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$S=1/2$ antiferromagnetic chains and dimers on hole-doped edge-sharing CuO_2 chains

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Abstract

Holes doped on edge-sharing CuO_2 chains are almost localized because of nearly orthogonal Cu–O–Cu bonds. Consequently, only spin degrees of freedom survive at low temperatures, which sometimes presents unusual quantum magnetism. Quasi-one-dimensional cupric oxides $Ca_{1-x}CuO_{2+\delta}$ and $Sr_{14}Cu_{24}O_{41}$, both containing 25–50% hole-doped edge-sharing CuO_2 chains, are studied by uniform magnetic susceptibility and specific heat measurements on a series of polycrystalline samples with controlled metal and oxygen contents. Most spins are always dimerized in $Sr_{14}Cu_{24}O_{41}$, while, in contrast, antiferromagnetic chains made of nearly 50% spins exist with the remainder forming dimers of variable density in $Ca_{1-x}CuO_{2+\delta}$. A two-sublattice model is proposed by considering that the nearest-neighbor couplings are negligibly small, due to both geometrical frustration and the special Cu–O–Cu bond angle of ~95°.

Keywords: Quantum spin system; CuO_2 chain; Hole-doping

1. Introduction

Low-dimensional Heisenberg antiferromagnets (HAFs) with $S=1/2$ spins have attracted many solid state physicists because of their intriguing ground states where quantum fluctuations play a crucial role. Particularly exciting is to observe what happens when localized spins begin to move together with doped hole carriers. Cupric oxides have been found to present versatile materials for such studies. For two-dimensional systems, this was clearly demonstrated by finding high-T_C superconductivity in CuO_2 planes, while another form of superconductivity discovered recently in Cu_2O_3 ladder planes [1] illustrates the rich mine of physics on the way from two-dimensional to one-dimensional (1D) systems. However, there are few experimental reports on pure 1D CuO_2 chains doped with hole carriers, in spite of the many theoretical studies available.

Two kinds of CuO_2 chains made of CuO_4 squares are known: a corner-sharing chain, as seen in Sr_2CuO_3, and an edge-sharing chain as in many other cupric oxides such as Li_2CuO_2, $CuGeO_3$, $GeCu_2O_3$ [2], $Ca_{1-x}CuO_2$ (Fig. 1a), and $Sr_{14}Cu_{24}O_{41}$ (Fig. 1b). The former type exhibits large antiferromagnetic interactions because of the linear Cu–O–Cu bonds, while the latter shows rather complicated magnetism. Fig. 2 shows magnetic susceptibility measured on powder samples for these compounds with edge-sharing CuO_2 chains, where the magnitude and the temperature dependence are very different among them. This implies that magnetic interactions depend on subtle change in the crystal structure. Mizuno et al. [3] have studied systematically the edge-sharing chain systems, and suggested that nearest-neighbor interactions J_1 depends sensitively on the Cu–O–Cu bond angle θ; for example, $J_1/k_B \sim -100$ K (ferromagnetic) for Li_2CuO_2 ($\theta \sim 94°$) and 140 K (antiferromagnetic) for $CuGeO_3$ ($\theta = 99°$). In contrast, next-nearest-neighbor interactions J_2 is always antiferromagnetic, with values 62 K for Li_2CuO_2 and 18 K for $CuGeO_3$. Note that J_1 can be zero at a certain bond angle around $\theta = 95°$.

Among many compounds containing edge-sharing CuO_2 chains, $(Ca,Sr)_{14}Cu_{24}O_{41}$ [4] and $Ca_{1-x}CuO_2$ [5–7] are especially interesting because they both have doped chains with variable hole number. Since the holes are almost localized owing to small transfer integrals or large charge transfer gaps [3], only spin degrees of freedom survive at low temperature. This raises an interesting question of what kind of ground states should appear as spins are

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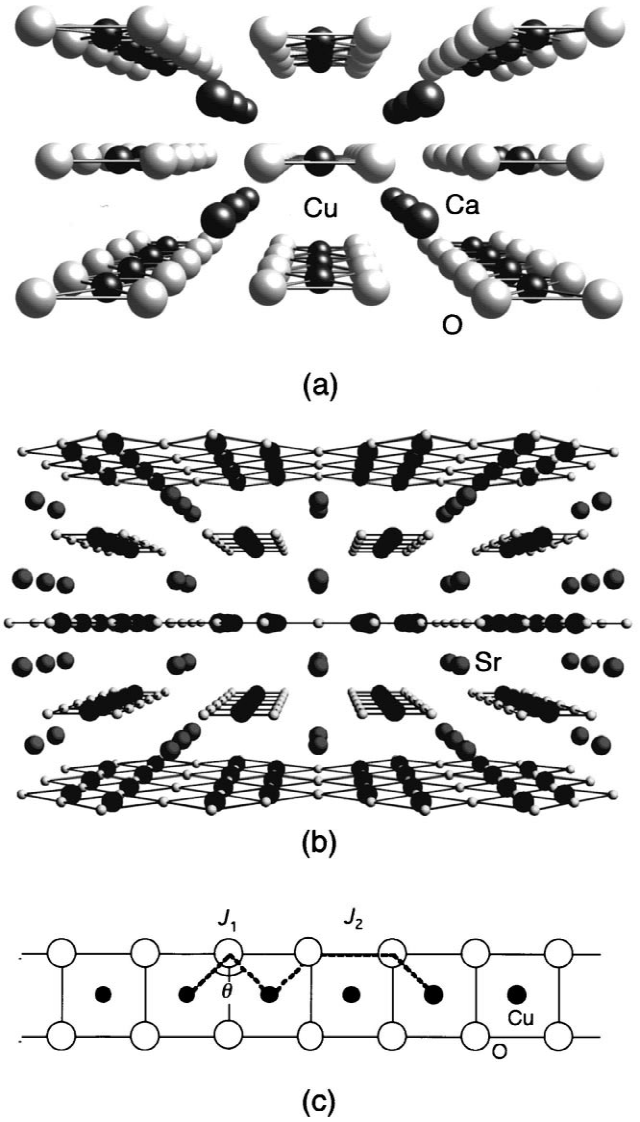

Fig. 1. Structure of $Ca_{1-x}CuO_{2+\delta}$ (a) and $Sr_{14}Cu_{24}O_{41}$ (b) viewed in perspective along the CuO_2 chains, which are made of CuO_4 squares linked by their edges (c). The chain is illustrated schematically to show the nearest- and next-nearest-neighbor interactions, J_1 and J_2, respectively. θ is the Cu–O–Cu bond angle which is close to 95°.

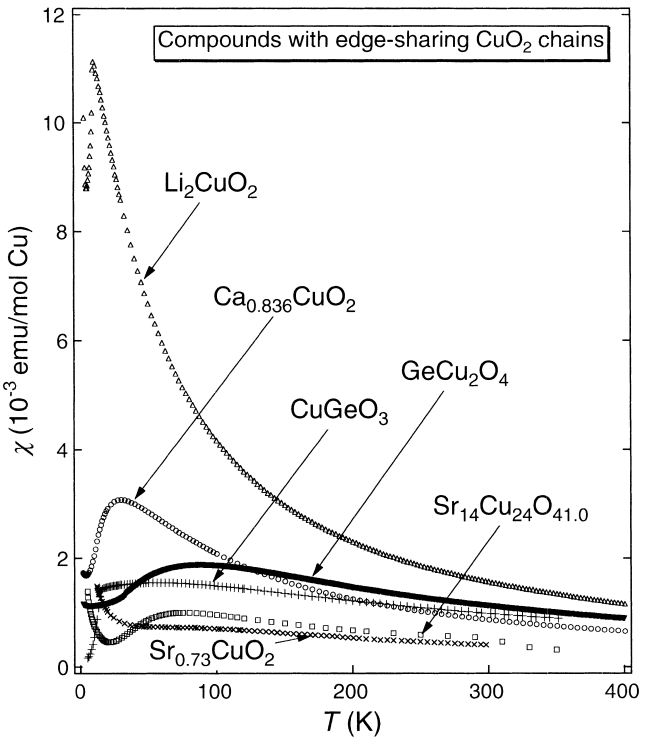

Fig. 2. Magnetic susceptibility χ of various compounds containing edge-sharing CuO_2 chains.

extracted successively from a half-filled 1D HAF chain down to a quarter-filled one, which is actually accessible in both compounds. In the 50 or 60% doped chains of $Sr_{14}Cu_{24}O_{41}$, it is believed that all the spins are dimerized to form singlets on pairs of Cu sites separated by one Zhang-Rice singlet site. Moreover, those dimers are ordered with periodicity along the chains of four or five lattice constants [8,9].

On the other hand, in $Ca_{1-x}CuO_{2+\delta}$, which was previously studied in the forms $Ca_{0.828}CuO_2$ [5], $Ca_{0.85}CuO_2$ [6,10], $Ca_4Cu_5O_{10}$ [11,12], $Ca_5Cu_6O_{12}$ [13] and $Ca_{0.83}CuO_2$ [14], the magnetic susceptibility shows a broad maximum around 30 K and decreases rapidly at low temperature toward a large, non-zero value at $T=0$. The decrease is too large to explain with a simple HAF chain model, but too small to assume a perfect singlet ground state with a gap in the spin excitation spectrum. Although a new kind of short-range ordered state has been suggested [12], this issue remains mysterious. Recently a 1D model consisting of isolated, short segments with an even number of spins, such as quartets, has been proposed on the basis of the electron-spin resonance and magnetic susceptibility measurements [15]. These authors analyzed susceptibility data after subtracting a very large Curie component, and concluded that the ground state was nonmagnetic. On the other hand, Meijer et al. proposed a modified alternating chain model [14]. A Sr analogue of this compound, $Sr_{0.73}CuO_2$, reported by Karpinski et al. [16] seems to present the opportunity to study the opposite case of reduced spin density (N_S), because the nominal N_S value derived from the chemical formula is 0.46, close to quarter-filling. The susceptibility data reported for $Sr_{0.73}CuO_2$ show a broad maximum around 80 K, followed by a ferromagnetic increase below 10 K [17], which led to the suggestion that the compound is composed of alternating chains.

Here we have prepared with care a series of polycrystalline samples of $Ca_{1-x}CuO_{2+\delta}$ with controlled metal and oxygen contents. The metal composition was uniquely determined by measuring the superlattice period. The purpose of this report is to clarify the essential feature of the short-range ordered state in diluted spin chains of $Ca_{1-x}CuO_{2+\delta}$.

Table 1
Summary of samples and parameters obtained by fitting the susceptibility and the specific heat data to the chain-dimer model

Sample	Composition	Data	N_N	N_C	N_D	N_{CW}	N_S	J_C/k_B (K)	J_D/k_B (K)	$\chi_0(10^{-5}$ emu/mol)/Θ_D(K)[a]
A	$Ca_{0.836}CuO_{1.97}$	$\chi(T)$	0.732	0.466(2)	0.194(2)	0.023(2)	0.683	85.4(5)	48.8(3)	−5.0(2)
		$C(T)$	0.732	0.50(5)	0.251(2)	–	0.75	90(5)	42.9(3)	327(3)
B	$Ca_{0.832}CuO_{2.00}$	$\chi(T)$	0.664	0.473(1)	0.139(1)	0.024(1)	0.636	92.5(5)	50.8(3)	1.1(2)
		$C(T)$	0.664	0.50(1)	0.180(5)	–	0.68	76(2)	47.0(7)	305(1)
C	$Ca_{0.810}CuO_{2+\delta}$	$\chi(T)$	–	0.442(1)	0.102(1)	0.029(1)	0.573	98.0(3)	52.8(3)	−1.2(1)
		$C(T)$	–	0.50(3)	0.015(6)	–	0.52	64(3)	52.8[b]	272(5)
D	$Sr_{14}Cu_{24}O_{41.0}$[c]	$\chi(T)$	0.4	–	0.324(2)	0.016(1)	0.340	–	130.9(4)	4.4(2)

[a] χ_o and Θ for the $\chi(T)$ and $C(T)$ data, respectively.
[b] Parameter was fixed to be that obtained from $\chi(T)$ data.
[c] It is assumed that holes exist only in the chain part.

2. Experimental

A series of polycrystalline samples of $Ca_{1-x}CuO_{2+\delta}$ and $Sr_{14}Cu_{24}O_{41}$ were prepared by the standard solid-state reaction method. For $Ca_{1-x}CuO_{2+\delta}$ appropriate mixtures of $CaCO_3$ and CuO powders were pressed and calcined at 800°C in an oxygen flow for 1 week, with intermittent grindings (sample A). In order to prepare more oxidized samples, high-pressure treatments were carried out: the starting powders were sealed in gold capsules with $KClO_4$ as an oxidizer, and treated at $P=3$ GPa and $T=800$°C (B), and 4.5 GPa and 1000°C (C). The samples thus obtained were investigated by means of powder X-ray diffraction (XRD) with graphite-monochromated CuKα radiation. The Ca content was decided on the basis of the structural analyses [18]. It was found that the more oxidizing preparation conditions resulted in larger x values as shown in Table 1. The compound showed also nonstoichiometry in oxygen content, depending on annealing conditions. The oxygen content of our samples A–C was determined thermogravimetrically by measuring weight loss when a sample was heated up to 800°C in a 95% N_2–5% H_2 atmosphere. Magnetic susceptibility was measured between 1.8 and 400 K in an external field of 1 kOe in a quantum design SQUID magnetometer (MPMS-XL). Specific heat was measured by the heat-relaxation method in a temperature range between 1.7 and 50 K on a quantum design physical-property-measurement-system (PPMS).

3. Results

Fig. 3 shows the temperature dependence of magnetic susceptibility χ for the three samples of $Ca_{1-x}CuO_{2+\delta}$ and $Sr_{14}Cu_{24}O_{41.0}$. The former shows a broad, rounded maximum at 30 K, followed by a large decrease at low temperature, as reported previously. The broad maximum indicates short-range antiferromagnetic correlations characteristic of low-dimensional HAFs, while the large decrease below 30 K suggests dominant singlet correlations at low temperature. Below 4 K a small upturn is detected, probably due to a Curie-like contribution. However, it seems impossible to ascribe the observed large residual susceptibility at $T\rightarrow 0$ only to such a small Curie-like contribution. As the nominal spin density N_N decreases from sample A to C, the maximum χ value decreases monotonically, while those at the lowest and the highest temperatures do not change appreciably. Moreover, the peak temperature does not shift significantly, suggesting similar antiferromagnetic couplings for all the samples.

In contrast, the χ value of $Sr_{14}Cu_{24}O_{41}$ shows a gap-like decrease below 80 K, followed by an upturn due to a Curie contribution at low temperature. This susceptibility mostly shows the contribution from Cu^{2+} spins on the chains, because the Cu_2O_3 plane with a large spin gap of 400 K should be almost magnetically inactive in this temperature range. Fitting of the χ data was performed assuming $\chi=\chi_0+\chi_{CW}+\chi_D$, where χ_0 is a small, temperature-independent term, χ_{CW} is the Curie–Weiss (CW) contribution from N_{CW} spins, and χ_D is a contribution from dimers consisting of N_D spins per mol Cu only in the chain part

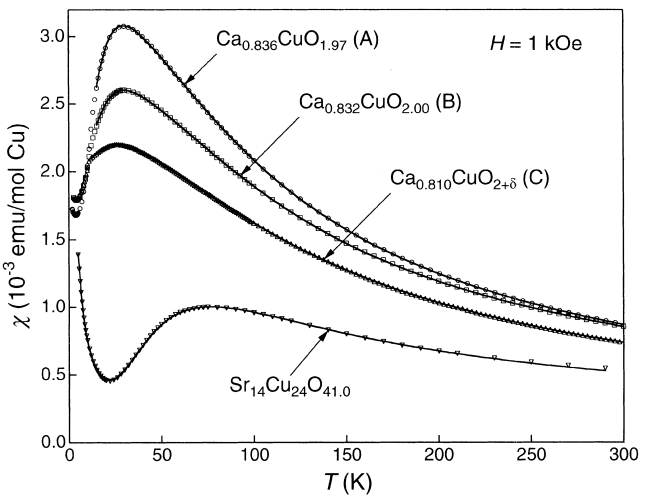

Fig. 3. Magnetic susceptibility of a series of the polycrystalline samples of $Ca_{1-x}CuO_{2+\delta}$ with different metal and oxygen contents as well as that of $Sr_{14}Cu_{24}O_{41.0}$. The solid line on each data set is a fit to the chain-dimer model described in the text.

which are coupled by the superexchange J_D. The results are summarized in Table 1. Note that the fitting converged well with small N_{CW} and χ_0, suggesting that most spins on the CuO_2 chains form dimers in $Sr_{14}Cu_{24}O_{41}$.

It is obvious in the case of $Ca_{1-x}CuO_{2+\delta}$ that such a simple dimer model is inapplicable. We have in fact tried to fit the data with the dimer model or the alternating chain model and found that unacceptably large CW contributions are always necessary to reproduce the data [18]. We have reached, alternatively, more reliable and reasonable fit by assuming a three-component model containing chains and dimers as well as CW contributions: $\chi = \chi_0 + \chi_{CW} + \chi_C + \chi_D$, where χ_C is a contribution from Heisenberg antiferromagnetic chains consisting of N_C spins coupled by the superexchange J_C. The results are excellent for the three samples with different spin density as shown in Fig. 3 and listed in Table 1. The details of fitting are shown also in Fig. 4a, typically for sample A, where each contribution is shown separately. The most important implication is that

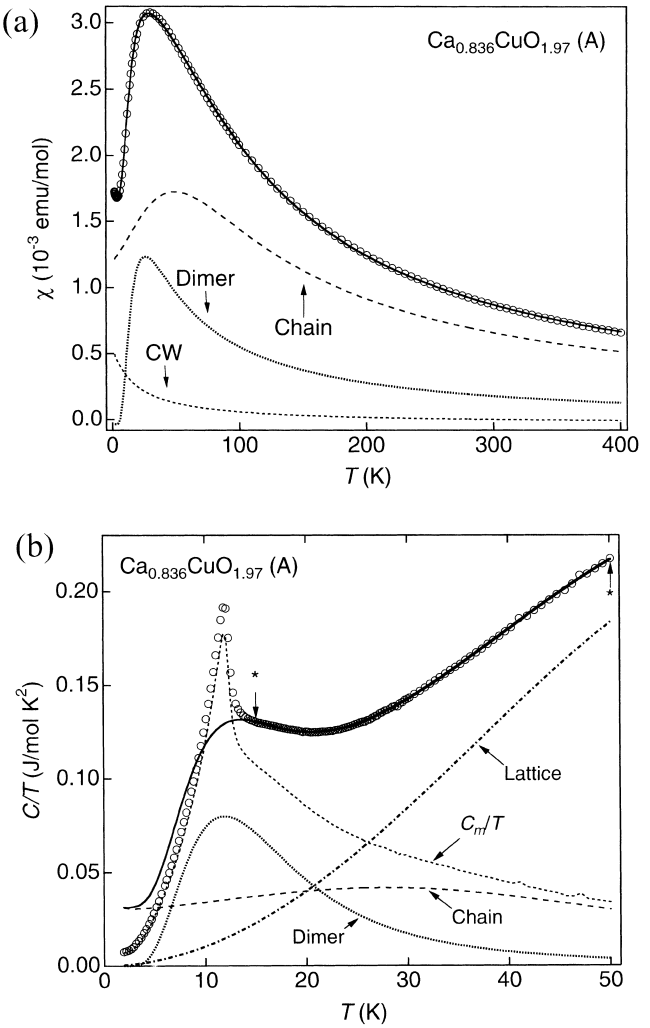

Fig. 4. Fitting the (a) $\chi(T)$ and (b) $C(T)/T$ data for sample A to the chain-dimer model. The dotted curves in the bottom of these figures show each contribution separately.

N_C is always nearly half of the Cu sites, and most of the remaining spins form dimers with a density which seems to decrease with decreasing total spin density.

In order to gain more insight into the unusual magnetism of $Ca_{1-x}CuO_{2+\delta}$, we have measured the specific heat C of the samples. Fig. 4b shows a graph C/T versus T between 1.7 and 50 K for sample A. A sharp anomaly was found at 12.0 K, suggesting an onset of long-range magnetic order, in good agreement with the recent results of Meijer et al. [19]. They found a similar peak at 12 K for their $Ca_{0.83}CuO_2$. As the temperature is lowered from 50 K, the specific heat decreases as the lattice contribution falls, but then exhibits an unusual upturn with a minimum around 22 K. Such an upturn was not observed in the previous data. This upturn cannot be explained by incorporating an additional magnetic specific heat from the simple HAF chains. We believe that it is clear evidence for dimer contributions as derived from the $\chi(T)$ data.

Therefore, we have fitted the data using the same dimer-chain model as in the $\chi(T)$ analyses: $C = C_L + C_C + C_D$, where C_L, C_C and C_D are the respective contributions from lattice, chains and dimers. For lattice contributions the simple Debye model with the Debye temperature Θ_D was assumed. The best fit to the data for sample A between 15 and 50 K (Fig. 4b) was obtained with $\Theta_D = 327(3)$ K, $N_C = 0.50(5)$, $N_D = 0.251(2)$, $J_C/k_B = 90(5)$ K, and $J_D/k_B = 42.9(3)$ K. The Debye temperature of 327 K is smaller than the value (420 K) reported for the isomorphous compound $Ca_2Y_2Cu_5O_{10}$ [20]. But N_C (close to half) and N_D (to a quarter) are in reasonably good agreement with the values derived from the $\chi(T)$ analysis. Moreover, the values obtained for J_D and J_C are also consistent with the $\chi(T)$ results. Therefore, we conclude that the chain-dimer model gives a plausible description for the magnetism of the present heavily hole-doped CuO_2 chains. Each contribution from lattice, chains, and dimers is depicted separately in Fig. 4b. The upturn below 25 K is certainly due to magnetic excitations from singlet to triplet states in the dimers. The total magnetic contribution C_m was calculated by subtracting C_L from the experimental data, and is plotted also in the figure. The total amount of magnetic entropy between 1.7 and 50 K is 3.14 J/mol K, which is 73% of the total entropy, $N_S N_A k_B \ln 2 = 4.32$ J/mol K ($N_S = 0.75$). The amount of magnetic entropy which is already gained below the cusp ($T_N = 12.0$ K) is 0.7 J/mol K, which corresponds to only 17% of the total magnetic entropy: most of the entropy has been lost by short-range ordering above T_N, as generally seen in low-dimensional antiferromagnets.

The upturn is gradually fading away with increasing the spin density as shown in Fig. 5, suggesting that the dimer density is reduced. Then, finally it disappears completely for sample C which may have spin density close to quarter-filling. The result of fitting to the chain-dimer model is shown in Fig. 5 and presented in Table 1. The calculated curves successfully reproduce the data above 15

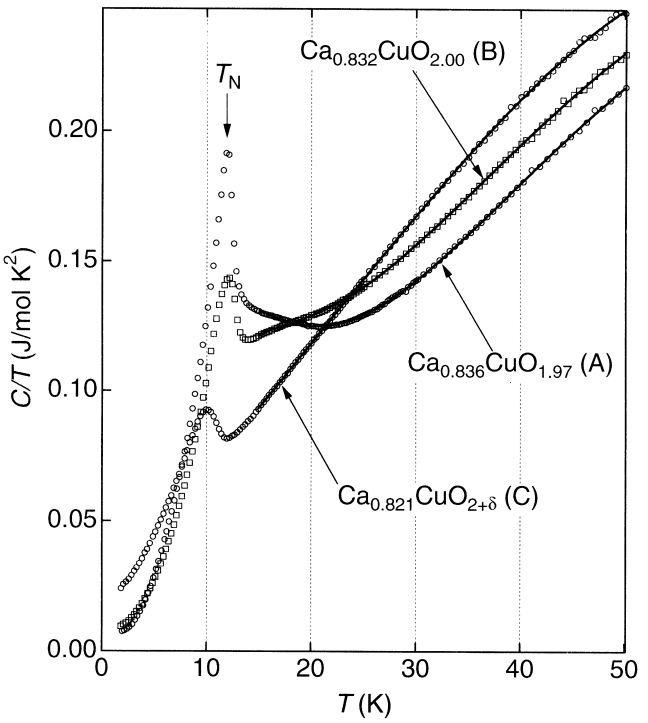

Fig. 5. Specific heat divided by temperature C/T for the series of samples. The solid curve above 15 K shows the calculated specific heat.

K in each sample. The N_C value is nearly half for all the samples and the N_D decreases systematically from 0.25 (A) to 0.02 (C). The estimated total spin density N_S ($=N_C+N_D$) is in very good agreement with the chemically expected N_N.

4. Discussion

The analyses of magnetic susceptibility and specific heat presented here have demonstrated clearly that the complicated magnetism of $Ca_{1-x}CuO_{2+\delta}$ is quantitatively described by assuming the coexistence of chains and dimers. It is surprising that such well-defined spin chains are realized in such heavily hole-doped CuO_2 chains. It is also unusual that chains and dimers are mixed on the same CuO_2 chains. We now discuss the physical background of the model, to elucidate a possible and interesting scenario for this unique system. The arrangement of holes is apparently a key to the problem. We will start with the spin Hamiltonian for $N_S = 1$ (half-filling), $H = J_1 \Sigma S_i \cdot S_{i+1} + J_2 \Sigma S_i \cdot S_{i+2}$, with the nearest- and next-nearest-neighbor couplings, J_1 and J_2, as usually used to represent edge-sharing CuO_2 chains. The problem is then the behavior of this system as spins are extracted successively down to $N_S \sim 1/2$ (quarter-filling).

The electronic states of various compounds comprising edge-sharing CuO_2 chains have been studied extensively, particularly with regard to $CuGeO_3$ [21]. The significance of J_2 contributions to understanding their magnetic properties has been emphasized by many authors. The important theoretical implications of the work by Mizuno et al. are that J_1 depends sensitively on the Cu–O–Cu bond angle θ, while J_2 does not [3]. In particular, J_1 changes its sign at ~95° from ferromagnetic ($\theta < 95°$) to antiferromagnetic ($\theta > 95°$). Then, it is natural to expect that J_1 becomes negligibly small around a critical θ value near 95°. This must be the case for the present CuO_2 chains in $Ca_{1-x}CuO_{2+\delta}$ and $(Ca,Sr)_{14}Cu_{24}O_{41}$. The θ value from a previous study on the average structure appears to be 94–95° [6]. As a consequence, one CuO_2 chain at half-filling can be divided into two identical spin chains connected antiferromagnetically by J_2, which couple to each other with a relatively small, frustrating zigzag coupling J_1. Note that the frustration is always present apart from the sign of J_1.

If $J_1/k_B = 0$, the system would consist of identical, independent pairs of chains (sublattices) at half-filling ($N_S = 1$). In contrast, at quarter-filling, we expect that it is energetically favorable to put all the spins on one of the sublattices forming a single chain, as depicted in Fig. 6a, which may decrease the total magnetic energy and also reduce the intersite Coulomb interactions compared to a random distribution. This is considered to be charge ordering on every Cu site, as discussed by Mutou et al. [22]. In the actual situation for $Ca_{1-x}CuO_{2+\delta}$, N_S is variable between 0.5 and 0.75. The present analyses of susceptibility and specific heat indicate that there are always (i) a chain consisting of spins on nearly one half of the Cu sites with $J_2/k_B \sim 90$ K and (ii) dimers coupled by $J_2'/k_B \sim 50$ K, the number of which varies with N_S. This means that the intermediate state consists of a perfect chain on one sublattice and isolated dimers scattered on the other sublattice. It is fully plausible that for sufficiently small $|J_1|/J_2$ either adding spins to a quarter-filled CuO_2 chain or extracting spins from a half-filled chain keeps intact a perfect chain on the sublattice a, and creates or annihilates spins on the sublattice b. It is possible that a small amount of spins on the sublattice b tends to be phase-separated to form small clusters such as dimers and trimers, rather than being scattered randomly, as depicted in Fig. 6b. A lattice distortion expected from the lattice mismatch between the Ca and Cu–O sublattices would help the formation of such clusters. The experimental results indicate that most of the spins form dimers.

The relevance to the dimerized states found in the similar CuO_2 chains of $(Ca,Sr)_{14}Cu_{24}O_{41}$ is interesting. In the case of the pure Sr compound, $N_S \sim 0.4$ and all the spins are coupled into dimers which order with a periodicity of five lattice constants as illustrated in Fig. 6c. Remarkably, similar spin gaps were observed even for $N_S \sim 0.7$ in the Ca-substituted compounds. We believe that the CuO_2 chains in $(Ca,Sr)_{14}Cu_{24}O_{41}$ can be described also by the above two-sublattice model with $J_2 \gg |J_1| \sim 0$, because θ in $Sr_{14}Cu_{24}O_{41}$ is 94.6° [23]. A substantial

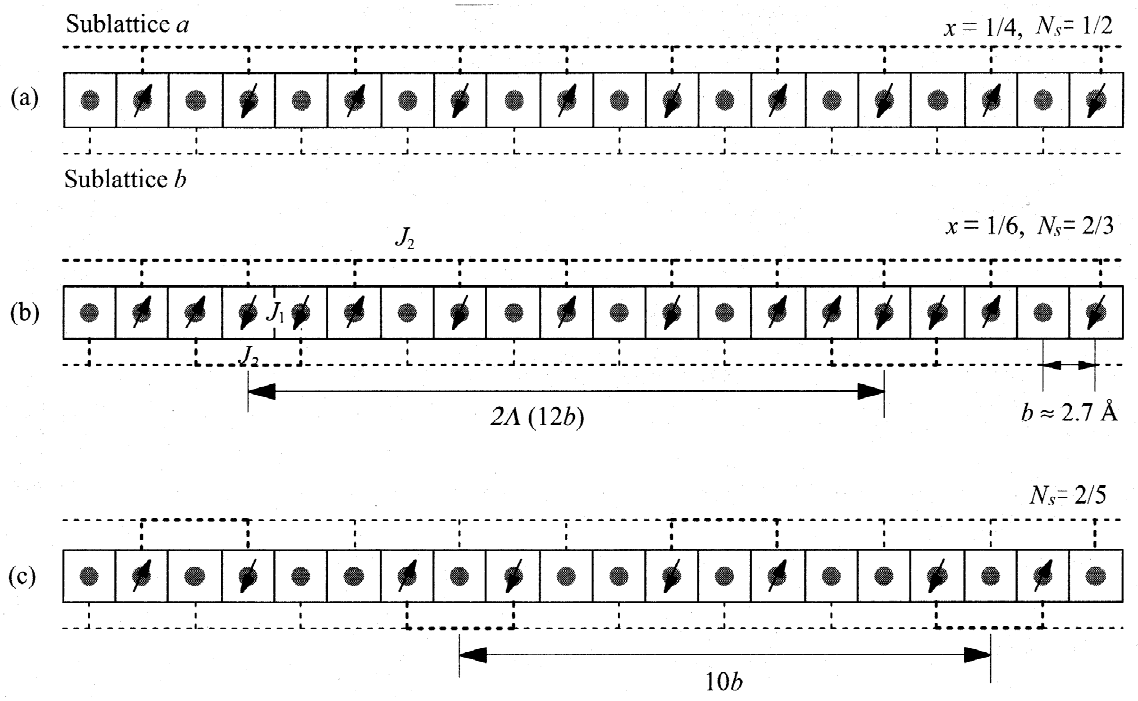

Fig. 6. Chain-dimer (two-sublattice) model proposed for the edge-sharing CuO_2 chains in $Ca_{1-x}CuO_{2+\delta}$. J_1 and J_2 correspond to those shown in Fig. 1c. Spins of Cu^{2+} ions are represented by arrows. Assuming $J_2 \gg |J_1| \sim 0$, possible spin arrangements are depicted for quarter-filling ($x=1/4$, $N_S=1/2$) (a), intermediate-filling ($x=1/6$, $N_S=2/3$) (b), and the case of $Sr_{14}Cu_{24}O_{41}$ with $N_S=2/5$ (c).

difference between $Ca_{1-x}CuO_{2+\delta}$ and $(Ca,Sr)_{14}Cu_{24}O_{41}$ is whether a 1D chain on one of the sublattices, or dimers on both of the sublattices, are preferred for quarter-filling. The latter may be preferable in $(Ca,Sr)_{14}Cu_{24}O_{41}$, because large lattice distortions with a nearly five-fold periodicity are present there. Otherwise, a small difference in J_1 might lead to a substantial difference in the ground state.

5. Concluding remarks

In summary, hole-doped or spin-depleted CuO_2 chains have been studied in the insulating compound $Ca_{1-x}CuO_{2+\delta}$. The results suggest a coexistence of spin chains and dimers on a single chain with $J_2 \gg |J_1| \sim 0$. The nature of antiferromagnetic ordering observed below 12 K and the ground state of $Ca_{1-x}CuO_{2+\delta}$ is not yet clear. Recent experiments have suggested a coexistence of an antiferromagnetic order and a gapped state in the ground state [24,25]. It may be plausible to assume in our two-sublattice model that only the chains order antiferromagnetically, keeping the dimers intact, because 1D HAF chains are in a quantum critical regime.

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References

[1] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori, K. Kinoshita, J. Phys. Soc. Jpn. 65 (1996) 2764.
[2] T. Yamada, Z. Hiroi, M. Takano, M. Nohara, H. Takagi, J. Phys. Soc. Jpn. 69 (2000) 1477.
[3] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, S. Uchida, Phys. Rev. B 57 (1998) 5326.
[4] T. Siegrist, L.F. Schneemeyer, S.A. Sunshine, J.V. Waszczak, Mat. Res. Bull 23 (1988) 1429.
[5] R.S. Roth, N.M. Hwang, C.J. Rawn, B.P. Burton, J.J. Ritter, J. Am. Ceram. Soc. 74 (1991) 2148.
[6] T.G.N. Babu, C. Greaves, Mat. Res. Bull. 26 (1991) 499.
[7] T. Siegrist, R.S. Roth, C.J. Rawn, J.J. Ritter, J. Chem. Mater. 2 (1990) 192.
[8] M. Matsuda, T. Yoshihama, K. Kakurai, G. Shirane, Phys. Rev. B 59 (1998) 1060.
[9] Z. Hiroi, S. Amelinckx, G.V. Tendeloo, N. Kobayashi, Phys. Rev. B 54 (1996) 15849.
[10] O. Milat, G.V. Tendeloo, S. Amelinckx, T.G.N. Babu, C. Greaves, Solid State Commun. 79 (1991) 1059.
[11] P.K. Davies, J. Solid State Chem. 95 (1991) 365.
[12] A. Hayashi, B. Batlogg, R.J. Cava, Phys. Rev. B 58 (1998) 2678.
[13] M. Kibune, S. Miyasaka, T. Tonogai, M. Nohara, H. Takagi, S. Adachi, K. Tanabe, unpublished.
[14] G.I. Meijer, C. Rossel, E.M. Kopnin, M. Willemin, J. Karpinski, H. Schwer, K. Conder, P. Wachter, Europhys. Lett. 42 (1998) 339.

[15] J. Dolinsek, D. Arcon, P. Cevc, O. Milat, M. Miljak, I. Aviani, Phys. Rev. B 57 (1998) 7798.
[16] J. Karpinski, H. Schwer, G.I. Meijer, K. Conder, E.M. Kopnin, C. Rossel, Physica C 274 (1997) 99.
[17] A. Shengelaya, G.I. Meijer, J. Karpinski, G.-M. Zhao, H. Schwer, E.M. Kopnin, C. Rossel, H. Keller, Phys. Rev. Lett. 80 (1998) 3626.
[18] Z. Hiroi, M. Okumura, T. Yamada, M. Takano, J. Phys. Soc. Jpn. 69 (2000) 1824.
[19] G.I. Meijer, C. Rossel, W. Henggeler, L. Keller, F. Fauth, J. Karpinski, H. Schwer, E.M. Kopnin, P. Wachter, R.C. Black, J. Diederichs, Phys. Rev. B 58 (1998) 14452.
[20] M. Matsuda, K. Katsumata, J. Mag. Mag. Mat. 177–181 (1998) 683.
[21] M. Hase, I. Terasaki, K. Uchinokura, Phys. Rev. Lett. 70 (1993) 3651.
[22] T. Mutou, N. Shibata, K. Ueda, Phys. Rev. B 57 (1998) 13702.
[23] E.M. McCarron, M.A. Subramanian, J.C. Calabrese, R.L. Harlow, Mat. Res. Bull. 23 (1988) 1355.
[24] A. Ueda, H. Ohta, S. Okubo, Z. Hiroi, M. Okumura, M. Takano, Appl. Magnetic Resonance, in press.
[25] K. Yoshimura, T. Mitsui, N. Tujii, M. Kato, K. Kosuge, in: Proceedings of the Spring Meetings of the Physical Society of Japan, 54th, Hiroshima, 1999, p. 418.