Low-temperature specific-heat studies on two square-kagome antiferromagnets

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We studied the low-temperature specific heats of two antiferromagnets with the two-dimensional square-kagome structure, i.e., $KCu_6AlBiO_4(SO_4)_5Cl$ (KCu_6) and $Na_6Cu_7BiO_4(PO_4)_4[Cl,(OH)]_3$ ($NaCu_7$), with the structural difference that there are interlayer Cu^{2+} ions in $NaCu_7$. Both materials show no magnetic ordering down to 50 mK. At zero field, the C/T of KCu_6 has a finite value when the temperature is close to 0 K. Under the magnetic field, an apparent T^2 dependence appears and its coefficient is progressively suppressed by the field. For $NaCu_7$, the specific heat exhibits the T^2 dependence at zero field and under fields. The ratio of the quadratic coefficients of KCu_6 and $NaCu_7$ at high fields is inversely proportional to that of the squared Weiss temperatures, which indicates these two compounds host the same ground state under fields. Our results suggest that the interlayer Cu^{2+} ions in $NaCu_7$ play a negligible role in determination of its ground state. We discuss the possible quantum-spin-liquid states in these compounds and further directions to pursue based on our results.

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I. INTRODUCTION

Geometrical frustrated magnetic materials have long been thought to be the playgrounds for searching for quantum spin liquids (QSLs) [1]. The triangle-based lattice structures have drawn particular attention as a triangle is one of the basic building blocks to produce frustrations. One of the most popular examples is the two-dimensional (2D) kagome lattice [2–6], which consists of corner-sharing triangles with the smallest loop of six sites. Experimentally, herbertsmithite and its related compounds with the kagome structure show strong signatures for the existence of QSLs although there are still debates on the exact nature of their ground states [7–17]. Starting from the kagome lattice, it has been proposed that the shuriken or square-kagome lattice (SKL) may also host exotic ground states including QSLs [18–26]. The triangles are also corner sharing as those in the kagome lattice, but the SKL has the smallest loops with four and eight sites. Moreover, the square loops of the SKL endure stronger quantum fluctuations and thus the system exhibits long-range correlations of virtual singlets [22]. The ground states of the SKL could be incommensurate orders, pinwheel valence bond crystal, $U(1)$, or topological QSLs [24,25].

The material realization of the SKL was only achieved recently in $KCu_6AlBiO_4(SO_4)_5$ (KCu_6) [28] and $Na_6Cu_7BiO_4(PO_4)_4[Cl,(OH)]_3$ ($NaCu_7$) [29]. Extensive studies have been made on KCu_6 down to 50 mK and shown that it may host a gapless QSL ground state [28]. Magnetic-susceptibility and specific-heat measurements on $NaCu_7$ down to 2 K also suggest it may be a promising candidate for the QSLs [29]. It should be noted that KCu_6 and $NaCu_7$ have different crystal structures with the space groups of $P4/ncc$ and $P4/nmm$, respectively. We show the structures of Cu^{2+} ions in Table I and Fig. 1. The most significant difference between the magnetic systems of these two structures is that there are interlayer Cu^{2+} ions for $NaCu_7$. It is known that for kagome magnetic systems interlayer Cu^{2+} ions act as magnetic impurities and can significantly affect the system properties [10,12–14,16,30–34]. While it seems that the interlayer Cu^{2+} ions in $NaCu_7$ are magnetically isolated from the SKL layers, their effects are only studied down to 2 K [29], which makes it unclear whether similar impurity issues also exist in $NaCu_7$. Another important difference between these two compounds is that the Cu1 in KCu_6 is not in a symmetrical position so there are two different superexchanges between Cu1 and Cu2, as shown in Fig. 1(a), which means that a minimal $J_1 - J_2 - J_3$ SKL model is necessary [28]. In contrast, there is only one J_2 between Cu1 and Cu2 in $NaCu_7$ as shown in Fig. 1(b), which probably makes the spin system of $NaCu_7$ closer to the proposed SKL model [18–25]. These differences make it necessary to compare the properties of KCu_6 and $NaCu_7$.

In this paper, we studied the low-temperature specific heats of KCu_6 and $NaCu_7$. We confirm that none of them shows magnetic ordering down to 50 mK. We find that magnetic impurities are few in both compounds. The specific heat of $NaCu_7$ shows a quadratic temperature dependence, the coefficient of which linearly decreases with increasing field.

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TABLE I. The structures of Cu^{2+} ions in KCu_6 and $NaCu_7$ with the space groups of $P4/ncc$ and $P4/nmm$, respectively. The structure file of KCu_6 can be found in the Supplemental Material [27], which is similar to previous reports [28]. The structure of $NaCu_7$ has been reported in Ref. [29].

KCu_6	x	y	z	Occupancy
Cu1	0.4879(3)	0.2741(4)	0.89703(14)	1
Cu2	0	0	0	1
$NaCu_7$	x	y	z	Occupancy
Cu1	0.46981(6)	0.25	0.69285(6)	1
Cu2	0.5	0.5	0.5	1
Cu3	0.25	0.25	0.14102(12)	1

For KCu_6, the specific heat exhibits almost linear temperature dependence at zero field but quickly changes to the T^2 dependence under fields. Interestingly, their specific heats at high fields are very similar and may be directly associated with the values of superexchanges. Our results suggest that both compounds could host QSL ground states predicted by the SKL model but further studies are needed to solve some issues.

II. EXPERIMENTS

Polycrystals of KCu_6 and $NaCu_7$ were grown by the solid-state reaction and hydrothermal method, respectively, as reported previously [28,29]. The crystal structures and magnetization of KCu_6 were confirmed by powder x-ray diffraction and a superconducting quantum interference device magnetometer (MPMS 3, Quantum Design), respectively. The specific heats were measured on a physical property measurement system (PPMS, Quantum Design) with the dilution refrigerator option, which used the relaxation method. The samples were cold pressed into small pellets and attached on the heat-capacity platform by Apiezon N grease.

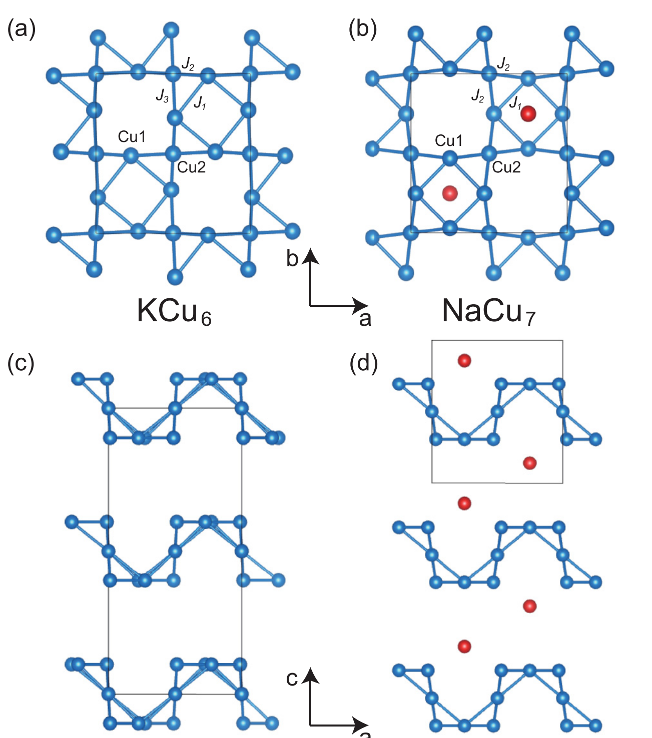

FIG. 1. Structures of Cu ions in (a, c) KCu_6 (top and side views) and (b, d) $NaCu_7$ (top and side views). The interlayer Cu^{2+} ions in $NaCu_7$ are shown as red balls. The configurations of superexchanges for KCu_6 and NCu_7 are in panels (a) and (b), respectively. The black solid lines indicate unit cells.

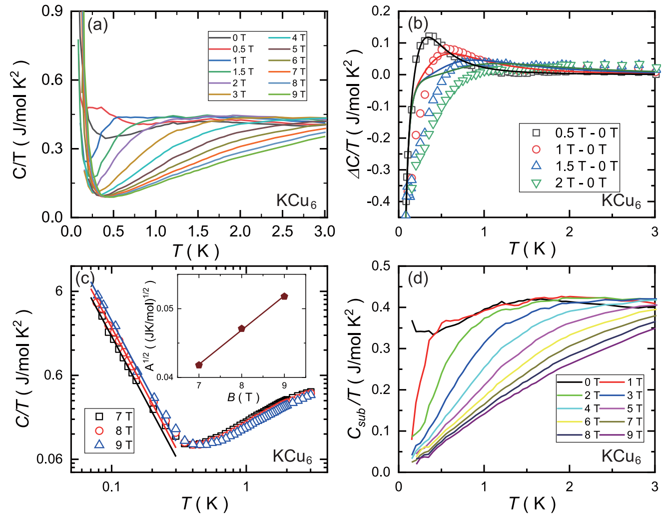

FIG. 2. (a) The temperature dependence of C/T of KCu_6 under different fields. (b) Field difference of C/T below 2 T as a function of temperature. The solid line for 0.5–0 T is the fitted result by Eq. (1), while other lines are calculated results based on Eq. (1). (c) The C/T above 7 T as a function of temperature in the log-log scale. The solid lines are the fitted results by the nuclear Schottky anomaly function as described in the text. The inset shows the field dependence of the fitted values of $A^{1/2}$. The solid line is the linear fitting result. (d) The temperature dependence of C/T of KCu_6 under different fields with the impurity and nuclear contributions subtracted.

III. RESULTS AND DISCUSSIONS

Figure 2(a) shows the temperature dependence of C/T of KCu_6. Consistent with a previous report [28], there is no magnetic order down to 50 mK. In analyzing the low-temperature specific heat of a QSL candidate, we typically need to remove two kinds of contributions that are not intrinsic to the magnetic system. The first one is from orphan or weakly correlated magnetic impurities, which are usually weakly correlated and so can be described by the Schottky anomaly [30]. The specific heat from the Schottky anomaly takes the form $C_{\rm Sch} = NR(\Delta/T)^2 e^{\Delta/T}/[1+e^{\Delta/T}]^2$, where N is the impurity concentration, R is the gas constant, and $\Delta = \Delta_0 + g\mu_B H$ is the energy level. Assuming that the change of the whole specific heat mainly comes from these magnetic impurities, we have

$$\Delta C = C(H) - C(0) \approx C_{\rm Sch}(H) - C_{\rm Sch}(0). \quad (1)$$

As shown in Fig. 2(b), this equation can nicely describe the 0.5–0-T data with $g = 2.7$, $\Delta_0 = 0.132$ K, and $N = 0.0133$, which suggests that there are about 1.33% orphan magnetic

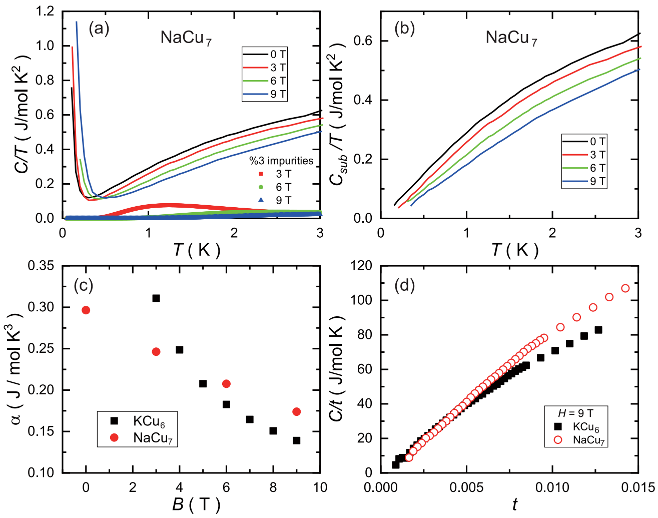

FIG. 3. (a) The temperature dependence of C/T of $NaCu_7$ at several fields (lines). The symbols are calculated specific heat for 3% of magnetic impurities per molecular formula with $g = 2$ and $\Delta_0 = 0$. (b) The temperature dependence of C/T with the nuclear contributions subtracted. (c) The field dependence of α for KCu_6 and $NaCu_7$, which is defined in the main text. (d) The t dependence of C/t for KCu_6 and $NaCu_7$ at 9 T. Here t is the temperature normalized by the Weiss temperature as defined in the main text.

impurities per molecular formula. With these fitted parameters, we can calculate the contribution of magnetic impurities based on Eq. (1). With increasing field, the deviation from the data becomes larger, which indicates that there is an intrinsic change of the specific heat from the magnetic system. The second nonintrinsic contribution to the specific heat is the nuclear Schottky anomaly, the energy levels of which are very small and so we only observe its high-temperature tail as $C = A/T^2$. As shown in Fig. 2(c), this function can well describe the data below 0.2 K for the field larger than 7 T. The inset of Fig. 2(c) shows $A^{1/2}$ as the function of field, which shows a linear field dependence. Accordingly, the contribution from the nuclear Schottky anomaly can be calculated based on the fitted value of A.

Figure 2(d) shows C/T of KCu_6 with the contributions from both magnetic impurities and nuclear Schottky anomaly subtracted as described above. We note that the phonon part of the specific can be neglected since its C/T at 3 K would be just about 0.03 J/mol K^2 with the Debye temperature of 100 K, which should be a very conservative estimate. At 0 T, there seems to be a residual C/T at 0 K, larger than 0.3 J/mol K^2. With field applied, the low-temperature C/T is quickly suppressed and shows almost linear temperature dependence at high fields. In other words, the specific heat probably has a quadratic temperature dependence.

The low-temperature C/T of $NaCu_7$ is shown in Fig. 3(a). The nuclear Schottky anomaly still clearly presents at very low temperature. After removing the nuclear Schottky anomaly, all C/T tend to linearly decrease to zero, as shown in Fig. 3(b). The specific heat from the magnetic system is also progressively suppressed by the magnetic field, which cannot be explained by the existence of orphan magnetic impurities in this system. To see this, we can calculate the specific heat of 3% magnetic impurities per molecular formula by using the Schottky anomaly function, as shown in Fig. 3(a). The field dependence of the calculated values clearly suggests that if there are any weakly correlated magnetic impurities their content should be negligible and thus the field dependence of the specific heat is from the SKL magnetic system. It is particularly interesting that the C/T at 9 T in $NaCu_7$ looks to be very similar to that in KCu_6. We note that both of them show a bending-over feature with increasing temperature, which may come from low-energy singlet excitations [26]. We can fit the specific heat of both KCu_6 and $NaCu_7$ below certain temperatures by the function $C/T = A/T^3 + \alpha T$. The field dependence of α is shown in Fig. 3(c). For $NaCu_7$, α linearly depends on the magnetic field, whereas it increases quickly with decreasing field below about 6 T for KCu_6.

Our low-temperature specific-heat results provide some key information on the square-kagome magnets. The first important result is that the existence of interlayer Cu^{2+} ions in $NaCu_7$ does not result in any magnetic ordering. This result suggests that unlike the well-known herbertsmithite and its siblings [10,12–14,16,30–34] the interlayer Cu^{2+} ions in the SKL materials may not significantly affect the ground states. This is a good news for further studies on these materials. While this may be understood that the interlayer Cu^{2+} ions are probably magnetically isolated from the SKL layers, our specific-heat measurements suggest that they do not act as orphan or weakly correlated spins. In this case, a gap may exist in the magnetic system of the interlayer Cu^{2+} ions in $NaCu_7$ so that its contribution to the low-temperature specific heat is absent. Alternatively, the interlayer spins may be actually correlated with the SKL ones but the interactions should be weak so that the nature of the SKL layers does not change. Further studies are needed to see whether the spins of the interlayer Cu^{2+} magnetic system themselves are strongly correlated or they are not independent of the SKL layers.

The second important result is that the specific heats of KCu_6 are $NaCu_7$ are very similar at high magnetic fields. As shown above, the specific heat at high fields of both materials roughly shows T^2 dependence at low temperatures. The ratio of the coefficient α for the quadratic term between $NaCu_7$ and KCu_6 is about 1.27–1.33 at 9 T depending on the fitting ranges. The Weiss temperatures Θ_{CW} for $NaCu_7$ and KCu_6 are −212 and −237 K, respectively [28,29]. Assuming that the superexchange J is proportional to the Weiss temperature, this suggests that the ratio of α may be related to the ratio of $1/J^2$, which is about 1.25. We thus define the normalized temperature $t = T/|\Theta_{CW}|$ and plot C/t vs t in Fig. 3(d). It is clear that the data of KCu_6 and $NaCu_7$ are almost overlapped with each other below $t \approx 0.005$, which is about 1 K.

Our results suggest that both KCu_6 and $NaCu_7$ are good candidates for QSLs. Neither of them shows magnetic ordering down to 50 mK despite their large Weiss temperatures. In the optimistic view, both of them can host QSL ground states. At zero field, the C/T of KCu_6 seems to have a finite value at 0 K, which indicates a linear temperature dependence of C that could come from spinon Fermi surfaces. At high fields, the specific heat shows a T^2 temperature dependence. For $NaCu_7$, the specific heat always exhibits the T^2 temperature dependence. This quadratic temperature dependence of the specific heat for QSLs has been shown to exist in the $U(1)$ Dirac

QSL, the coefficient of which is proportional to $1/J^2$ [35]. Interestingly, the SKL model could indeed host a $U(1)$ Dirac spin liquid [25,36]. It should be pointed out that although our data indicate gapless states for both compounds we cannot rule out that very small gaps may exist, which are covered by the large nuclear Schottky anomaly at low temperatures.

Of course, there exist a few potential problems to be clarified before one confirms the above note of optimism. First, the low-temperature specific heat of the $U(1)$ Dirac QSLs should have a linear-T component under magnetic field and increase with the increasing field due to the formation of spinon Fermi pockets [17,35]. However, for both KCu_6 and $NaCu_7$, the low-temperature specific heats are suppressed by the field. We also note that for a trivial 2D magnetism the low-temperature specific heat could also exhibit a T^2 temperature dependence with the coefficient proportional to $1/J^2$ [37,38]. Second, it is rather hard to understand a crossover or transition from a spinon Fermi-surface state to a $U(1)$ Dirac state with such small change of the magnetic field in KCu_6. One may also expect some signatures for this kind of crossover or transition between two distinct ground states, which cannot be identified in our measurements. Third, the different configuration of superexchanges in these two compounds, as shown in Fig. 1, seems to have no effect on the nature of the ground states under fields. If assuming that J_1 is proportional to the Cu_1-O-Cu_1 bond angle, we can estimate that the ratio of J_1^2 between KCu_6 and $NaCu_7$ is about 1.3 according to previous results on the 2D copper oxide compounds [39,40]. This value is consistent with the normalized factor in Fig. 3(d) and seems to suggest that the low-energy excitations in the SKL model are probably mainly associated with J_1 since we cannot find such coincidence if J_2 and J_3 are also considered. If this is true, the finite value of C/T at 0 K in KCu_6 may be related to the different values of J_2 and J_3, especially the large value of J_2. Of course, this is rather a naive hypothesis. All these issues need to be investigated further both experimentally and theoretically.

IV. CONCLUSIONS

Our studies on the low-temperature specific heats of KCu_6 and $NaCu_7$ provide some basic key information that is important to further study their magnetic ground states. We show that magnetic impurities are few in both compounds and the existence of interlayer Cu^{2+} ions probably has negligible effects on the magnetic system of the SKL layers. The zero-field specific heat of KCu_6 may consist of a large linear temperature dependence, which is easily suppressed by the magnetic field. The low-temperature specific heat of KCu_6 under magnetic fields and that of $NaCu_7$ are very similar, which suggests that both of them may be good platforms to study the SKL model.

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