Valence-Bond-Glass State with Singlet Gap in the Spin-1/2 Square-Lattice Random $J_1 - J_2$ Heisenberg Antiferromagnet Sr$_2$CuTe$_{1-x}$W$_x$O$_6$

Masari Watanabe$^1$ Nobuyuki Kurita$^1$, Hidekazu Tanaka$^1$ Wataru Ueno$^2$, Kazuki Matsui$^2$, and Takayuki Goto$^2$

$^1$Department of Physics, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan
$^2$Physics Division, Sophia University, Chiyoda-ku, Tokyo 102-8544, Japan

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The double-perovskite compounds Sr$_2$CuTeO$_6$ and Sr$_2$CuWO$_6$ are magnetically described as quasi-two-dimensional spin-1/2 square-lattice $J_1 - J_2$ Heisenberg antiferromagnets with predominant $J_1$ and $J_2$ exchange interactions, respectively. We report the low-temperature magnetic properties of Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ with randomness in the magnitudes of $J_1$ and $J_2$. It was found that the low-temperature specific heat for $0.1 \leq x \leq 0.5$ has a large component proportional to the temperature $T$ above 1.2 K, although the low-temperature specific heat for the two parent systems is approximately proportional to $T^3$. With decreasing temperature below 1.2 K, the $T$-linear component decreases rapidly toward zero, which is insensitive to the magnetic field up to 9 T. This is suggestive of the singlet excitation decoupled from the magnetic field. The NMR spectrum for $x = 0.2$ exhibits no long-range order down to 1.8 K. These results indicate that the ground state of Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ is a valence-bond-glass state with singlet gaps.

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I. INTRODUCTION

In most magnets except for one-dimensional (1D) magnets, the ordered ground state is robust and can survive even in a spin-1/2 triangular-lattice Heisenberg antiferromagnet [1–3], which is a prototypical frustrated quantum magnet. Thus, the disordered ground state induced by the quantum fluctuation has been of great interest and is one of the central topics in condensed matter physics. Quantum disordered ground states (QDGSs) such as the spin liquid state [4–7] and valence-bond-solid state [8] have been predicted to exist in frustrated quantum magnets such as spin-1/2 kagome-lattice Heisenberg antiferromagnets [9–16].

Recently, it has been theoretically demonstrated that the exchange randomness in frustrated quantum magnets suppresses the spin ordering and induces a QDGS [17–20]. This randomness-induced QDGS is considered to be composed of randomly frozen singlets, which are formed between not only nearest-neighbor spins but also distant spins. This QDGS is termed the random singlet [21–24] or valence-bond-glass (VBG) state [25, 26]. The randomness-induced QDGS is characterized by a finite magnetic susceptibility and a low-temperature specific heat proportional to the temperature $T$, which arise from the many singlet spin pairs that can be easily excited to triplets with a small or zero energy [17–19]. The suppression of spin ordering and the $T$-linear specific heat caused by exchange randomness were observed in the spin-1/2 spatially anisotropic triangular-lattice antiferromagnet Cs$_2$CuBr$_{4-x}$Cl$_x$ [27], kagome-lattice antiferromagnet (Rb$_{1-x}$Cs$_x$)$_2$Cu$_3$SnF$_{12}$ [28] and a honeycomb-lattice organic magnet with random competing exchange interactions [29]. However, the systematic changes in the ground states and low-temperature magnetic properties upon varying the exchange randomness have not been sufficiently elucidated.

The spin-1/2 square-lattice Heisenberg antiferromagnet with the nearest-neighbor ($J_1$) and next-nearest-neighbor ($J_2$) exchange interactions, referred to as the $S = 1/2$ $J_1 - J_2$ SLHAF, is a prototypical quantum magnet with bond frustration. The most noteworthy point of this model is that a QDGS emerges in the range of $\alpha_1 < J_2/J_1 < \alpha_2$ with $\alpha_1 \approx 0.4$ and $\alpha_2 \approx 0.6$ [30–40]. The ground states for $J_2/J_1 < \alpha_1$ and $\alpha_2 < J_2/J_1$ are Néel antiferromagnetic and collinear antiferromagnetic states, respectively. In this paper, we report the QDGS observed in the spin-1/2 square-lattice random $J_1 - J_2$ Heisenberg antiferromagnet Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ with $0.1 \leq x \leq 0.5$.

The two parent compounds, Sr$_2$CuWO$_6$ and Sr$_2$CuTeO$_6$, have the tetragonal structure, in which CuO$_6$ and MO$_6$ octahedra are arranged alternately in the $ab$ plane, sharing their corners as shown in Fig. 1(a). Because the hole orbitals $d(x^2 - y^2)$ of Cu$^{2+}$ ions with spin-1/2 are spread in the $ab$ plane, exchange interactions in the $ab$ plane are much stronger than those between the $ab$ planes. Consequently, Sr$_2$CuWO$_6$ and Sr$_2$CuTeO$_6$ are described as quasi-2D $S = 1/2$ $J_1 - J_2$ SLHAFs [41–43].

Sr$_2$CuWO$_6$ and Sr$_2$CuTeO$_6$ undergo three-dimensional magnetic orderings at $T_N = 24$ and 29 K, respectively, owing to the weak interlayer exchange interactions [42–43]. However, the spin structures in their ordered states are different. The collinear antiferromagnetic and Néel antiferromagnetic states are realized in Sr$_2$CuWO$_6$ [44] and Sr$_2$CuTeO$_6$ [45], respectively. This indicates that the dominant exchange interaction is $J_2$ in Sr$_2$CuWO$_6$, while $J_1$ is dominant in Sr$_2$CuTeO$_6$. 

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$^*$Electronic address: watanabe.m.bm@m.titech.ac.jp
$^1$Electronic address: tanaka@lee.phys.titech.ac.jp
A powder sample withing a physical property measurement system (Quantum measured down to 0.36 K in magnetic fields of up to 9 T us-
diffraction, we confirmed that W
for 24 h in an oxygen atmosphere. Using X-ray powder
magnetometer (Quantum Design MPMS XL). The spe-
samples were measured down to 1.8 K using a SQUID
magnetic properties.

II. EXPERIMENTAL DETAILS

Powder samples of Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ were synthesized from mixtures of SrCO$_3$, CuO, TeO$_2$, and WO$_3$ with
molar ratios of 2 : 1 : 1 − x : x by a solid-state reaction. Each
mixed powder was ground well with an agate mortar and
fired at 1000°C in air for 24 h. The powder was then re-
ground, pelletized, and calcined twice at 1000 − 1100°C
for 24 h in an oxygen atmosphere. Using X-ray powder
diffraction, we confirmed that W$^{6+}$ ions substitute for
Te$^{6+}$ ions in Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ and that the phase sepa-
arion of the two parent compounds does not occur.

The magnetic susceptibilities of the Sr$_2$CuTe$_{1-x}$W$_x$O$_6$
powders were measured down to 1.8 K using a SQUID
magnetometer (Quantum Design MPMS XL). The spe-
cific heat of the Sr$_2$CuTe$_{1-x}$W$_x$O$_6$ powders was mea-
sured down to 0.36 K in magnetic fields of up to 9 T us-
ing a physical property measurement system (Quantum
Design PPMS) by the relaxation method. Nuclear mag-
netic resonance (NMR) measurements were performed on
a powder sample with $x = 0.2$ using a 16 T superconduct-
ing magnet in the temperature range between 1.8 and 20
K.

III. RESULTS AND DISCUSSION

Figure 2 shows the temperature variation of the mag-
netic susceptibility for 0 ≤ $x$ ≤ 0.5 and $x = 1$ measured at
$\mu_0 H = 0.1$ T. The susceptibility data of the two parent
compounds ($x = 0$ and 1) coincide with those reported in
Refs. [42] and [43], respectively. With decreasing tem-
perature, the susceptibilities of the parent compounds
display broad maxima at approximately $T_{\text{max}} = 70 − 90$
K owing to the short-range spin correlation. This sus-
ceptibility behavior is characteristic of two-dimensional
S = 1/2 SLHAFs [47–49]. With further decreasing tem-
perature, the magnetic susceptibilities for $x ≠ 0$ and 1 ex-
hibit a Curie-like upturn. As the tungsten concentration
$x$ increases, the upturn is more enhanced, which gives rise
to a shift of $T_{\text{max}}$ toward the low-temperature side. This
upturn probably originates from almost free or uncou-
pled spins, which are produced by exchange randomness.
We also measured field-cooled (FC) and zero-field-cooled
(ZFC) magnetic susceptibilities to clarify whether or not
the ground state is the ordinary spin-glass state. Because
no significant difference was found between the FC and
ZFC data, the possibility of a spin-glass ground state is
ruled out.

The nearest-neighbor interaction $J_1$ in Sr$_2$CuTeO$_6$ was
evaluated as $J_1/k_B = 80$ and 83 K from the magnetic
susceptibility by the Padé approximation [42] and from the
dispersion relations of magnetic excitations [50], respec-
tively. The next-nearest-neighbor interaction $J_2$ is neg-
ligible in Sr$_2$CuTeO$_6$. However, for Sr$_2$CuWO$_6$, the sus-
cceptibility data have only been analyzed by the classical
molecular-field approximation [41]. Here, we estimate

FIG. 1: (Color online) (a) Linkage of CuO$_6$ and MO$_6$ octa-
hedra in the ab plane of Sr$_2$CuMO$_6$ (M = W and Te). (b) Illustration of exchange interactions around W$^{6+}$ ions that substitute for Te$^{6+}$ ions.
FIG. 3: (Color online) (a) Temperature dependence of $C/T$ of $\text{Sr}_2\text{CuTeO}_6$ powders measured at zero magnetic field for $x = 0, 0.1, 0.2, 0.5$, and 1. The inset shows an enlargement of the data below 8 K. (b) Temperature dependence of $C/T$ for $x = 0.1, 0.2$, and 0.5 measured at zero field (open symbols) and 9 T (closed symbols). The inset shows the coefficient $\gamma$ of the $T$-linear component vs $x$ obtained at zero field and 9 T.

the exchange constants of $\text{Sr}_2\text{CuWO}_6$ from the susceptibility data by the [5, 5] Padé approximation using the result of the high-temperature expansion of $\beta = 1/k_B T$ up to the tenth order [19]. We assume that $J_2 > J_1$ in $\text{Sr}_2\text{CuWO}_6$. The best fit between 45 and 300 K is obtained with $J_1/k_B = 22.6$ K and $J_2/k_B = 91.2$ K using $g = 2.18$, which was determined from the paramagnetic resonance. The solid line in Fig. [2] shows the susceptibility calculated with these parameters.

Figure 3(a) shows the temperature dependence of the specific heat divided by the temperature $C/T$ for $x = 0, 0.1, 0.2, 0.5$, and 1 measured at zero magnetic field. No anomaly indicative of magnetic ordering was observed even for the parent compounds $\text{Sr}_2\text{CuTeO}_6$ and $\text{Sr}_2\text{CuWO}_6$, which undergo magnetic phase transitions at $T_N = 29$ K [45] and 24 K [43, 44], respectively. We can see from the inset of Fig. 3(a) that the partial substitution of $\text{W}^{6+}$ for $\text{Te}^{6+}$ causes a large change in the low-temperature specific heat. The low-temperature specific heat $C(T)$ of the parent compounds ($x = 0$ and 1) is described as $C(T) = \beta T^2 + \alpha T^3$, where the $T^2$ component is much smaller than the $T^3$ component. The small $T^2$ component can be attributed to quasi-2D magnetic excitations of the parent compounds. In contrast to the specific heat of the parent compounds, a $T$-linear component is clearly observed in the low-temperature specific heat for $0.1 \leq x \leq 0.5$ above 1.5 K. With decreasing temperature from 1.5 K, the $T$-linear component decreases rapidly toward zero, resulting in a shoulder anomaly appearing in $C/T$ near 1.2 K.

Figure 3(b) shows $C/T$ for $x = 0.1, 0.2$, and 0.5 measured at $\mu_0 H = 0$ and 9 T. The shoulder anomaly in $C/T$ observed at zero magnetic field is partly suppressed at 9 T for $x = 0.2$ and 0.5, whereas for $x = 0.1$, $C/T$ is almost independent of the applied magnetic field. Above 2 K,
no significant difference is observed in the specific heat data measured at $\mu_0 H = 0$ and $9$ T. Applying the formula $C(T) = \gamma T + \alpha T^3$ for $3 \leq T \leq 7$ K, we estimate the coefficient $\gamma$ of the $T$-linear component. The inset of Fig. 3(b) shows $\gamma$ as a function of $x$. $\gamma$ increases with increasing $x$ and saturates at $\approx 54 \text{ mJ/(K}^2\text{mol)}$ around $x = 0.3$. Recent theory [17–20] has demonstrated that the specific heat has a $T$-linear component in frustrated quantum magnets with random bonds, which arises from the low-energy gapless excitations. The maximum $\gamma$ value in $\text{Sr}_2\text{CuTe}_1-x\text{W}_x\text{O}_6$ is the same order of magnitude as that calculated for the $S = 1/2$ triangular-lattice random bond Heisenberg antiferromagnet [17].

From the analysis shown below, we deduce that the difference between the values of $C/T$ at $\mu_0 H = 0$ and $9$ T below $2$ K arises from the Schottky specific heat due to the Zeeman splitting of loosely coupled spin pairs. The inset of Fig. 4 shows the temperature dependence of the difference $\Delta(C/T)$ between $C/T$ measured at $\mu_0 H = 0$ and $9$ T for $x = 0.2$, and $0.5$. With increasing temperature from $0.36$ K, $\Delta(C/T)$ displays a rounded maximum at $0.6 - 0.7$ K and decreases to be negative. This is typical of the Schottky specific heat due to the Zeeman splitting. Specific heat of spin pairs coupled via exchange interaction $J$ in magnetic field is expressed as

$$C(T, H, J) = \frac{nN_A \beta}{2T} \left[ (J^2 + (g\mu_B H)^2) e^{\beta J} + (g\mu_B H)^2 \right] \cosh (\beta g\mu_B H) - 4J g\mu_B H e^{\beta J} \sinh (\beta g\mu_B H) + 4(g\mu_B H)^2 + J^2 e^{\beta J} \right],$$

where $N_A$ is the Avogadro’s number and $n$ is the fraction of the spins that are loosely coupled to form spin pairs. In this analysis, we assume that the coupling constant $J$ is uniformly distributed between $J - \Delta J$ and $J + \Delta J$. Solid lines in the inset of Fig. 4 are $\Delta(C/T) = C(0 T)/T - C(9T)/T$ for $x = 0.2$, and $0.5$ calculated with $n = 1.7 \times 10^{-3}$, $J/k_B = 2.3$ K and $\Delta J/k_B = 0.63$ K, and $n = 3.4 \times 10^{-3}$, $J/k_B = 3.1$ K and $\Delta J/k_B = 1.3$ K, respectively. The $g$ factor is set to be $g = 2.18$. Experimental results of $\Delta(C/T)$ are well described in terms of the Schottky specific heat due to the Zeeman splitting of loosely coupled spin pairs. Because the coupling constant $J$ is of the order of $1$ K, these spins give rise to the Curie-like term in the magnetic susceptibility at low temperatures. The fraction of spins that produce the Curie-like term is estimated as $n = 1.9 \times 10^{-3}$ and $3.5 \times 10^{-3}$ for $x = 0.2$, and $0.5$, respectively, which coincide with those obtained from the analysis of low-temperature specific heat. Thus, we can deduce that the magnetic field dependence of the low-temperature specific heat and the Curie-like term in the magnetic susceptibility arise from the loosely coupled spin pairs.

Figure 4 shows $C(T)$ at $\mu_0 H = 0$ and $9$ T for $x = 0.2$, and $0.5$ after the correction of the Schottky specific heat. Down to the lowest temperature of $0.36$ K, no significant difference is observed in $C(T)$ at $\mu_0 H = 0$ and $9$ T. The shoulder anomaly around $1.2$ K is not sharp and the temperature that gives the shoulder anomaly is almost independent of the tungsten concentration $x$. The shoulder anomaly and the rapid decrease in $C(T)$ toward zero persist even at $9$ T, the Zeeman energy of which is much larger than the energy corresponding to $1.2$ K. These results indicate that the shoulder anomaly in $C(T)$ cannot be ascribed to the magnetic ordering or spin-glass transition. Because the low-temperature specific heat is insensitive to the magnetic field, we deduce that the shoulder anomaly originates from the singlet excitations, which are decoupled from the magnetic field.

Figure 5(a) shows two typical $63/65^{\text{Cu}}$-NMR spectra measured with two different frequencies $\nu_0$. One can observe well-resolved peaks corresponding to the singular points in the quadrupolar powder pattern for the $I = 3/2$ nuclei. To extract $K$, which is the in-plane component of the Knight shift, from the observed spectra, we measured the positions of the $90^\circ$ peak for the $65^{\text{Cu}}$ central transition denoted by the dashed arrows in Fig. 5(a) at ten different frequencies between $109$ and $132$ MHz and analyzed them using the second-order perturbation formula [51]. The values of $K$ and the nuclear quadrupolar parameter $63\nu_Q$ at $3.8$ K were determined to be $1.3\%$ and $52$ MHz, respectively. The positive value of $K$ suggests that it includes an appreciable orbital contribution.

Next, to obtain the temperature dependence of $K$, we traced the peak position. Typical spectral profiles are shown in the inset of Fig. 5(b). No anomalous broadening or splitting, indicative of a magnetic order, was observed down to $1.8$ K. Assuming that $63\nu_Q$ is temperature-independent at low temperatures, the temperature dependence of $K$ was simply determined from the peak position and is shown in Fig. 5. It decreased with decreasing temperature and scales well with the uniform susceptibility, from which the tiny Curie-like term was subtracted. From the scaling factor, the hyperfine coupling constant $A$ was estimated to be $-13 (T/\mu_B)$. Its negative sign and its magnitude are typical for divalent copper, indicating that the present NMR effectively probes the magnetism of the copper spin. Consequently, we can safely conclude at this stage that the bulk spin susceptibility of this system decreases with decreasing temperature and approaches a finite value at low temperatures.
The many loosely coupled singlet spins, which can be easily excited, tend to form singlet excitations. In the VBG state, there are characteristic features for frustrated quantum magnets, including a linear component and Curie term. The linear component in the low-temperature specific heat increases with increasing magnetic concentration. The small amount of substitution of W produces marked suppression of the magnetic ordering. The absence of magnetic ordering down to 1.8 K indicates the magnetic suppression due to a singlet excitation.

As shown above, the NMR spectrum for \( x = 0.2 \) indicates the absence of magnetic ordering down to 1.8 K. The small amount of substitution of W\(^{6+}\) for Te\(^{6+}\) induces marked suppression of the magnetic ordering. The partial substitution of W\(^{6+}\) for Te\(^{6+}\) also produces a T-linear component in the low-temperature specific heat and a Curie term in the magnetic susceptibility. The T-linear component and Curie term increase with increasing tungsten concentration x. These properties are characteristic of the VBG state for frustrated quantum magnets with random bonds. In the VBG state, there are many loosely coupled singlet spins, which can be easily excited. The T-linear component in the specific heat and the Curie term in the magnetic susceptibility arise from the low-energy excitations of these spins. Thus, we deduce that the ground state of Sr\(_2\)CuTe\(_{1-x}\)W\(_x\)O\(_6\) is the VBG state at least for \( 0.2 \leq x \leq 0.5 \), as predicted by the theory. It is considered that there is a critical point that separates the ordered state and the VBG state. In the present experiments, \( x_c \) was not determined. The data of \( C/T \) show a rapid decrease below 1.2 K, which is insensitive to the magnetic field. Thus, we infer that the VBG ground state is accompanied by singlet excitations.

As shown in Fig. 5, the temperature that gives the shoulder in \( C/T \) is almost independent of the tungsten concentration x. This suggests that the singlet excitations are determined by the local structure of the exchange interactions. Figure (b) illustrates the exchange interactions when Te\(^{6+}\) ions are substituted by W\(^{6+}\) ions. We assume that \( J_1 \) and \( J_2 \) are almost the same as those in Sr\(_2\)CuTeO\(_6\) and Sr\(_2\)CuWO\(_6\), respectively, which are \( J_1/k_B \simeq 80 \) and \( J_2/k_B \simeq 90 \) K. \( J'_1 \) and \( J'_2 \) are the nearest-neighbor exchange interactions via TeO\(_6\) and WO\(_6\) octahedra and two WO\(_6\) octahedra, respectively, which are estimated to be \( J'_1/k_B \simeq 50 \) and \( J'_2/k_B \simeq 20 \) K using the exchange constants for SrCuWO\(_6\) obtained in this study and those for SrCuTeO\(_6\).

Very recently, Mustonen et al. reported the magnetic properties of Sr\(_2\)CuTe\(_{0.5}\)W\(_{0.5}\)O\(_6\). Their magnetic susceptibility and specific heat data measured down to 2 K are consistent with our data for \( x = 0.5 \). From muon spin relaxation and rotation measurements, they observed the absence of magnetic ordering or a spin-glass transition in Sr\(_2\)CuTe\(_{0.5}\)W\(_{0.5}\)O\(_6\) down to 19 mK.

**IV. CONCLUSION**

In conclusion, we have reported the results of magnetization, specific heat, and NMR measurements on Sr\(_2\)CuTe\(_{1-x}\)W\(_x\)O\(_6\), which is characterized as an \( S = 1/2 \) square-lattice random \( J_1 - J_2 \) Heisenberg antiferromagnet. The partial substitution of W\(^{6+}\) for Te\(^{6+}\) causes a marked change in the ground state and low-temperature thermodynamic properties. The magnetic ordering observed in the parent compounds is strongly suppressed. The ground state, at least for \( 0.2 \leq x \leq 0.5 \), is concluded to be the VBG state with a singlet excitation gap of about 1 K.

*Note added in proof.* At the proof stage, we noticed that Walker et al. estimated the exchange interactions in Sr\(_2\)CuWO\(_6\) as \( J_1/k_B = 14 \) K and \( J_2/k_B = 110 \) K from the magnetic excitation data obtained by inelastic neutron scattering on powdered sample.

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