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Recent neutron results on magnetic superconductors and related systems

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Abstract

We briefly summarize the presentation at the conference discussing our recent neutron scattering results on magnetic superconductors. We give some historical perspective, and then focus on the coexistence and competition between the magnetic and superconducting order parameters in the cuprate superconductors. We also discuss our very recent work on the Na_xCoO_2 system, where the Co ions carry $S = \frac{1}{2}$ as in the square–planar cuprates, but with the Co ions occupying a triangular lattice.

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1. Introduction

The behavior of magnetic spins in superconducting systems has had a rich and interesting history [1,2]. Initially, magnetic impurities substituted into a superconductor were found to quickly suppress superconductivity due to the strong spin scattering that disrupts the Cooper pairs, with typically ~1% substitution being enough to completely extinguish the superconducting state. Such small concentrations of magnetic moments precluded the possibility of cooperative magnetic states forming and competing with the superconducting order parameter. The first exception to this behavior was realized for the $(Ce_{1-x}{-}R_x)Ru_2$ system, where over 30% of non-magnetic Ce^{4+} could be replaced by the magnetic heavy lanthanides before superconductivity was suppressed. Strong ferromagnetic correlations were found to develop in the superconducting state, but no long-range order was present [3]. The first examples of true long-range magnetic order coexisting with superconductivity were provided by the ternary Chevrel-phase superconductors (RMo_6S_8) and related (RRh_4B_4) compounds [2]. In these materials there is a separate, fully occupied lanthanide sublattice, and the fact that

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these materials were superconducting at all suggested that the magnetic ions and the superconducting electrons must belong to different, "isolated" sublattices. The magnetic ordering temperatures were all low ($\sim$1 K), indicating that dipolar interactions dominate the magnetic energetics. For antiferromagnets the magnetization averages to zero on the length scale of a unit cell (a), which results in a weak influence on the superconducting state ($a << \xi,\lambda$), and the antiferromagnetic order and superconductivity were found to readily accommodate one another. In the rare and more interesting situation where the magnetic interactions are ferromagnetic, there is strong coupling to the superconducting state that originates from the internally generated magnetic field, and the competition with the superconducting order gives rise to long wavelength oscillatory magnetic states and/or reentrant superconductivity [2,4–6].

The cuprate superconductors offer new and interesting perspectives into our understanding of "magnetic superconductors" for a number of reasons. Many of the rare-earth ions order at low temperatures and behave as conventional "magnetic superconductors", but some magnetic ordering temperatures (e.g. Sm in Sm_2CuO_4 [7] or Ru in $RuSr_2GdCu_2O_8$ [8]) are much too high to be explained by dipolar interactions, and it has become clear that R–R exchange interactions actually must play a dominant role in the magnetism [9], as is also clearly the case for the new RNi_2B_2C class of superconductors [10–12]. Moreover, one of the most interesting aspects of the cuprates concerns the magnetism associated with the $S = \frac{1}{2}$ Cu ions, where quantum fluctuations are maximal [13] and are now thought to be intimately intertwined in the d-wave superconducting pairing. We have thus come full circle, from the early days when magnetic impurities were extremely detrimental to the superconducting state, to the cuprates where the spin fluctuations appear to play an essential role in high-temperature superconductivity.

2. Field-induced magnetic order in the cuprates

The undoped "parent" cuprates are Mott insulators where the strong copper–oxygen bonding within the layered crystal structure renders the magnetism two-dimensional in nature, with an exchange interaction within the layers that is much stronger than between the layers and typically an order-of-magnitude more energetic than the lattice dynamics. The $S = \frac{1}{2}$ Cu^2 spins order at relatively high temperatures ($\sim$250–500 K) in a simple antiferromagnetic (AF) structure that doubles the crystallographic unit cell in the CuO planes. Superconductivity occurs when holes (e.g. in $La_{2-x}Sr_xCuO_4$) or electrons (e.g. $Nd_{2-x}Ce_xCuO_4$) are doped into the CuO planes. In the latter electron-doped materials, AF order persists to much larger x ($\geqslant$0.12) compared to the hole-doped materials and coexists with superconductivity for even the highest T_C (=25 K) materials ($x = 0.15$). In contrast, superconductivity in the hole-doped systems emerges from a spin-glass regime and occurs over a much wider composition range.

Superconductivity in the copper oxides is a subtle phenomenon that competes with other possible quantum ground states, and the close proximity of AF order to the superconducting state raises the interesting question concerning the possible role of magnetic order and spin fluctuations in the superconductivity of cuprates. Given the delicate balance of interactions in these highly correlated electron systems, it would be particularly helpful in developing an overall description of the physical properties to determine the nature of the energetically closest competing ground state, and establish if that state is the same for all the cuprates. Magnetic field provides a simple tuning parameter to suppress the superconductivity, and theoretically it was predicted that when an applied field creates vortices in these superconductors AF order would be induced in the core of each vortex [14]. Indeed, neutron diffraction experiments in doped La_2CuO_4 found that the static incommensurate spin density wave order was enhanced in field, suggesting that such order competes directly with superconductivity [15–17].

One experimental difficulty with investigating the hole-doped superconductors is the enormous upper critical fields, while the electron-doped materials generally have upper critical fields (for fields along the c-axis) less than 10-T [18–20], which are accessible in neutron scattering experiments. For $(Nd–Ce)_2CuO_4$, in particular, the magnetic structure is the usual antiferromagnetic configuration in-plane, but is non-collinear between planes [21]. The Nd spins are weakly coupled to the Cu spins and tend to "dress" them with a relatively large moment, making their behavior much easier to observe [22]. Field-dependent measurements on high-quality single crystals of $Nd_{1.85}Ce_{0.15}CuO_4$ reveal that the induced AF moment increases approximately linearly with field up to B_{c2} and then decreases for higher fields, indicating that the field-induced AF order competes directly with superconductivity [23–25] as for the hole-doped materials.

Although electron-doped $Nd_{2-x}Ce_xCuO_4$ offers a unique opportunity for studying the superconductivity-suppressed ground state of high-T_C cuprates, the system has one important complication. The as-grown material is non-superconducting, and has to be oxygen reduced to render the system superconducting. This reducing process has been found to produce a small quantity of impurity that has been identified as cubic $(Nd–Ce)_2O_3$. Generally a small amount ($\sim$0.01–0.1%) of impurity would be unobservable, but this phase is lattice matched to the *a–b* plane of the cuprate and grows epitaxially [26], giving structural impurity peaks that match some of the magnetic peaks (such as $(\frac{1}{2},\frac{1}{2},0)$). In the paramagnetic state of $(Nd–Ce)_2O_3$ a field induces a net magnetization, which can then contaminate the intensity of the cuprate magnetic peak such as $(\frac{1}{2},\frac{1}{2},0)$. This issue can be resolved in three different ways. Since the impurity and cuprate peaks are not lattice matched along the *c*-axis direction, the impurity peaks can be measured separately and then the cuprate signal can be corrected (a correction of $\sim$20%). The second course of action is to measure magnetic peaks in the cuprate that are not lattice matched, such as $(\frac{1}{2},\frac{1}{2},l)$ where $l \neq 0$ [23–25,27]. Both procedures show unambiguously that there is a field-induced moment in electron-doped $(Nd–Ce)_2CuO_4$, whose behavior is similar to that observed in the hole-doped systems. Our experiments therefore indicate that antiferromagnetic order (accompanied by insulating behavior) is the competing ground state in $(Nd–Ce)_2CuO_4$. Third, measurements on $(Pr–Ce)_2CuO_4$, where the Pr ion does not carry a significant moment in either the impurity or the cuprate [28,29], also reveal an induced AF moment [29,30].

The data for both hole-doped and electron-doped systems indicate that an induced AF order, particularly in the underdoped materials, is universal in the high-T_c copper oxides. These experimental observations, however, do not unambiguously answer the question of whether this antiferromagnetism is central to the superconducting pairing. The observed induced moments are quite small in size, and it is not unambiguous whether they occur uniformly throughout the bulk. The importance of these questions and the difficulty of the experiments assures that this will be an active area of research until the issue is resolved.

3. Structure and dynamics of the sodium cobaltates

Cobalt oxide systems are now a focus of materials researchers because of their interesting magnetic and thermoelectric properties, as well as for possible analogies to colossal magnetoresistive manganite materials or high superconducting transition temperature cuprate oxides. For the Na_xCoO_2 system of particular interest here, the spin entropy has been found to play an essential role in the dramatically enhanced thermopower for large sodium content ($x \sim 0.7$) [31], while the recent discovery of superconductivity in hydrated Na_xCoO_2 has been of particular interest with regard to the superconducting cuprates [32]. This is a layered system where the Co^{4+} ions are in the low-spin state and carry $S = \frac{1}{2}$ so that quantum effects are maximal, while the underlying lattice is triangular rather than square like the cuprates. These observations suggest that this may be the first new class of "high-T_C" superconductors since the discovery of the cuprates over 18 years ago, but of course the nature and mechanism of superconducting pairing is in the early stages of being addressed. The appropriate underlying model may be a Mott insulator in two-dimensions, with $S = \frac{1}{2}$ where quantum fluctuations are optimal. The Co spins would then play a critical role in forming Cooper pairs that might have triplet symmetry as in Sr_2RuO_4 or d-wave symmetry as in the cuprates. On the other hand, the traditional electron–phonon interaction may be establishing conventional s-wave pairing, with the possibility that the anharmonic motion of the hydrogen and oxygen ions might be playing a role in enhancing the superconducting properties, in a manner similar to MgB_2 [33]. In recent studies, we have investigated the crystal structure of Na_xCoO_2 as a function of doping x, and related the structure to the observed physical properties [34–36]. We have also determined the lattice dynamics for the superconducting hydrate, and compared the behavior with the related non-superconducting $Na_{0.3}CoO_2$ compound [37].

Each Na ion nominally donates an electron to the CoO_2 plane, but the phase diagram and the behavior of the Na is much more complicated than this simple picture would suggest. In particular, the Na ions occupy two different sites over a wide range of x, while the CoO_2 layer is structurally robust. The system is a paramagnetic metal for $x<1/2$, with both the Na(1) and Na(2) sites being partially occupied, and the Na(2) being further split into a threefold site that is again randomly occupied [35]. This is designated the H1 structure. At $x=\frac{1}{2}$ the system exhibits a special charge and orbitally ordered structure that is insulating, with the Na ions occupying ordered positions that form one-dimensional zigzag chains [34]. For $x>\frac{1}{2}$ the system returns to the H1 structure and is a Curie–Weiss metal [35]. Around $x\sim\frac{3}{4}$ the Na structure transforms to the more ordered H2 structure, where the randomness in the Na(2) site is absent. This transition can also be driven thermally, where we observe the quite unusual behavior of transforming from an ordered state at low T to a randomly occupied threefold degenerate site at elevated T [36]. This transition is first-order in nature in both temperature and composition. Finally, with further increase of the Na composition we realize the H3 structure, where the Na(2) site is fully occupied and the Na(1) is completely vacant [35]. The transition from the H2 to the H3 structure as a function of composition is also discontinuous in nature.

One of the amazing characteristics of this system is the discovery of superconductivity when the material is hydrated. Initially water goes into the Na layer, but then the water forms its own layer between the Na and CoO_2 layers, with the c-axis expanding from 11.2 to 19.5 Å and the material becoming a 5 K superconductor. Both the structure and lattice dynamics indicate that this separate water layer has the basic structure of ice [37]. It is noteworthy that the structure of the Na is different than in the parent compound, with the Na shifting to the other side of the unit cell to accommodate the water. A central question is whether the water is playing an active role in the superconducting pair formation, or is simply expanding the lattice and making the system more two-dimensional in nature. So far, however, only water has been found to render the system superconducting.

The present work has elucidated the basic crystal structure for the Na_xCoO_2 and superconducting systems, and determined the changes in the bonding and structure as the electron count is varied. The results suggest that conducting triangular lattice systems exhibit their own type of structural and electronic phases that are distinct from square-planar systems like the cuprates, providing a rich new variety of physical phenomena to explore for both fundamental and technological purposes.

4. Summary

In this brief article, we have presented some of the highlights of recent work carried out primarily at the NIST Center for Neutron Research, focusing in the area of magnetic superconductors and the related Na_xCoO_2 oxide materials. Details can be found in the references. These are very active areas of research and there are of course many groups working on these materials, and this short article was not intended to review this work and cannot provide a balanced perspective. We note that a detailed review of the magnetic properties of the cuprates is presently in preparation [38].

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