Real Space Imaging of Spin Polarons in Zn Doped SrCu$_2$(BO$_3$)$_2$

M. Yoshida,$^1$ H. Kobayashi,$^1$ I. Yamauchi,$^1$ M. Takigawa,$^1$ S. Capponi,$^2$
D. Poilblanc,$^2$ F. Mila,$^3$ K. Kudo,$^4$ Y. Koike,$^5$ and N. Kobayashi$^6$

$^1$Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
$^2$Laboratoire de Physique Théorique, Université de Toulouse and CNRS, UPS (IRSAMC), F-31062 Toulouse, France
$^3$Institut de Théorie des Phénomènes Physiques, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
$^4$Department of Physics, Okayama University, Okayama 700-8530, Japan
$^5$Department of Applied Physics, Tohoku University, Sendai 980-8579, Japan
$^6$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

(Dated: July 24, 2014)

We report on the real space profile of spin polarons in the quasi two-dimensional frustrated dimer spin system SrCu$_2$(BO$_3$)$_2$ doped with 0.16% of Zn. The $^{11}$B nuclear magnetic resonance spectrum exhibits 15 additional boron sites near non-magnetic Zn impurities. With the help of exact diagonalizations of finite clusters, we have deduced from the boron spectrum the distribution of local magnetizations at the Cu sites with fine spatial resolution, providing direct evidence for an extended spin polaron. The results are confronted with those of other experiments performed on doped and undoped samples of SrCu$_2$(BO$_3$)$_2$.

PACS numbers: 75.25.-j, 76.60.Pc, 75.10.Jm

Impurities and defects in strongly correlated quantum systems often produce significant effects over an extended spatial region, which can be studied by local probes such as nuclear or electron magnetic resonance (NMR or ESR) [1]. The best example is the edge states in Heisenberg spin chains. The spin 1/2 edge state in spin 1 Haldane chains is a direct consequence of the valence-bond-solid ground state of the pure system. The ESR experiments have played vital roles in identifying the edge spins [2, 3] and their interactions [4]. The edge states are not localized at a single site but associated with local staggered magnetization due to the antiferromagnetic interaction of the bulk, and the spatial extent of such a polaronic structure is given by the correlation length of the bulk. The real space profile of spin polarons have been actually observed by NMR experiments in both spin 1 [5] and spin 1/2 [6] Heisenberg chains, from which the temperature dependence of the correlation length was deduced.

Although there have been less studies on two-dimensional (2D) systems, an interesting example is the Shastry-Sutherland lattice [11], which is known to be the exact ground state of Eq. (1) for $x = J'/J$ not too large [11, 12], less than $\alpha_x \simeq 0.675$ [13, 14]. SrCu$_2$(BO$_3$)$_2$ exhibits a number of fascinating properties, most notably the unique sequence of quantized magnetization plateaus in magnetic fields [17, 22], which have been a subject of intense research in the last decade [23, 24].

A nonmagnetic impurity creates an unpaired Cu$^{2+}$ site in the dimer singlet state, producing a free spin-1/2. The structure factor of this spin-1/2 has been measured by inelastic neutron scattering experiments [8], which clearly point to an extended object. Theories have confirmed this picture: the spin density forms a spin polaron that extends over several sites around the impurity [8, 10], a prediction that clearly calls for further experimental investigation.

In this Letter, we report the observation of such a spin polaron in real space by $^{11}$B NMR experiments on Zn doped SrCu$_2$(BO$_3$)$_2$ performed in a sufficiently high magnetic field to saturate unpaired spins. With the help of exact diagonalization results, a nearly complete assignment of the 15 additional boron sites has been achieved, leading to the determination of microscopic structure of a localized spin polaron with unprecedented accuracy.

Single crystals of SrCu$_{2-x}$Zn$_x$(BO$_3$)$_2$ were grown by the traveling-solvent floating-zone method [25, 26]. Two crystals were used, $x = 0.0174$ and 0.0032 as determined by the inductively coupled plasma atomic emission spectrometry. Presence of free spins at low temperatures was confirmed by the magnetization measurements (see Supplementary Material [20]). The crystals were cut into a rod ($1 \times 1 \times 5$ mm$^3$) for NMR measurements, which were performed in a magnetic field $B$ of 6.615 T precisely along the c axis (within $\sim 0.2$ degree).

The NMR spectra were obtained by summing the Fourier transform of the spin-echo signal obtained at equally spaced rf-frequencies. Figure 1 shows the $^{11}$B NMR spectrum for $x = 0.0032 \ (0.16\% \ of \ Zn)$ at 1.6 K. The Zeeman energy for the magnetic field of 6.615 T is
FIG. 1: (color online) $^{11}$B NMR spectrum at $T = 1.6$ K and $B = 6.615$ T. The black arrows mark the position of the reference line (zero internal field). 15 additional lines named $B_1$ to $B_{15}$ have been resolved. Note that $B_1$ is about twice as intense as $B_2$, and that $B_{12}$ (shaded in blue) is also about twice as intense as $B_{11}$ (shaded in orange).

much smaller than the zero-field energy gap for the triplet excitation in the bulk ($\Delta = 35$ K) but large enough to completely polarization the impurity induced free spins [30]. To understand the $^{11}$B NMR spectra, we first recall that one boron site generates three NMR lines at the frequencies $\nu_r = \gamma (B + B_{\text{int}}) + k \nu_Q$, $(k = -1, 0, 1)$, where $\nu_Q$ is the quadrupole splitting along the $c$ axis, $\gamma = 13.66$ MHz/T is the nuclear gyromagnetic ratio, and $B_{\text{int}}$ is the internal magnetic field produced by nearby Cu spins. Since the Zn concentration is extremely dilute, most of Cu spins form singlet dimers generating $B_{\text{int}} \sim 0$ at the majority of B sites. The NMR lines from these B sites (shown by black arrows) are very intense, far exceeding the range of display in Fig. 1.

In addition to this reference line, we have been able to identify 15 weaker lines with non-zero $B_{\text{int}}$ ($B_1$ - $B_{15}$) indicated by the thin lines in Fig. 1 and to determine the values of $B_{\text{int}}$ and $\nu_Q$ for each of them. We confirmed that the sample with $x = 0.0174$ has a nearly identical NMR spectrum, ensuring that the distribution of $B_{\text{int}}$ and $\nu_Q$ represents the properties of an isolated impurity [30].

As we shall now demonstrate, it is possible to assign most of the lines to specific boron sites, and to deduce the polarization of the Cu sites around the impurity as shown in Fig. 2. To perform this line assignment, it is useful to have some idea a priori of the local magnetization that can be expected in the neighborhood of a Zn impurity. We have thus performed exact diagonalizations (ED) calculation for finite-size clusters of the 2D Shastry-Sutherland lattice with 32 sites (31 spins and one vacancy) and 36 sites (35 spins and one vacancy), with periodic boundary conditions in both cases [30]. The ED results of Fig. 3(c) show that the local magnetization is distributed primarily over five spins surrounding the defect. A single spin at Cu$_A$ with a large positive $\langle S^B_A \rangle \sim 0.18 - 0.30$, two spins at Cu$_C$ with also a large positive $\langle S^B_C \rangle \sim 0.18 - 0.21$, and two spins at Cu$_B$ with a large negative $\langle S^B_C \rangle \sim -0.1$ which add up approximately to the saturated value of 0.5. In addition, eight spins at four other sites (Cu$_{0-C}$) carry a small and oscillating magnetization less than 0.1 in absolute value. The local magnetization is much smaller for the remaining sites ($\sim 10^{-3}$) and cannot be determined accurately for the cluster size of our calculation. Interestingly, there is a strong dependence on $\alpha$. First of all, the polaronic structure collapses very rapidly when $\alpha$ exceeds 0.68, consistent with the first order transition in the pure system from the dimer singlet to the plaquette singlet phase [13, 16, 29]. Besides, and more remarkably, the magnetization of the unpaired site Cu$_A$, $\langle S^A_C \rangle$, strongly depends on $\alpha$. It decreases steeply with $\alpha$ and becomes smaller than $\langle S^C_C \rangle$ at $\alpha \sim 0.66$, an observation that will turn crucial for the analysis of the experimental spectrum.

To make contact between the local magnetization at Cu sites and the boron spectrum, we need some information on the internal field $B_{\text{int}}$ at a given boron site. It is given by the sum of contributions from neighboring Cu sites

$$B_{\text{int}}^i = \sum_j A_{ij} \langle S^j_C \rangle,$$

(2)

Here $A_{ij}$ is the hyperfine coupling constant from the $i$-th boron site to the $j$-th Cu site. It is the sum of the dipolar and transferred hyperfine couplings, $A_{ij} = D_{ij} + T_{ij}$, and it depends only on the relative position between the boron site and the Cu site. The dominant couplings are illustrated in Fig. 3(a) and summarized in Table I. The transferred hyperfine couplings are short-ranged and limited to in plane nearest and next-nearest neighbors, $T_1$ and $T_2$. They satisfy the condition $T_1 + 2T_2 = -0.431$ T imposed by the NMR shift data in undoped SrCu$_2$(BO$_3$)$_2$ [13], leaving only one adjustable parameter, say $T_1$. The analysis of B NMR spectra in the magnetization plateau phases has led to the estimation $-0.711 < T_1 < -0.531$ T.
FIG. 2: (color online) Real space sketch of the spin polaron formed around a Zn impurity (cross). The solid (open) circles on the Cu sites represent the spin moments parallel (antiparallel) to the external field. The area of the circles is proportional to $|\langle S_z \rangle|$ as calculated on a 36-site cluster with $J'/J = 0.67$. The circled numbers show the assignment of the B sites to the NMR lines of Fig. 1 deduced from the analysis described in the text. Primed numbers have been used when different sites are assigned to the same line.

The dipolar couplings decrease as the inverse of the cube of the distance and can be calculated from the crystal parameters. In addition to the nearest and next nearest neighbors in the same layer, two neighbors on the adjacent layers have significant dipolar couplings with different values $D_3 > D_4$ because of the buckling of the layers. Looking at Table I, we can anticipate that the boron sites close to the impurity both in the layer of the impurity and in the two adjacent layers will have internal fields large enough to give rise to additional peaks.

The absolute value $|A_j|$ is by far the largest for the nearest neighbor ($j = 1$). The value of $B_{\text{int}}$ for the B sites in the layer of the impurity should, therefore, be primarily determined by $\langle S^A_c \rangle$ of the nearest neighbor Cu site. We then conclude that $B_1$ and $B_2$, which show a large negative $B_{\text{int}}$ ($\sim -0.14$ T, see Fig. 1), must correspond to boron sites either close to CuA or to CuC in Fig. 2. Likewise, $B_{15}$, with its large positive $B_{\text{int}}$ ($\sim 0.07$ T), should be assigned to boron sites close to CuB. The values of $\langle S^A_c \rangle$ and $\langle S^C_c \rangle$ can be estimated approximately as $B_{\text{int}}/A_j \sim 0.2$, which is significantly smaller than the saturated value of 0.5. Thus the distribution of $B_{\text{int}}$ provides a direct experimental proof for the polaronic spin structure near defects.

Interestingly, the integrated intensity of the low frequency satellite line of $B_1$ at 87.12 MHz is twice as large as that of $B_2$ at 87.24 MHz, indicating that the $B_1$ sites are more abundant than the $B_2$ sites. Therefore, $B_1$ ($B_2$) must be assigned to sites near CuC (CuA). Since $|B_{\text{int}}|$ is larger close to CuC than to CuA, we conclude that $\langle S^A_c \rangle < \langle S^C_c \rangle$. Fig. 3(c) shows that this condition is only met in a very narrow range of $\alpha$ between 0.65 and 0.68.

Thanks to this assignment, we are now in a position to fix $\alpha$ and $T_1$ by fitting the experimental value of $B_{\text{int}}$ at the $B_1$ and $B_2$ sites using the 36-site cluster results (interpolated between $\alpha = 0.66$ and 0.67). This leads to $\alpha = 0.665$ and $T_1 = -0.563$ T ($A_1 = -0.724$, $A_2 = -0.009$ T), compatible with the values in Table 1. The full theoretical histogram of $B_{\text{int}}$ deduced from Eq. (2) is plotted in the upper panels of Fig. 4(a) and (b). The isolated red lines in Fig. 4(a) represent $B_{\text{int}}$ at the boron sites in the same layer as the impurity. Each of them is nearest to one of the seven Cu sites (CuA-C) carrying appreciable magnetization. The overall agreement between the ED results and experiment is very good, leading to the assignment of the lines $B_3$, $B_{14}$, $B_{13}$, $B_{14}$ and $B_{15}$ (see Fig. 2).

All other boron sites in the layer of the impurity have much smaller internal fields. So let us turn to the boron sites on the neighboring layers. They have smaller values

![FIG. 3: (color online) (a) Main hyperfine couplings between a Cu spin and the B nuclei in the same layer ($A_1$ and $A_2$) or in the neighboring layers ($A_3$ or $A_4$). (b) Quadrupolar splitting $\nu_q$ for B sites near a Zn impurity. (c) Dependence on $\alpha = J'/J$ of the local magnetization calculated with exact diagonalizations on a 32-site cluster (open symbols) and 36-site cluster (solid symbols).](image)

| $j$ | $T_j$ | $D_j$ | $A_j$ |
|-----|-------|-------|-------|
| 1   | -0.711 $\sim$ -0.531 | -0.161 | -0.872 $\sim$ -0.692 |
| 2   | 0.05 $\sim$ 0.14 | -0.075 | -0.025 $\sim$ 0.065 |
| 3   | 0 | 0.103 | 0.103 |
| 4   | 0 | 0.065 | 0.065 |

TABLE I: Hyperfine coupling constants in Tesla.
of $B_{\text{int}}$ coming from the interlayer dipolar couplings $D_3$ or $D_4$ as shown in the upper panel of Fig. 1(b). Again, the agreement with the experimental results is very good. Let us first focus on the experimental lines $B_{11}$ and $B_{12}$. Since $B_{12}$ is twice as intense as $B_{11}$ (see Fig. 1), we must assign $B_{12}$ to the neighbors of CuC in the layer above, and $B_{11}$ to the neighbor of the CuA in the layer below. Since both couplings are given by $D_3$, the larger $B_{\text{int}}$ at $B_{12}$ than $B_{11}$ provides an independent confirmation that $\langle S_5^A \rangle < \langle S_5^C \rangle$.

With its strongly negative $B_{\text{int}}$, the line $B_5$ must be attributed to the neighbors of CuB in the layer above. For the other peaks, the experimental resolution is not sufficient to achieve a one to one correspondence with the calculated lines, but the line $B_{10}$ can be assigned to the theoretical lines 10 and 10’ with a high level of confidence given the asymmetric form of the line consistent with two Lorentzians of unequal weight [30]. Likewise, the assignment of lines $B_8$ and $B_9$ to pairs of theoretical lines is plausible since they are well separated from the others. The lines $B_6$ and $B_7$ develop on top of the broad tail of the main line, consistent with the numerous theoretical lines on the negative side of the main line, even though specific assignment is not possible.

So far we have not considered possible lattice distortion induced by Zn doping, which could cause local variation of the hyperfine coupling or exchange interaction. The quadrupole splitting $\nu_Q$ is sensitive to local structural distortion. The inset (b) of Fig. 3 shows the values of $\nu_Q$ for all the observed B NMR lines. Remarkably, most sites have exactly the same value $\nu_Q = 1.25$ MHz as in undoped SrCu$_2$(BO$_3$)$_2$ (solid line). Only the lines $B_{11}$ and $B_{15}$ show minor deviation of about 0.02 MHz, indicating that the lattice distortion is small and limited in the immediate vicinity of the Zn impurities. Note that $\nu_Q$ at the boron sites close to CuA and CuC is unchanged, an indication that the hyperfine couplings are likely not to be influenced. Furthermore, the dipolar coupling, which varies slowly with distance as $1/r^3$, should not be affected by small lattice distortion. Therefore, our conclusion $\langle S_5^A \rangle < \langle S_5^C \rangle$ should remain valid even allowing for a local distortion around the impurity.

Finally, let us comment on the value of $\alpha = 0.665$ necessary to account for the internal structure of the polaron. This value is significantly larger than the value $\alpha \simeq 0.63$ deduced early on from thermodynamic measurements [23]. In addition, the recent determination of the width of the 1/2 plateau in very high magnetic fields by Matsuda et al. [22] also points to a value of $\alpha \simeq 0.63$. We can think of several possible explanations for this apparent discrepancy. First of all, we examined the effects of the Dzyaloshinsky-Moriya (DM) interaction with the help of ED for the Zn doped system. We found, however, that neither the intradimer nor the interdimer DM coupling is able to account for the discrepancy. Another possibility is that the exchange coupling constants take different values in high magnetic field due to magnetostription, an effect already observed in that system [24, 31]. Alternatively, local lattice distortions due to Zn doping could modify the exchange couplings, even though the distortion is spatially confined. In fact, the conclusions of our analysis are compatible with a smaller ratio of $J'/J$ in the bulk if this ratio is allowed to take a larger value close to the impurity [30]. A definitive interpretation would however require to have a better understanding of the modification of the electronic structure around the impurity on the basis of e.g. ab initio calculations. This definitely goes beyond the scope of the present paper.

We acknowledge useful discussions with C. Berthier and M. Horvatić. The work was supported by Grant-in-Aids for JSPS KAKENHI (B) (No. 21340093), the MEXT-GCOE program, and the Swiss National Foundation. Numerical simulations were performed at CALMIP and GENCI.

[1] H. Alloul, J. Bobroff, M. Gabay, and P. J. Hirschfeld, Rev. Mod. Phys. 81, 45 (2009).
[2] M. Hagiwara, K. Katsumata, I. Affleck, B. I. Halperin, and J. P. Renard, Phys. Rev. Lett. 65, 3181 (1990).
[3] S. H. Glarum, S. Geschwind, K. M. Lee, M. L. Kaplan, and J. Michel, Phys. Rev. Lett. 67, 1614 (1991).
[4] M. Yoshida, K. Shiraki, S. Okubo, H. Ohta, T. Ito, H. Takagi, M. Kaburagi, and Y. Ajiro, Phys. Rev. Lett. 95, 117202 (2005).
[5] F. Tedoldi, R. Santachiara, and M. Horvatić, Phys. Rev.
A. Lauchli, S. Wessel, and M. Sigrist, Phys. Rev. B 66 (1997).

K. Kudo, T. Noji, Y. Koike, T. Nishizaki, and N. Kobayashi, J. Phys. Soc. Jpn. 73, 3497 (2004).

S. El Shawish and J. Bonča, Phys. Rev. B 74, 174420 (2006).

S. Haravifard, S. R. Duniger, S. El Shawish, B. D. Gaulin, H. A. Dabkowska, M. T. F. Telling, T. G. Perring, and J. Bonča, Phys. Rev. Lett. 97, 247206 (2006).

Y. Narumi, N. Teradai, Y. Tanaka, M. Iwaki, K. Kato, K. Kindo, Y. Ueda, and T. Goto, J. Phys. Soc. Jpn. 84, 043702 (2009).

For an early review, see S. Miyahara and K. Ueda, J. Phys.: Condens. Matter 14, L319 (2002).

S. Miyahara and K. Ueda, Phys. Rev. Lett. 82, 3701 (1999).

A. Koga and N. Kawakami, Phys. Rev. Lett. 84, 4461 (2000).

C. Knetter, A. Buhler, E. Muller-Hartmann, and G. S. Uhrig, Phys. Rev. Lett. 85, 3958 (2000).

A. Läuchli, S. Wessel, and M. Sigrist, Phys. Rev. B 66, 014401 (2002).

See supplemental material for details about the experiments and the theory.

Y. Narumi, N. Teradai, Y. Tanaka, M. Iwaki, K. Katsumata, K. Kindo, H. Kageyama, Y. Ueda, H. Toyokawa, T. Ishikawa, and H. Kitamura, J. Phys. Soc. Jpn. 78, 043702 (2009).

SUPPLEMENTAL MATERIALS

A. Comparison of the NMR spectra for different Zn concentration

Figure 5 shows the $^{11}$B NMR spectra for $x = 0.0032$ and 0.0174 at 1.6 K and 6.615 T. Both samples show nearly identical spectra. All the resolved peaks are exactly at the same frequencies, indicating that the average distance between Zn$^{2+}$ ions is sufficiently large and effects of interaction between impurity-induced spins can be neglected. However, the widths of the individual lines for $x = 0.0174$ are slightly larger than those for $x = 0.0032$, which is likely due to the difference in the distribution of the demagnetizing fields inside the crystals.

B. Magnetization due to impurity-induced free spins

Figure 6(a) shows the temperature dependence of the magnetization $M$ of SrCu$_2$Zn$_x$(BO$_3$)$_2$ at the field of 1 T. The increase of $M$ for $x = 0.0174$ and 0.0032 at low temperatures should be ascribed to the impurity-induced unpaired spins. By subtracting the magnetization for $x = 0$ from these data and normalizing by $x$, we obtain the contributions from the impurity-induced spins $M_1$, which are plotted in Fig. 6(a). The values of $M_1$ are nearly identical for $x = 0.0174$ and 0.0032 in the whole temperature range, indicating that Zn$^{2+}$ ions effectively replace the Cu sites. The increase of $M_1$ below 10 K is described reasonably well by a free spin model $M_F = gS\mu_B B_S(X)$ with $S = 1/2$, where $B_S(X) = gS\mu_B B/k_B T$ is the Brillouin function. Above 10 K, on the other hand, $M_1$ is much smaller than $M_F$, indicating that Zn impurities can...
no longer generate free spins because of interaction between unpaired Cu spins and thermally excited triplets.

Figure 6(b) shows the magnetic field dependence of $M$ at 2 K. Although the magnetization of a free spin $M_F$ saturates completely above 4 T as indicated by the solid line, $M$ of SrCu$_{2-x}$Zn$_x$(BO$_3$)$_2$ keeps increasing almost linearly with $B$ at high fields. The NMR spectra shown in Fig. 7(a), on the other hand, indicate that the internal fields at boron sites stay exactly the same between 4.5 and 6.615 T, a clear indication of the saturation of the spin moments. The temperature dependence of the resonance frequency shown in Fig. 7(b) provides further support for the saturation of spin moments. Thus the linear increase of $M$ at high fields cannot be attributed to spin moments. It may be associated with orbital (van Vleck) magnetism, even though we do not understand the mechanism for such a behavior. By subtracting the $B$-linear component at high fields from $M$, we obtain the contributions of the unpaired spins $M_I$, which are normalized by $x$ and are plotted in Fig. 6(b). There is almost no difference between $M_I$ for $x = 0.0174$ and 0.0032. They also agree reasonably well with the free spin behavior $M_F$.

C. Numerical Methods

Exact Diagonalization (ED) have been performed using the standard Lanczos algorithm for the $S = 1/2$ Heisenberg model on Shastry-Sutherland lattices ($N = 32$ and 36 sites, see Fig. 5) having a single impurity. Periodic boundary conditions have been used to minimize finite-size effects. The presence of an impurity forbids the use of any translation symmetry, but we have still made use of the remaining reflection symmetry to reduce the size of the Hilbert space. After computing the ground-state, one can easily extract the average magnetization on each site. Note that since the polaron has a large but finite extension, we have checked that these magnetization values are almost independent on the size of the cluster and thus we are confident that they are close to their thermodynamical values (see Fig. 5 of main text).
D. Intensity and line shape of some specific lines.

One of our main conclusion that $\langle S_A^c \rangle < \langle S_C^c \rangle$ is based on the intensity ratio of the $B_1$ and $B_2$ lines, which are assigned to the B sites close to CuC and CuA on the layer of the Zn impurity. Equally important is the intensity ratio of the $B_{11}$ and $B_{12}$ lines assigned to the B sites on the adjacent layers coupled to CuC and CuA with the same dipolar coupling $D_3$. The spectrum of the center line of these sites are displayed in Fig. 9(a) with an enlarged scale. We can clearly see that the integrated intensity of the $B_{12}$ line is twice as large as the $B_{11}$ line. Since CuC is twice as abundant as CuA, the $B_{12}$ ($B_{11}$) line must be assigned to the neighbor of CuC (CuA). The fact that $B_{	ext{int}}$ is larger for the $B_{12}$ line than for the $B_{11}$ line then leads to the conclusion that $\langle S_A^c \rangle < \langle S_C^c \rangle$.

The ED calculation shows that there is another pair of lines (10 and 10') assigned to the B sites on the adjacent layers coupled to CuC and CuA with the smaller dipolar coupling $D_4$ (see the upper panel of Fig. 4(b)). Although the experimentally observed $B_{10}$ line shows only a single peak, the spectral shape can be actually fit well to a sum of two Lorentzians with the intensity ratio of 2 to 1 as indicated in Fig. 9(b). The fact that one of these lines with larger $B_{	ext{int}}$ has the double intensity is again consistent with the conclusion $\langle S_A^c \rangle < \langle S_C^c \rangle$.

E. Possible local change of exchange interaction due to lattice distortion

Here we employ a simple model to account for a possible change of exchange interaction due to local lattice distortion near Zn impurities and examine to what extent our best choice of $\alpha = 0.665$ is influenced by such effects. Since the distribution of $\nu_Q$ shown in Fig. 5(b) suggests that the lattice distortion is confined in the immediate vicinity of Zn, the simplest model consists in assuming that only the exchange interaction for the Cu-Cu bonds closest to the Zn impurity, i.e. the exchange between CuA and CuB, changes from the bulk $J'$ to $J_{\text{imp}}$.

We have calculated the moments at CuA and CuC sites by exact diagonalization using a cluster of 32 or 36 sites as a function of $\alpha_{\text{imp}} = J_{\text{imp}}/J$ for three values of the
the observed values of mental data, we extracted the local magnetization from ciable moments. The values of $C$ symbols) sites are plotted against finalization for a cluster with 32 (open symbols) or 36 (filled and $B$ A
FIG. 10: (color online) Local magnetization at Cu $B$ bor to one of the major Cu sites (Cu $B$ 13–15 in Fig. 4b), each of which is the nearest neighbor to one of the major Cu sites (Cu$_{A-C}$) carrying appreciable moments. The values of $\langle S^\Lambda_c \rangle$ can be determined by solving Eq. (2) after substituting the experimental values of $B_{\text{int}}$ into the left side and using the same values of the hyperfine coupling constants $T_1 = -0.563$ T. The values of Cu$_A$ and Cu$_C$ thus determined are shown by the solid lines in Fig. 10. Alternatively, we can use the values of $B_{\text{int}}$ at the B sites in the adjacent layers (B$_5$, B$_{11}$, and B$_{12}$) coupled to the three major Cu sites (Cu$_{A-C}$) by the dipolar coupling $D_3$ to determine $\langle S^\Lambda_{A-C} \rangle$. The re-
results are displayed by the dashed lines in Fig. 10. From these plots, we may conclude that the experimental results can be reconciled with $\alpha = 0.65$ by allowing a rather large modification of exchange coupling near Zn. However, the value $\alpha = 0.63$ seems difficult to reconcile with the experimental results within this simple model.

F. Dynamics of the impurity induced spins near saturation

When the impurity-induced moments become saturated as the temperature is decreased, we expect the thermal fluctuations to be gradually depressed and to slow down. Such a process has been indeed confirmed by measurements of the nuclear spin-lattice relaxation rate $1/T_1$ and of the spin-echo decay rate $1/T_2$. A standard inversion recovery method was used for the $1/T_1$ measurement. To determine $1/T_2$, the spin echo intensity $I(\tau)$ as a function of the time $\tau$ between the two rf-pulses was fit to the exponential function $I(\tau) = C_0 \exp(-2\tau/T_2)$.

Figure 11 shows the temperature dependences of $1/T_1$ and $1/T_2$ measured on the low frequency quadrupole satellite line of the B$_1$ site at 6.615 T. Both $1/T_1$ and $1/T_2$ exhibit a peak but at different temperatures. The peak in $1/T_1$ occurs at 3.8 K while the peak in $1/T_2$ appears near 2.5 K. In fact, $T_2$ becomes too short near 2.5 K to be able to observe NMR signal. At lower temperatures, both $1/T_1$ and $1/T_2$ show steep decrease, consistent with the excitation gap for impurity induced spins in a magnetic field.

Let us first discuss $1/T_1$, which is related to the time correlation function of the local field by the standard formula, $1/T_1 \propto G(\omega_N)$, where $G(\omega) = \int \langle h(t)h(t) \rangle \exp(i\omega t) dt$ and $\omega_N$ is the NMR frequency. A simple expression for the correlation function parametrized by the mean square amplitude of the fluctuation $\langle h^2 \rangle$ and the correlation time $\tau_c$, $\langle h(0)h(t) \rangle =
$\langle h^2 \rangle \exp(-t/\tau_c)$ leads to the following simple result,

$$\frac{1}{T_1} \propto \frac{\tau_c}{1 + (\omega_N \tau_c)^2}.$$  \hspace{1cm} (3)

The saturation of the impurity-induced moments is expected to proceed with the depression of $\langle h^2 \rangle$ and the growth of $\tau_c$. The peak in $1/T_1$ can be reproduced only by the latter process. Indeed $1/T_1$ exhibits a peak when $\tau_c = 1/\omega_N \sim 1.8 \times 10^{-9}$ s, a well known result in the context of motional narrowing in classical NMR [1].

The slowing down of the spin fluctuation can also cause a peak in $1/T_2$, with different criteria however. When the fluctuating local field slows down, the fastest spin-echo decay is achieved when $1/\tau_c$ becomes comparable to $\gamma \sqrt{\langle h^2 \rangle}$ and the peak value of $1/T_2$ has the same orders of magnitude as $1/\tau_c$ at the peak temperature [2, 3]. Although we were not able to determine the peak value of $1/T_2$ due to loss of NMR signal, it should be of the order of $10^6$ s$^{-1}$, judging from the data in Fig. indicating that $\tau_c \sim 10^{-6}$ s at 2.5 K, which is much longer than the value estimated at the peak temperature of $1/T_1$ (3.8 K). Thus, different peak temperatures of $1/T_1$ and $1/T_2$ provide evidence for a rapid but gradual slowing down of the fluctuation of the impurity-induced spins, which precedes the complete saturation at lower temperatures.

[1] A. Abragam, "The principles of Nuclear Magnetism" (Oxford Univ. Press, 1961).
[2] M. Takigawa and G. Saito, J. Phys. Soc. Jpn. 55, 1233 (1986).
[3] C. H. Recchia, K. Gorny, and C. H. Pennington, Phys. Rev. B 54, 4207 (1996).