Eur. Phys. J. B **13**, 417–420 (2000)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Rapid Note

An NMR approach to the superconducting regime of the spin ladder compound $Sr_2Ca_{12}Cu_{24}O_{41}$

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Received 21 October 1999

Abstract. ^{63}Cu–NMR experiments of Knight shift and relaxation time T_1 have been performed on the two-leg spin ladders of a $Sr_2Ca_{12}Cu_{24}O_{41}$ single crystal at several pressures up to the critical pressure P_c for the stabilization of a superconducting ground state. The data confirm the onset of low-lying spin excitations at P_c observed previously [Science **279**, 345 (1998)] and reveal a marked decrease of the spin gap under pressures above 20 kbar although a significant fraction of the spin excitations remains gapped at $P_c = 32$ kbar. A comparison between NMR and transport data under pressure suggests that the depression of the spin gap can be ascribed to an increase in the interladder exchange coupling, possibly mediated by the ladder-chain interaction along the *b*-direction.

PACS. 74.72.Jt Other cuprates – 74.25.Ha Magnetic properties

Introduction

The compound $Sr_2Ca_{12}Cu_{24}O_{41}$ is one of the rare examples in the vast cuprate family in which the superconducting ground state can be stabilized under pressure [1–3]. This peculiarity makes therefore the study of the approach to the superconducting regime *via* pressure experiments possible. The remarkable feature of the compound $(Sr/Ca)_{14}Cu_{24}O_{41}$ is the existence of Cu_2O_3 two-leg ladders running along the *c*-axis, *i.e.* two parallel Cu–O chains linked together by oxygen atoms with magnetic coupling between Cu^{2+} ions along rungs and legs being both of the same order of magnitude and much larger than the interladder coupling [4–6]. Consequently, in a first approximation, the ladders can be considered as isolated entities. This ladder structure is thus responsible for the absence of low-lying spin excitations, namely the existence of a spin gap due to the tendency of Cu^{2+} $(S = 1/2)$ ions on the same rung to form a spin singlet state at low temperature. The spin gapped structure survives the existence of a finite concentration of holes in the ladders, as suggested theoretically and also verified experimentally in the compound $(Sr/Ca)_{14}Cu_{24}O_{41}$ which comprises chemically doped ladders with a concentration of 0.06 hole per Cu in the Cu_2O_3 ladder of the parent compound $Sr_{14}Cu_{24}O_{41}$ [7].

The main interest of spin ladder superconductors lies in the theoretical prediction to observe superconductivity in the *d*-wave channel; a direct consequence of the spin gapped character of the magnetic excitations [8]. It has been recognized that the attempt to establish a link between the predicted theoretical superconducting phase of isolated ladders and the phase actually stabilized under high pressure in $(Sr/Ca)_{14}Cu_{24}O_{41}$, is one of the hottest challenges in the physics of strongly correlated low-dimensional fermions.

A previous study carried out on $Sr_2Ca_{12}Cu_{24}O_{41}$ [3] has concluded to the existence of low-lying spin excitations under high pressure conditions, *i.e.* $P = 32$ kbar, when superconductivity appears below $T_c \approx 5$ K. Consequently, it is of high importance to study how the transient domain between the spin gap regime and the situation with low-lying spin excitations develops under pressure. Recent NMR experiments at 17 kbar and inelastic neutron scattering experiments at 21 kbar have reported the observation of a spin gap which does not vary from that observed at ambient pressure [9–11].

Our work presents the results of a new study performed on $Sr_2Ca_{12}Cu_{24}O_{41}$ by high pressure NMR experiments, focusing on the pressure regime 20–32 kbar which is close to the critical pressure needed for the stabilization

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of superconductivity. Some preliminary measurements related to this study have appeared in [12].

Experimental

The experiments were carried out on the single crystalline sample of $Sr_2Ca_{12}Cu_{24}O_{41}$, grown by the travelling solvent floating zone method already used in a previous study [3].

^{63}Cu ($I = 3/2$) NMR measurements were performed at a fixed magnetic field of 9.3 T *via* a Fourier transform of the spin echo on the central transition (1/2, −1/2) using phase alternation techniques. The broad ^{63}Cu spectrum at low temperature was obtained by summing up the Fourier transforms of spin echo signals taken at different frequencies with a frequency increment such as $\Delta\nu_{\mathrm{in}} = n\Delta\nu_{\mathrm{res}}$ (where $\Delta\nu_{\mathrm{res}}$ is the resolution of the Fourier transformed spectrum) which is kept smaller than the FWHM of a single Fourier spectrum.

The magnetic shift of the ^{63}Cu–NMR line was determined using a simulation taking into account quadrupolar corrections to the Zeeman frequency in a second-order perturbation theory. For a magnetic field applied parallel to the b-axis of the sample, the resonance frequency of the central transition reads [13,14],

$$\nu_{(1/2,-1/2)} = (1 + K_{\mathrm{b}})\nu_{\mathrm{o}} + (\nu_{\mathrm{c}} - \nu_{\mathrm{a}})^2/12(1 + K_{\mathrm{b}})\nu_{\mathrm{o}} \quad (1)$$

where K_{b}, ν_{o} and $\nu_{\mathrm{c,a}}$ are the Knight shift, the Larmor frequency in a diamagnetic substance and the quadrupolar tensor components, respectively.

Following the determination of the quadrupole tensor in $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$, the second term in equation (1) amounts to about 42 kHz (400 ppm) with a negligible temperature dependence compared to the temperature dependence of the first contribution. The pressure dependence of the quadrupolar contribution is not easy to estimate. However, considering the 100 ppm change of the quadrupolar contribution at $B = 9.3$ T which is observed upon Ca substitution from $x = 0$ to $x = 11.5$ in $Sr_{1-x}Ca_xCu_{24}O_{41}$ [15,16] and the expected equivalence between the chemical pressure of Ca and the applied pressure, we can conclude that a change of the quadrupolar term exceeding 100 ppm is very unlikely under 32 kbar.

NMR data were obtained in a non magnetic high hydrostatic pressure cell. In order to take into account the slight field distortion generated by the tungsten carbide piston, the NMR signal from the RF coil was used as a field marker (known to be only weakly pressure dependent) [17]. All shift values reported in this work have been calculated relative to the ^{63}Cu resonance in a diamagnetic substance, namely $^{63}\nu_{\mathrm{o}} = {}^{63}\nu(\mathrm{met})/1.0023$, where $^{63}\nu(\mathrm{met})$ is the resonance frequency of copper metal.

The ^{63}Cu Knight shift consists of two contributions, the orbital $^{63}K_{\mathrm{orb}}$ and spin $^{63}K_{\mathrm{s}}$ contributions, which are both very anisotropic. Given the known anisotropy of the Knight shift, the situation $B \parallel b$ has been reached through a fine adjustment of the angular position of the pressure cell in the magnetic field.

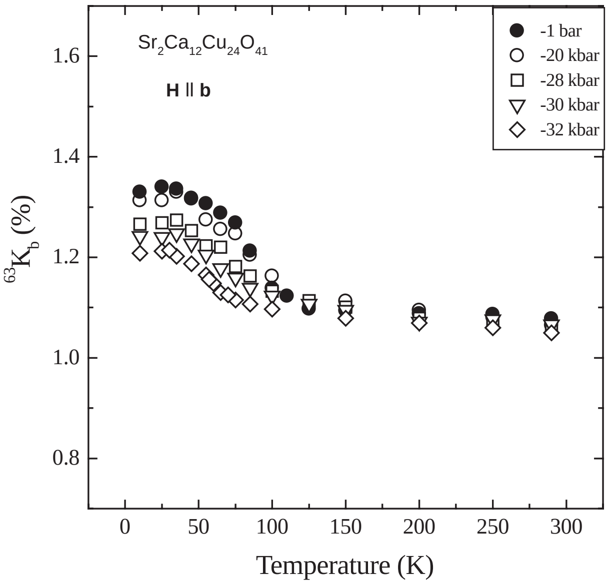

Fig. 1. Temperature dependences of the ^{63}Cu ladder nuclei Knight shift in $Sr_2Ca_{12}Cu_{24}O_{41}$ for $H \parallel b$ at different pressures.

Some measurements of the spin-lattice relaxation time T_1 have been performed by the saturation recovery method and will be presented more extensively in a forthcoming publication.

Results

Figure 1 shows the data of the ^{63}Cu Knight shift *versus* temperature at different pressures up to 32 kbar. The remarkable feature in Figure 1 is the very small pressure dependence of $K_{\mathrm{b}}(T)$ at $T > 150$ K as compared to the strong one which is observed in the low temperature regime. The Knight shift consists of two contributions K_{orb} and $K_{\mathrm{s,b}}$ which can both be pressure dependent while the orbital contribution is likely to be temperature independent. The published NMR study at 17 kbar has suggested the possibility of a slight decrease of the orbital shift under pressure [9]. However, according to the data presented in reference [9] we should have obtained a reduction of 0.11% of $K_{\mathrm{orb,b}}$ at $P = 32$ kbar. Our results of Figure 1, would thus impose the spin part $K_{\mathrm{s,b}}$ to be reduced by a factor of about two at room temperature and 32 kbar, an assumption which we find unlikely. Consequently, we have assumed the pressure dependence of $K_{\mathrm{orb,b}}$ to be negligible and the spin contribution reads then,

$$K_{\mathrm{s,b}}(P,T) = K_{\mathrm{b}}(P,T) - K_{\mathrm{orb,b}}(P = 1\ \mathrm{bar}). \quad (2)$$

The temperature dependence of the ^{63}Cu line position at ambient pressure leads to $K_{\mathrm{orb,b}} = 1.33\%$ assuming $K_{\mathrm{s,b}}$ (1 bar, O) to be zero at $T = 0$ in the spin gap regime, *vide infra*. The $K_{\mathrm{s,b}}$ data are displayed in Figure 2.

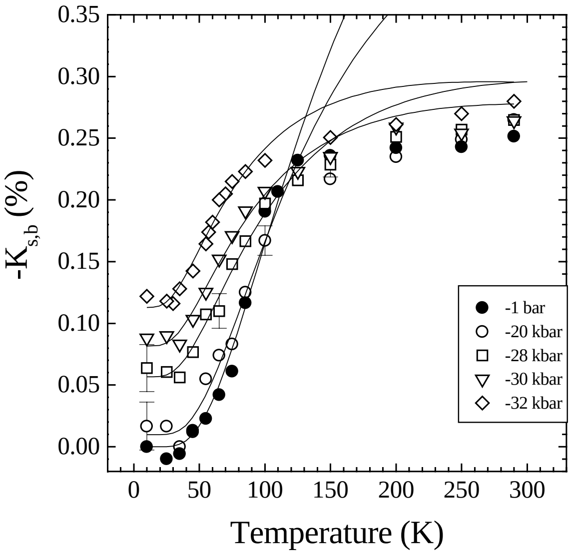

Fig. 2. T-dependences of the spin part of the ^{63}Cu Knight shift $K_{s,b}$. The lines are a fit to equation (3).

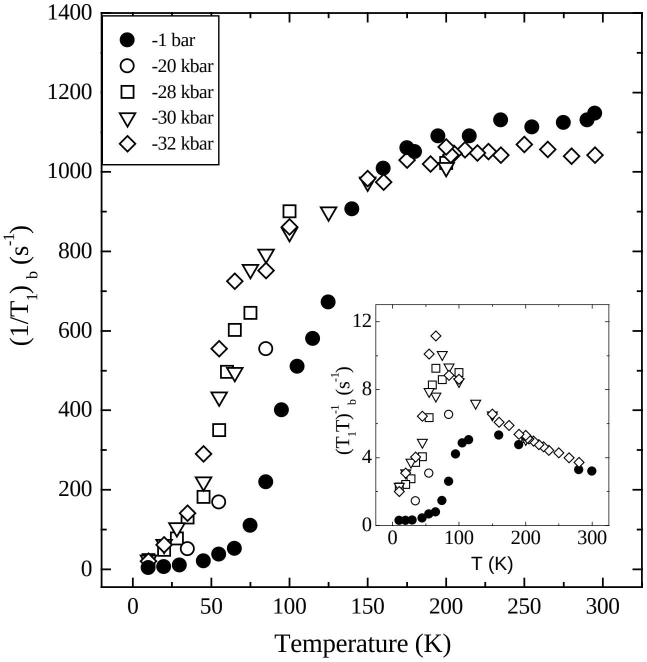

Fig. 3. Relaxation rate $^{63}\left(1/T_1\right)_b$ *vs.* temperature. In the insert, $(T_1T)^{-1}$ *vs.* T.

The temperature dependency of the spin-lattice rate is shown at various pressures in Figure 3 and plotted as $(T_1T)^{-1}$ *vs.* T (see inset). T_1 data have been extracted from the recovery of the magnetization using the theory of relaxation *via* magnetic hyperfine coupling for quadrupolar nuclei in metals [18].

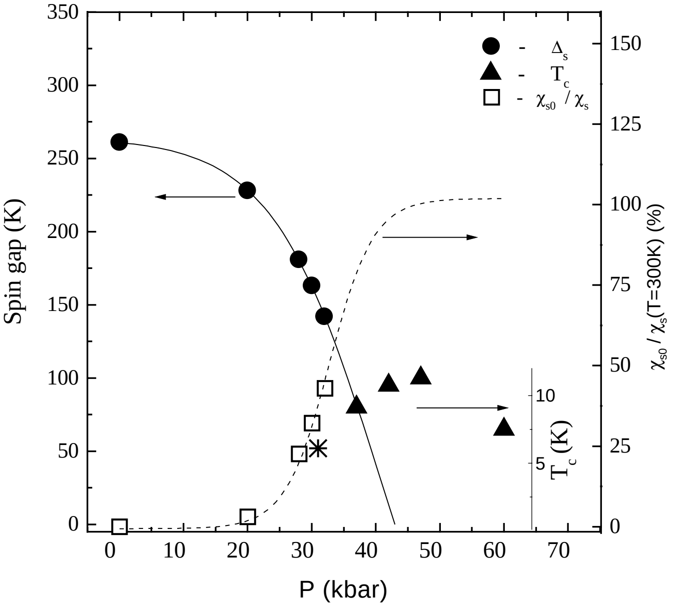

Fig. 4. Pressure dependence of the spin gap Δ_s (●), the residual spin susceptibility $\chi_{so}(P)$ (□) and the superconducting transition temperature, T_c, for $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ (▲) [2] and for $Sr_2Ca_{12}Cu_{24}O_{41}$ ($\star$) [3,12].

Discussion

The temperature dependence of the Knight shift, Figure 2, shows three characteristic temperature domains. The high temperature regime down to 140 K and 75 K at 1 bar and 32 kbar, respectively, in which $K_{s,b}$ reveals hardly any T and P dependence. An intermediate regime with both T and P dependences and the low T regime below 30–20 K which is only P-dependent. As far as low and intermediate temperature regimes are concerned, we shall assume that the temperature dependence of $K_{s,b}$ is related to the spin excitations above the spin gap Δ_s as for undoped two-leg ladders. Hence, we fit the spin susceptibility using the sum of two contributions,

$$\chi_s(T) = \frac{C}{\sqrt{T}} \exp\frac{-\Delta_s}{T} + \chi_{so}(P) \qquad (3)$$

where the first term of equation (3) represents the contribution to the susceptibility expected for triplet excitations in undoped spin ladders [19] and the second term is T-independent but could be P-dependent. The pressure dependence of the activation energy Δ_s and $\chi_{so}(P)$ are displayed in Figure 4. These results agree with earlier studies showing a spin gap value $\Delta_s \approx 260-270$ K at ambient pressure in similar samples [15,20] and also support the sharp decrease of the spin gap under pressure [3,9,21]. It is also clear from Figure 4 that the strong decrease of Δ_s occurs in the pressure domain above 17 kbar together with the emergence under pressure of spectral weight in the spin excitations at low energy.

The solid line in Figure 4 is a polynominal fit which suggests an extrapolation of Δ_s to a zero value in the pressure range 40–45 kbar which is close to the pressure where a maximum in the superconducting T_c is observed. What Figure 4 shows is that a significant fraction of the spin excitations remains gapped when superconductivity is stabilized around 32 kbar. This situation is indeed reminiscent of the growth of zero frequency spectral weight which is observed in the undoped two-leg ladders upon substitution of Cu^{2+} by non-magnetic impurities [22,23].

The border between high and intermediate T regimes is also visible on the $(T_1T)^{-1}$ *vs.* T data, Figure 3. The high temperature domain represents a regime in which the Cu^{2+} ($S = 1/2$) spins no longer feel the influence of the intra-rung AF coupling (when the temperature becomes larger than the spin gap ($T \geq \Delta_s/2$)) and in turn follow the dynamics of 1-D Heisenberg chains with $1/T_1 \approx 1/J_\parallel$. As the data of Figure 3 and in reference [3] do not show any significant pressure dependence we may conclude that the longitudinal coupling is not affected by pressure up to 32 kbar. The cross-over temperature between 1-D Heisenberg and spin-gapped regimes is depressed in the same proportion as Δ_s under pressure, Figure 4.

Using the direct derivation value of the parallel exchange coupling from inelastic neutron data, $J_\parallel = 990 \pm 165$ K [10], the experimental value of $\Delta_s \approx 260$ K leads to $\Delta_s/J_\parallel \approx 0.26 \pm 0.04$ and in turn to $J_\perp/J_\parallel \approx 0.6 \pm 0.05$ from the calculation of the excitation spectrum of Heisenberg spin ladders [24]. The perpendicular coupling thus obtained, $J_\perp \approx 644 \pm 50$ K, is in qualitative agreement with the INS data, $J_\perp \approx 715 \pm 110$ K [10]. This discussion suggests that the theory of undoped Heisenberg ladders is still rather satisfying to understand the spin excitations spectrum under ambient pressure.

In order to explain the suppression of the spin gap approaching the superconducting regime, several hypothesis can be taken into account. We first consider a possible pressure dependence of intra-ladder couplings (exchange and hopping terms). We have seen that a variation of $J_\parallel$ is not supported by our T_1 data under pressure in the 1-*D* regime. Furthermore, a variation of $J_\perp$ under pressure (and, in turn, of the ratio $J_\perp/J_\parallel$) is also unlikely since the rung exchange coupling comes from the same Cu–O–Cu 180° bond as the intra-leg bond coupling already found to be insensitive to pressure up to 30 kbar. The finding of a small pressure coefficient for the conductivity along the ladders at room temperature (2% per kbar) is also not in favour of a drastic increase of the hopping term along the legs of the ladders.

The next interactions to be considered are interladder couplings. It is known that the *b*-axis parameter plays a dominant role in the $(Sr/Ca)_{14}Cu_{24}O_{41}$ series as this parameter decreases by an amount of 6.5% going from $Sr_{14}Cu_{24}O_{41}$ to $Sr_2Ca_{12}Cu_{24}O_{41}$ while the drop of the *a* and *c* parameters are only 1.6% and 1.24%, respectively [25]. In addition, the compressibility is about ten times larger along *b* than along the *a* direction and the transport anisotropy shows hardly any *P*-dependence at room temperature in the ladder plane [26]. Consequently, the interladder hopping term does not seem to be more pressure dependent than the intra-leg one. Therefore, we may tentatively suggest that the dominant coupling which increases under pressure is an indirect interladder exchange between Cu^{2+} spins mediated by the Cu (ladder)–O (chain) interaction which is known to be very sensitive to pressure.

To summarize, the data of this new study of the ^{63}Cu–NMR properties of $Sr_2Ca_{12}Cu_{24}O_{41}$ performed in the pressure domain which goes up to the critical pressure for the stabilization of superconductivity have confirmed the collapse of the spin gap reported earlier [3] and are also in agreement with the transfer of population of spin excitations above 20 kbar from the modified gap position down to the low energy range. Gapped excitations extrapolate to zero at a pressure corresponding to the maximum T_c for superconductivity. We have suggested a possible relation between the strong depression of the spin gap and a chain-mediated interladder exchange coupling

Y.P wishes to acknowledge the support of a MENRT post-doc position. This work has benefited from the technical help of M. Nardone. We acknowledge the support of the Université Paris-Sud *via* a BQR contract for the year 1999.

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