Electronic and magnetic properties of $K_2CuP_2O_7$: A model $S = \frac{1}{2}$ Heisenberg chain system

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(Received 7 January 2008; revised manuscript received 19 March 2008; published 30 April 2008)

The electronic and magnetic properties of $K_2CuP_2O_7$ were investigated by means of susceptibility, specific heat and $^{31}P$ nuclear magnetic resonance (NMR) measurements and by local density approximation (LDA) band structure calculations. The temperature dependence of the NMR shift $K(T)$ is well described by the $S = \frac{1}{2}$ Heisenberg antiferromagnetic chain (HAF) model with nearest neighbor exchange $J_1 = (141 \pm 5) \text{ K}$. The corresponding mapping of an LDA-derived tight-binding model leads to $J_1^{\text{LDA}} = 196 \text{ K}$. The spin lattice relaxation rate $1/T_1$ decreases with temperature below 300 K but becomes nearly temperature independent between 30 and 2 K, as theoretically expected for an $S = \frac{1}{2}$ HAF chain. None of the investigated properties give any evidence for long range magnetic order above 2 K, which is in agreement with the results of the band structure calculation, which yield extremely weak exchange to the next nearest neighbor and a very small and frustrated interchain exchange. Thus, $K_2CuP_2O_7$ seems to be a better realization of a nearest neighbor $S = \frac{1}{2}$ HAF chain than the compounds reported so far.

DOI: 10.1103/PhysRevB.77.134451

I. INTRODUCTION

One-dimensional (1D) spin systems have attracted considerable attention because of their intriguing ground states where quantum fluctuations play a crucial role. Much attention in their magnetism has been caused by the theoretical prediction that the integer-spin chains have an energy gap in the excitation spectrum, while the half-integer spin chains have a gapless excitation spectrum. In particular, 1D $S = \frac{1}{2}$ Heisenberg antiferromagnetic (HAF) systems are interesting since enhanced quantum fluctuations due to reduced dimensionality and low spin value impede long range magnetic order (LRO). In the past decade, theoretical studies on these systems have achieved a remarkable progress but real material realizations for such compounds are limited to date.

The $S = \frac{1}{2}$ chains formed via direct linkage of CuO$_4$ units can be grouped into two categories: in one group, the chains are formed by edge-sharing CuO$_4$ units, while in the other compound family, they are built from corner-sharing CuO$_4$ units. CuGeO$_3$ and Li$_2$CuO$_2$ belong to the former category, where the nearest neighbor (NN) interaction $J_1$ and the next-nearest neighbor (NNN) interaction $J_2$ have comparable strength ($|J_2/J_1| = 1$), thereby leading to a strong frustration within the chain. In such a scenario, various ground states are possible. On the contrary, in Sr$_2$CuO$_4$ which has corner shared CuO$_4$ units $|J_2/J_1| = \frac{1}{20}$, which greatly reduces the in-chain frustration. With $J_1 \gg T_N$, Sr$_2$CuO$_4$ is a better quasi-1D $S = \frac{1}{2}$ chain system than CuGeO$_3$ and Li$_2$CuO$_2$. Recently, another system, Sr$_2$Cu(PO$_4$)$_2$, containing isolated CuO$_4$ units (neither edge nor corner shared) was reported to have $J_2 \approx \frac{3}{75}$ and a much reduced $T_N$ of 85 mK. The presence of interchain coupling (ic) normally provides LRO, but frustrating ic reduces the tendency to LRO. Along with $J_1 \gg T_N$, the presence of frustration between the chains strongly influences the 1D nature of this system, making it a nearly perfect realization for the 1D NN only HAF chain model. Unfortunately, the sample quality was not very good, thereby reducing the chains to a finite length. The analytical solution by Bethe ansatz provides a clear picture of the magnetic (thermodynamic) properties of a very good 1D material. Thus, deviations from these predictions can be assigned to other degrees of freedom (anisotropy, Dzyaloshinskii-Moriya (DM), and other spin-spin interactions), allowing us to analyze their influence on the ground state behavior. Therefore, strong interest still prevails in the experimental community to find possible ways to synthesize a system which keeps the in-chain geometry of Sr$_2$Cu(PO$_4$)$_2$, but with a smaller interchain coupling, which is still frustrating, along with an improved sample quality.

Formally, $K_2CuP_2O_7$ belongs to the family of $M_2CuP_2O_7$ ($M=Li,Na,K$) compounds, although the arrangement of the magnetic CuO$_4$ building blocks is modified within the family. The magnetic properties of Na$_2$CuP$_2$O$_7$ and Li$_2$CuP$_2$O$_7$ were reported earlier. $Na_2CuP_2O_7$ and $Li_2CuP_2O_7$ both have an in-chain exchange coupling $J_1$ of about 28 K and they undergo magnetic ordering at around 5 K. Unlike the other members of this family, our experiments reveal that $K_2CuP_2O_7$ shows a much stronger in-chain exchange interaction ($J_1 = 141 \text{ K}$) but no ordering down to 2 K. Due to such a wide $T_N - J_1$ temperature range, it can be considered as a very good candidate on which to test the theoretical predictions of both static and dynamic properties of an 1D HAF model.

In this paper, we present susceptibility, specific heat, $^{31}P$ NMR results and first principles band structure calculations on $K_2CuP_2O_7$ in order to shed light on the 1D character of the system. The paper is organized as follows: In Secs. II and III, we describe the structural aspects, measurement procedures, and the theoretical methodology. In Sec. IV, we present the experimental results followed by the electronic structure analysis. In Sec. V, we address the issues concerning the almost ideal 1D nature of this compound inferred from the $^{31}P$ NMR and band structure calculations. In Sec. VI we give a short summary and conclusions.

II. STRUCTURE

$K_2CuP_2O_7$ crystallizes in an orthorhombic unit cell with space group $Pbnm$. The reported lattice constants are $a$...
action techniques using K2CO3/H2O849/H11015/por\ldots
Magnetic properties of this compound have not been re-
shown here. NATH et al. direction. The potassium cations reside in between the chains
that of edge sharing CuO4 chains with every second CuO4
system will become
change between Cu2+ ions in K2CuP2O7 will be similar to
K2CuP2O7 crystal structure. The CuO4
tetrahedra, forming [Cu(PO4)2]∞ chains propagating along
the crystallographic c direction. A scheme of the basic building
blocks of the crystal is shown in Fig. 1. The superex-
change between Cu2+ ions in K2CuP2O7 will be similar to
that of edge sharing CuO4 chains with every second CuO4
unit cutoff. In such a situation, J2 (NN) in the edge shared
system will become J1 (NN) in our system (of the order of
100 K), and J2 in our system will be comparable to J4
(fourth neighbor interaction along the chain) in the edge
shared system, which is known to be quite negligible. The
chains are well separated from each other since the potas-
sium cations, K17+ reside in between the chains. The inter-
chain interactions are expected to be very weak, unlike
Sr2Cu(PO4)2 since the chains do not lie in the same plane.
Magnetic properties of this compound have not been re-
ported yet.

III. METHODS

A. Experiment

Polycrystalline K2CuP2O7 was prepared by solid state re-
action techniques using K2CO3 (99.9% pure), CuO (99.99% pure),
and NH4H2PO4 (99.9% pure) as starting materials. The stoichiometric mixtures were fired at 640 °C for 60 h
in air, with one intermediate grinding. The samples were
characterized using a STOE powder diffractometer with a
Cu target (λcu=1.541 82 Å). The powder pattern evidenced
single phase material. The lattice parameters obtained
using a least-squares fit procedure are a=9.541(3) Å, b =
14.407(5) Å, and c=5.253(1) Å, which are close to the
previously reported values.15

Magnetization (M) data were measured as a function of
temperature T between 2 and 400 K in fields up to 5 T on
powder samples in a commercial (Quantum design) super-
conducting quantum interference device (superconducting quantum interference device) magnetometer. Specific heat
Cp(T) measurements were performed on a pressed pellet using
relaxation method in a commercial PPMS (physical property measurement system) equipment (Quantum design). NMR measurements were carried out using pulsed NMR
techniques on 31P nuclei (nuclear spin I=\frac{1}{2} and gyromagnetic
ratio γ/2π=17.237 MHz/T) at 70 MHz, which corresponds
to an applied field of about 40.6 kOe. Spectra were obtained
by Fourier transform of the NMR echo signal using a π/2
pulse with width of about 2 μs. The NMR shift \kappa(T) =\left[n(T)−ν_{ref}\right]/ν_{ref} was determined by measuring the reso-
rance frequency of the sample \kappa(T) with respect to a stan-
dard H3PO4 solution (resonance frequency νref). The spin-
lattice relaxation rate (1/T1) was measured by the saturation
recovery method. Our attempt to see the 63Cu signal was not
successful due to the fast relaxation at the magnetic site.

B. Theory

The band structure calculations presented here utilized
version 5.00-18 of the full-potential local orbital band
structure16,17 (FPLO) method. The structure, lattice con-
stants, and atomic positions have been taken from experi-
ment.15 The core states have been treated fully relativ-
istically, while the semicore (K: 3s3p, Cu: 3s3p, and P:
2s2p) and the valence states (K: 3d4s4p, Cu: 3d4s4p, P:
3s3p3d, and O: 2s2p3d) are treated scalar relativistically.
The extent of the valence basis functions was optimized with
respect to the total energy.18 The Brillouin zone sampling
was based on 216 k points in the irreducible wedge. We have
used the Perdew and Wang19 flavor of the exchange and cor-
relation potential when performing the calculations within
the local density approximation (LDA).

IV. RESULTS

A. Susceptibility and specific heat

Bulk magnetic susceptibility \chi(T)=(M/H) was measured
as a function of temperature in an applied field of 5 kOe
(Fig. 2). As shown in Fig. 2, the sample exhibits a shoulder
at about 100 K, suggesting a maximum in this temperature
range, which is a hallmark of low-dimensional magnetic
interactions. With further decreasing temperature, \chi(T) in-
creases again in a Curie–Weiss manner. Common sources for
such an increase are the presence of paramagnetic impurities
or finite length chains due to disorder. However, an intrinsic
Curie-like tail is expected in a quasi-1D S=\frac{1}{2} chain, if DM
interaction and/or a staggered g-factor anisotropy are present.20,21 Among the 3d systems, Cu benzoate22 and pyri-
midine Cu dinitrate23 are well known examples. No obvious
features associated with LRO were observed for 1.8≤T ≤
400 K.

In order to fit the bulk susceptibility data, we decomposed \chi into
\chi = \chi_0 + \frac{C_{imp}}{T+t_{imp}} + \chi_{spin}(T),
(1)
where the first term \chi_0 is temperature independent and ac-
counts for the diamagnetism of the core electron shells and
Electronics and magnetic properties of K...

FIG. 2. (Color online) Magnetic susceptibility (M/H) vs temperature T for K$_2$CuP$_2$O$_7$ (open circles) in an applied field of 5 kOe. The solid line is best fit of the data to Eq. (1). Spin susceptibility $\chi_{\text{spin}}$ is plotted (open triangles) after subtracting the Curie contribution. In the inset, $C_p/T$ is plotted as a function of $T^2$ for the low temperatures. The solid line represents a linear fit.

Van-Vleck paramagnetism of the open shells of the Cu$^{2+}$ ions. The second term $C_{\text{imp}}$ is the low T Curie–Weiss contribution due to paramagnetic species in the sample. $\chi_{\text{imp}}(T)$ is the spin susceptibility for a uniform $S=\frac{1}{2}$ 1D HAF system, which is known quite precisely over the whole measured temperature range. This indicates that the leading term of the magnetic susceptibility is linear in $T$. For an $S=\frac{1}{2}$ HAF chain, theoretical calculations predict for low temperatures $(T<0.2J)$; $C_p=\frac{2g^2\mu_B^2}{K}\chi_{\text{hyp}}$. With $J_1=141$ K obtained from the NMR shift $\theta(T)$ analysis (presented later), this corresponds to a value $\gamma_{\text{theor}}=0.04 J/K^2$ mole. Fitting the measured data in the range $5\leq T\leq 12$ K, we obtained $\gamma_{\text{exp}}=0.042 J/K^2$ mole. The value of $\gamma_{\text{exp}}$ is close to the value predicted theoretically. This strongly supports the quasi-1D nature of the spin system in K$_2$CuP$_2$O$_7$. No other anomaly was observed down to 2 K in $C_p(T)$, suggesting the absence of magnetic order. Below 5 K, our experimental data deviates upward from the straight line fit (inset, Fig. 2). This is likely related to the contributions of paramagnetic impurities and of chain ends, which should follow a $C=A/T^2$ behavior.

B. 31P NMR

Although our analysis of the susceptibility and specific heat suggests the presence of a $S=\frac{1}{2}$ 1D HAF system, the evidence is only of preliminary nature because of the large Curie tail in $\chi(T)$ at low T. In order to gain a more reliable insight into this system, we turned our attention towards NMR results. NMR has the advantage to be much less sensitive to contribution of defects or impurities because usually only the nucleus on an undistorted site contributes to the narrow NMR line. As shown in the crystal structures (Fig. 1), K$_2$CuP$_2$O$_7$ has two inequivalent $^{31}$P sites, which are coupled inductively to Cu$^{2+}$ ions in the chain. Therefore, $^{31}$P NMR can probe accurately the low-lying excitations in the spin chain. Our $^{31}$P NMR spectra consist of a single spectral line as is expected for $I=\frac{1}{2}$ nuclei (Fig. 3). Although there are two inequivalent $^{31}$P sites present in the crystal structure, a single resonance line implies that both the $^{31}$P sites in this compound are nearly identical. With decreasing temperature, the NMR line shifts away from the Larmor frequency, paramagnetically broadens but the overall line shape remain same down to 2 K. The asymmetric shape of the spectra corresponds to a powder pattern due to an asymmetric hyperfine coupling.
The temperature dependence of the NMR shift $K$ is shown in Fig. 4. With decreasing temperature $K(T)$ paramagnetically increases, then passes through a broad maximum at 110 K, which is an indicative of short-range correlations, and decreases again smoothly toward low temperatures. Below $T_c \approx 0.028$, $K(T)$ shows a much steeper decrease toward zero. As mentioned before, the NMR has an advantage over bulk susceptibility. One accurately measures the $\chi_{spin}$ by NMR shift without suffering from the contribution from the free spins and extrinsic foreign phases, which limits the accuracy of the bulk susceptibility measurements. Therefore, it is more reliable to extract the magnetic parameters from the temperature dependence of the NMR shift rather than from the bulk susceptibility. The conventional scheme of correlating $K(T)$ and $\chi(T)$ is to plot, $K$ vs $\chi_{spin}$ with $T$ as an implicit parameter. Then, the slope yields the average hyperfine coupling $A_{hf}$ between the $^{31}P$ nucleus and the two nearest-neighbor Cu$^{2+}$ ions. In the case of K$_2$CuP$_2$O$_7$, because of the low $T$ Curie tail in $\chi(T)$, this $K(T)$ vs $\chi(T)$ plot shows a straight line only for $T \geq 110$ K (see upper inset of Fig. 4). Nevertheless, we can estimate $A_{hf} \approx 4400 \pm 400$ Oe/µ$_B$, which is about two times stronger than in other phosphate systems.\(^9\)\(^,\)\(^28\) We then define $J_1$ and $g$ by fitting the temperature dependence of $K$ to the following equation:

$$K = K_0 + \left( \frac{A_{hf}}{N\mu_B} \right) \chi_{spin} (T, J_1),$$

where $K_0$ is the temperature independent chemical shift. As shown in Fig. 4, the $K(T)$ data fit rather well to Eq. (2) in the temperature range $9 \leq T \leq 300$ K. By using $A_{hf} \approx 4400$ Oe/µ$_B$ (obtained from the $K$ vs $\chi$ analysis), we obtained $K_0 \approx -890$ ppm, $J_1 \approx (141 \pm 5)$ K, and $g \approx 2.2$. Below about 8 K, $K(T)$ show a significant deviation from the fit (see lower inset of Fig. 4), which shall be discussed later.

The temperature dependence of $^{31}P$ $1/T_1$ is presented in Fig. 5. For a $I = \frac{1}{2}$ nucleus the recovery of the longitudinal magnetization is expected to follow a single exponential behavior. In the experiment, we indeed observed single exponential behavior down to 30 K, while below 30 K, it fitted nicely to the stretch exponential with a reduced exponent. We did not observe any anomaly or divergence in $1/T_1(T)$ down to 2 K, which indicates the absence of magnetic ordering. For $2 \leq T \leq 30$ K, $1/T_1$ almost remains constant, while for $T \geq 30$ K, it strongly increases with temperature. A slight shoulder is visible in the plot $1/T_1$ versus ln $T$ around 180 K, i.e., just above $J_1$, suggesting a regime crossover in this temperature range.

### C. First principles and tight binding

Collected in Fig. 6 are the nonmagnetic band structure and the density of states (DOS). The antibonding is made from a half-filled Cu 3$d_{x^2}$, 2$p_x$ molecular orbital belonging to the CuO$_4$ plaquettes. The band structure shows strong dispersion of about 55 meV parallel to the chain direction $\Gamma Z$ and $X A$ but is nearly dispersionless within the crystallographic $a$-$b$ plane (i.e., perpendicular to the direction of the chains), indicative of the strong 1D character in this system. Within LDA, we get a metallic behavior, though the system is an insulator, suggested by its blue color.\(^14\) This is a well known artifact of LDA wherein the effect of strong correlations is under estimated. Including the strong correlations for the Cu 3$d$ states will open up the insulating gap. This can be achieved via two possible ways: (a) performing an LDA+$U$ calculation self-consistently, (b) mapping the results from LDA first to a tight-binding model (TBM). The TBM is then mapped on to a Hubbard model, and subsequently to a Heisenberg model because the system belongs to the strong correlation limit $U \gg t$ ($t$ is the leading transfer integral) at half filling.

In order to better understand the microscopic magnetic interactions in this system, we have followed the second option mentioned above. First, we have considered the TBM,

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} C_{i, \sigma}^\dagger C_{j, \sigma} + \sum_i \epsilon_i n_i,$$

where $t_{ij}$ are the hopping integrals, $C_{i, \sigma}^\dagger$ and $C_{j, \sigma}$ are annihilation and creation operators. From the LDA band structure, we
have extracted only the four antibonding Cu $3d_{z^2-r^2}$ bands and performed a fit to the TBM. All the hopping paths considered in our model are shown in Fig. 7. The hopping integrals were calculated using the steepest descent method. The resulting parameters, which provided the best fit to the LDA band structure, are collected in Table I. The strength of the NN hopping $t_1$ along the chain is 2 orders of magnitude larger than all the other hoppings, attributing the strong one dimensionality to the interaction of the plaquettes along the chain. The individual exchange constants are calculated by using $J_{ij}^{\text{AFM}} = 4t_{ij}^2/U_{\text{eff}}$. The value of $U_{\text{eff}}$ for K$_2$CuP$_2$O$_7$ is set to 4.5 eV, the same as the choice in related 1D compounds (Sr,Ba)$_2$Cu(PO$_4$)$_2$. The total exchange constant is given by $J_{\text{total}} = J_{\text{AFM}} + J_{\text{FM}}$. The $J$ values collected in Table I are indicative of the $J_{\text{FM}}$ only. In K$_2$CuP$_2$O$_7$, the CuO$_4$ plaquettes are separated from each other, with no corner-or edge-sharing oxygens. The absence of direct connections between the plaquettes largely suppresses ferromagnetic interactions between the copper sites. The strength of the FM interactions was shown to be very small in the related systems (Sr,Ba)$_2$Cu(PO$_4$)$_2$, and this result should equally hold for our system.

V. DISCUSSION

The quality of the fit for the NMR shift supports the presence of an $S = \frac{1}{2}$ HAF chain. The exchange coupling ($J_1 = 141$ K) is comparable to that found in other phosphates and in nice agreement with the effective NN superexchange constant, $J_1^{\text{LDA}} = 196$ K obtained from the TBM. The slight overestimation may stem from the fact that $U_{\text{eff}}$ is not exactly known, along with some FM contributions. Such a overestimation of $J$ by LDA is well known and is also observed in (Sr,Ba)$_2$Cu(PO$_4$)$_2$. The NNN superexchange

FIG. 6. (Color online) Left panel: The nonmagnetic band structure of K$_2$CuP$_2$O$_7$ along the high-symmetry directions of a standard orthorhombic unit cell. X-A and Z-Γ denote the directions along the chain (i.e., along crystallographic $c$ axis), wherein the dispersion is the largest, while the perpendicular-to-chain directions Γ-X and Γ-Y are rather nondispersive. There are four copper sites per unit cell leading to four half-filled metallic bands at the Fermi level, well separated from all other bands. Right panel: The total DOS for K$_2$CuP$_2$O$_7$ along with the Cu $d_{z^2-r^2}$ orbitally resolved contributions. A comparison to the band structure clearly elucidates that the half-filled metallic band at the Fermi level is primarily from Cu $d_{z^2-r^2}$ and O $p_m$ molecular plaquette orbital.

FIG. 7. (Color online) The various hopping paths considered in our tight-binding model to reproduce the half-filled metallic LDA band are shown here. We have considered two hoppings along the chain ($t_1$, $t_2$) and four interchain hoppings ($t_{1c1}$,$t_{1c2}$,$t_{1c3}$,$t_{1c4}$) in all. Starting from one chain, Cu in the next neighbor chain are shifted by half of the in-chain Cu-Cu distance, leading to two identical interactions to two Cu sites in each adjacent chains.
constant \(J_{\text{ic}}^{\text{LDA}} = 0.04 \text{ K}\) is extremely small, so frustration coupling, if any, should be negligible. The ratio of first and second neighbor in-chain coupling is \(J_1^{\text{LDA}}/J_{\text{ic}}^{\text{LDA}} \approx 5000\), the largest found in \(S = \frac{1}{2}\) chain system. The ratio of in chain to the strongest (frustrating) interchain coupling is \(J_1^{\text{LDA}}/J_{\text{ic}}^{\text{LDA}} \approx 1000\), which is 2 orders of magnitude larger than in \(\text{Sr}_2\text{Cu}(\text{PO}_4)_2\) (Ref. 11) and 1 order of magnitude larger than \(\text{Sr}_2\text{CuO}_3\) \((J_1^{\text{LDA}}/J_{\text{ic}}^{\text{LDA}} \approx 500)\) (Refs. 8 and 29) and making \(\text{K}_2\text{CuP}_2\text{O}_7\) an even better realization of 1D HAF behavior than the Sr analog. We have estimated the Néel temperature of \(\text{K}_2\text{CuP}_2\text{O}_7\) \((T_N^\text{K})\) by adapting a simple mean field approximation\(^8,30\) and comparing it to the Sr analogue \((T_N^\text{Sr})\). Assuming that the anisotropy are the same in both compounds, we can write according to Ref. 8

\[
\frac{T_N^\text{K}}{T_N^\text{Sr}} = \sqrt{\frac{J_1^{\text{LDA}}}{J_{\text{ic}}^{\text{LDA}}}},
\]

where, \(T_N^\text{Sr} = 85 \text{ mK}\).\(^{10}\) Since the incompleteness in the mapping should be the same for both the compounds, we can directly compare the values of \(T_N\). We have used \(J_{\text{ic}}^{\text{K}} = 187 \text{ K}\), \(J_{\text{ic}}^{\text{Sr}} = 0.23 \text{ K}\) (geometrical average of the 2 inter-chain exchanges), \(J_1^{\text{K}} = 196 \text{ K}\), and \(J_1^{\text{Sr}} = \sqrt{J_1^{\text{LDA}} J_{\text{ic}}^{\text{LDA}}} = 0.037 \text{ K}\). By plugging these values in the above equation, we get \(T_N^\text{K} = 37 \text{ mK}\), which is a factor of 2 smaller than the Sr analog. This value sets an upper bound because the value of \(J_{\text{ic}}\) is calculated by using a mean-field approximation. The absence of anomalies in \(K(T)\), \(1/T_1(T)\), and the invariant spectral shape down to low temperatures rules out the possibility of LRO down to 2 \text{ K}\), which is consistent with the theoretical prediction of an extremely low \(T_N\). In \(\text{K}_2\text{CuP}_2\text{O}_7\), each CuO\(_4\) plaquettes in one chain has two identical neighbors in each adjacent chains, with the same exchange interactions. For a strong in-chain AFM exchange, this leads to a complete frustration of the interchain interactions. Quantum fluctuations are therefore enhanced here which suppresses \(T_N\) to lower values.

For a 1D \(S = \frac{1}{2}\) HAF, theoretical calculations predict a weak logarithmic decrease of \(\chi(T)\) upon approaching \(T = 0 \text{ K}\) (see Fig. 4). The lower inset of Fig. 4 clearly shows that the decrease we observe in \(\chi(T)\) below \(2 \text{ K}\) is much lower, only 180 ppm, and \(K(T)\) is still decreasing steeply with \(T\) at this temperature. Thus, at the quantitative level, the theoretically predicted logarithmic term fails to describe our experimentally observed decrease. A similar feature has been experimentally found in \(^{17}\)O NMR on \(\text{Sr}_2\text{CuO}_3\) below \(T/J_1 \approx 0.015\) (Ref. 31) and \(^{31}\)P NMR on \((\text{Sr},\text{Ba})_2\text{Cu}(\text{PO}_4)_2\) below \(T/J_1 = 0.003\).\(^9\) In both the cases, it is argued that the decrease

### Table I. Hopping parameters (in meV) and the corresponding exchange constants \(J\) (in K) from an effective one-band tight-binding model. The hopping paths used are indicated in Fig. 7.

<table>
<thead>
<tr>
<th>(t_1)</th>
<th>(t_2)</th>
<th>(t_{ic1})</th>
<th>(t_{ic2})</th>
<th>(t_{ic3})</th>
<th>(t_{ic4})</th>
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<td>138</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0.8</td>
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<tr>
<td>(J_1^{\text{LDA}})</td>
<td>(J_2^{\text{LDA}})</td>
<td>(J_{ic1}^{\text{LDA}})</td>
<td>(J_{ic2}^{\text{LDA}})</td>
<td>(J_{ic3}^{\text{LDA}})</td>
<td>(J_{ic4}^{\text{LDA}})</td>
</tr>
<tr>
<td>K</td>
<td>196</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.007</td>
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FIG. 8. (Color online) The superposition of the total band structure from the FPLO density functional theory (DFT) calculations along with the calculated eigenvalues from the four-site one-band TBM. The TBM fit is quite consistent with the DFT results.
is unrelated to the onset magnetic order or a spin-Peierls transition. In K$_2$CuP$_2$O$_7$, we neither saw any indication of ordering in $1/T_1(T)$ nor in $C_p(T)$. Similarly, there is no signature of exponential decrease (or singlet ground state) observed in $1/T_1(T)$ as is expected for a spin-Peierls transition. One possibility to account for this drop in $K(T)$ is the presence of DM interaction arising from the fact that in K$_2$CuP$_2$O$_7$, there is no center of inversion symmetry-relating two neighboring copper atoms along the chain. In the presence of DM interaction, application of a magnetic field parallel to the DM vector opens a gap $\Delta$ in the magnetic excitation spectra. Since in a first approximation $\Delta$ increases with $B$ to the power $2/3$, it shall not be visible in the $B=0$ specific heat data or the low field susceptibility shown in Fig. 2.

However, further experiments are needed to confirm or discard this explanation.

In NMR valuable information on the dynamic of low-energetic spin excitations can be gained from the analysis of the temperature dependence of nuclear spin-lattice relaxation rates. Therefore, it is essential to analyze $1/T_1(T)$ carefully, which yields information about the imaginary part of the dynamic susceptibility $\chi(q,\omega)$. Thus, $1/T_1$ should include contributions from both the uniform ($q=0$) and staggered ($q=\pm\frac{2}{a}$) spin fluctuations. A theoretical analysis by Sachdev$^{32}$ shows that the staggered component is dominant at low temperatures ($T \ll J_1$). Indeed, the uniform component leads to $1/T_1 \propto T$, while the staggered component gives $1/T_1=\text{constant}$. Monte Carlo calculations by Sandvik supported the validity of these results over an appropriate temperature range.$^{33}$ As shown in Fig. 5, our experimentally observed constant $1/T_1$ at low temperatures ($2 \leq T \leq 30$ K) suggests the dominance of staggered fluctuations at low temperatures. The $^{31}$P form factor for such systems is defined in Ref. 9. Since $^{31}$P is symmetrically located between the Cu ions, the fluctuations are expected to be filtered out provided the hyperfine couplings are equal. Moreover, in this case, we still have a significant remnant contribution from $q=\pm\pi/a$, which plays a dominant role at low temperatures. The possible origin of the remnant staggered fluctuations could be the unequal hyperfine couplings. In fact, such features have been previously observed in a few other 1D $S=\frac{1}{2}$ HAF systems, where $J_1 > T_N$. The strong increase of $1/T_1$ with $T$ above 30 K could be attributed to the uniform fluctuations. When the dominant contribution is from $q=0$, then one expects a constant $1/(KT_1T)$. In K$_2$CuP$_2$O$_7$, for $T \geq 30$ K, we rather observe a weak temperature dependency (inset of Fig. 5), which might be due to some remnant contributions from the staggered fluctuations and/or some additional relaxation mechanisms. This weak temperature dependence as well as the reduction of the slope in the plot $1/T_1$ versus $T$ above 180 K might be related to spin diffusion as observed in $\alpha$-VO(PO$_3$)$_2$ above $J_1$. The relaxation rate due to staggered fluctuations can be calculated following the prescription of Barzykin. For the purpose of comparison of theory with experiment, he defined the normalized dimensionless NMR spin-lattice relaxation rate at low temperature $(1/T_1)_\text{norm} = \frac{\hbar J_1}{A_B T_1} \approx 0.3$, where $A_B$ is $A_B/2\gamma^2/2\pi$. Assuming the fluctuations to be correlated because of the exchange $J_1$ along the chains, $1/T_1$ can be written as $1/T_1 = \frac{\alpha T}{\lambda J_1 T_1}$. By using this expression, $(1/T_1)$ at the $^{31}$P site was calculated to be about 129 s$^{-1}$, whereas our experimental value is 50 s$^{-1}$ in the 2$\leq T\leq 30$ K range. The experimental value is about two times smaller than the theoretical value, likely due to the effect of the geometrical form factor. Further on a weak logarithmic increase in $1/T_1$ is theoretically expected at low temperatures.$^{37}$ In the present case, our measurements were not done down to low enough temperatures to rise this contribution above our experimental error.

VI. CONCLUSION

In conclusion, our experimental and theoretical studies of K$_2$CuP$_2$O$_7$ demonstrate that this compound presents a very uniform and strongly 1D $S=\frac{1}{2}$ HAF chain system. Our NMR, specific heat, and susceptibility measurements show good agreement with theoretical predictions for a 1D $S=\frac{1}{2}$ HAF chain. Thus, the temperature dependence of the NMR shift $K$ can be fitted in good agreement with model calculations giving $J_1 \approx 141 \pm 5$ K. A calculation of the exchange interactions using a TBM fitted to the results of $ab$ initio LDA band structure calculations, subsequently mapped onto a Heisenberg model, leads to a quite similar value of $J_1=190$ K and evidences extremely weak NNN interactions as well as extremely weak and “frustrated” interchain exchange of the order of $J^c \approx -0.1$ K, which is in contrast to Sr$_2$Cu(PO$_4$)$_2$ with $J^c \approx -9$ K (Ref. 11) and to Sr$_2$CuO$_3$ “nonfrustrated” $J^c \approx -10$ K.$^8$ The absence of any evidence for magnetic order above 2 K in the experimental data confirms the weakness of the interchain exchanges. By using the TBM results, a rough estimate of the Neél temperature results in a value of $T_N \approx 37$ mK only. K$_2$CuP$_2$O$_7$ has the smallest in-chain as well as frustrating smallest interchain exchanges, which do not suppress quantum systems, thereby making this system an even better example of a 1D $S=\frac{1}{2}$ HAF system than the compounds reported so far.

We further studied the magnetic fluctuations by analyzing the temperature dependence of $1/T_1$. At low temperatures $1/T_1$ remains constant, which is in reasonable agreement with Sachdev’s predictions for 1D $S=\frac{1}{2}$ HAF system where relaxation is dominated by $q=\pm\pi/a$ at low $T$. Below 5 K, we obtained a decrease of the NMR shift $K$, which is more pronounced than that expected for 1D $S=\frac{1}{2}$ HAF. Its origin is not clear yet but might be due to DM interactions.

ACKNOWLEDGMENTS

We thank A. V. Mahajan and F. Haarmann for their critical suggestions on NMR. We would like to acknowledge Alois Loidl for some preliminary NMR measurements done in his group laboratory. D.K. and H.R. acknowledge financial support from the “Emmy-Noether-program” of the DFG.
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14. L. Alexander et al. (private communication)
25. Using g as a free parameter results in a reduced value of about 1.8. Nevertheless, in either case it does not lead to a significant change in the value of J1 (~130 K).
29. Taking the measure of J1=190 meV from the magnetic susceptibility experiment of Ref. 7 and the empirical J2:0.2 meV, calculated from the ordering temperature T_N=5 K, using coupled quantum spin chain approach as in Ref. 8, we find J1/J2 ~ 600 still 1 order of magnitude smaller than K2CuP2O7.