Spin gap behavior in Cu$_2$Sc$_2$Ge$_4$O$_{13}$ by $^{45}$Sc nuclear magnetic resonance

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We report the results of a $^{45}$Sc nuclear magnetic resonance (NMR) study on the quasi-one-dimensional compound Cu$_2$Sc$_2$Ge$_4$O$_{13}$ 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 negative broad maximum at $T_{\text{max}} \approx 170$ K. Below $T_{\text{max}}$, the NMR shifts and spin lattice relaxation rates clearly indicate activated responses, confirming the existence of a spin gap in Cu$_2$Sc$_2$Ge$_4$O$_{13}$. The experimental NMR data can be well fitted to the spin dimer model, yielding a spin gap value of about 275 K which is close to the 25 meV peak found in the inelastic neutron measurement. A detailed analysis further points out that the nearly isolated dimer picture is proper for the understanding of spin gap nature in Cu$_2$Sc$_2$Ge$_4$O$_{13}$.

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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. Prominent examples like the spin-Peierls transition and the spin ladder compounds have been characterized by ground states of the spin singlet with a finite spin gap. For a quasi-one-dimensional chain with half-integer spin ($S = 1/2$), the gap can be opened via either frustration due to next nearest neighbor antiferromagnetic exchange or dimerization due to an alternating coupling to nearest neighbors along the chain. Several $S = 1/2$ chain systems such as (VO)$_2$P$_2$O$_7$, BaCu$_2$V$_2$O$_8$, and PbCu$_2$(PO$_4$)$_2$ have been reported to possess spin gaps and their characteristics have been interpreted in accordance with these scenarios.

Cu$_2$Sc$_2$Ge$_4$O$_{13}$, which crystallizes in a monoclinic structure with the space group $P2_1/m$, was recently synthesized by one of the present authors (G.J.R.). A schematic picture of the crystal structure is illustrated in Fig. 1. Taking into account the known oxidation states of O$^{2-}$ and Ge$^{4+}$, the remaining valences are non-magnetic Sc$^{3+}$ and Cu$^{2+}$ ($S = 1/2$). The spin chain in Cu$_2$Sc$_2$Ge$_4$O$_{13}$ can be described as an arrangement of spin dimers oriented along the crystallographic $b$-axis, separated by GeO$_4$ tetrahedra and crankshaft-like chains of ScO$_6$ octahedra (Fig. 1). Each dimer consists of two Cu$^{2+}$ ions in a Cu$_2$O$_2$ plaquette and weak interdimer interactions could be possible to induce a quantum phase transition from a gapless state into a gapped state for Cu$_2$Sc$_2$Ge$_4$O$_{13}$.

The bulk magnetic susceptibility of Cu$_2$Sc$_2$Ge$_4$O$_{13}$ exhibits a broad maximum at around 170 K and decreases rapidly at low temperatures, indicative of spin gap behavior for this material. Also the magnetization data have been fitted well to the dimer chain model, yielding a spin gap of 290 K (25 meV). Furthermore, the result of heat capacity has confirmed no magnetic ordering above 2 K. Recently, Masuda et al. have performed a neutron inelastic-scattering experiment on Cu$_2$Sc$_2$Ge$_4$O$_{13}$ and found a narrow-band excitation of about 25 meV, which is quite consistent with the value extracted from the susceptibility. They thus attributed the observation to the spin-gap excitation and proposed Cu$_2$Sc$_2$Ge$_4$O$_{13}$ as a new spin-gapped dimer material.

FIG. 1: Crystal structure for Cu$_2$Sc$_2$Ge$_4$O$_{13}$.

In order to further identify the existence of a spin gap in Cu$_2$Sc$_2$Ge$_4$O$_{13}$, we carried out a detailed $^{45}$Sc 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$_2$Sc$_2$Ge$_4$O$_{13}$, a transfer of magnetic $d$-spin from the Cu$^{2+}$ onto Sc$^{3+}$ 4$s$ orbital allows us to probe the Cu$^{2+}$ spin dynamics and determine the spin gap through the transfer hyperfine interaction. The experimental NMR results clearly reveal spin gap behavior in this material. Data analysis using the isolated dimer model is found to give good agreement with the observations. Interestingly, the deduced spin gap value of 275 K is close to the 25 meV peak revealed by the inelastic neutron experiment, indicating the same energy excitation detected by both measurements.

II. EXPERIMENTS AND DISCUSSION

A polycrystalline Cu$_2$Sc$_2$Ge$_4$O$_{13}$ sample was synthesized by a ceramic sintering solid-state reaction technique. A mixture of CuO, Sc$_2$O$_3$ and GeO$_2$, weighted in a predetermined molar ratio of Cu$_2$Sc$_2$Ge$_4$O$_{13}$, was carefully ground under alcohol, pressed into pellets, put into an open platinum crucible, and fired under ambient pressure and ambient oxygen fugacity in a temperature range between 900 °C and 1100 °C. After each of six heating cycles, the sample was reground, pressed, and reheated. In initial stages the product consisted of a mixture of the title compound and CuGeO$_3$. The amount of CuGeO$_3$ reduced successively as increasing synthesis temperature and heating time. In a final synthesis cycle, the sample was fired at 1150 °C and a light blue product was thus obtained. A room-temperature x-ray diffraction confirmed the single phase for Cu$_2$Sc$_2$Ge$_4$O$_{13}$ with the lattice parameters $a=12.336(2)$ Å, $b=8.7034(9)$ Å, $c=4.8883(8)$ Å, and $\beta=95.74(2)^\circ$.

NMR experiments were performed using a Varian 300 spectrometer, with a constant field of 7.05 T. A home-built probe was employed for the low-temperature measurements. The powder specimen was put in a plastic vial that showed no observable $^{45}$Sc NMR signal. The NMR spectrum was obtained from spin echo fast Fourier transforms using a standard $\pi/2-\tau-\pi$ sequence. Within the $P2_1/n$ space group for Cu$_2$Sc$_2$Ge$_4$O$_{13}$, scandium atoms occupy one crystallographic site having octahedral oxygen coordination, yielding an one-site $^{45}$Sc NMR powder pattern, as demonstrated in the inset of Fig. 2. Here the observed NMR line shape is manifested by the anisotropic Knight shift as well as the quadrupole effects. However, no visible quadrupole edges have been detected with our static NMR probe, suggesting that the value of quadrupole frequency $\nu_Q$ is essentially small. Such a result indicates that the Sc atoms are located in a symmetric environment, probably at the center of the Sc$^{4+}$ octahedron. It is of great importance to note that the line shape of the spectrum remains unchanged with temperature. This phenomenon confirms the nonmagnetic ground state for Cu$_2$Sc$_2$Ge$_4$O$_{13}$ and no structural changes above 4 K.

![Fig. 2: Temperature dependence of the observed $^{45}$Sc NMR shift in Cu$_2$Sc$_2$Ge$_4$O$_{13}$. Note that $K_{obs}$ is shown by the negative direction. Dashed curve: fit to the dimer model plus a constant term. Inset: $^{45}$Sc NMR spectrum for Cu$_2$Sc$_2$Ge$_4$O$_{13}$ measured at 24 K.](image)

In Fig. 2, we displayed the observed temperature-dependent NMR shift ($K_{obs}$) for the Sc site. The shift was taken at the peak position of the resonance line referred to the $^{45}$Sc resonance frequency of aqueous ScCl$_3$. Here $K_{obs}$ has different sign from that of the susceptibility since the transfer hyperfine field arising from 3$d$ electrons of Cu$^{2+}$ ions is negative. In spite of the sign difference of $K_{obs}$, the whole temperature variation is quite consistent with the bulk susceptibility data, with a broad maximum at around $T_{max} \simeq 170$ K and a rapid decrease as lowering temperature. In general, $K_{obs}$ can be decomposed into $K_{obs} = K_o + K_{spin}(T)$. The first term $K_o = 112$ ppm, mainly arising from the orbital shift, is independence of temperature. On the other hand, the spin shift $K_{spin}$, which reflects the Cu$^{2+}$ spin behavior through the transfer hyperfine interaction, is a function of temperature.

![Fig. 3: Plot of $K_{spin}$ against $1/T$ for Cu$_2$Sc$_2$Ge$_4$O$_{13}$. Solid curve: fit to the function described by the dimer model with $\Delta K$ of 270 K.](image)

As mentioned above, the spin chain configuration of
spin dimers could be responsible for the magnetic behavior of Cu2Sc2Ge4O13. Accordingly, the temperature dependence of the spin shift will obey the relation $K_{spin} \propto 1/T(3 + e^{\Delta K/T})$. Here $\Delta K$ is the gap energy determined from the NMR shift based on the dimer model. As demonstrated in Fig. 3, $K_{spin}$ can be fitted well in a fairly wide temperature range to this relation (solid curve in Fig. 3). It is also found that $K_{spin}$ vanishes to almost zero at low temperatures, indicative of the gap in the spin excitation spectrum. With this fit, we extracted $\Delta K = 270 \pm 20$ K, consistent with 290 K obtained from the susceptibility measurement.\(^{(10)}\)

The spin shift here is related to the magnetic susceptibility $\chi$ by the expression

$$K_{spin}(T) = \frac{H_{hf}^t}{N_A \mu_B} \chi(T), \quad (1)$$

where $H_{hf}^t$ is the transfer hyperfine field due to an intermixing of Sc and Cu spin states, $N_A$ is the Avogadro’s constant, and $\mu_B$ is the Bohr magneton. The Clogston-Jaccarino plot\(^{(13)}\) which shows the observed shift against constant, and behavior of Cu Sc K K behavior of Cu K Sc K for the understanding of the spin gap nature.\(^{(18)}\)

FIG. 4: Variation of $K_{obs}$ versus $\chi$ (deduced from Ref. 10)

To gain more insight into the spin gap characteristics of Cu2Sc2Ge4O13, we performed spin-lattice relaxation rate (1/$T_1$) measurements, 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 $T_1$ measurement was carried out using the saturation recovery method. The saturation rf comb with 30 short 2 μs pulses was employed. We recorded the recovery of the signal strength by integrating the $^{45}$Sc spin echo signal. For the central transition with $I = 7/2$, the recovery of the nuclear magnetization follows\(^{(14)}\)

$$\frac{M(t)}{M(0)} = 0.012e^{-\frac{t}{T_1}} + 0.068e^{-\frac{t}{T_2}} + 0.206e^{-\frac{t}{T_3}} + 0.714e^{-\frac{t}{T_4}}.$$  \quad (2)

Here $M(t)$ is the magnetization at the recovery time $t$ and $M(0)$ is the initial magnetization. The $T_1$ value was thus obtained by fitting to this multi-exponential function. To provide accurate values, each $T_1$ has been measured several times and the averaged $T_1$ for the corresponding temperature is shown in the inset of Fig. 5. It is apparent that 1/$T_1$ exhibits activated behavior at low temperatures. Based on the dimerized scenario, the spin-lattice relaxation rate should be fitted to the form 1/$T_1 \propto 1/(3 + e^{\Delta R/T})$ by analogy to the treatment of NMR shift.\(^{(12)}\) The fitting result, drawn in Fig. 5 as a solid curve, is quite satisfactory and yields an energy gap $\Delta R = 275 \pm 25$ K. Remarkably, this excitation energy is almost identical with the 25 meV (290 K) peak obtained in the inelastic neutron experiment.\(^{(10)}\) pointing to the same energy excitation probed by both measurements.

Our NMR investigation thus provides clear evidence for the existence of spin gap in Cu2Sc2Ge4O13. The extracted $\Delta K$ was found to be close to $\Delta R$. As a matter of fact, the ratio of $\Delta K/\Delta R \approx 1$ is commonly seen in the dimerized systems.\(^{(13, 16)}\) Within the isolated dimer limit, $T_{max}$, the temperature at which magnetic susceptibility or NMR shift display a maximum, will appear at around 0.63$\Delta R$.\(^{(17)}\) For the present case of Cu2Sc2Ge4O13, the determined $\Delta R = 275$ K results in $T_{max} = 173$ K, in excellent agreement with the observed $T_{max} \approx 170$ K. In this regard, it seems reasonable to characterize Cu2Sc2Ge4O13 as a nearly isolated dimer chain compound.

At this moment, we did not attempt to fit the temperature dependence of spin shift and 1/$T_1$ to other models such as the alternating chain model. In fact, our previous analyses of NMR data for BaCu2V2O8 indicated that both alternating chain and dimer chain models are suitable for the understanding of the spin gap nature.\(^{(18)}\) However, a convincing result can be established unambiguously from the comparison of static and dynamic excitations. Within the dimer picture, the excitation is
temperature dependence of \( T \) gap description for \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) chain \( \text{BaCu}_2\text{S}_4 \). Such a phenomenon has been observed in the \( T \) ing to a larger spin gap deduced by \( 1/2 \) dimer gap compound \( \text{Y}_2\text{BaNiO}_5 \) and the \( S =1/2 \) spin gap in this material. The spin gap of about 275 K deduced from the spin shifts and spin-lattice relaxation rates was found to be identical. A detailed analysis further indicates that the spin gap nature can be well accounted for by the free dimer model. These findings thus allow us to add \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) to the family of \( S =1/2 \) dimerized spin gap compounds.

III. CONCLUSIONS

In conclusion, we report the first NMR investigation of \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) and present evidence for the existence of spin gap in this material. The spin gap of about 275 K deduced from the spin shifts and spin-lattice relaxation rates was found to be identical. A detailed analysis further indicates that the spin gap nature can be well accounted for by the free dimer model. These findings thus allow us to add \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) to the family of \( S =1/2 \) dimerized spin gap compounds.

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