Rapid Note

An NMR approach to the superconducting regime of the spin ladder compound \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \)

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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 \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) 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 \textbf{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 \( P_c \approx 32 \) 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 \( c \)-direction.

PACS. 74.72.Jt Other cuprates \(–\) 74.25.Ha Magnetic properties

Introduction

The compound \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) 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 \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) is the existence of \( \text{Cu}_2\text{O}_3 \) two-leg ladders running along the \( c \)-axis, \( i.e. \) two parallel \( \text{Cu}–\text{O} \) chains linked together by oxygen atoms with magnetic coupling between \( \text{Cu}^{2+} \) 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 \( \text{Cu}^{2+} \) \( (S = 1/2) \) 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 \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) which comprises chemically doped ladders with a concentration of 0.06 hole per \( \text{Cu} \) in the \( \text{Cu}_2\text{O}_3 \) ladder of the parent compound \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) [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 \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \), is one of the hottest challenges in the physics of strongly correlated low-dimensional fermions.

A previous study carried out on \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) [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 \( \text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41} \) by high pressure NMR experiments, focusing on the pressure regime 20–32 kbar which is close to the critical pressure needed for the stabilization...
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 Sr2Ca12Cu24O41, grown by the travelling solvent floating zone method already used in a previous study [3].

63Cu (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 63Cu 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 ∆νn = n ∆νres (where ∆νres 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 63Cu-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],

\[ \nu_{1/2,-1/2} = (1 + K_b)\nu_o + (\nu_c - \nu_o)^2/12(1 + K_b)\nu_o \]  

(1)

where \( K_b, \nu_o \) and \( \nu_c, a \) 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 Sr2.5Ca11.5Cu24O41, 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 Sr1−xCa5Cu24O41 [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 63Cu resonance in a diamagnetic substance, namely \( 63\nu_o = 63\nu(\text{met})/1.0023 \), where \( 63\nu(\text{met}) \) is the resonance frequency of copper metal.

The 63Cu Knight shift consists of two contributions, the orbital \( 63K_{\text{orb}} \) and spin \( 63K_s \) 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.

Results

Figure 1 shows the data of the 63Cu Knight shift versus temperature at different pressures up to 32 kbar. The remarkable feature in Figure 1 is the very small pressure dependence of \( K_{\text{orb}}(T) \) 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 \( K_{\text{orb}} \) and \( K_{s,b} \), 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 \( K_{\text{orb},b} \) at \( P = 32 \) kbar. Our results of Figure 1, would thus impose the spin part \( K_{s,b} \) 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 \( K_{\text{orb},b} \) to be negligible and the spin contribution reads then,

\[ K_{s,b}(P,T) = K_{b}(P,T) - K_{\text{orb},b}(P = 1 \text{ bar}) \]  

(2)

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