ELSEVIER

Physica B 312–313 (2002) 614–616

PHYSICA B

www.elsevier.com/locate/physb

ESR study of $(Sr, La, Ca)_{14}Cu_{24}O_{41}$

V. Kataev[a,*,1], K.-Y. Choi[a,2], M. Grüninger[a], U. Ammerahl[a,b], B. Büchner[a,2], A. Freimuth[a], A. Revcolevschi[b]

[a] *II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*
[b] *Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay, France*

Abstract

We report an electron spin resonance (ESR) study of single crystals of the spin-chain spin-ladder compound $(Sr, La, Ca)_{14}Cu_{24}O_{41}$. The data suggest that in intrinsically hole doped $Sr_{14-x}Ca_xCu_{24}O_{41}$, only a *small* amount of holes is transferred from the chains to the ladders with increasing x, resulting in a crossover from spin dimerized to uniform spin chains. In the samples of $La_{14-x}Ca_xCu_{24}O_{41}$ with reduced hole content a very broad signal is observed in the paramagnetic state, indicative of a surprisingly strong anisotropy of the nearest neighbor exchange in the chains.

Keywords: Spin chains and ladders; Magnetic resonance

Spin ladders have recently attracted much attention, in particular, due to superconductivity with $T_c \approx 10$ K observed under pressure in $Sr_{14-x}Ca_xCu_{24}O_{41}$ (SCCO) with $x \geqslant 11.5$ [1]. SCCO contains 2-leg $S = \frac{1}{2}$ Cu_2O_3 ladders showing a large spin gap $\Delta_{ladder} \approx 400$ K [2] and $S = \frac{1}{2}$ CuO_2 chains, both running along the c-axis. It is 'self-doped' with 6 holes per formula unit. For $x = 0$ almost all holes reside in the chains and show quasi-2D order [3,4]. In this charge ordered state spin dimers with a gap $\Delta_{dimer} \approx 130$ K are formed between next-nearest-neighbor Cu spins via a localized hole [3,4]. The conductivity of SCCO increases with x. The prevailing viewpoint is that the chemical pressure due to Ca-doping causes a substantial hole transfer from the chains to the ladders [5], i.e., both metallic conductivity and superconductivity are confined to the ladders. However, recent X-ray absorption data indicate only a marginal increase of the hole content in the ladders with increasing x [6].

We measured electron spin resonance (ESR) of Cu^{2+} ions in single crystals of $(Sr, La, Ca)_{14}Cu_{24}O_{41}$ at 9.47 GHz. A single resonance line of a Lorentzian shape with an anisotropic g-factor is observed. The principal values of g determined for the b- and c-axis are $g_b = 2.29 \pm 0.05$ and $g_c = 2.05 \pm 0.03$, respectively. Since Δ_{ladder} is large, the ESR signal at $T < 300$ K is attributed to the chains. The spin susceptibility χ_{ESR}^{spin} derived from the ESR intensity is similar to the static susceptibility χ_{stat}. In SCCO χ_{ESR}^{spin} and χ_{stat} for small x are well described by the spin-dimer model. A consistent description of χ_{stat} in SCCO *for all* x is obtained [7,8] in terms of a *smooth crossover* from spin dimers to a uniform antiferromagnetic (AF) spin chain with increasing Ca content, which assumes a *small* reduction of the hole content in the chains from ~ 6 to ~ 5. This scenario is proved by the following analysis of the ESR line width ΔH (Fig. 1). For SCCO with small x (Fig. 1, left panel) the curves above 30 K can be well approximated as $\Delta H(T) = \Delta H_0 + \Delta H^*(T)$. ΔH_0 is due to T-independent spin–spin interactions and inhomogeneities. $\Delta H^*(T)$ accounts for other, T-dependent spin-relaxation mechanisms. For $x = 0$ it emerges as a strong and almost linear in T contribution to ΔH only above a certain

*Corresponding author. Tel.: +49-0-221-470-3592; fax: +49-0-221-470-6708.

E-mail address: kataev@ph2.uni-koeln.de (V. Kataev).

[1] On leave from Kazan Physical Technical Institute, RAS, Kazan, Russia.

[2] Currently at: 2. Physikalisches Institut, RWTH Aachen, 52056 Aachen, Germany.

0921-4526/02/$ - see front matter
PII: S0921-4526(01)01288-1

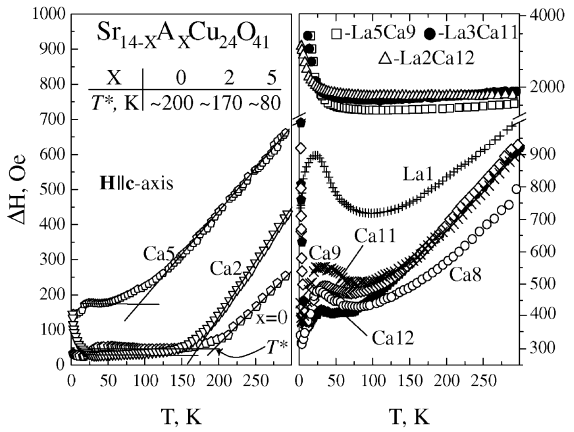

Fig. 1. T-dependence of the ESR line width ΔH of $(Sr, La, Ca)_{14}Cu_{24}O_{41}$. Solid lines in the left panel denote the constant and linear contributions to $\Delta H(T)$, as explained in the text. T^* indicates the charge ordering temperature.

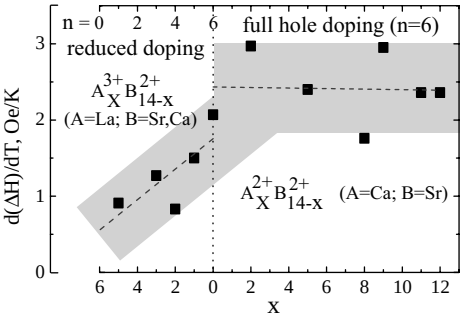

Fig. 2. High temperature slope of the $\Delta H(T)$ dependence of the samples with full ($n = 6$) and reduced ($n < 6$) hole doping.

temperature $T^* \approx 200$ K. T^* decreases rapidly with Ca-doping to 170 K for $x = 2$ and to ~ 80 K for $x = 5$. For still larger x, it is not possible to define a T^* below which ΔH is constant. We identify T^* as the charge ordering temperature, consistent with the results of other techniques [3,4,7]. Activated hole motion in the chains above T^* breaks spin dimers, causes spin flips and thus broadens the ESR signal. A rapid reduction of T^* with increasing x indicates a growing instability of the spin dimer state. Remarkably, a strong increase of $\Delta H(T)$ is found for all x, suggesting the presence of a substantial amount of mobile holes in the chains even at large Ca-doping. A consecutive reduction of the total number of holes due to heterovalent substitution from $n = 6$ in SCCO to $n = 5, 4, 3$, and 1, as in $Sr_{13}La_1-$, $La_2Ca_{12}-$, $La_3Ca_{11}-$ and $La_5Ca_9Cu_{24}O_{41}$, respectively, results in a much weaker increase of ΔH with T. The slopes $d(\Delta H)/dT$ are summarized in Fig. 2. According to Ref. [6] all holes reside in the chains in the compounds with reduced hole doping. Therefore, the comparison of $d(\Delta H)/dT$ in the left and right part of Fig. 2 gives an *upper border* of approximately *one hole* being transferred from the chains to the ladders in fully hole doped SCCO.

The steep increase of ΔH at $T < 10$ K in SCCO with large x is due to the development of AF order in the chains. A detailed analysis of the data [8] shows that the increase of the Ca content continuously drives the system towards an AF instability. This is expected, if spin dimerized chains gradually transform into uniform chains which eventually order at low T due to weak interchain couplings.

With increasing x the T-independent part of the line width ΔH_0 in SCCO increases by a factor of 10. In the samples with reduced hole doping, it grows up to ~ 1.5 kOe in nearly undoped $La_5Ca_9Cu_{24}O_{41}$. A careful analysis of the spectra suggests that this effect is not related to structural or magnetic inhomogeneities [10]. At $T < 50$ K the resonance line experiences additional broadening when long-range AF order at $T_N \approx 10$ K with an extreme magnetic anisotropy is approached [9]. The width of the ESR signal in the *paramagnetic* regime above ~ 50 K, where static short-range correlations vanish, is therefore determined mainly by the anisotropy of the spin–spin interactions, which in concentrated paramagnets is the major broadening mechanism. The dominant isotropic exchange in the chains with a small hole content is ferromagnetic and occurs between *nearest* neighbors, $H_{iso} = J_{iso} \sum \mathbf{S_i S_{i+1}}$, with $J_{iso} \approx -20$ K [3]. The leading anisotropy is of a symmetric type, $H_{aniso} = \sum \mathbf{S_i} A_{i,i+1} \mathbf{S_{i+1}}$. A conventional estimate of $A_{i,i+1}$ with $\Delta H \sim 1.5$ kOe yields $A_{i,i+1} \sim 2$ K [10], which is as large as 10% of J_{iso}. Such a strong anisotropy is surprising for copper oxides, which are considered to be the best experimental realizations of an isotropic Heisenberg magnet. It can be explained by the specific geometry of two symmetrical 90° Cu–O–Cu bonds, connecting nearest neighbor Cu sites. In this geometry the influence of the spin–orbit coupling on the superexchange is found to be considerably enhanced [11]. The ESR data indeed show that low-dimensional cuprates with certain bonding geometries may deviate significantly from the isotropic Heisenberg model.

References

[1] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Môri, K. Kinoshita, J. Phys. Soc. Japan 65 (1996) 2764; T. Nagata, M. Uehara, J. Goto, J. Akimitsu, N. Motoyama, H. Eisaki, S. Uchida, H. Takahashi, T. Nakanishi, N. Môri, Phys. Rev. Lett. 81 (1998) 1090.

[2] R.G. Eccleston, M. Uehara, J. Akimitsu, H. Eisaki, N. Motoyama, S. Uchida, Phys. Rev. Lett. 81 (1998) 1702;

S. Katano, T. Nagata, J. Akimitsu, M. Nishi, K. Kakurai, Phys. Rev. Lett. 82 (1999) 636.
[3] S.A. Carter, B. Batlogg, R.J. Cava, J.J. Krajewski, W.F. Peck Jr., T.M. Rice, Phys. Rev. Lett. 77 (1996) 1378.
[4] L.P. Regnault, J.P. Boucher, H. Moudden, J.E. Lorenzo, A. Hiess, U. Ammerahl, G. Dhalenne, A. Revcolevschi, Phys. Rev. B 59 (1999) 1055;
M. Matsuda, T. Yosihama, K. Kakurai, G. Shirane, Phys. Rev. B 59 (1999) 1060.
[5] T. Osafune, N. Motoyama, H. Eisaki, S. Uchida, Phys. Rev. Lett. 78 (1997) 1980.
[6] N. Nücker, M. Merz, C.A. Kuntscher, S. Gerhold, S. Schuppler, R. Neudert, M.S. Golden, J. Fink, D. Schild, S. Stadler, V. Chakarian, J. Freeland, Y.U. Idzerda, K. Conder, M. Uehara, T. Nagata, J. Goto, J. Akimitsu, N. Motoyama, H. Eisaki, S. Uchida, U. Ammerahl, A. Revcolevschi, Phys. Rev. B 62 (2000) 14384.
[7] U. Ammerahl, Ph.D. Thesis, University of Cologne, 2000.
[8] V. Kataev, K.-Y. Choi, M. Grüninger, U. Ammerahl, B. Büchner, A. Freimuth, A. Revcolevschi, Phys. Rev. B 64 (2001) 104442.
[9] U. Ammerahl, B. Büchner, C. Kerpen, R. Gross, A. Revcolevschi, Phys. Rev. B 62 (2000) R3592.
[10] V. Kataev, K.-Y. Choi, M. Grüninger, U. Ammerahl, B. Büchner, A. Freimuth, A. Revcolevschi, Phys. Rev. Lett. 86 (2001) 2882.
[11] V.Yu. Yushankhai, R. Hayn, Europhys. Lett. 47 (1999) 116;
S. Tornow, O. Entin-Wohlman, A. Aharony, Phys. Rev. B 60 (1999) 10206.