Dynamical coupling of dilute magnetic impurities with quantum spin liquid state in the $S = 3/2$ dimer compound Ba$_3$ZnRu$_2$O$_9$

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Received 17 April 2018, revised 23 July 2018
Accepted for publication 25 July 2018
Published 8 August 2018

Abstract
We have investigated the dilute magnetic impurity effect on the magnetic properties of a quantum spin liquid candidate Ba$_3$ZnRu$_2$O$_9$ and a spin gapped compound Ba$_3$CaRu$_2$O$_9$. The magnetic ground state of each compound stands against 2% substitution of magnetic impurities for Zn or Ca. We have found that the magnetic response of these impurities, which behave as paramagnetic spins, depends on the host materials and the difference of the two manifests itself in the Weiss temperature, which can hardly be explained by the dilute magnetic impurities alone in the case of Ba$_3$ZnRu$_2$O$_9$. We consider a contribution from the Ru$^{5+}$ ions which would appear only in the substituted Ba$_3$ZnRu$_2$O$_9$ and discuss a possible physical meaning of the observed Weiss temperature.

Keywords: quantum spin liquid, impurity effects, magnetic susceptibility, magnetic oxide

(Some figures may appear in colour only in the online journal)
simple localized spins of the Ru$^{5+}$ ions are responsible for the magnetism of the system.

The magnetic ground state of Ba$_3$MRu$_2$O$_9$ depends on the species of $M$. For $M = \text{Co, Ni, and Cu}$ [27–29], an antiferromagnetic ordering is observed below $T_N \sim 100$ K. When the $M$ sites are occupied by Ca, Sr, and Mg [27, 30], paired spins in the Ru$_2$O$_9$ dimer form a spin singlet, and then the system is in a non-magnetic SG ground state. In the case of the $M = \text{Zn}$ sample, we have found neither a long-range magnetic order nor a spin glass transition down to 37 mK [26], despite the magnetic interaction has been evaluated to be an energy scale of around 200 K in this family [30–32]. The magnetic susceptibility at low temperatures exhibits a nearly temperature-independent value of about $10^{-3}$ emu mol$^{-1}$, and the specific heat shows a temperature-linear contribution. These features suggest the presence of a QSL state. We have proposed that the competition between intra- and inter-dimer interactions play important role in stabilizing this QSL state. The exchange coupling pathways are shown in figure 1(b).

We underline several advantages of Ba$_3$ZnRu$_2$O$_9$ in investigating the impurity effects on the magnetism, compared with other QSL candidates. One is that this compound is free from tigating the impurity effects on the magnetism, compared with the competition between intra- and inter-dimer interactions which would be present only in the substituted Ba$_3$ZnRu$_2$O$_9$.

2. Experimental

Polycrystalline samples of Ba$_3$MRu$_2$O$_9$ and Ba$_3$M$_{0.98}$A$_{0.02}$Ru$_2$O$_9$ ($M = \text{Zn and Ca}; A = \text{Co, Ni, and Cu}$) were prepared by solid state reaction using high-purity reagents of BaCO$_3$ (4N), RuO$_2$ (3N), ZnO (4N), CaCO$_3$ (4N), Co$_2$O$_4$ (3N), NiO (3N), and CuO (4N). Stoichiometric mixtures of the oxides were ground, pressed into pellets, and pre-sintered in air at 1000 °C for 12 h. The pre-sintered samples were then re-pelletized after regrinding and sintered in air at 1200 °C for 72 h. Powder x-ray diffraction measurements (Cu Kα radiation) at room temperature showed that all the prepared samples have the hexagonal structure without any trace of a secondary phase and the lattice parameters were unchanged by substitution. The magnetization measurements were conducted by a Quantum Design superconducting quantum interference device magnetometer. The magnetic susceptibility ($\chi$) was measured between 2 and 300 K in an external magnetic field ($H$) of 10 kOe. The magnetization ($M$) data were collected at 2, 3, and 5 K in the magnetic field range from 0 to 70 kOe.

3. Results and discussion

Figures 2(a) and (b) show the temperature dependence of the magnetic susceptibility of Ba$_3$MRu$_2$O$_9$ and Ba$_3$M$_{0.98}$A$_{0.02}$Ru$_2$O$_9$ ($M = \text{Zn and Ca}; A = \text{Co, Ni, and Cu}$) on a logarithmetic scale. With decreasing temperature, the susceptibility of both host materials decreases in its magnitude from similar values of about $2 \times 10^{-3}$ emu mol$^{-1}$ at 300 K, reflecting the development of short-range correlation between Ru$^{5+}$ ions. Note that the features of which at high temperatures above 100 K are similar to those reported the previous works [30, 31] and BaCu$_3$V$_2$O$_9$ (OH)$_2$ Cl$_2$ [34], and thus one can introduce an impurity into a specific site in a controlled way. Another is that a Curie tail is hardly visible at low temperatures in the title compound unlike BaCu$_3$V$_2$O$_9$ (OH)$_2$ [10] and Cu$_3$V$_2$O$_7$ (OH)$_2$ · 2 H$_2$O [35], in which a substantial contribution of unwanted impurities obscures the intrinsic physical properties in macroscopic measurements.

Here we report the dilute magnetic impurity effect on the magnetic properties of Ba$_3$ZnRu$_2$O$_9$ in comparison with Ba$_3$CaRu$_2$O$_9$. We have found that the magnetic ground state of each compound stands against 2% substitution of magnetic impurities of Cu, Ni, and Co for Zn or Ca, and these impurities behave as paramagnetic spins. We have further found that the magnetic response of the paramagnetic spins depends on the host materials, which appears in the difference of the Weiss temperature, which can be hardly explained by the simple impurity–impurity interaction alone in the case of the substituted QSL candidate. We discuss a possible origin in terms of a coupling of the magnetic impurities with the Ru$^{5+}$ ions.
and (b) Ba$_3$CaRu$_2$O$_9$ and Ba$_3$Ca$_{0.98}$Ru$_2$O$_9$.

Weiss spin state of the Ru$^{5+}$ of the corresponding parent compound, implying that the susceptibility at around 300 K is almost the same as that measured in 10 kOe for (a) Ba$_3$ZnRu$_2$O$_9$ and Ba$_3$Zn$_{0.98}$Ru$_2$O$_9$ (A = Co, Ni, and Cu). The broken curve in (b) depicts the fit using the Curie–Weiss law (see text).

Figure 2. Temperature dependence of the magnetic susceptibility measured in 10 kOe for (a) Ba$_3$ZnRu$_2$O$_9$ and Ba$_3$Zn$_{0.98}$Ru$_2$O$_9$, and (b) Ba$_3$CaRu$_2$O$_9$ and Ba$_3$Ca$_{0.98}$Ru$_2$O$_9$ (A = Co, Ni, and Cu). The broken curve in (b) depicts the fit using the Curie–Weiss law (see text).

In all the impurity-substituted samples, the magnetic susceptibility at around 300 K is the order of Cu$^{2+}$ ions out of the total Ru ions. The inverse susceptibility, which is consistent with the spin gapped dimer state of Ba$_3$CuRu$_2$O$_9$.[30]

In the all impurity-substituted samples, the magnetic susceptibility at around 300 K is almost the same as that of the corresponding parent compound, implying that the spin state of the Ru$^{5+}$ ions is little affected by substitution. On the other hand, $\chi$ increases significantly below 50 K as the spin value of the substituent ions increases in order of Cu$^{2+}$ ($S_{\text{imp}} = 1/2$), Ni$^{2+}$ ($S_{\text{imp}} = 1$), and Co$^{2+}$ ($S_{\text{imp}} = 3/2$). Furthermore, it exhibits a Curie–Weiss-like temperature dependence without any sign of a magnetic transition down to 2 K. These results suggest that the Ru$^{5+}$ ions are still responsible for the ground state of each parent compound, and the substituted magnetic impurities behave as paramagnetic spins. Note that the impurity substitution for the M sites does not directly disrupt the network of the Ru$_2$O$_9$ dimers.

Let us evaluate the low-temperature susceptibility in the substituted samples. We assume that this can be divided into two terms, a contribution from the magnetic impurities and the Ru$^{5+}$ ions, i.e. $\chi = \chi_{\text{imp}} + \chi_{\text{Ru}}$. The former may follow the Curie–Weiss law as $\chi_{\text{imp}} = C_{\text{imp}}/(T + \theta_{\text{imp}})$. We note here that not only the substituted impurities but also unwanted impurities can contribute to this term, and it is difficult to distinguish them in the susceptibility data. Namely, $C_{\text{imp}}$ may include both contributions and $\theta_{\text{imp}}$ may reflect the interaction between all these impurities. At sufficiently low temperatures below 50 K, the latter term may be regarded as the temperature-independent term in the corresponding parent compound. Accordingly, we fit the data with a constant $\chi_{\text{Ru}}$ of $1.12 \times 10^{-3}$ emu mol$^{-1}$ for Ba$_3$Zn$_{0.98}$Ru$_2$O$_9$ and $2.5 \times 10^{-5}$ emu mol$^{-1}$ for Ba$_3$Ca$_{0.98}$Ru$_2$O$_9$, respectively.

The results of the fit are summarized in table 1, together with $x_{\text{imp}} = C_{\text{imp}}/C_0$. Here $C_0$ is the Curie constant expected for a mole of magnetic impurities with $S_{\text{imp}}$ and $g = 2$. Thus ideally, $x_{\text{imp}}$ means the concentration of the substituted magnetic impurities per formula unit, and equals 0.02 in the nominal compositions. One finds that $x_{\text{imp}} \sim 0.02$ except for (M, A) = (Zn, Ni). The reason of the exception of the sample is to be explored at this stage, but it may reflect that a magnetic transition is about to occur at lower temperatures, as anticipated from the saturation of $\chi$. Besides, we notice that the contribution from unwanted magnetic impurities observed in Ba$_3$CuRu$_2$O$_9$ may not be ignored for (M, A) = (Ca, Cu). If one simply subtracts the contribution from $C_{\text{imp}}$, the corrected value is obtained to be $3.05 \times 10^{-3}$ emu K mol$^{-1}$, which corresponds to $x_{\text{imp}} \sim 0.01$. Such a value is also implied by the fact that the saturation magnetization of the sample is estimated to be half of that expected for $x_{\text{imp}} = 0.02$, while the details are to be clarified by investigating the compositional dependence.

Figure 3 shows the temperature dependence of $1/(\chi - \chi_{\text{Ru}})$ below 30 K of (a) Ba$_3$Zn$_{0.98}$Ru$_{0.02}$O$_9$ and (b) Ba$_3$Cu$_{0.98}$Ru$_{0.02}$O$_9$ (A = Cu and Co). The inverse susceptibility goes to nearly zero in the limit of $T = 0$ in the Ca-based materials, as expected for free spins which obey the Curie law. On the contrary, $1/\chi_{\text{imp}}$ takes a finite value in the same limit.

| Material | $C_{\text{imp}}$ (emu K mol$^{-1}$) | $\theta_{\text{imp}}$ (K) | $x_{\text{imp}}$ |
|----------|---------------------------------|------------------|----------------|
| (M, A) = (Zn, Cu) | $8.37 \times 10^{-3}$ | 3.42 | 0.022 |
| (M, A) = (Zn, Ni) | $4.96 \times 10^{-2}$ | 9.00 | 0.050 |
| (M, A) = (Zn, Co) | $5.51 \times 10^{-2}$ | 9.92 | 0.029 |
| (M, A) = (Ca, Cu) | $6.37 \times 10^{-3}$ | 1.36 | 0.017 |
| (M, A) = (Ca, Ni) | $3.07 \times 10^{-2}$ | 2.21 | 0.031 |
| (M, A) = (Ca, Co) | $4.77 \times 10^{-2}$ | 2.27 | 0.025 |
for the Zn-based materials, clearly indicating a substantial contribution of the magnetic interaction. Thus, the magnetic response of the impurity spins seems to depend on the host materials. The difference between them can also be seen from the Curie–Weiss fitting, as depicted in figure 3 with the broken lines. In Ba₃Ca₀.₉₈Co₀.₀₂Ru₂O₉, θ_imp is estimated to be about 1 or 2 K independently of the magnetic ion in the A site, whereas it increases in the magnitude with increasing θ_imp in Ba₃Zn₀.₉₈A₀.₀₂Ru₂O₉, from about 3 K for the A = Cu sample to about 10 K for the A = Co sample. These estimated values of θ_imp is anomalously large, considering that the magnetic interaction between a few percent of magnetic impurities is usually found to be of the order of 1 K in various spin gapped systems and QSL candidates [1, 10, 37, 38]. Note that the positive θ_imp implies an antiferromagnetic coupling.

To further investigate the difference of the magnetic response, we measure the field dependence of the magnetization at several temperatures. For the free spins, the magnetization saturates for $\mu_B H \gg k_B T$, and follows the Brillouin function as a function of $\mu_B H/k_B T$. Here $\mu_B$ is the Bohr magneton and $k_B$ is the Boltzmann constant. Figures 4(a) and (b) show the magnetization at 2, 3, and 5 K plotted against $\mu_B H/k_B T$ for Ba₃Zn₀.₉₈Co₀.₀₂Ru₂O₉ and Ba₃Ca₀.₉₈Co₀.₀₂Ru₂O₉, respectively. We find the distinct differences between the two. In the former sample, the magnetization curves at each temperature deviate from each other with increasing magnetic field. Moreover, $M$ is unlikely to saturate even at 2 K in 70 kOe. In contrast, all the experimental data are about to fall into a single curve with a sign of saturation in the latter sample.

The slight deviation observed in Ba₃Ca₀.₉₈Co₀.₀₂Ru₂O₉ can be explained by considering the impurity–impurity interaction. When the paramagnetic spins weakly interact with each other, the Brillouin function is modified, and then $M$ scales to $\mu_B H/k_B (T + θ_w)$ [37, 38], which means the reduction of the field effect. As shown in the inset of figure 4(b), a good scaling is indeed established with a small $θ_w$, which is adopted the same value as $θ_imp$. This fact allows us to attribute $θ_imp$ to the weak interaction between the dilute magnetic impurities. We attempt the same analysis on the magnetization curves in Ba₃Zn₀.₉₈Co₀.₀₂Ru₂O₉ (the inset of figure 4(a)). They overlap each other at low magnetic fields, but the scaling gets worse as $H$ increases, implying that the magnetic response is affected by other contributions. A similar trend is found for the Cu-substituted samples (not shown).

Now let us discuss a possible origin of the relatively larger Weiss temperature found in Ba₃Zn₀.₉₈Co₀.₀₂Ru₂O₉. The difference in the magnetic response suggests that the substituted magnetic impurities in each host lattice exist under different environments. This would be related to the magnetism of the Ru⁵⁺ ions: the impurities can interact with the Ru⁵⁺ ions only in the Zn-based compounds. In this context, it is worth noting that the low-T upturn of the susceptibility due to the impurities is strongly suppressed below $θ_imp$ in Ba₃Zn₀.₉₈Co₀.₀₂Ru₂O₉. This feature is reminiscent of the low-temperature susceptibility in Kondo systems [39, 40], in which localized spins are screened by conduction electrons via an antiferromagnetic coupling between them. Therefore, we propose that the large Weiss temperature observed in the substituted Ba₃ZnRu₂O₉ is
the implication of such screening effect on the impurity spins, which results from the magnetic coupling of these spins and the Ru$^{3+}$ spins. If that were the case, the spin fluctuation rates of impurity spins should be enhanced, leading to the magnetic moment instability [41]. In this sense, the Weiss temperature is interpreted as a measure of the degree of the spin fluctuations. The screening effect would also be suggested from the absence of a Curie tail in the parent Ba$_3$ZnRu$_2$O$_9$ despite unwanted magnetic impurities should exist, as in Ba$_3$CaRu$_2$O$_9$.

Unlike Kondo systems, there are no conduction electrons in the title compound. Nevertheless, QSL candidates are believed to possess a kind of quasiparticles as fermionic elementary excitations, because a gapless $T$-linear term of the specific heat has been generally observed [10, 26, 42, 43]. Thus, one possible explanation of the screening effect is that a magnetic impurity couples with the quasiparticles. However, this scenario is incompatible with the $S_{\text{imp}}$ dependence of $\theta_{\text{imp}}$ in our system because the Weiss temperature exhibits the opposite $S_{\text{imp}}$ dependence in the framework of the Kondo model [44]. As another possible scenario, we suggest that the enhancement of the spin fluctuation rates is caused by the quantum fluctuations originating from the Ru$_2$O$_9$ dimers. In our previous study [26], we have pointed out that the spin state of the Ru$_2$O$_9$ dimers dynamically changes in the range between $S_{\text{tot}} = 0$ and $S_{\text{tot}} = 2$ for the title compound, where $S_{\text{tot}}$ is the total spin. In such a situation, a magnetic coupling of the magnetic impurities with the Ru$_2$O$_9$ dimers will be dynamical and produces a fluctuating internal field at each impurity site. The increase in $S_{\text{imp}}$ would imply a stronger exchange coupling between them, resulting in the observed $S_{\text{imp}}$ dependence of $\theta_{\text{imp}}$. The NMR and neutron scattering measurements are indispensable to examine this scenario through direct observation of the spin fluctuation.

4. Summary

We have investigated the effect of the magnetic impurity on the magnetic properties of the quantum spin liquid candidate Ba$_3$ZnRu$_2$O$_9$ through the comparison with the spin gapped compound Ba$_3$CaRu$_2$O$_9$. The magnetic ground state of these systems is robust against the 2% impurity substitution, and the introduced magnetic impurities behave as paramagnetic spins. We have found that the magnetic response of these paramagnetic spins is dependent on the host materials and the difference between the two manifest itself in the Weiss temperature. We have proposed a possible picture that the enhanced Weiss temperature observed in the substituted QSL candidate is the implication of a kind of screening effect on the impurity spins, which arises from a dynamical magnetic coupling between the magnetic impurities and the Ru$_2$O$_9$ dimers.

Acknowledgments

We gratefully acknowledge Y Hara, T Matsushita, and N Wada at Nagoya University for the collaboration in the magnetic and thermodynamic measurements at very low temperatures. This work was partly supported by Grants-in-Aid for Scientific Research (18H01173). One of the authors (TDY) was supported by the Program for Leading Graduate Schools ‘Integrative Graduate Education and Research in Green Natural Sciences’, MEXT, Japan and a Grant-in-Aid for JSPS Research Fellow (No. 17J04840), MEXT, Japan.

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