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# Suppression of the mass enhancement in $CaCu_3Ru_4O_{12}$

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We have investigated heavy-fermion behavior of the transition-metal oxides $ACu_3Ru_4O_{12}$ ($A$=Na, Ca, La, and their mixtures). It has been known that $CaCu_3Ru_4O_{12}$ exhibits Kondo-like behavior attributable to $Cu^{2+}$ $3d$ electrons, similar to that of some Ce-based heavy-fermion systems. However, we find striking *suppression* of the mass enhancement in $CaCu_3Ru_4O_{12}$, in which the Kondo-type effect is most pronounced. Such decrease in the density of states is reminiscent of the coherent-gap formation in Kondo lattice systems. Nevertheless, the behavior can not be interpreted within the conventional Kondo picture with localized moments because the Cu electrons are apparently itinerant. The present results indicate the importance of the duality of localized and itinerant nature, found also in some other $d$-electron systems which exhibit the Kondo-like behavior.

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## I. INTRODUCTION

Since the discovery of high-$T_c$ superconductivity in the cuprates $(La,Ba)_2CuO_4$ (Ref. 1) and spin-triplet superconductivity in the ruthenate $Sr_2RuO_4$,[2] considerable attention has been paid to electronic properties of perovskite-related transition-metal oxides. In some of these oxides electron correlations play important roles. Cupro ruthenates $ACu_3Ru_4O_{12}$ ($A$=Na, Ca, La) (Refs. 3–10) are transition-metal oxides with a perovskite-related structure and have recently been widely studied because of their relatively large electronic specific-heat coefficients $\gamma = 70-140\ \mathrm{mJ/(f.u.\ mol\ K^2)}$ (f.u.: formula unit), as well as their metallic conductivity originating from the $d$ electrons. The values of $\gamma$ of $ACu_3Ru_4O_{12}$ are much larger than $\gamma \simeq 6\ \mathrm{mJ/(mol\ K^2)}$ of the metallic transition-metal oxide $RuO_2$ without strong electron correlations[11] but comparable to $\gamma = 38\ \mathrm{mJ/(mol\ K^2)}$ of the strongly correlated metal $Sr_2RuO_4$.[2] The large values of $\gamma$ indicate a realization of a Fermi-liquid state with a heavy effective mass, which is rare among $d$-electron systems.

More interestingly, only for $CaCu_3Ru_4O_{12}$ with the formal valence of 2+ for Cu, similar to the insulating parent compounds of high-$T_c$ cuprates, Kondo-like behavior has been reported.[5,9,10] A broad peak at around 200 K in the magnetic susceptibility $\chi(T)$ was found by Kobayashi *et al.*,[5] reminiscent of those for some Ce-based heavy-fermion compounds with high Kondo temperatures (valence-fluctuation systems).[12] Kobayashi *et al.* regarded the peak in $\chi(T)$ of $CaCu_3Ru_4O_{12}$ as possible evidence of the lattice Kondo effect between the localized $Cu^{2+}$ electrons ($S=1/2, 3d^9$) and the itinerant electrons originating from the Ru $4d$ orbitals. However, more recent experiments revealed profound duality of localized and itinerant characters of the Cu electrons. First, for the origin of the mass enhancement, we recently clarified that electron correlations among the itinerant Ru electrons should be dominant and the Kondo-type effect provides, if any, only a minor contribution.[9] Moreover, recent copper core-level x-ray photoemission spectroscopy (XPS) at room temperature by Sudayama *et al.*[10] revealed that $CaCu_3Ru_4O_{12}$ shows the largest Cu DOS around $E_F$ among $ACu_3Ru_4O_{12}$, indicating that the Cu electrons are in fact itinerant. Therefore, the conventional Kondo picture with localized electrons in a metal clearly fails to account for the Kondo-like behavior with enhanced mass in $CaCu_3Ru_4O_{12}$. Nevertheless, the Kondo-like picture is supported by high-resolution photoemission spectroscopy (PES) measurements, which revealed that a prominent peak in the density of states (DOS) exists just at the Fermi level $E_F$ and grows below 100 K.[10] For the clarification of the duality of the Cu electrons in $CaCu_3Ru_4O_{12}$, namely the presence of the Kondo-like resonant state without localized moments, a detailed comparison with the other members of $ACu_3Ru_4O_{12}$, which exhibit the enhanced mass without Kondo-like behavior, is a promising experimental approach.

For $f$-electron-based heavy-fermion systems, the lattice Kondo effect is widely accepted as the dominant origin of the heavy mass. Among metallic oxides with $f$ electrons, the pyrochlore iridate $Pr_2Ir_2O_7$ with localized Pr moments also exhibits both the lattice Kondo effect and the mass enhancement.[13] In contrast with the $f$-electron-based systems, a general picture is still lacking to explain the Kondo-like behavior found in a few metallic $d$-electron systems with strong electron correlations.[14] In these systems, the duality of localized and itinerant characters appears to be an important common feature. For example, the spinel vanadate $LiV_2O_4$ with local magnetic moments as well as itinerant electrons of vanadium exhibits physical properties similar to those of heavy-fermion systems.[15] For this compound, the importance of hybridization between two distinct orbitals[16] and the closeness to orbital selective Mott transition[17] have been emphasized as the origin of the enhanced mass. However, alternative explanations are also given based on the geometrical frustration, which suppresses long-range order and leads to fluctuations giving Kondo-like behavior.[18] Another example is the ruthenate $Ca_{1.8}Sr_{0.2}RuO_4$ on the verge of Mott transition to an insulator with antiferromagnetic order of ruthenium local moments. In high-resolution angle-resolved PES, quasiparticle peaks that grow at low temperatures have been observed.[19] In $CaCu_3Ru_4O_{12}$, the additional presence of the itinerant heavy-mass Ru electrons allows us to control the duality of the Cu electrons which is responsible to the Kondo-like behavior. Thus, $CaCu_3Ru_4O_{12}$ may provide an important clue to gain a general picture of the Kondo-like behavior found in some $d$-electron systems.

In this paper, in order to examine the role of the Kondo-like effect on the mass enhancement of $CaCu_3Ru_4O_{12}$, we

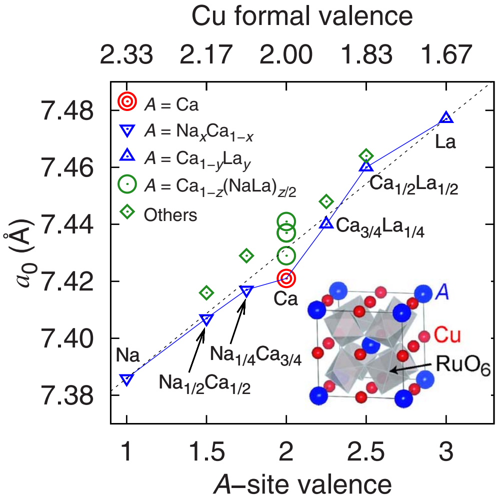

FIG. 1. (Color online) Variation in the cubic lattice parameter $a_0$ against the average valence of $A$ ions. The small blue triangles represent Na$_x$Ca$_{1-x}$Cu$_3$Ru$_4$O$_{12}$ and Ca$_{1-y}$La$_y$Cu$_3$Ru$_4$O$_{12}$ (valence series). The large green circles represent Ca$_{1-z}$(NaLa)$_{z/2}$Cu$_3$Ru$_4$O$_{12}$ (charge-disorder series). The broken line connects the data points for $A$=Na and La for a guide to the eyes. Inset: crystal structure of $A$Cu$_3$Ru$_4$O$_{12}$, generated using the program "VESTA" (Ref. 20). The corner-sharing octahedra represent RuO$_6$, in which the Ru ion is located at the center and the O ions occupy the corners.

compare the magnetic susceptibility and electronic specific heat of not only the end members NaCu$_3$Ru$_4$O$_{12}$, CaCu$_3$Ru$_4$O$_{12}$, and LaCu$_3$Ru$_4$O$_{12}$ but also the solid solutions (Na,Ca,La)Cu$_3$Ru$_4$O$_{12}$, in which Na$^+$ and La$^{3+}$ ions are partially substituted for Ca$^{2+}$ in CaCu$_3$Ru$_4$O$_{12}$. We use the Cu formal valence in this paper although the Cu valence may not be well-defined. While $\chi(T)$ suggests the presence of a Kondo-like effect only in compositions close to CaCu$_3$Ru$_4$O$_{12}$, we have revealed an additional, apparently *negative* effect on the mass enhancement. Such decrease in the DOS cannot be interpreted within the conventional Kondo scenario and suggests a possible formation of a gap structure in the electronic DOS at low temperatures.

## II. EXPERIMENTAL

Polycrystalline samples of (Na,Ca,La)Cu$_3$Ru$_4$O$_{12}$ were prepared by a solid-state reaction as described in Ref. 9. Powder x-ray diffractometry with Cu $K_{\alpha 1}$ radiation at room temperature indicates that the samples were almost single phased, containing at most a few percent of CuO and RuO$_2$ (not shown). Their structure, shown in the inset in Fig. 1, is cubic with a calculated lattice parameter $a_0$ at room temperature that increases from 7.386 ± 0.001 Å for $A$=Na to 7.477 ± 0.001 Å for $A$=La as shown in Fig. 1. Among the samples in this paper, we will focus on the following two groups. The members with $A$=Na$_x$Ca$_{1-x}$ and Ca$_{1-y}$La$_y$ are referred to as the valence series, where the formal valence of Cu varies, and the members with $A$=Ca$_{1-z}$(NaLa)$_{z/2}$ are referred to as the charge-disorder series, where the average valence of $A$ ions is kept at two, corresponding to the Cu formal valence of two.

## III. RESULTS

### A. Susceptibility

Figure 2 displays their DC susceptibility $\chi(T)=M(T)/H$ measured at 10 kOe from 1.8 to 350 K with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, model MPMS). First, we compare $\chi(T)$ for the valence series. As shown in Fig. 2(a), a broad peak at around 180 K is observed for CaCu$_3$Ru$_4$O$_{12}$, consistent with earlier reports,[5,9] relating the temperature dependence with a Kondo-like effect. As $x$ or $y$ increases, the peak is gradually obscured as evident in Fig. 2(b) with an enlarged vertical scale for $A$=Na$_{1/4}$Ca$_{3/4}$, Ca, and Ca$_{3/4}$La$_{1/4}$. The clear peak suggests a peculiarity of CaCu$_3$Ru$_4$O$_{12}$ with the Cu formal valence of two. Next, we examine $\chi(T)$ for the charge-disorder series with the Cu formal valence of two in Fig. 2(c). As $z$ increases, it is expected that the local-charge disorder at the $A$ site increases. It is clear that the peak disappears for large $z$, indicating that the charge disorder disturbs the peculiarity of CaCu$_3$Ru$_4$O$_{12}$.

### B. Specific heat

Figure 3 displays their specific heat $C_P(T)$ at low temperatures measured with a commercial calorimeter (Quantum Design, model PPMS). The relation $C_P(T)/T=\gamma+\beta T^2$ holds from 5 to 15 K for all the samples, yielding the electronic specific-heat coefficients $\gamma$ consistent with our earlier

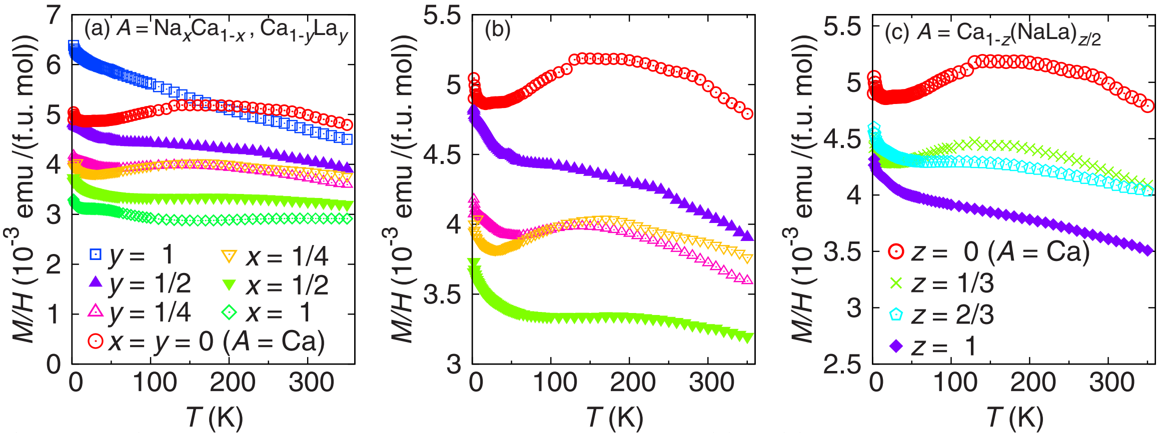

FIG. 2. (Color online) Temperature dependence of DC magnetic susceptibility $\chi(T)=M(T)/H$ under 10 kOe for the valence series (a), for the valence series plotted in an enlarged vertical scale (b), and for charge-disorder series (c).

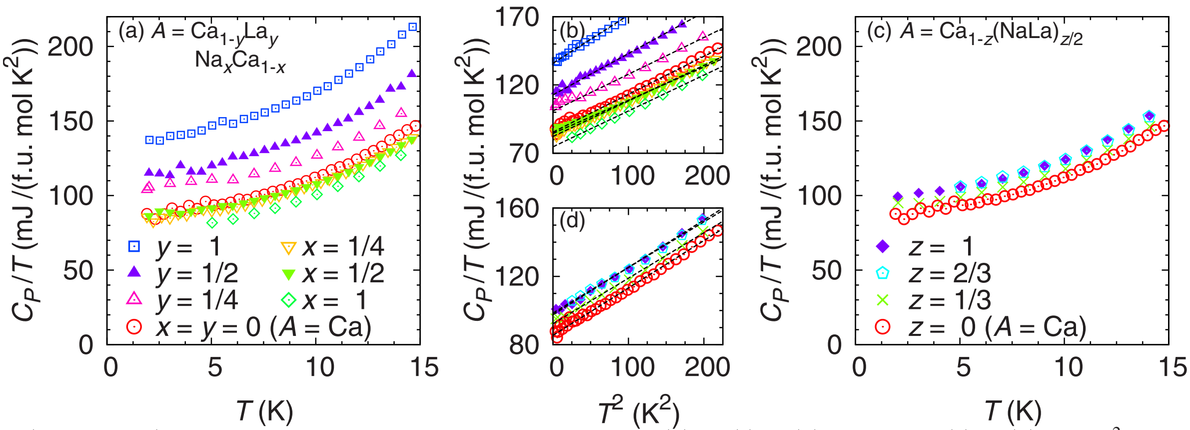

FIG. 3. (Color online) Electronic specific heat divided by temperature $C_P(T)/T$. (a) $C_P(T)/T$ vs $T$ and (b) $C_P(T)/T$ vs $T^2$ for the valence series. (c) $C_P(T)/T$ vs $T$ and (d) $C_P(T)/T$ vs $T^2$ for the charge-disorder series. The number of displayed data points are reduced to avoid overlap in the plots for a clear presentation. The dashed lines in (b) and (d) are obtained by fitting the equation $C_P(T)/T = \gamma + \beta T^2$ to the data from 5 to 15 K.

report.[9] The values of $\gamma$ of all the present samples are relatively large. Here, let us focus on the valence series and the charge-disorder series separately. In the valence series, $\gamma$ increases as the $A$ ions vary from $Na^+$ to $Ca^{2+}$ to $La^{3+}$ as shown in Figs. 3(a) and 3(b). In the charge-disorder series, interestingly, the samples with less disorder have smaller values of $\gamma$ as shown in Figs. 3(c) and 3(d).

In order to clarify these tendencies, the variations in both the magnetic susceptibility $\chi$ and the electronic specific-heat coefficient $\gamma$ as functions of the average valence of $A$ are plotted in Figs. 4 and 5. There is a general tendency of $\chi$ and $\gamma$ to increase with the $A$-site valence. We note that the lattice parameter also exhibits a systematic increase, as shown in Fig. 1. Since this variation in the lattice parameter is known to cause little change in the bond angles of Ru-O-Ru as well as of Cu-O-Ru,[3] it is perhaps not the main origin of the change in $\chi$ and $\gamma$, as already argued by Ramirez *et al.*[4] Rather, the change in the number of Cu and Ru electrons filling the states near the Fermi level is considered as the main origin for the change in the DOS.[9]

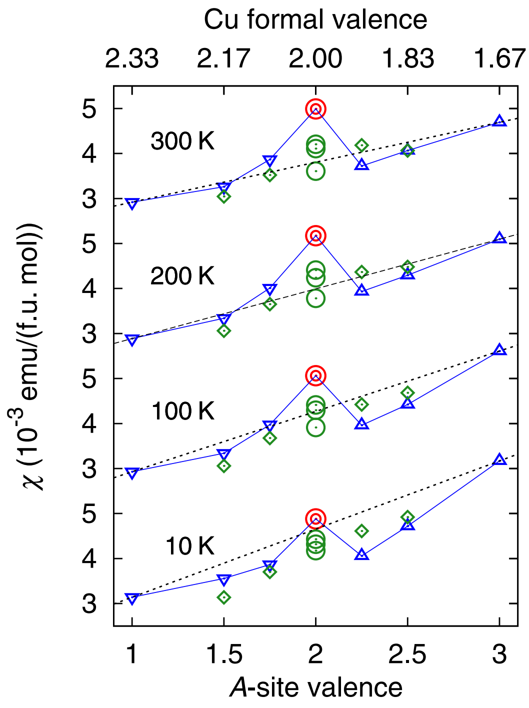

FIG. 4. (Color online) Variation in the susceptibility $\chi$ at various temperatures against the average valence of the $A$-site ions in $ACu_3Ru_4O_{12}$.

It is evident from Figs. 4 and 5 that $CaCu_3Ru_4O_{12}$ exhibits peculiar properties among the $ACu_3Ru_4O_{12}$ systems. As a function of the $A$-site valence, $\chi$ shows a distinct peak below room temperature, although at low temperatures the peak becomes weaker. Because of the peak, one may expect a larger DOS and thus larger $\gamma$ for $A$=Ca. Contrary to the expectation, $\gamma$ exhibits a *dip*, rather than a peak, at $A$=Ca. The peak in $\chi$ as well as the dip in $\gamma$ is readily obscured by introducing charge disorder at the $A$ site, indicating the importance of a well-ordered lattice. These peak and dip lead to a large Wilson ratio of 4.0 for $CaCu_3Ru_4O_{12}$,[9] indicative of enhanced magnetic fluctuations.

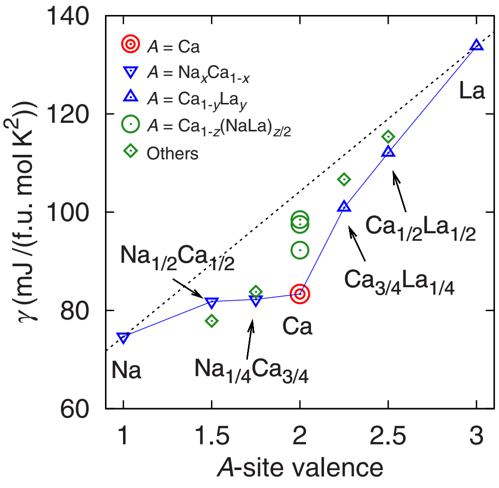

FIG. 5. (Color online) Variation in the electronic specific-heat coefficient $\gamma$ against the average valence of the $A$-site ions.

## IV. DISCUSSION AND CONCLUSION

As we have previously reported,[9] the large values of $\gamma$ of all (Na,Ca,La)$Cu_3Ru_4O_{12}$ suggest that the mass enhancement is mainly ascribable to correlations among itinerant Ru electrons. This is the major premise in the following discussions.

Since $CaCu_3Ru_4O_{12}$ exhibits Kondo-like behavior, $\gamma$ is expected to be enhanced at low temperatures in view of the conventional Kondo effect. In contrast, the dip is observed in $\gamma$ for $CaCu_3Ru_4O_{12}$, for which the formal valence of Cu is exactly two. In analogy with the insulating parent phase of the high-$T_c$ cuprates, it may seem that the reduction in the Cu DOS at $E_F$ occurs due to the localization of the $Cu^{2+}$ electrons for $CaCu_3Ru_4O_{12}$. Such localization may overcome the enhancement of the DOS due to the Kondo-like effect.

However, the large value of $\chi$ for $CaCu_3Ru_4O_{12}$ suggests that the Cu DOS is actually higher for this compound even at room temperature, in contrast to the expectation for the localized $Cu^{2+}$ states. In fact, the Cu core-level XPS indicates that the Cu DOS at $E_F$ is higher for $CaCu_3Ru_4O_{12}$ among the $ACu_3Ru_4O_{12}$ compounds even at room temperature.[10]

Thus, an alternative interpretation is required to explain the suppression in $\gamma$ for $CaCu_3Ru_4O_{12}$, compatible with the enhanced susceptibility as well as the optical evidence for the enhanced Cu DOS at $E_F$. In heavy-fermion systems, it has been shown both experimentally and theoretically[21,22] that a gap structure is formed from hybridization between localized $f$ electrons and conduction electrons at half filling, leading to the Kondo semiconductor state. We speculate that a similar hybridization gap is formed at low temperatures.[10] In $CaCu_3Ru_4O_{12}$, a metallic state with a substantial DOS at $E_F$ is maintained because of the multiband nature of the electronic states originating from the Ru orbitals. The observed reduction in the peak in $\chi$ and the recovery of $\gamma$ for the charge-disorder series shown in Figs. 4 and 5 are consistent with the coherence nature required in such a hybridization gap.

In summary, we have systematically investigated unusual electronic states in a series of transition-metal oxides $ACu_3Ru_4O_{12}$ ($A$=Na,Ca,La and their mixtures). While all of these materials exhibit heavy-mass behavior, a striking *suppression* of the mass enhancement occurs in compositions close to $CaCu_3Ru_4O_{12}$, although the Kondo-like effect is most pronounced in $CaCu_3Ru_4O_{12}$. We argued that a many-body effect in the presence of the enhanced Cu DOS, in addition to the correlated bands of Ru 4$d$ electrons, leads to a phenomenon of reduction in DOS at $E_F$ at low temperatures. We speculate that a formation of a gap structure just at $E_F$ is responsible for this reduction. Such development of the electronic structure at low temperatures is different from the conventional lattice Kondo effect in $f$-electron systems with clear localized moments. The distinct electronic state of $CaCu_3Ru_4O_{12}$ among the $ACu_3Ru_4O_{12}$ compounds, including the striking suppression of the DOS, demonstrated the importance of the duality of localized and itinerant nature of the $d$ electrons. The results of this investigation should provide a useful viewpoint in clarifying the mechanisms of the mass enhancement and Kondo-like effect found in some other $d$-electron systems.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).

[2] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994); A. P. Mackenzie and Y. Maeno, Rev. Mod. Phys. **75**, 657 (2003), and references therein.

[3] S. G. Ebbinghaus, A. Weidenkaff, and R. J. Cava, J. Solid State Chem. **167**, 126 (2002).

[4] A. P. Ramirez, G. Lawes, D. Li, and M. A. Subramanian, Solid State Commun. **131**, 251 (2004), and references therein.

[5] W. Kobayashi, I. Terasaki, J. Takeya, I. Tsukada, and Y. Ando, J. Phys. Soc. Jpn. **73**, 2373 (2004).

[6] T. T. Tran, K. Takubo, T. Mizokawa, W. Kobayashi, and I. Terasaki, Phys. Rev. B **73**, 193105 (2006).

[7] H. P. Xiang, X. J. Liu, E. J. Zhao, J. Meng, and Z. J. Wu, Phys. Rev. B **76**, 155103 (2007).

[8] A. Krimmel, A. Günther, W. Kraetschmer, H. Dekinger, N. Büttgen, A. Loidl, S. G. Ebbinghaus, E. W. Scheidt, and W. Scherer, Phys. Rev. B **78**, 165126 (2008) and references therein.

[9] S. Tanaka, N. Shimazui, H. Takatsu, S. Yonezawa, and Y. Maeno, J. Phys. Soc. Jpn. **78**, 024706 (2009), in Table I of this paper the unit of $\beta$ should be corrected to $\mu J/(f.u.\ mol\ K^4)$.

[10] T. Sudayama, Y. Wakisaka, K. Takubo, T. Mizokawa, W. Kobayashi, I. Terasaki, S. Tanaka, Y. Maeno, M. Arita, H. Namatame, and M. Taniguchi (unpublished).

[11] B. C. Passenheim and D. C. McCollum, J. Chem. Phys. **51**, 320 (1969).

[12] Y. Kishimoto, Y. Kawasaki, and T. Ohno, Phys. Lett. A **317**, 308 (2003).

[13] S. Nakatsuji, Y. Machida, Y. Maeno, T. Tayama, T. Sakakibara, J. van Duijn, L. Balicas, J. N. Millican, R. T. Macaluso, and J. Y. Chan, Phys. Rev. Lett. **96**, 087204 (2006).

[14] H.-A. Krug von Nidda, R. Bulla, N. Büttgen, M. Heinrich, and A. Loidl, Eur. Phys. J. B **34**, 399 (2003).

[15] S. Kondo *et al.*, Phys. Rev. Lett. **78**, 3729 (1997).

[16] V. I. Anisimov, M. A. Korotin, M. Zölfl, T. Pruschke, K. Le Hur, and T. M. Rice, Phys. Rev. Lett. **83**, 364 (1999).

[17] R. Arita, K. Held, A. V. Lukoyanov, and V. I. Anisimov, Phys. Rev. Lett. **98**, 166402 (2007), and references therein.

[18] C. Lacroix, Can. J. Phys. **79**, 1469 (2001).

[19] A. Shimoyamada, K. Ishizaka, S. Tsuda, S. Nakatsuji, Y. Maeno, and S. Shin, Phys. Rev. Lett. **102**, 086401 (2009).
[20] K. Momma and F. Izumi, J. Appl. Crystallogr. **41**, 653 (2008).
[21] H. Ikeda and K. Miyake, J. Phys. Soc. Jpn. **65**, 1769 (1996).
[22] K. Shimada, K. Kobayashi, T. Narimura, P. Baltzer, H. Namatame, M. Taniguchi, T. Suemitsu, T. Sasakawa, and T. Takabatake, Phys. Rev. B **66**, 155202 (2002).