Observation of spin freezing and relaxation at microwave frequencies in the spin ladder compound \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41} \)

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We report the observation of a frequency \((\omega)\) and temperature \((T)\) -dependent loss peak in \(\chi''\) and accompanying dispersion in \(\chi'\) from microwave \((2 - 18\,\text{GHz})\) measurements of the complex susceptibility \(\tilde{\chi}(\omega,T) = \chi' + i\chi''\) of \(\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41}\). We associate this phenomenon with a rapid decrease of spin disorder and corresponding spin relaxation rate, representing a “spin freezing transition” accompanying charge ordering which occurs at temperatures \(\sim 250\,\text{K}\) (for the \(x = 0\) compound). Our results enable direct quantitative measurements of the spin relaxation rate, and also display superconductivity.

The dynamics of the basic \(\text{Cu} - \text{O}\) building blocks of the high temperature superconducting cuprates is of great interest, as they may provide insights into the fundamental magnetic and superconducting interactions in these materials. To this end the synthesis of the structurally simpler but related chain / ladder compounds in these materials is of great interest, as they may provide insights into the functionality. These features are strongly temperature dependent in the microwave frequency range and are not observed in static (dc) magnetization or resistivity measurements. The cause of this is a rapid decrease of the spin-spin relaxation rate which is extracted from the data, and indicates a rapid decrease in spin disorder below approximately \(250\,\text{K}\) in the \(x = 0\) compound. The peak temperature decreases with \(\text{Ca}\) doping. This is a dynamic magnetic signature of the onset of charge ordering suggested by structural [12] and NMR measurements [15]. Additional magnetic relaxation processes due to holes at high temperatures and dimer formation at low temperatures are also observed. The precision microwave measurements, which have a dynamic range over several orders of magnitude, are thus a sensitive probe of electron spin relaxation in condensed matter systems.

Samples of \(\text{Sr}_{14}\text{Cu}_{24}O_{41}\), \(\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41}(x = 2, 8, 11.5)\), \(\text{Sr}_2\text{CuO}_2\) and \(\text{Sr}_2\text{CuO}_3\) were prepared by the floating zone technique [3]. These single crystal samples have been extensively characterized by a vast array of measurements: dc resistivity, ac and dc SQUID susceptibility, XRD, neutron scattering, high pressure studies, and numerous other techniques. All of these measurements are in good agreement with those reported in the literature and indicate single phase, high quality crystals.

The principal measurements reported here are carried out using a superconducting microwave cavity at \(10\,\text{GHz}\), with additional measurements at \(2\,\text{GHz}\) and \(18\,\text{GHz}\). These experiments have been extensively utilized previously for measuring a variety of materials, including superconducting cuprate, nickelate and borocarbide crystals. Typical samples were \(2 \times 2 \times 2 \,\text{mm}\) in size. The anisotropic response was studied by orienting the sample with the microwave magnetic field \(H_{\parallel}\) parallel to one of the \(a, b, c\) crystal axes. In all of the measurements, the sample was placed in maximum microwave magnetic field and in zero microwave electric field. The cavity parameters can be related to the sample microwave susceptibility \(\chi\) by: \(f(0) - f(T) + i\Delta f = a(\delta \chi'(T) + i\delta \chi''(T))\), where \(f(0)\) is the resonant frequency, \(\Delta f(T)\) is the width of the resonance, and \(a\) is a sample geometric factor. While the loss term \(\chi''(T)\) is measured absolutely, the technique yields changes \(\delta \chi'(T) = \chi'(T) - \chi'(0)\) in susceptibility with very high precision.

The microwave susceptibility \(\delta \chi'(10\,\text{GHz},T)\) and \(\chi''(10\,\text{GHz},T)\) versus \(T\) for \(\text{Sr}_{14}\text{Cu}_{24}O_{41}\) are shown in Fig. 1. The subscript \(c\) indicates that the microwave field \(H_{\parallel}||c\), i.e. parallel to the chains. Similar results were obtained on measurements of other crystal samples of this material. The most striking feature of the data is the rapid drop with decreasing \(T\) in susceptibility \(\chi''(10\,\text{GHz},T)\) below approximately \(200\,\text{K}\). This is accompanied by a relatively sharp peak in \(\chi'(10\,\text{GHz},T)\), with a peak temperature of \(T_{\text{peak}} \sim 170\,\text{K}\). It is worth noting that below the peak the absorption has dropped by nearly a factor of 100 between \(170\,\text{K}\) and \(100\,\text{K}\). Indeed the rapid decreases in susceptibility (\(\delta \chi'(T)\)) and large
absorption($\chi''_c$) can be easily mistaken for a (broad) superconducting transition.

Another striking aspect is a very strong frequency dependence. At 2GHz, the peak is shifted downward to $T_{p2GHz} \sim 152K$ while at 18GHz it is shifted upwards to $T_{p18GHz} \sim 189K$. The strong variation with frequency of the temperature dependence of $\delta\chi_c(f, T)$ and $\chi''_c(f, T)$ is shown in Fig.3. Due to differences in the techniques, the measurements at different frequencies are shown in arbitrary units.

It is important to note that similar features are not observed in static and low frequency measurements. dc SQUID susceptibility measurements shown in Fig.1 (inset, bottom panel) are consistent with those available in the literature and only indicate a gradual increase of the susceptibility with decreasing $T$. We have also measured the susceptibility at 1KHz and 3MHz and do not see these features. Thus the phenomenon seen in Fig.1 is observable only at high frequencies in the microwave spectral range.

We have carried out extensive measurements to check the validity of these remarkable results. Similar results were observed in 3 samples. In particular we have confirmed that these data cannot arise from a purely resistive (eddy-current) sample size effect, since the resistivity increases with decreasing $T$, while the observed $\delta\chi_c(10GHz, T)$ in Fig.1 can only be consistent with $\rho(T)$ decreasing with decreasing $T$. (The eddy-current contribution is relevant at high temperatures and is included in the analysis later). Taken together these checks confirm that the observed phenomenon is magnetic and due to the spin system.

Important insights can be gained by plotting the data as $\chi''_c$ vs. $\delta\chi_c$, as shown in Fig.4. This so-called “arc-plot” can be regarded as the magnetic equivalent of a Cole-Cole plot used in dielectric spectroscopic studies of liquids. However here we are varying temperature as a parameter rather than frequency. The data show a dominant relaxation process represented by the nearly semi-circular arc for most of the temperature 100K to 220K, above which temperatures another process dominates.

A close examination shows that the totality of our results can be expressed as $\tilde{\chi}_c(\omega, T) = \tilde{\chi}_{co}(\omega, T) + \tilde{\chi}_{c}\prime(\omega, T) + i \chi''_c(T)$, where $\chi_{co}(<< \tilde{\chi}_{c}\prime)$ represents a low temperature dimer contribution which is discussed later, $\tilde{\chi}_{c}\prime$ the loss peak and accompanying susceptibility transition in Fig.1 and Fig. 3, and $\chi''_c$, the high temperature relaxation which we attribute to the eddy-current contribution arising from the finite resistivity. (See Fig.1 top panel for the location in $T$ of these processes).

The eddy-current term due to the resistivity $\rho(T)$ can be written as $\tilde{\chi}_{c}\prime(T) = g(2a/\delta)$, where $g$ is a function of the ratio of the sample radius $a$ and the skin depth $\delta = (2\rho/\omega\mu_0)^{1/2}$. While the exact expressions depend on the sample shape, we have carried out careful numerical analysis and verified that the present data are in the limit $a << \delta$, where $\chi''_c \approx (2a/\delta)^2/20$. From the experimental data, we get $\chi''_c \sim 1.5 \exp(-\Delta_c/kT)$, which is consistent with an activated resistivity $\rho(T)$ with a gap value of $\Delta_c = 1200K$, and is hence in reasonable agreement with typical dc resistivity measurements. Note that in this regime $\chi''_c << \chi''_c$. The numerical estimates show that the $\chi''_c$ process leads to a peak at a much higher temperatures $>> 300K$, accompanied by a corresponding decrease in $\chi''_c$ at the same temperature.

Subtracting the $\chi''_c = 1.5 \exp(-1200/T)$ contribution leads to a nearly pure relaxation $\tilde{\chi}_{c}\prime$ as is evident from the arc plot in Fig.3 (bottom curve). We therefore analyze the results in terms of spin relaxation leading to a susceptibility $\tilde{\chi}_{c}\prime(\omega, T) = \Delta\chi_{\beta}(1 + i\omega\tau_c(T))$. (Although the data of Fig.3 do not lie exactly on a semi-circle, they are close enough to justify the use of a single relaxation time for convenience). As the relaxation time $\tau_c(T)$ changes with $T$, a loss peak occurs in the absorption at the temperature $T_p$ when $\omega\tau(T_p) = 1$, i.e. when the relaxation rate $(2\pi\tau(T_p))^{-1}$ crosses the measurement frequency $f$.

This is accompanied by a net change of the susceptibility $\Delta\chi_{\beta}$. The sharpness of the peak is determined by the rate of variation of $\tau_c$ with $T$. (Note that the peak in the measured $\chi''_c$ is at a different location than that inferred from $\chi''_c$ because of the contribution of the $\gamma$ relaxation).

The relaxation time $\tau_c(T)$ can be directly obtained from the data of Fig.1 as $\tau_c(T) = \omega^{-1}(\chi''_c(\omega, T)/\chi'_c(\omega, T))$. This is shown in Fig.4 as the relaxation rate $(2\pi\tau(T_p))^{-1}$ (T). The relaxation rate $\tau_c^{-1}(T)$ clearly drops dramatically in the vicinity of approximately 250K. The relaxation rate is due to spin-spin interactions and can therefore be related to a spin fluctuation rms field $H_s$ from the relation $\tau = (8\pi\mu_0 H_s)$. Thus the data in Fig.4 indicate a rapid slowing of spin fluctuations below 250K leading to a sharp drop in the relaxation rate. The phenomenon represented by Fig. 1 is very similar to the “spin freezing transition” that is seen in probes of spin dynamics such as NMR (e.g. ref. [22]) and $\mu$SR [23] but characterized there by lower (MHz) frequencies. A key feature of our present experiments is the much higher frequency range and the direct coupling to the electron spins.

There are several other experiments [15,14,12] which have observed anomalies in the vicinity of 200K in Sr$_{14}$Cu$_{23}$O$_{41}$. NMR and NQR experiments [12] reported that the $Cu^{3+}$ NMR signal splits into 2 peaks below $\sim 200K$, suggesting the occurrence of charge ordering. Neutron scattering experiments [14] have reported charge ordering at 50K eventually disappearing close to 300K. Cox et al. [12] interpret their synchrotron X-ray scattering results in terms of a charge-ordered model involving both dimerization between two next-neighbor $Cu^{2+}$ ions surrounding a $Cu^{3+}$ ion on a Zhang-rice singlet site comprised of a $Cu^{2+}$ ion and a hole on the surrounding O atoms, and dimerization between $Cu^{2+}$ ions, in the linear $Cu - O$ chains. Thus the NMR and synchrotron radiation experiments on Sr$_{14}$Cu$_{23}$O$_{41}$ are consistent with an ordered arrangement of $Cu^{2+}$ and Zhang-Rice singlets below approximately 300K. Such a spin ordering
reduces the spin susceptibility. However, our data shows that there is no static ordering, but only the a reduction in the rate of fluctuations of the spins.

Further insight into the microscopic origin of this phenomenon can be achieved by comparing with our measurements of $\chi''(10GH z, T)$ and $\chi''(10GH z, T)$ versus $T$ for $SrCuO_2$. This is shown in Fig.2. Although the magnitudes of the susceptibilities are a factor 10 lower in $SrCuO_2$, a weak peak is also observed, which is however not as sharp, indicating that the spin relaxation rate does not vary as strongly as in $Sr_{14}Cu_{24}O_{41}$, probably because of the smaller hole density, and the absence of any reported charge ordering. It is worth noting that static susceptibility measurements on $SrCuO_2$ do not show any features at this temperature $[3,4]$. Since a structural unit common to both is the zig-zag $CuO_2$ chain, the data suggests that this is the magnetic sub-unit that is dominant at these temperatures in both $Sr_{14}Cu_{24}O_{41}$ and $SrCuO_2$.

In the zig-zag chains in $SrCuO_2$ both $J_1$ (the 180° $Cu - O - Cu$ AFM interaction) and $J_2$ (the nearly 90° FM interaction) are present. In $Sr_{14}Cu_{24}O_{41}$ there is additional coupling ($J_3$) along the ladder rung. Competition between $J_1$, $J_2$ and $J_3$ could lead to frustration. The increase in the strength of the loss peak (Fig. 5) by orders of magnitude in $Sr_{14}Cu_{24}O_{41}$ could possibly be due to enhanced frustration, besides the increasing hole density, both leading to more dissipation. It has, recently, been suggested theoretically that the frustrated zigzag chain-ladder system possesses incommensurate spin correlations $[2]$. The present results (Fig. 5) suggest that incommensurate spin correlations in the zig-zag chains caused by frustration may also be responsible for the loss peak.

The above conclusion is further confirmed by measurements on $Sr_2CuO_3$ (Fig.3), which only possesses linear $Cu - O$ chains and is regarded as an ideal 1-D Heisenberg AFM. Here the microwave measurements show only signatures of the 3-D static AFM order below $TN = 5.5K$ $[1]$. At high temperatures in the vicinity of 160 – 300K the features discussed above in $Sr_{14}Cu_{24}O_{41}$ and $SrCuO_2$ are absent.

We have studied the systematics of $\chi(\omega, T)$ with $Ca$ doping (see Fig.4). Focussing on the peak in $\chi''(10GH z, T)$ for the present, we find that it is shifted to a lower temperature 140K in $Sr_{12}Ca_2Cu_{24}O_{41}$ with greatly decreased amplitude. It is further shifted to a very broad, weak peak at around 110K in $Sr_4Ca_8Cu_{24}O_{41}$. In $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ it is not visible and is perhaps overwhelmed by a low temperature ($\chi_{co}$) process. An extensive discussion of these results of the doping dependence, as well as extensive studies of anisotropy where the field $H_{ab}||b$ and $a$ axes in $Sr_{14-x}Ca_xCu_{24}O_{41}$ for $x = 0, 2, 8, 11.5$ will be provided in a detailed publication.

The extraordinary sensitivity of the superconducting cavity measurements enables us to see additional phenomena (which we call $\chi_{co}$) at low temperatures. This is evident from the semi-log plot in Fig.4(bottom panel), which reveals a low temperature feature in $Sr_{14}Cu_{24}O_{41}$ below about 100K. This temperature scale has been identified with singlet dimer formation in the $CuO_2$ chains with a spin gap value 140K, as has been observed in ac susceptibility and NMR/NQR studies $[3]$. As two neighboring $Cu^{2+}$ spins in the 1D chains couple antiferromagnetically to form a singlet, most of the $Cu^{2+}$ ($S=1/2$) spins among the comparable amount of $Cu^{2+}$ ($S=0$) ions will form dimers $[3]$. This mechanism has been used to explain the dc magnetic susceptibility $[3]$ and is likely to be responsible here also for the low temperature features in Fig.4, modified by frequency-dependent corrections. Note also that this is the first measurement of $\chi''(10GH z, T)$ and hence spin relaxation at these temperatures.

The present results show clearly the presence of spin relaxation mechanisms with time scales corresponding to the GHz frequency ranges. These results have a greater relevance to superconductivity in the cuprates since the presence of strongly $T$-dependent relaxation times is essential to understanding the microwave response of the cuprate superconductors $[3]$. The microwave measurements yield information on dynamics at short time scales $10^{-11}$ sec. and longer, comparable to NS but shorter than NMR and NQR ($10^{-7}$ sec.) and $\mu$SR ($10^{-8}$ sec.). Thus the present precision measurements are a new probe of spin dynamics in the form of a spin relaxation spectroscopy in quantum magnets and superconductors. This will also require further theoretical developments, such as microscopic calculations of $\chi''(\omega, T)$, to quantitatively describe the various interactions observed in the present work.

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FIG. 1. (Top) Microwave susceptibility $\delta \chi'_c(10\text{GHz}, T)$ and $\chi''_c(10\text{GHz}, T)$ versus $T$ for $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$. (Bottom) Semilog plot of the data in the top panel. The large dynamic range of the experiment is evident. Note the large drop in absorption, i.e. $\chi''_c$. This plot also shows the low $T \chi_{c\alpha}$ process below 100K. (Inset, bottom panel) dc susceptibility $\chi(10^{-3} \text{ emu/mole} - \text{Cu})$ which shows no features between 100K and 300K.

FIG. 2. $\delta \chi'_c(f, T)$ and $\chi''_c(f, T)$ versus $T$ for $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, at $f = 2, 10$ and 18 GHz. Note that the peak temperature is frequency dependent.

FIG. 3. $\chi''_c(f, T)$ vs. $\delta \chi'_c(f, T)$ at 10GHz using the data in Fig. 1. Note that temperature $T$ is the parameter that is varied. This is equivalent to a Cole-Cole plot used in dielectric spectroscopy. The plot shows a dominant relaxation labelled $\beta$ followed by another relaxation labelled $\gamma$ at higher temperature. The low $T \alpha$ relaxation is not visible on this scale. The bottom curve represents the data with the $\chi_{c\gamma}$ contribution subtracted out leaving a pure $\beta$ relaxation.

FIG. 4. Spin relaxation rate $1/2\pi \tau_{\beta}(T)$ vs. $T$ obtained from the data of Fig. 1.

FIG. 5. $\chi''_c(10\text{GHz}, T)$ versus $T$ for $\text{Sr}_2\text{CuO}_3$, $\text{SrCuO}_2$ and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$.
$\chi_c''$ vs $\delta \chi_c'$ for $10\text{GHz}$

- $\tilde{\chi}_{c\beta} + \tilde{\chi}_{c\gamma}$
- $\tilde{\chi}_{c\beta}$
$10\text{GHz}$
\( \chi_c \) vs. \( T (K) \)

- \( x = 11.5 \) for \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \)
- \( x = 8 \) for \( \text{SrCuO}_2 \)
- \( x = 0 \) for \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \)
- \( x = 2 \) for \( \text{Sr}_{12}\text{Cu}_2\text{O}_3 \)