ring circumference of 100 km, the dipole field needed to reach 100 TeV must be about 16 T (the energy at the collision is given by $E[TeV] = 3 \cdot 10^{-4} \cdot B \cdot R$, where B is the intensity of the magnetic field and R is the radius of the ring, both in SI units). Such a field level is about twice that of the Nb-Ti magnets installed in the Large Hadron Collider (LHC), which represent the end-of-the-line in terms of performance of accelerator magnets based on this material. Nb_3Sn is the superconducting material poised to take the place of Nb-Ti as the next step in accelerator magnet technology. High temperature superconductors (HTS) also have promising properties, with high in-field critical current density that indicate the potential for 20 T-range accelerator magnets. However, FCC would require superconducting materials in massive quantities, an estimate of 10000 tons in a time frame of 30 years. Even if we extrapolate with optimism the present industrial capabilities of about 1 ton/year, HTS cannot represent a credible option. Over the last two decades, high-field Nb_3Sn magnet technology has made great progresses thanks to the ITER conductor development [2] and various R&D programs funded by the European Commission and the US Department of Energy [3,4]. The first milestone for Nb_3Sn applications in HEP research programs will be achieved with the installation of the Nb_3Sn dipole and quadrupole magnets built for the High-Luminosity upgrade of the LHC (HL-LHC) at CERN [5]. These will be the first Nb_3Sn magnets ever operating in a particle accelerator and thus represent an important test bench in the perspective of the FCC developments.

A field of 16 T in a dipole configuration translates into a requirement of a minimum critical current density, J_c, of more than 1500 A/mm^2 at 16 T and 4.2 K [6], which is a target currently beyond state-of-the-art for commercial Nb_3Sn wires [7,8]. The work reported here is motivated by the need to push Nb_3Sn technology towards its ultimate performance in view of achieving and exceeding the requirements of the FCC study. The in-field critical current capabilities for any type-II superconductor rely on its ability to impede vortex motion, i.e. to pin the vortex lines into the material. This ability is given by the presence of the so-called pinning centers, features in the material that interact attractively with individual vortices. Grain boundaries represent the primary pinning centers in Nb_3Sn: higher current densities are thus obtained in materials that have finer grains. In the present day high-performance wires, Nb_3Sn has average grain sizes of typically 100 - 200 nm [9,10]. The Group of Applied Superconductivity at UNIGE is working in close collaboration