Magnetism and field-cycling induced domain walls in staircase Kagomé antiferromagnet PbCu$_3$TeO$_7$ revealed by $^{125}$Te NMR

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We report $^{125}$Te nuclear magnetic resonance (NMR) studies on single crystals of staircase Kagomé antiferromagnet PbCu$_3$TeO$_7$ ($T_{N1} \approx 36$ K). The Knight shifts give a large hyperfine coupling constant $^{125}A_{hf} = -67$ kOe/$\mu_B$, implying a strong interlayer coupling bridging the neighboring Kagomé layers. The ordered static moment is about 0.4 $\mu_B$/Cu, indicating moderate magnetic frustration in the system. At $T = 2$ K, the broad zero-field NMR spectrum and the rf enhancement suggest that the magnetic structure is not a simple collinear antiferromagnetic type. We also find a second type of zero-field NMR signal, which is only seen after a field-cycling process. The signal is identified as domain wall contributions created by field cycling in frustrated antiferromagnets.

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I. INTRODUCTION

The ground states and excitations of geometrically frustrated quantum magnet have attracted enormous interests in condensed matter physics. Particularly, two-dimensional (2D) $S = 1/2$ Kagomé Heisenberg antiferromagnet (KHAF) may have novel quantum disordered states, such as spin liquids, due to strong quantum fluctuation and magnetic frustration. $^{14}$ ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite) is one $S = 1/2$ KHAF with weak magnetic anisotropy and nearly perfect magnetic layer structure. Until now, the absence of magnetic ordering and the low-lying continuum excitations observed in this system make it a promising candidate for spin liquids. However, in many systems with imperfect Kagomé structure, magnetic anisotropy induced by Dzyaloshinsky-Moriya (DM) interactions or spatially anisotropic exchange may reduce geometry frustration and lead to magnetic ordering at low temperatures.

In real materials, the interplay of geometric frustration, magnetic anisotropy, and quantum fluctuation produces competing ground states with complex magnetic structures. For example, a staircase Kagomé lattice with buckled Kagomé layers has been realized in several materials, such as $A_2V_2O_8$ ($A$ = Cu,Co,Ni) $^{10,11}$ and PbCu$_3$TeO$_7$. $^{13}$ Among them, consecutive magnetic transitions and magnetism induced ferroelectricity were reported in $A_2V_2O_8$, characterizing a multiferroic material with strong magnetoelectric coupling. The magnetic properties of PbCu$_3$TeO$_7$ have not been well studied yet.

The lattice structure of PbCu$_3$TeO$_7$ is illustrated in Fig. 1. The planes are stacked along the crystalline $a$ direction with Pb and Te atoms as spacer layers. The buckled Kagomé layer has two inequivalent copper sites, Cu(1) in CuO$_6$ octahedrons and Cu(2) in CuO$_4$ tetrahedrons. Cu(1) spins and neighboring Cu(2) spins are not uniform through corner and edge sharing oxygen. $^{13}$ The Weiss constant $\theta$ obtained from the magnetic susceptibility is about 150 K, whereas three magnetic transitions were reported at much lower temperatures with $T_{N1} \sim 36$ K, $T_{N2} \sim 25$ K, and $T_{N3} \sim 17$ K, indicating magnetic frustration. $^{13}$

In this paper, we present our $^{125}$Te NMR ($S = 1/2$) and magnetization studies on PbCu$_3$TeO$_7$ single crystals. The hyperfine coupling constant is calculated to be $^{125}A_{hf} = -67$ kOe/$\mu_B$. The zero-field (ZF) NMR on

FIG. 1: (color online) Crystal structure of PbCu$_3$TeO$_7$. Cu(1) in CuO$_6$ octahedrons and Cu(2) in CuO$_4$ tetrahedrons (oxygen not drawn) form the buckled Kagomé lattice. Te and Pb separates the Kagomé layers.
$^{125}$Te at $T=2$ K reveals an average static moment about 0.4 $\mu_B$/Cu. The large hyperfine coupling and the small magnetic moment indicate strong interlayer coupling and moderate magnetic frustration, the interplay of which helps to understand the finite Néel temperature of this system. From the NMR spectra, a broad distribution of local field is observed, which suggests a complex magnetic structure. Spin canting under magnetic field is also suggested. At low temperatures, a second type of NMR signal emerges only after a large magnetic field is applied and then reduced to zero. Our detailed NMR measurements under different field and cooling conditions suggest that the signal comes from dense magnetic domain walls created by field cycling, which is probably a generic phenomenon in frustrated antiferromagnet.

II. MATERIALS AND METHODS

PbCu$_3$TeO$_7$ single crystals were grown by flux growth method with NaCl/KCl as flux$^{125}$. Our X-ray diffraction and susceptibility data, and the nêel temperatures are consistent with literature$^{125}$, implying good quality of the sample. The bulk susceptibility was measured in a superconducting quantum interference device (SQUID) magnetometer, and the magnetization measurements were performed with a vibrating sample magnetometer (VSM). NMR measurements were conducted on a single crystal with mass $\sim$3.3 mg, under zero field or with field applied along the crystalline [0 1 1] direction. The NMR spectra were collected by the standard spin-echo sequence $\pi/2$-$\tau$-$\pi$ optimized by different pulse length for different NMR signals. We did not find $^{63}$Cu and $^{65}$Cu signal, probably due to their very fast spin relaxation. The $^{125}$Te signal is seen at temperatures above $T_{N1}$ and below $T_{N3}$, and not detectable between $T_{N3}$ and $T_{N1}$ also because of fast spin relaxation. The high-temperature narrow spectra were obtained by Fourier transform of the spin-echo signal, and the low-temperature broad spectra were obtained by integrating the spin-echo intensity as rf frequency was swept through the resonance line. The knight shift in the paramagnetic phase was calculated by $^{125}K = (f/^{125}\gamma H) - 1$, where $f$ is the center frequency of the resonance line, $H$ is the external field, and the gyromagnetic ratio $^{125}\gamma = 13.454$ MHz/T.

III. RESULTS

The $^{125}$Te NMR spectra, with temperature from 275 K down to 37 K are first shown in Fig. 2(a). Upon cooling, the spectra shift to lower frequencies. The NMR signal is wiped out because of very fast spin relaxation below 37 K, which is consistent with the reported $T_{N1}$ at 36 K$^{125}$. The Knight shift $^{125}K$ is calculated and shown as a function of temperature in Fig. 2(b). $^{125}K$ is close to zero at 275 K and decreases with temperature as cooling, indicating a negative hyperfine coupling transferred from copper ions$^{125}$. The Knight shift above 100 K can be fit with a Curie-Weiss form, $^{125}K(T) = A + C/(T + \theta)$, as shown by the dashed line in Fig. 2(b). The fitting gives $\theta \approx 140 \pm 20$ K, which also suggests strong magnetic frustration, and is consistent with the susceptibility data$^{125}$.

In Fig. 2(b), we also plot the bulk susceptibility data $\chi$, measured as a function of temperature under 1 T field. In the inset of Fig. 2(b), $^{125}K$ is plotted against $\chi$ with temperature as an implicit parameter, where a linear relation between them is clearly seen. From the formula $^{125}K = ^{125}A_B f x$, the hyperfine coupling is calculated as $^{125}A_B f = -67$ kOe/$\mu_B$. Such a large hyperfine coupling indicates that Te is strongly coupled to Cu moments. From the crystal structure, the strongest superexchange
pathway should be Cu(1)-O-Te-O-Cu(1) because of its short bond distance, where two Cu(1) are in neighboring Kagomé planes. Therefore, our data is a direct evidence for strong interlayer coupling of the material.

The low-temperature NMR measurements were performed under different cooling conditions and magnetic fields. In Fig. 3(a), the $^{125}$Te spectra are shown with different measurement field at $T = 2$ K after zero-field cooling (ZFC). The spin-spin relaxation time $T_2$ is about 60 $\mu$s at this temperature, and the rf excitation power about $h_{ac} \approx 10$ Oe is used. The rf pulse length is about 1/2 of that required for high-temperature NMR. Therefore, a rf enhancement factor $\eta \approx 2$ is suggested below $T_{N1}$. Usually, the rf enhancement is seen in ferromagnet or incommensurate antiferromagnet. Furthermore, the zero-field spectrum is broadly distributed in the frequency range from 70 MHz to 140 MHz with several prominent peaks, while no signal is found below 70 MHz. Such a broad spectrum indicates a large distribution of hyperfine field on the Te sites. Since $^{125}$Te is a $S = 1/2$ nucleus and all Te sites are equivalent in the lattice, the distributed hyperfine field suggests a magnetic modulation with incommensurate, ferrimagnetic, or other complex patterns. In parallel, broad NMR spectra from incommensurate ordering have been reported in several frustrated magnets, such as Ni$_3$V$_2$O$_8$ and TbMn$_2$O$_{12}$. Therefore, the magnetic structure of PbCu$_2$TeO$_7$ is not a simple collinear type, where magnetic frustration should play an essential role in this system.

From the zero field spectrum, the average internal hyperfine field on the $^{125}$Te site is about 8.9 T. With $^{125}$A$_{hf}$ determined at high temperatures, the average ordered moment of Cu(1) and Cu(2) is estimated to be 0.4 $\mu_B$/Cu. This is much less than the typical value of $\sim 1$ $\mu_B$ for the Cu$^{2+}$ ion. The reduced static moment is another character of magnetic frustration, like many other systems.

With increasing field, the NMR lineshape changes dramatically as shown in Fig. 3(a). Evidences for changes of magnetic structure under field are seen in the first moment and the integrated spectral weight of the spectra. The first moments of each spectra is shown by solid circles in the figure, which is almost a constant below 6 T, and then increases with field above 6 T. The integrated spectral weight of the whole spectra at each field is shown in the inset of Fig. 3(a), which increases slightly below 6 T. From 6 T to 11.5 T, the spectral weight increases significantly by a factor of ten, whereas the first-moment is only increased by 0.4 times. The prominent increase of the spectral weight, in contrast to the first moment, indicates that the total local field on the Te site, including the external field and the internal field, is aligned toward $H$, which maximizes the NMR signal due to geometry configuration of the NMR coil. Therefore, our data suggest that the magnetic structure changes gradually below 6 T field and then flops to a new magnetic structure above 6 T. Although we cannot resolve the magnetic structure by our NMR, we think that a spin flop transition is possible at 6 T.

We also conducted magnetization measurements at 2.2 K for comparison. As shown in Fig. 3(b), the magnetization increases linearly with field up to 12 T. The bulk magnetization moment is only $\sim 0.05 \mu_B$/Cu at 12 T, which suggests that the system remains in the antiferromagnetic phase. The small increase of the bulk magnetization suggests a weak spin canting effect toward the external field, although local AFM structure may vary largely as revealed by NMR.

In the following, we show another NMR signal created by a field cycling process far below $T_{N3}$. Two zero-field NMR spectra are demonstrated in Fig. 3(a). The solid triangles represent the regular zero-field spectra (marked...
that they come from different regions of the sample. We
in the cycling field, but suppressed with measurement field.
above 7 T. Clearly, the signal strength is enhanced with
while \( H \)
and with different cycling field \( H_{\text{cycle}} \).
FIG. 4: (color online) (a) The low-temperature, zero-field
\( ^{125}\text{Te} \) spectra measured with a normal rf excitation power
\( \text{(A1, solid triangles), and with a low rf power after a 6 T field}
\text{cycling (A2, open circles).} \)
\( (c) \) The echo intensity of \( A2 \) after
6 T field cycling, as a function of escalated measurement field
with fixed resonance frequency \( f = 116 \text{ MHz} \). (d) The echo
intensity of \( A2 \) as a function of the cycling field \( H_{\text{cycle}} \) with
fixed \( f = 116 \text{ MHz} \).

as \( A1 \). The open circles represent a second spectra
(marked as \( A2 \)) obtained after field cycling with a 6 T
field. The field cycling refers to a process that after ZFC,
a finite magnetic field \( (H_{\text{cycle}}) \) is first switched on and
then reduced to zero. The \( A2 \) signal is not seen after
ZFC without field cycling, whereas \( A1 \) does not change
under different cooling or magnetization process. Com-
pared with \( A1 \), \( A2 \) is optimized with only 1% rf excita-
tion power, which suggests a large rf enhancement with
\( \gamma = 20 \). Furthermore, \( A2 \) has a large intensity and a broad
linewidth over 220 MHz. The \( T_2 \) of \( A2 \) is about 14 \( \mu s \),
shorter than that of \( A1 \) (60 \( \mu s \)). Therefore, \( A2 \) is char-
erized by very large rf enhancement, strong magnetic
fluctuations, and inhomogeneous hyperfine fields.

The \( A2 \) spectrum is further checked with different mea-
surement fields \( H \) and with different cycling field \( H_{\text{cycle}} \).
With the same \( H_{\text{cycle}} = 6 \text{ T} \), the echo intensity at 116
MHz is quickly suppressed to zero when \( H \) is swept from
zero to 0.4 T, as shown in Fig. (b). In Fig. (c), the echo
intensity is shown as a function of cycling field \( H_{\text{cycle}} \),
while \( H \) remains zero. The echo intensity is absent with
\( H_{\text{cycle}} \) from 0 (ZFC) to 2 T, then starts to increase rapidly
with \( H_{\text{cycle}} \) from 3 T to 6 T, and saturates with \( H_{\text{cycle}} \)
above 7 T. Clearly, the signal strength is enhanced with
the cycling field, but suppressed with measurement field.
The coexistence of \( A1 \) and \( A2 \) after field cycling indicates
that they come from different regions of the sample. We
will discuss the mechanism for \( A2 \) later.

IV. DISCUSSIONS

Our data of the large Weiss temperature \( (\theta \approx 140 \text{ K}) \)
and the small ordered moment of \( \sim 0.4 \mu_B/\text{Cu} \) are con-
sistent with the magnetic frustration in this staircase
Kagomé lattice. On the other hand, the large hyper-
fine coupling constant on the \( ^{125}\text{Te} \) site suggests a strong
interlayer coupling bridged through the Cu(1)-O-Te-O-
Cu(1) path, which may favor the 3D magnetic ordering.
The interplay of interlayer coupling and intralayer fra-
stration provides helpful information for understanding
the finite Néel temperature in this system.

Furthermore, the multiple peak feature of the \( ^{125}\text{Te} \)
zero-field NMR spectrum, and a finite rf enhancement in
the magnetic ordered state suggest a complex magnetic
structure as a results of magnetic frustration. Although
we cannot determine the exact magnetic structure by
our NMR data, we think that incommensurate antifer-
romagnetic order or ferrimagnetic structure is possible in
PbCu$_3$TeO$_7$, which needs to be investigated by neutron
scattering.

Finally, we attempt to understand the origin of the
field-cycling induced NMR signal. In ferromagnet, mag-
netic domains walls have large NMR signal excited with
very low rf power, which is characterized by fast relax-
ation and broad linewidth, and is easily erasable under
field[12]. Our \( A2 \) spectra is consistent with domain wall
NMR signals. Our separation of \( A1 \) and \( A2 \) signals by
different rf power is a direct evidence for coexisting mag-
netic domains (\( A1 \)) and magnetic domain walls (\( A2 \)) after
field cycling.

However, in principle, the NMR signal in ferromag-
net is suppressed upon field cycling, because the domain
walls are reduced as seen by magnetization hysteresis.
Our data are opposite, as the signal strength increases
largely with \( H_{\text{cycle}} \). At \( T = 2 \text{ K} \), the integrated spectral
intensity of \( A2 \) is about six times of \( A1 \), whereas its rf en-
hancement factor is ten times larger. From this, we esti-
mate that the volume fraction of the domain walls, which
is proportional to the NMR spectral weight divided by
the rf enhancement factor, is slightly smaller than that of
the magnetic domains. Such a large volume fraction sug-
gests that very dense or thick domain walls are created
upon field cycling, in contrast to the suppression effect
in ferromagnet. The large volume fraction also suggests
that the domain wall is an intrinsic effect of the material,
rather than the impurity effect. In fact, we found simi-
lar field-cycling induced zero-field NMR signal in FeVO$_4$
and CuBr$_2$ (data not shown), both of which are frus-
trated antiferromagnet with incommensurate magnetic
ordering[21,24]. Therefore, field-cycling induced magnetic
domain walls are probably generic in many frustrated
magnets.

Field induced domain walls are rarely reported in an-
tiferromagnet. Enhanced NMR signal upon field cycling
was seen in spin glass system Cu-Mn alloy\textsuperscript{25} and antiferromagnet TbMn$_2$O$_5$\textsuperscript{26}, which is linked to the dynamics of magnetic domains. In the case of spin-glass Cu-Mn alloy, field cycling induces remnant magnetization, and results in enhanced bulk NMR signal from coherence of neighboring spins.\textsuperscript{27} For TbMn$_2$O$_5$, the enhanced NMR signal is attributed to the antiferromagnet domain walls, which is coupled to ferromagnetic Tb moment. These two scenarios cannot describe the domain wall signal in PbCu$_3$TeO$_7$, where no spin glass or bulk ferromagnetic moment is observed.

However, from our magnetization data, spin canting is suggested by a weak increase of magnetization with field (Fig. 3(b)). As field is removed, although the bulk magnetization is reduced, remnant ferromagnetism may exist and forms domain walls between antiphase antiferromagnetic domains. In particular, for frustrated antiferromagnet, we think it is easier to created local ferromagnetism from highly degenerate magnetic states. We notice that the $A_2$ signal saturates with $H_{\text{cycle}} \approx 6$ T (Fig. 3(c)), in coincidence with the change of magnetic structure at the same field (Fig. 3(a)). This supports our view that the domain wall formation is intrinsically coupled to the bulk magnetism.

Our data suggests that in frustrated magnet, magnetic domains walls can be created after the field cycling treatment. The density of the domain walls may be controlled by the strength of the cycling field. This may be an efficient method for domain engineering in frustrated magnet, which may have application potentials in functional applications and storage carriers.

V. SUMMARY AND ACKNOWLEDGMENTS

In summary, we studied the magnetic properties of frustrated staircase Kagomé compound PbCu$_3$TeO$_7$ by $^{125}$Te NMR. Strong interlayer coupling was evidenced by the large $^{125}$Te Knight shift. The magnetic frustration is indicated by the large Weiss constant in the Knight shift data and the low ordered magnetic moment. Complex magnetic structure is suggested by the broad spectrum of $^{125}$Te and the rf enhancement. In addition to the normal NMR signal, a second NMR signal is discovered, which requires field cycling and is excited by low rf power. We propose that the second NMR signal comes from remnant domain walls, which is probably a generic phenomenon in strongly frustrated antiferromagnet.

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