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NMR evidence for the spin gap behavior in Cu_2PO_4OH

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We report on the results of a ^{31}P nuclear-magnetic-resonance (NMR) study on Cu_2PO_4OH at temperatures between 4 and 300 K. This material has been a subject of current interest due to indications of spin gap behavior. The temperature-dependent NMR shift exhibits a character of low-dimensional magnetism with a broad maximum at $T_{max} \simeq 110$ K. Below T_{max}, the NMR shifts and spin-lattice relaxation rates clearly indicate activated responses, confirming the existence of a spin gap in Cu_2PO_4OH. The experimental NMR data can be well fitted to the square spin tetramer (SQST) model, yielding a spin gap size of about 140 K. It thus points out that the nearly isolated SQST picture is proper for the understanding of the spin gap nature in Cu_2PO_4OH.

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I. INTRODUCTION

The physics of low-dimensional magnetic systems continues to attract attention because of the association with peculiar quantum effects.[1,2] Strong quantum fluctuations due to low dimensionality may suppress the long-range magnetic ordering, resulting in an opening of a finite spin gap separated from the spin singlet ground state and magnetic excited states.[3–7] During the past decades, several quantum spin systems such as $SrCu_2O_3$, $BaCu_2V_2O_8$, $Na_2Cu_2TeO_6$, and $Cu_2Sc_2Ge_4O_{13}$ have been discovered to possess spin gaps.[8–12] The spin gap characteristics have been interpreted in accordance with the strong spin-exchange interactions of particular configurations along the specific low-dimensional pathways in these compounds.[13–16]

Mineral libethenite Cu_2PO_4OH, although it was discovered in 1823, has been a subject of current interest due to indications of spin gap behavior. The bulk magnetic susceptibility of Cu_2PO_4OH exhibits a broad maximum at around $T_{max} \simeq 110$ K and decreases rapidly at low temperatures.[17] In addition, the result of the heat-capacity measurement has further confirmed no long-range magnetic ordering above 2 K. These features are in reminiscence of a spin gap characteristic for this material. Cu_2PO_4OH crystallizes in an orthorhombic structure with the space group *Pnnm*.[18] Within this crystal structure, copper atoms have two nonequivalent crystallographic sites denoted as Cu1 and Cu2, respectively. A very recent theoretical study of the relative strengths of the spin-exchange interactions between Cu^{2+} ($S=1/2$) ions of Cu_2PO_4OH indicated that the strongest superexchange interaction (J_1) occurs along the path between the Cu1 and Cu2 atoms,[17] as illustrated by solid lines in Fig. 1. The J_1 interactions form square spin tetramer (SQST) units via Cu1-Cu2-Cu1-Cu2, and these SQSTs are weakly coupled through another exchange interaction J_2 (shown as dashed lines) between the Cu2 atoms. Since the calculated ratio of $J_2/J_1 \simeq 0.2$ is rather small, it is suitable to employ the isolated SQST scenario for the understanding of the magnetic property of Cu_2PO_4OH. With this respect, the spin Hamiltonian can be approximated by

$$\hat{H}_{SQST} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_1), \qquad (1)$$

with $J_1 = J$ and $J_2 = 0$. The magnitude of the spin-exchange constant J represents the separated energy between the adjacent pairs of the spin levels which corresponds to the size of the spin gap in Cu_2PO_4OH.

In order to further identify the existence of a spin gap in Cu_2PO_4OH, we carried out a detailed ^{31}P nuclear-magnetic-resonance (NMR) study invoking NMR shifts and spin-lattice relaxation rates on this compound. The NMR shift provides a local measurement of the susceptibility which is less sensitive to the presence of impurities and other phases. The spin-lattice relaxation rate is a sensitive probe for the low-energy spin excitations, yielding direct evidence for the presence of an energy gap. Regarding the title compound Cu_2PO_4OH, a transfer of magnetic $3d$ spin from the copper ions onto the phosphorus orbital allows us to probe the Cu^{2+} spin dynamics and determine the spin gap characteristic through the transferred hyperfine interaction. The experimental NMR results clearly reveal spin gap behavior in Cu_2PO_4OH. In addition, the data analysis using the isolated SQST model was found to give good agreement with the observations.

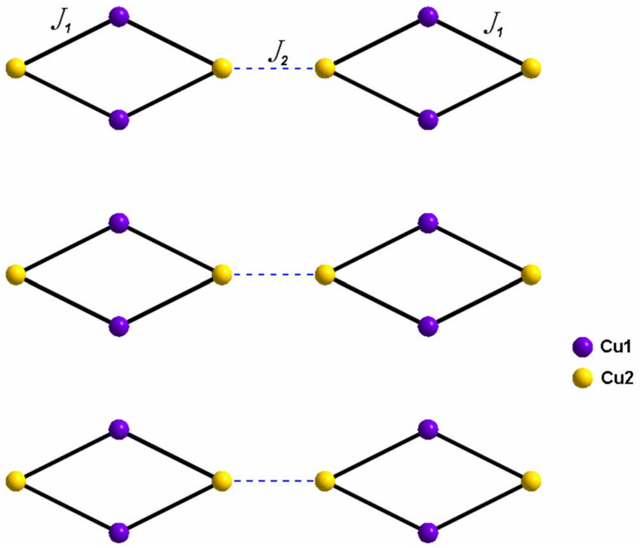

FIG. 1. (Color online) A schematic view of the weakly interacting SQSTs of Cu_2PO_4OH. Only Cu1 and Cu2 ions are shown. The solid lines represent the spin-exchange interactions between Cu1 and Cu2 ions defined by J_1 and the dashed lines illustrate the intertetramer interaction via J_2.

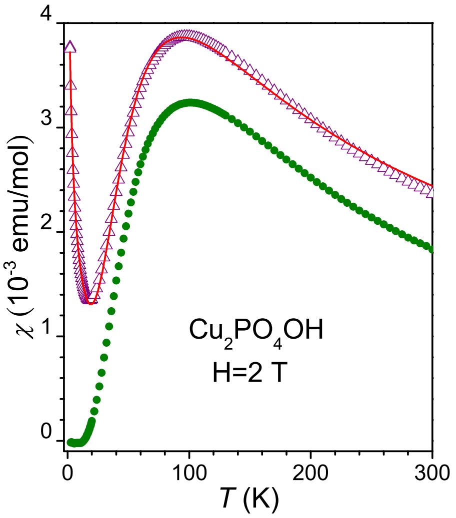

FIG. 2. (Color online) Magnetic susceptibility of Cu_2PO_4OH in a field of 2 T (triangles). The solid curve corresponds to a fit to the equation of $\chi(T)=\chi_0+\chi_{cw}(T)+\chi_{spin}(T)$ described in the text. The resulting $\chi_{spin}(T)$ is shown as the solid circles.

II. EXPERIMENT AND DISCUSSION

A polycrystalline Cu_2PO_4OH sample was synthesized by a ceramic sintering solid-state reaction technique described elsewhere.[17] The dc magnetic susceptibility χ was measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) under an external field of 2 T. The temperature dependence of $\chi(T)$ in the range between 2 and 300 K was given in Fig. 2. The feature of the curve is similar to that reported by Belik *et al.*,[17] showing a broad maximum near 110 K. After passing this maximum, the susceptibility decreases rapidly with lowering temperature and an upturn appears below 15 K. The susceptibility data can be decomposed into $\chi(T)=\chi_0+\chi_{CW}(T)+\chi_{spin}(T)$ where χ_0 is a temperature-independent part, $\chi_{CW}(T)=C/(T-\theta)$ is the Curie-Weiss term responsible for the low-temperature upturn, and $\chi_{spin}(T)$ is the uniform spin susceptibility corresponding to the intrinsic magnetic nature of Cu_2PO_4OH. From the theoretical prediction,[17] the magnetic property of Cu_2PO_4OH can be described by an ensemble of noninteracting SQSTs with a single spin-exchange interaction J. Based on this proposed picture, $\chi_{spin}(T)$ can be expressed as[19]

$$\chi_{spin}(T)=\frac{N_A g^2\mu_B^2}{2k_BT}\,\frac{2+e^{-J/T}+5e^{J/T}}{7+3e^{-J/T}+5e^{J/T}+e^{-2J/T}}, \tag{2}$$

where N_A is the Avogadro's constant, μ_B is the Bohr magneton, and k_B is the Boltzmann constant. As one can see, the fitting of the susceptibility data to the above expression, shown as a solid curve in Fig. 2, is quite satisfactory. With this fit, we obtained the parameters of $\chi_0=4.8\times10^{-4}$ emu/mol, $\theta=-2.85$ K, $C=1.57\times10^{-2}$ emu K/mol, and $J=-125$ K. From the Curie constant C, the concentration of the paramagnetic defects arising from the isolated Cu^{2+} ions was estimated to be 4.18%/mol.

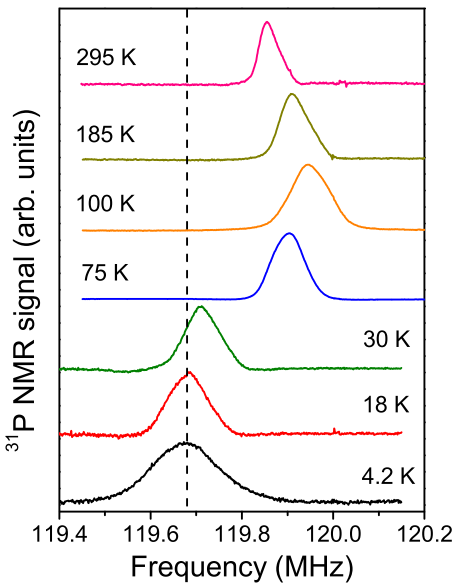

FIG. 3. (Color online) ^{31}P NMR spectra of Cu_2PO_4OH measured at various temperatures under a constant field of 6.9437 T. The dashed vertical line denotes the position of the ^{31}P reference frequency.

The NMR experiments were performed using a Varian 300 spectrometer, with a constant field of 6.9437 T. A homebuilt probe was employed for the low-temperature measurements. The powder specimen was put in a plastic vial that showed no observable ^{31}P NMR signal. The ^{31}P NMR spectra were obtained by the Fourier transform of a half of the spin-echo signal using a standard $\pi/2$-τ-π sequence. Within the *Pnnm* space group for Cu_2PO_4OH, the phosphorus atoms occupy one crystallographic site, yielding a single ^{31}P NMR resonance line, as demonstrated in Fig. 3. Upon lowering temperature, the resonance line gradually shifts to higher frequency. Below about 100 K, the line moves toward the reference position shown as a vertical dashed line. The reference frequency here was referred to the ^{31}P resonance frequency of aqueous H_3PO_4.

In Fig. 4, we displayed the observed temperature-dependent NMR shift (K_{obs}) for the phosphorus site of Cu_2PO_4OH. The shift here was taken at the center of the gravity of the resonance line at each temperature. As one can see, the whole temperature variation in K_{obs} is quite consistent with $\chi_{spin}(T)$ deduced from the susceptibility data, showing a broad maximum at around $T_{max}\simeq110$ K and a rapid decrease by lowering temperature.[17] In general, K_{obs} is a combination of two parts as $K_{obs}=K_0+K_{spin}(T)$. The first term $K_0=-0.0034\%$, mainly arising from the diamagnetic shift, is temperature independent. On the other hand, the spin shift K_{spin}, which reflects the Cu^{2+} spin behavior through the transferred hyperfine interaction, is a function of temperature. As mentioned above, the configuration of SQSTs could be responsible for the magnetic property of Cu_2PO_4OH. Accordingly, the temperature dependence of the spin shift will obey the relation[20]

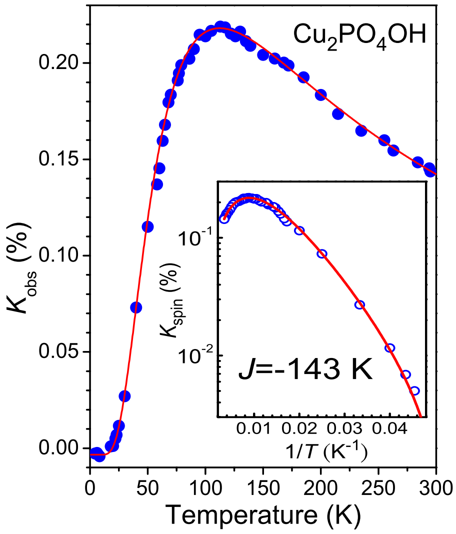

FIG. 4. (Color online) Temperature dependence of the observed ^{31}P NMR shift in Cu$_2$PO$_4$OH. Solid curve: fit to the isolated square spin tetramer model plus a constant term. Inset: a semilogarithmic plot of K_{spin} against $1/T$ for Cu$_2$PO$_4$OH.

$$K_{spin}(T) \propto \frac{1}{T}\frac{2+e^{-J/T}+5e^{J/T}}{7+3e^{-J/T}+5e^{J/T}+e^{-2J/T}}. \qquad (3)$$

As demonstrated in the inset of Fig. 4, K_{spin} can be fitted well in a fairly wide temperature range to this expression, yielding $J=-143\pm5$ K. The magnitude of this value is a bit larger than 125 K extracted from the susceptibility measurement, but it should be more reliable because the bulk susceptibility analysis is somewhat hampered by the low-temperature Curie term. Also note that K_{spin} vanishes to almost zero at low temperatures, indicative of the existence of an energy gap in the spin excitation spectrum.

The NMR shift here is related to the spin susceptibility χ_{spin} by the expression

$$K_{obs}(T) = K_0 + \frac{A_{hf}}{N_A\mu_B}\chi_{spin}(T), \qquad (4)$$

where A_{hf} is the hyperfine coupling constant due to an intermixing of P and Cu spin states. The Clogston-Jaccarino-Yafet plot[20] which shows the observed NMR shift against χ_{spin} is given in Fig. 5. The linear behavior indicates a unique hyperfine coupling constant over the entire temperature range we investigated. The slope yields a value of $A_{hf}=3.04\pm0.02$ kOe for Cu$_2$PO$_4$OH.

To gain more insight into the spin gap characteristics of Cu$_2$PO$_4$OH, we performed the spin-lattice relaxation rate ($1/T_1$) measurement, being sensitive to the low-energy magnetic excitations. It thus provides direct information about the low-energy spin dynamics and the presence of a spin gap. Here the relaxation-time T_1 measurement was carried out using the saturation recovery method. The saturation rf comb with 50 short 2 μs pulses was employed. We recorded the recovery of the signal strength by integrating the ^{31}P spin-echo signal. For the nuclear spin $I=1/2$, the recovery of the nuclear magnetization follows single exponential behavior. Each T_1 value was thus obtained by fitting to the single exponential function. In Fig. 6, we show the temperature dependence of $1/T_1$ of Cu$_2$PO$_4$OH. It is apparent that $1/T_1$ exhibits activated behavior at low temperatures, being consistent with the NMR shift observation.

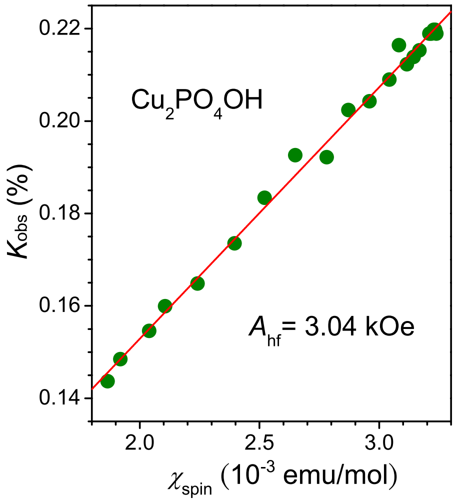

FIG. 5. (Color online) Variation in K_{obs} versus χ_{spin}. The solid line indicates the linear relationship.

In general, the four copper ions ($S=1/2$) are coupled to give a quintet, three triplet, and two singlet states. The energetic order and the number of the spin levels strongly depend on the relative strength of the spin interactions. For the present noninteracting SQST configuration of Cu$_2$PO$_4$OH, four discrete levels (J, 0, $-J$, and $-2J$) can be revealed from the spin Hamiltonian in Eq. (1) with $J<0$. Within the low-temperature limit where the lowest-energy excitation is predominant, only a single spin gap between the adjacent spin levels will be probed. Therefore, the local dissipative suscep-

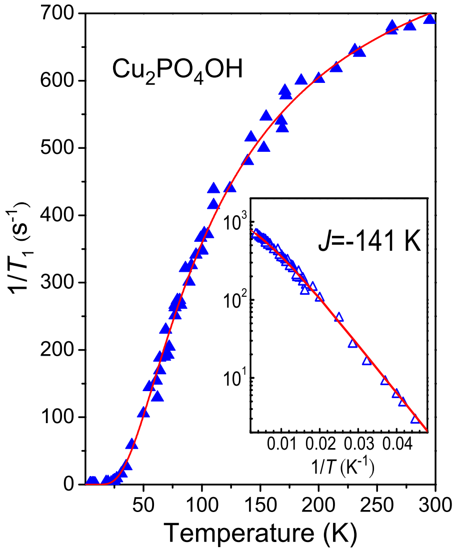

FIG. 6. (Color online) Temperature dependence of the spin-lattice relaxation rate for Cu$_2$PO$_4$OH. The solid curve is the fitted function based on the free square spin tetramer picture. The inset shows a semilogarithmic plot of $1/T_1$ as a function of the inverted temperature for Cu$_2$PO$_4$OH.

tibility sensed by $1/T_1T$ and the static susceptibility sampled by K_{spin} would be almost identical. With this accordance, both static and dynamic excitations follow the same temperature variation and the spin-lattice relaxation rate should be fitted to the form

$$\frac{1}{T_1} \propto \frac{2 + e^{-J/T} + 5e^{J/T}}{7 + 3e^{-J/T} + 5e^{J/T} + e^{-2J/T}} \tag{5}$$

by analogy to the treatment of the NMR shift. The fitting result, drawn in Fig. 6 as a solid curve, is quite satisfactory and yields the parameter $J = -141 \pm 5$ K, which is very close to the value of -143 K deduced from the NMR spin shift.

Our NMR investigation thus provides clear evidence for the existence of a spin gap in Cu_2PO_4OH. The analyses of the NMR shift and $1/T_1$ further indicated that the free SQST scenario is a suitable realization for the spin gap nature of this compound. From the noninteracting SQST model, the gap size is equal to the value of the interaction J which has been determined to be about 140 K for Cu_2PO_4OH. It is worthwhile mentioning that several copper phosphates such as Cu_2PO_4, $SrCu_2(PO_4)_2$, and $PbCu_2(PO_4)_2$ have been reported to possess spin gaps and their magnetic characteristics have been well interpreted in terms of the similar spin tetramer configurations.[21–23] Therefore, it seems appropriate to add the present Cu_2PO_4OH compound to the family of the spin gap copper phosphates arising from spin tetramerization.

III. CONCLUSIONS

We report on the NMR investigation of Cu_2PO_4OH and present evidence for the existence of a spin gap in this material. The spin gap of about 140 K revealed from the spin shift and the spin-lattice relaxation rate was found to be identical. A detailed analysis further indicates that the magnetic nature of Cu_2PO_4OH can be well accounted for by an ensemble of noninteracting square spin tetramers.

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