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Microscopic evidence for magnetic ordering in $NdCu_3Ru_4O_{12}$: ^{63,65}Cu nuclear quadrupole resonance study

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ABSTRACT

We have conducted ^{63,65}Cu nuclear quadrupole resonance (NQR) measurements on *A*-site ordered perovskite compounds $LaCu_3Ru_4O_{12}$ and $NdCu_3Ru_4O_{12}$ to investigate their ground state and spin fluctuations. While there is only one Cu site in the crystal structure, multiple NQR resonance lines were observed. This is presumed to be due to the presence of slight distortion and lattice defects in the samples. The nuclear spin-lattice relaxation rate divided by temperature, $1/T_1T$, for $LaCu_3Ru_4O_{12}$ showed almost constant value indicating the Fermi-liquid state. A remarkable increase in $1/T_1T$ due to spin fluctuations was observed in $NdCu_3Ru_4O_{12}$. Furthermore, an evident magnetic phase transition at $T_M = 0.6$ K was revealed from the distinct peak of $1/T_1T$ and the broadening of the NQR spectrum.

1. Introduction

Transition-metal oxides with a perovskite-related crystal structure are one of the systems showing various interesting physical properties. One well-known example is the itinerant-electron ferromagnetism in $SrRuO_3$ [1,2]. On the other hand, $CaRuO_3$ shows paramagnetic behavior with antiferromagnetic exchange interactions [1,2]. Among the compounds which contain a perovskite structure, *A*-site ordered perovskite compounds were examined in this study. The crystal structure of the *A*-site ordered perovskite is shown in Fig. 1. In the *A*-site ordered perovskite structure, three-fourths of *A* ions of the parent perovskite structure ABO_3 are replaced with a *C*-ion [3]. Due to the collective rotation of the BO_6 octahedral, the unit cell doubles in all directions, resulting in a unique cubic structure (space group: $Im\bar{3}$, T_h^5 No. 204). Its chemical formula is described as $AC_3B_4O_{12}$ [4], which is similar to the filled skutterudite structure RT_4X_{12} (R=rare earth, T=transition metal, X = pnictogen) [5]. Therefore, the structure is sometimes called oxyskutterudite [6]. The *A*-ion in $AC_3B_4O_{12}$ compounds is surrounded by 12 O ions, which is similar to the filled skutterudite compounds in which the *R* ion is surrounded by 12 *X* ions. The various physical properties in the *A*-site ordered perovskite compound are produced by a combination of *A*, *B*, and *C*. Among them, the ruthenates $ACu_3Ru_4O_{12}$ exhibit metallic behavior [3]. $CaCu_3Ru_4O_{12}$ was reported to exhibit heavy-fermion behavior with a moderately enhanced Sommerfeld coefficient of $\gamma = 84$ mJ/(f. u. mol K^2) [7]. Extensive research has been promoted to clarify the origin of the heavy fermion behavior without the *f* electrons [7–13]. Comprehensive NMR and NQR have been performed, and detailed temperature dependence of $1/T_1T$ was measured for $CaCu_3Ru_4O_{12}$. As a result, an abrupt change in the density of states below 100 K and non-Fermi liquid behavior below 1 K were revealed [8–10].

Heavy-fermion-like behavior was also reported in the rare-earth ruthenates $ACu_3Ru_4O_{12}$ with $A =$ La, Pr, and Nd. The Sommerfeld coefficient in the compounds with A = La, Pr, and Nd amounts to $\gamma = 139$ mJ/(f. u. mol K^2), 295 mJ/(f.u. mol K^2), and 195 mJ/(f.u. mol K^2), respectively [12,14]. It was further reported that for $LaCu_3Ru_4O_{12}$, the 4*d* electrons of Ru play a significant role in the formation of the heavy-fermion state [15]. In our knowledge, no magnetic (or more higher order) phase transition has been reported in $PrCu_3Ru_4O_{12}$ and $NdCu_3Ru_4O_{12}$.

In this study, we carried out ^{63,65}Cu nuclear quadrupole resonance (NQR) measurements in the compounds $LaCu_3Ru_4O_{12}$ and $NdCu_3Ru_4O_{12}$ in order to investigate the electronic state of these compounds from a microscopic point of view. Through the detailed measurements of the NQR spectrum and the nuclear spin-lattice relaxation time T_1, we found characteristic spin fluctuations and evident magnetic phase transition in $NdCu_3Ru_4O_{12}$.

2. Experimental

Polycrystalline samples of $LaCu_3Ru_4O_{12}$ and $NdCu_3Ru_4O_{12}$ were prepared by a solid-state reaction method. Powder x-ray diffraction

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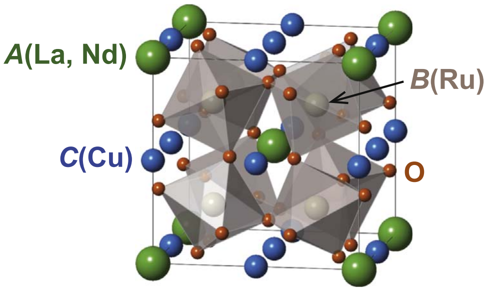

Fig. 1. The crystal structure of $AC_3B_4O_{12}$.

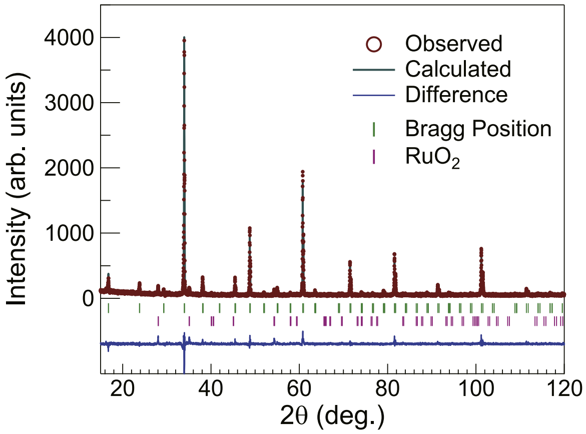

Fig. 2. The x-ray powder diffraction pattern of $NdCu_3Ru_4O_{12}$ at room temperature. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The upper set of vertical bars represents the Bragg peak positions corresponding to the $NdCu_3Ru_4O_{12}$ phase, while the lower set refers to the positions of the impurity phase of RuO_2 (space group $P4_2/mnm$). The lower solid line represents the difference curve between experimental and calculated spectra.

(XRD) characterized the samples. The room-temperature XRD pattern of $NdCu_3Ru_4O_{12}$ is shown in Fig. 2. From the results of the Rietveld refinement using the Rietan-FP program [16], this XRD data in Fig. 2 sufficiently explained the structure of $NdCu_3Ru_4O_{12}$ [4] and confirmed that it contained a second phase of starting material RuO_2 (space group $P4_2/mnm$) in the amount of 4.2 wt%. For the NQR measurements, the crystals were powdered to facilitate applied RF-field penetration. The pulse NQR measurements were performed on ^{63}Cu (nuclear spin $I = 3/2$, nuclear quadrupole moment $Q = -2.20 \times 10^{-29}$ m^2, nuclear gyromagnetic ratio $\gamma_n/2\pi = 11.289$ MHz/T) and ^{65}Cu ($I = 3/2$, $Q = -2.04 \times 10^{-29}$ m^2, $\gamma_n/2\pi = 12.093$ MHz/T) nuclei, by a spin-echo method using a conventional phase-coherent spectrometer in the temperature range of 0.3–300 K. A ^{3}He-^{4}He dilution refrigerator was used for measurements below 1.4 K. The NQR spectra were obtained by sweeping the frequency and integrating the spin-echo signal intensity step by step. T_1 was measured by a saturation-recovery method.

3. Results and discussion

Fig. 3 shows the ^{63,65}Cu NQR spectra for $LaCu_3Ru_4O_{12}$ and $NdCu_3Ru_4O_{12}$ measured at $T = 4.2$ K. Three distinct peaks and one small peak were observed in both compounds. The NQR Hamiltonian is described as:

$$\mathcal{H}_Q = \frac{h\nu_Q}{6}\left[3I_z^2 - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2)\right], \qquad (1)$$

with $\nu_Q \equiv \frac{3eQV_{zz}}{2I(2I-1)h}$ and $\eta \equiv \frac{V_{xx} - V_{yy}}{V_{zz}}$, where ν_Q is the nuclear quadrupole frequency, and η is the asymmetry parameter. Here, $V_{\alpha\alpha} \equiv \partial^2 V/\partial\alpha^2$ ($\alpha = x, y, z$) are three components of the electric field gradient (EFG)

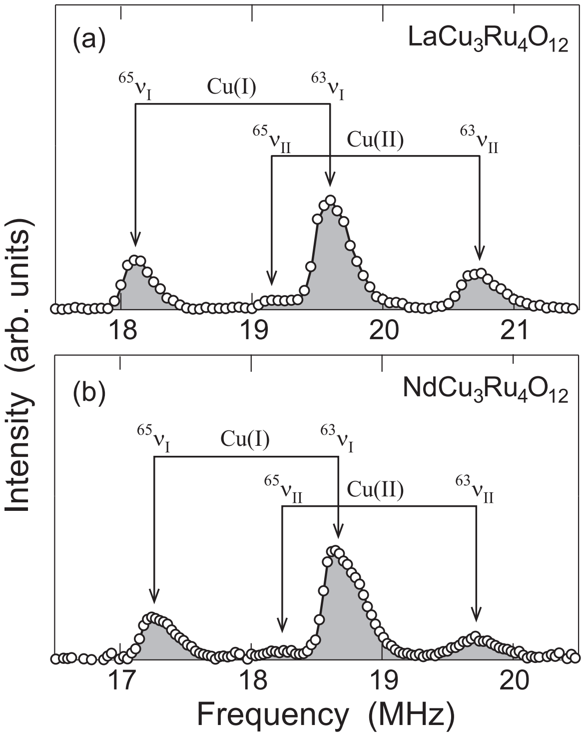

Fig. 3. $^{63,\,65}$CuNQR spectra of (a) $LaCu_3Ru_4O_{12}$ and (b) $NdCu_3Ru_4O_{12}$ at $T = 4.2$ K.

tensor, and where V is the electrostatic potential at the nuclear position. The crystal structure of $ACu_3Ru_4O_{12}$ has one Cu site whose local symmetry is expressed in *mmm* by Hermann-Mauguin notation or International notation. This local symmetry means there is the existence of nonaxisymmetric EFG at the Cu site. In the case of $I = 3/2$, one resonance line appears at frequency

$$\nu_{NQR} \equiv \nu_Q\sqrt{1 + \frac{\eta^2}{3}}. \qquad (2)$$

Therefore, two resonance lines corresponding to each nucleus of ^{63}Cu and ^{65}Cu should be expected in the paramagnetic state. However, as shown in Fig. 3, three distinct peaks and one small peak were observed in both samples. These results indicate multiple Cu sites in the crystal. We infer that lattice defects, strain, and distortions produce the various Cu sites with slightly different EFG. Usually, the effects of lattice distortion and random defects appear in the broadening of resonance lines. The presence of the observed two Cu sites suggests some particular ordering of lattice defects, however, the details are unknown. Further purification of the sample, such as the growth of single crystals, eliminates strange distortions and defects, and a single Cu site resonance line may be observed. Since the NQR frequency ν_Q is proportional to the nuclear quadrupole moment Q, the following relation holds for the two isotopes:

$$\frac{^{63}\nu_Q}{^{65}\nu_Q} = \frac{^{63}Q}{^{65}Q}. \qquad (3)$$

By using this relation, each peak was assigned assuming two Cu sites as indicated by arrows in Fig. 3. The site with the largest intensity is labeled as Cu(I) and the other as Cu(II). The resonance frequency at Cu(I) site of $LaCu_3Ru_4O_{12}$ is almost the same as that for the isostructural compound $CaCu_3Ru_4O_{12}$ [8]. In $NdCu_3Ru_4O_{12}$, the resonance frequencies were shifted to the low-frequency side due to the change of the lattice constant and the influence of 4*f* electrons.

Fig. 4 shows the temperature dependence of the NQR spectrum below 1 K. The spectrum starts to broaden below $T_M \sim 0.6$ K. This behavior indicates an occurrence of an internal magnetic field accom-