Relevance of magnetism to cuprate superconductivity: Lanthanides versus charge-compensated cuprates

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We address what seemed to be a contradiction between the lanthanide series REBa$_2$Cu$_3$O$_y$ (RE123) and the charge-compensated series (Ca$_x$La$_{1-x}$)$_{(Ba_1_{75-x}, La_0_{25+x})}$Cu$_3$O$_y$ (CLBLCO) regarding the superexchange ($J$) dependence of the maximum superconductivity (SC) critical temperature $T_{c\text{\,max}}(J)$; $RE$ and $x$ are implicit variables. This is done by measuring the Néel temperature and the temperature dependence of the magnetic order parameter for $RE = Nd, Sm, Eu, Gd, Dy, Yb, Y$, and for $Y(BaSr)$Cu$_3$O$_y$, at various very light dopings. The doping is determined by thermopower and the magnetic properties by muon spin rotation. We find that the normalized-temperature dependence of the order parameter is identical for all RE123 in the undoped limit (with the exception of Gd123) implying identical out-of-plane magnetic coupling. The extrapolation of $T_N$ to zero doping suggests that, despite the variations in ionic radii, $J$ varies too weakly in this system to test the relation between SC and magnetism. This stands in contrast to CLBLCO, where both $T_{c\text{\,max}}$ and $T_{c\text{\,max}}$ vary considerably in the undoped limit and a positive correlation between the two quantities was observed.

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I. INTRODUCTION

Recently, the group of Tallon [1] measured the in-plane superexchange parameter $J$ in a series of samples similar to YBa$_2$Cu$_3$O$_y$, where $Y$ was replaced by one of the lanthanides: La, Nd, Eu, Gd, Dy, Yb, Lu, or the Ba$_2$ was modified to BaSr. The measurements were done using two-magnon Raman scattering. The samples were prepared with as low doping ($p$) as possible, although the actual value was not determined. They found that as one progresses in the lanthanide series and the atomic number increases, $J$ also increases. They justify this $J$ increase by the famous lanthanide contraction where the atomic radius becomes smaller as the atomic number increases. They also found anticorrelation between the maximum $T_N$ ($T_{c\text{\,max}}$) of each family of materials and $J$. The internal pressure (induced by substitution of isovalent ions of smaller size) seems to increase $J$ but decrease $T_{c\text{\,max}}$.

The RE123 result stands in strong contrast to experiments on the charge-compensated compound (Ca$_x$La$_{1-x}$)$_{(Ba_1_{75-x}, La_0_{25+x})}$Cu$_3$O$_y$ (CLBLCO) performed by the Keren group. The name “charge-compensated” comes from the fact that Ca and Ba have the same valance and their replacement does not formally dope the system. However, from the fact that Ca and Ba have the same valance and their doping suggests that, despite the variations in ionic radii, $J$ varies too weakly in this system to test the relation between SC and magnetism. This stands in contrast to CLBLCO, where both $T_{c\text{\,max}}$ and $T_{c\text{\,max}}$ vary considerably in the undoped limit and a positive correlation between the two quantities was observed.

measurements were done with muon spin rotation ($\mu$SR) [3], Raman scattering [4], angle resolved photoemission [5], and resonant inelastic x-ray scattering [6] and all methods agree qualitatively. The RE123 results are also in contradiction with external pressure experiments on Y123 as pointed out by Tallon and co-workers [1]. External pressure raises $T_{c\text{\,max}}$ and $J$ simultaneously.

An attempt was made to resolve the contradiction using new two-magnon Raman scattering measurements [7]. In this experiment only samples that are prepared under the same conditions, and with the doping determined by thermopower, were remeasured. It was found that within experimental uncertainty the $RE = Y, Dy, Gd, and Sm$ have the same two-magnon Raman peak frequency. The $RE = Nd$ has a peak at substantially lower energy than its counterparts. This indicates that at least among the first four superconducting families $J$ is not changing appreciably with lanthanide substitution.

In this manuscript we address the same discrepancy from the perspective of magnetic measurements. We apply the $\mu$SR technique to 27 samples with different RE compositions and doping, including the Y(BaSr)Cu$_3$O$_y$. The doping is determined from the thermopower Seebeck coefficient ($S$) [8]. For each sample we measure the Néel temperature ($T_N$) and the muon spin angular rotation frequency $\omega$ as a function of temperature. Since $T_N$ is set by both in-plane and out-of-plane coupling $J$, respectively, two measured quantities are required to determine both couplings. These quantities are $T_N$ and the order parameter $\sigma(T) = \omega(T)/\omega_0$, where $\omega_0$ is the muon spin rotation frequency at $T \to 0$ [3]. This type of analysis works best in the fully undoped case which is

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FIG. 1. Raw data of lightly doped samples. The \( \mu \)SR asymmetry as a function of time for different RE123 samples with Seebeck coefficient \( S \sim 350 \mu V/K \). The sample name, exact \( S \), and temperatures are written in the labels. Results from temperatures near \( T_N \) and deep in the ordered state are presented.

The RE123 and Y(BaSr)Cu_3O_y samples are prepared by solid-state reaction at ambient pressure [9]. Each sample is an agglomerate of single crystals of sizes up to 100 \( \mu \)m pressed into a pellet typically 10 mm in diameter and 1 mm thick. The doping of the crystals is set by argon annealing at \( T \sim 650 \) C, followed by quenching into liquid nitrogen. The doping is determined from the room-temperature thermopower Seebeck coefficient, \( S(290) \), measured on the same samples used for the \( \mu \)SR measurements prior to the beam time. The results from temperatures near \( T_N \), below \( T_N \), and high above \( T_N \), for several samples are presented in Fig. 1. The exact value of \( S \) is written in each panel. For all samples, apart from Gd123, there is a temperature high enough that the asymmetry does not relax on the time scale presented in the figure. In all cases the asymmetry develops a strong relaxation within a temperature range of 10 K below \( T_N \). In the Gd case the asymmetry increases its relaxation from a high temperature saturated value. A finite, temperature independent relaxation rate at high temperatures in samples containing Gd is ubiquitous (e.g., Ref. [11]). In all cases, at very low temperatures oscillations develop indicating an ordered state of the material with a site-average magnetic field at the muon site larger than its fluctuation from site to site. The oscillation frequency is similar in all samples. The signal from YBaSr indicates that only part of this sample is actually magnetic.

Raw data from the various RE123 systems with \( S \sim 350 \mu V/K \) are shown in Fig. 2. Again, the relaxation in the Gd case is not zero at high temperatures but it saturates. For all families, the relaxation increases over a narrow temperature range (relative to the \( T_N \)). At low temperatures asymmetry oscillations develop. The time-dependent \( \mu \)SR asymmetry \( A(t) \) data is analyzed with the function

\[
A(t) = A_N \exp(-\Delta t^\alpha) + A_m \exp(-t/T_{||}) + R \exp(-t/T_{\perp}) \gamma \cos(\omega t) \gamma].
\]

(1)

In this function \( A_N \) represents the nonmagnetic fraction of the sample and \( \Delta \) the relaxation rate of the muon spin in this part of the sample. \( A_m \) is proportional to the magnetic fraction of the samples. \( \alpha = 2 \) except for the Gd samples where \( \alpha = 1 \) above room temperature. \( \gamma = 1 \) apart from Gd and Sm where \( \gamma = 0.5 \) and 2 respectively provide the best fit. \( T_{||} \) and \( T_{\perp} \) are the muon spin
relaxation times in the direction of the local field at the muon site and perpendicular to it, respectively. The relaxation rate $\Delta$ varies between samples but is kept fixed in the fit for each sample. In principle $R$ should be 2 since there are two field components perpendicular to the muon spin compared to only one longitudinal component. In practice $R$ is a fit parameter. Also the total asymmetry should be shared at all temperatures. In practice it is shared for temperatures between 5 and 200 K and between 200 to 470 K separately. Finally, $\omega$ is the muon rotation frequency. It is set to zero when no oscillations are observed in the data, in which case $R$ is also set to zero and $T_N$ has no directional association.

The relevant fit parameters are depicted in Fig. 3. Panel (a) shows the magnetic fraction $A_m$ as a function of temperature for samples with $S \sim 350 \mu V/K$. A straight line is fitted to the sharp rise in $A_m$ and the point of abscissa crossing defines $T_N$. The value of $T_N$ varies between 385 and 435 K and is indicated next to each line. The sharpness of the phase transition also varies between families. The symbols in panel (b) show the temperature-dependent order parameter. Eu, Sm, Dy, and Y families have the same rate of order parameter reduction with increasing temperature. Gd has a smaller and Nd and YBaSr have higher reduction rates than the common one. $\sigma(T)$ is a measure of the magnetic coupling anisotropy. The smaller $\frac{d\sigma}{dT}$ at $T \to 0$ the more isotropic 3D-like is the magnetic system [12].

The solid lines in panel (b) are the self-consistent Schwinger-boson mean-field theory calculations [12] of $\sigma(\alpha_{\text{eff}}, T)$, where $t = T/J$, $\alpha_{\text{eff}} = \alpha_{y} + \alpha_{\perp}$, the $z$'s are the number of neighbors, $\alpha_{y}$ is the in-plane anisotropy, and $\alpha_{\perp} = J_{\perp}/J$. Since RE123 has two types of $J_{\perp}$, this parameter represents an average perpendicular coupling. More details are given in Ref. [3]. However, this model is valid for the Heisenberg Hamiltonian, and the samples presented in Fig. 3(b) are slightly doped. The analysis becomes more accurate as $S$ increases further.

Figure 3 panels (c) and (d) also present $A_m$ and $\omega/\omega_0$ but for samples with $S \sim 500 \mu V/K$. In this case the lowest value of $T_N$ is 400 K and therefore the spread in $T_N$ between different families is smaller. In addition, apart from Gd, all $\sigma(T)$ at $T \to 0$ nearly overlap and $\alpha_{\text{eff}}$ is on the order of $10^{-5}$. This result suggests that as the doping decreases the different families converge to the same magnetic behavior.

### III. Discussion

Our main results are depicted in Fig. 4. We present $T_N$ as a function of the thermopower $S$ in the lower abscissa for various RE123 families and Y(BaSr)Cu$_2$O$_y$; $S$ decreases with increasing doping and hence the reverse axis. For all families, $T_N$ increases with increasing $S$ (decreasing doping). For some of the families such as RE = Y, and Dy, a saturation is clearly reached which reflects the fact that for these families doping is not changing at these high thermopower values. In RE = Gd and Eu it is not clear if saturation has been reached. For RE = Yb, Sm, and Nd it is clear that saturation has not been reached, and if it was possible to extract more oxygen from the sample, $T_N$ could have increased. In all families $T_N$ never exceeds 450 K. This is particularly peculiar for the YBaSrCu$_2$O$_y$ where $J$ is larger by 10%, according to new
measurements, and according to the original measurements [1] in YBa$_{0.3}$Sr$_{1.5}$Cu$_3$O$_{y}$ by 50%, than in RE = Y. Therefore, $T_{N\text{max}}$ of YBaSrCu$_3$O$_y$ is expected to be higher than 495 K, which is not the case. The solid lines in the figure are guides to the eye. It is conceivable but not guaranteed that all these lines meet at $S \cong 700$, which would then correspond to zero doping. These lines suggest that $T_{N\text{max}}$ for all examined families may be identical. Assuming that (i) all lines flatten by $S \cong 700$, (ii) that at an estimated doping level $p \cong 0.02$, $T_N$ drops to zero, and (iii) that the relation between $S$ and $p$ is exponential, then we may convert $S$ to zero, and (iii) that the relation between $S$ and $p$ is exponential, then we may convert $S$ to zero, and (iii) that the relation between $S$ and $p$ is exponential, then we may convert $S$ to zero, and (iii) that the relation between $S$ and $p$ is exponential, then we may convert $S$ to zero.

A different way of looking at the same data is depicted in the inset of Fig. 4. Here we plot $T_N$ versus $T_{N\text{max}}$ for each SC family at two, roughly fixed $S$, namely fixed doping. The room temperature thermopower has been shown to be an excellent correlate of the doped hole concentration, $p$, in units of holes/Cu [8]. Closer to optimal doping and beyond, it is a highly sensitive and a precise measure of doping, but at very low doping it becomes increasingly uncertain as $p \to 0$. For this reason we bin our doping states separately for all examined families.

The inset shows data from the Raman measurements, also plotted on a full scale, but only for samples which are prepared under the same condition (ambient pressure) and measured by both Müllner [7] and Mallett [1]. Close examination of this data shows an anticorrelation between $T_{N\text{max}}$ and $T_{N\text{max}}$.
The doping. In particular, we focus on the Néel temperature and the reduction of the order parameter $\sigma = \omega/\omega_0$ as a function of temperature. It is possible (yet not essential) to extrapolate the data for each family to zero doping in a way where all the RE123 have the same magnetic properties. In particular, they have the same $T_N$. This is quite surprising considering the changes in unit cell parameters [14]. Similarly, within experimental errors all RE123 presented here have nearly identical $T_c^{\text{max}}$. Therefore, RE123 is not the system with which one would like to test the relation between superconductivity and magnetism. In contrast CLBLCO shows large variation in both quantities and indicates a positive correlation between magnetic properties and superconductivity.

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