Difference in Ru ionic state between Ru1212 and Ru1222 from ESR measurements

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Abstract

We performed ESR measurements for polycrystalline samples of $RuSr_2GdCu_2O_8$ (Ru1212) and its analogous $RuSr_2(Gd_{1.4}Ce_{0.6})Cu_2O_{10}$ (Ru1222). Resonance spectra indicate a ferromagnetic correlation between the Ru ions, which appears below $T_M = 135$K (Ru1212) and 170K (Ru1222). Our most interesting finding is that the signal can be clearly separated into two components only in Ru1212. A charge segregation of Ru^{4+} and Ru^{5+} in the RuO_2 layers in Ru1212 is an intriguing candidate, in contrast to an ionic valence of Ru^{5+} in Ru1222.

Key words: $RuSr_2GdCu_2O_8$; $RuSr_2(Gd_{1.4}Ce_{0.6})Cu_2O_{10}$; ESR ; (anti)ferromagnetic correlation

1. Introduction

$RuSr_2GdCu_2O_8$ (Ru1212) is expected to give a good opportunity to understand a coexistence of ferromagnetism with superconductivity [1]. Recent neutron diffraction, however, shows a predominant antiferromagnetic correlation among Ru ions with a field-induced ferromagnetic component [2]. Therefore, a detailed magnetic structure is still controversial.

In order to investigate the magnetic structure, we performed ESR measurements for Ru1212 and its analogous compound $RuSr_2(Gd_{1.4}Ce_{0.6})Cu_2O_{10}$ (Ru1222). The tetragonal structure of Ru1212 is similar to $YBa_2Cu_3O_7$, where CuO chains are replaced by RuO_2 planes. In Ru1222, each unite cell of Ru1212 is stacked along the c axis with a shift of ($a/2$, $a/2$), where a is a lattice parameter.

2. Experimental

Polycrystalline samples of Ru1212 and Ru1222 were prepared by conventional solid-state reactions. In X-ray diffraction patterns, we cannot find any impurity peaks. The superconducting and magnetic transition temperatures (T_c, T_M) determined by the resistivity and the magnetic susceptibility are (45, 135) K for Ru1212 and (41, 170) K for Ru1222, respectively. ESR measurement was performed at ~ 9 GHz from 10 K to 300 K for fine samples diffused in paraffin.

3. Results and Discussion

The magnetic resonance spectra $d\chi''/dH$ of Ru1212 and Ru1222 are plotted in Fig. 1. At all measuring temperature regime, we observed an electron paramagnetic resonance (EPR) of Gd ions near 320 mT ($g \sim 2$). The EPR signal can be described well as a Lorenz resonance curve, indicating importance of the exchange interaction, in addition to the dipole-dipole interaction.

Figure 2 (a) shows the temperature dependence of the peak-to-peak line width ΔH_{pp} for the Gd^{3+} EPR. The line widths of Ru1212 and Ru1222 roughly exhibit a similar temperature dependence which is expressed by $\Delta H_{pp}(T) = (1 + \theta/T)\Delta H_{pp}(\infty) + bT$, where θ is a Weiss temperature of antiferromagnetic Gd^{3+} ($T_N \sim$ 2.5 K). Through T_M, we found a small negative jump

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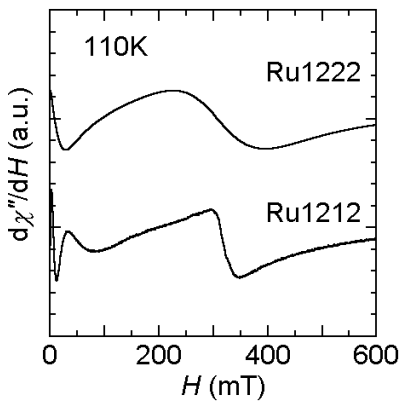

Fig. 1. Magnetic resonance spectra dχ"/dH of Ru1212 and Ru1222

in $\Delta H_{\rm pp}$for both Ru1212 and Ru1222. This could be caused by a decrease of the dipole magnetic field at the Gd site.

Below $T_{\rm M}$, the EPR signal shifts to a lower field. We define the inner field $H_{\rm i}$ as the shift, that is, $H_{\rm i}(T) = H_{\rm r}(300{\rm K}) - H_{\rm r}(T)$, where $H_{\rm r}$ is a resonance field (Fig. 2 (b)). In Ru1212, $H_{\rm i}$ increases with decreasing temperature. After taking a maximum value of 6 mT, further decreasing temperature results in $H_{\rm i} = 3$ mT as a saturated value. On the other hand, in Ru1222, a large enhancement of $H_{\rm i}$ curiously appears below 100 K $< T_{\rm M}$. The maximum value of $H_{\rm i}$ is 23 mT for Ru1222.

Now we concentrate on the resonance signals below 200 mT (Fig. 1), which cannot be observed above $T_{\rm M}$ within our resolution. Together with the appearance of $H_{\rm i}$ at Gd site, it is naturally concluded to originate from a ferromagnetic correlation of Ru ions. On the other hand, the decrease of the dipole field which explains the negative jump in $\Delta H_{\rm pp}$ at $T_{\rm M}$ could suggest a predominant antiferromagnetic correlation in Ru ions. Therefore, we suppose a ferrimagnetism or a weak ferromagnetism as the magnetic structure in the Ru site.

Our most interesting finding is that the resonance signal for Ru ions can be clearly separated into two components only in Ru1212, as shown in Fig. 1. This separation is also observed in $RuSr_2EuCu_2O_8$, suggesting a common feature among Ru1212 compounds. The most fascinating scenario, which explains this separation, is a mixed-valence state of the Ru ions. NMR measurements [3] suggest an almost equal charge segregation of Ru^{4+} and Ru^{5+}. Assuming an alternative alignment of Ru^{4+} and Ru^{5+}, a ferrimagnetism might be realized. In this case, one can expect two kind of resonance signals (normal mode and exchange mode) for Ru ions. However, it should be noted that the separation becomes unclear below 90 K. Therefore, the mechanism of the separation still remains an open question.

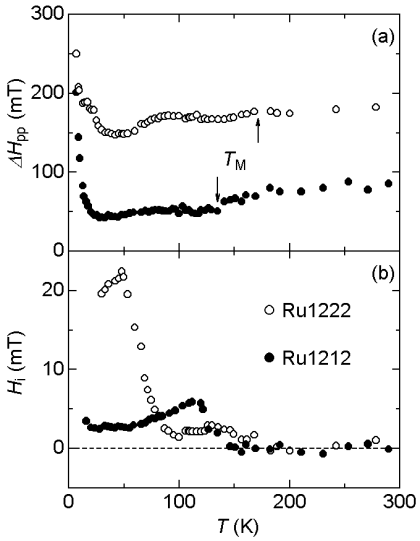

Fig. 2. Temperature dependence of $\Delta H_{\rm pp}$ and $H_{\rm i}$ obtained from Gd EPR signals.

Finally, we comment on why the difference in the Ru resonance signals between Ru1212 and Ru1222 exists. It is known that rich physical properties in $(Ca,Sr)_2RuO_4$ [4] depend on the rotation of the RuO_6. Therefore, we imagine that the band structure induced by such a structural change is also important for this ruthenocuprates.

4. Summary

We investigated the magnetic properties of Ru1212 and Ru1222 by ESR measurements. The resonance spectra consist of the Gd EPR and the Ru magnetic resonance. We found some evidences for a ferromagnetic correlation in each Ru ions, in addition to a predominant antiferromagnetic correlation. In order to understand the magnetic structure in detail, it could be a crucial factor that the Ru resonance signal can clearly be separated into two components only in Ru1212.

References

[1] C. Bernhard, J. Tallon, Ch. Niedermayer, Th. Blasius, A. Golnik, E. Brucher, R.K. Kremer, D.R. Noakes, C.E. Stronach, E.J. Ansaldo, Phys. Rev. B **59** (1999) 14099.

[2] J.W. Lynn, B. Keimer, C.Ulrich, C. Bernhard, J. Tallon, Phys. Rev. B **61** (2000) R14964.

[3] Y. Tokunaga, H. Kotegawa, K. Ishida, Y. Kitaoka, H. Takagiwa, J. Akimitsu, Phys. Rev. Lett. **86** (2001) 5767.

[4] S. Nakatsuji, Y. Maeno, Phys. Rev. Lett **84** (2000) 2666.