Local Magnetic Properties and Spin State of $YBaCo_2O_{5.5}$: ^{59}Co NMR Study

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Abstract

^{59}Co NMR studies have been made to clarify the spin state and local magnetic properties of $YBaCo_2O_{5.5}$, a new cobalt oxide with an oxygen-deficient and A-site ordered perovskite structure. In the antiferromagnetic state we observed four Co NMR spectra with internal fields of 216, 24, 19, 0 kOe. This means that the crystal structure at low temperatures does not have the 2×1×1 superstructure observed at room temperature.

Key words: spin state; $YBaCo_2O_{5.5}$; NMR

Complex phenomena due to spin, charge, and orbital degrees of freedom have attracted much attention in 3*d* transition metal oxides. Recently $YBaCo_2O_{5.5}$ was reported as a member of a new cobalt oxide with an oxygen-deficient and A-site ordered perovskite structure, $YBaCo_2O_{5+x}$, which has one phase with no superstructure ($0.00 \leq x \leq 0.19$) and two phases with 3×3×1 ($0.25 \leq x \leq 0.44$) and 2×1×1 ($0.50 \leq x$) superstructures in the structural properties [1,2]. The 2×1×1 superstructure in $YBaCo_2O_{5.5}$ comes from the alternative ordering of the CoO_6 octahedral and CoO_5 square pyramidal chains along the *b*-axis. It should be noted that the cobalt ions in the octahedra and the pyramids have a single valence of Co^{3+}. $YBaCo_2O_{5.5}$ was reported to undergo a metal-insulator transition at 297 K [2]. Also it has a paramagnetic to week ferromagnetic transition at 290 K and a week ferromagnetic to antiferromagnetic one at 270 K. These magnetic and electric properties are expected to closely relate to the spin state of the Co^{3+} ions. However, the spin state of $YBaCo_2O_{5.5}$ has not been clarified up to now. In this study we have made ^{59}Co NMR measurements to study local magnetic properties and the spin state of $YBaCo_2O_{5.5}$.

Powdered samples of $YBaCo_2O_{5.5}$ were prepared by the solid state reaction method as was described in Ref. 1. Field-swept NMR spectra were taken by using a coherent pulsed spectrometer, whereas frequency-swept NMR spectra were taken point by point of frequency in zero external field by using a coherent superheterodyne pulsed spectrometer.

The spin state of the Co^{3+} ions in $YBaCo_2O_{5.5}$ is closely related to the magnetic properties of the Co sites. NMR is a powerful technique to study the local magnetic properties. In a magnetically ordered state, NMR spectra can be in principal observed in zero external field, because the Co nuclei are governed by the hyperfine field from the ordered magnetic moments. At 1.5 K we observed the three ^{59}Co NMR spectra, Co(1)-Co(3), in zero external field as is shown in Fig. 1. The Co(1) spectrum with an electric quadrupole splitting is located at 217 MHz, whereas the peaks of the Co(2) and Co(3) spectra with a broad weak tail spread

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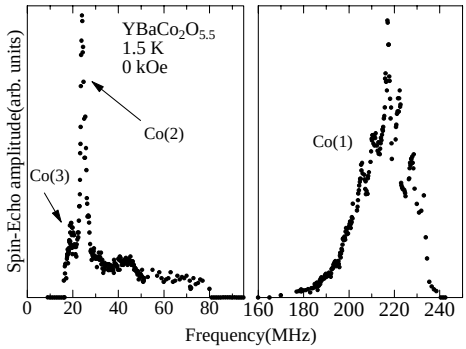

Fig. 1. ^{59}Co frequency-swept NMR spectra coming from the Co(1), Co(2) and Co(3) sites in $YBaCo_2O_{5.5}$ taken at 1.5 K in zero external field.

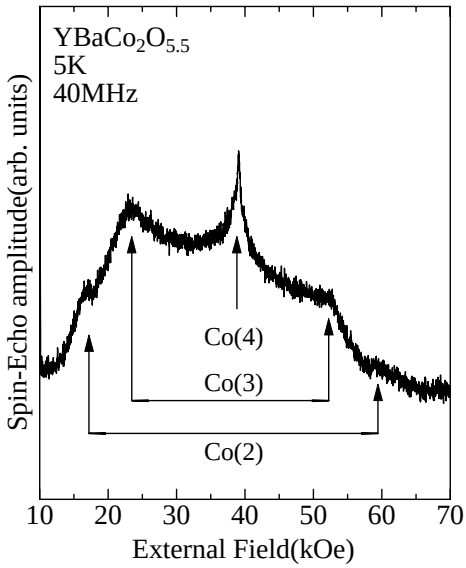

Fig. 2. ^{59}Co field-swept NMR spectra in $YBaCo_2O_{5.5}$ taken at 5 K and 40 MHz. The powder ^{59}Co spectra coming from the Co(2), Co(3), and Co(4) sites are presented by the arrows.

up to ∼80MHz are located at 24 and 19 MHz, respectively. In addition to these spectra, a ^{59}Co NMR spectrum, Co(4), was observed as is seen in Fig. 2 where the ^{59}Co field-swept NMR spectrum at 5 K is presented. It should be noted that the Co(4) site has no internal filed $H_{\rm n}$. Also powder patterns coming from the Co(2) and Co(3) sites with staggered internal fields are observed in Fig. 2 as are shown by the arrows which present peaks and shoulders in the NMR spectra. Thus it can be concluded that there are the four Co sites, Co(1)-Co(4), with $H_{\rm n}$= 216, 24, 19, 0 kOe, respectively, in the antiferromagnetic state of $YBaCo_2O_{5.5}$. This fact clearly shows that a crystal structure at the antiferromagnetic state does not have the 2×1×1 superstructure, which provides only two kinds of Co site, observed at room temperature.

As is well known, a Co^{3+} ion has a high-spin (HS), intermediate-spin (IS) or low-spin (LS) state due to the competition between the crystal field and the intra-atomic exchange interaction [3,4]. The Co(1) site with $H_{\rm n}$=216 kOe observed in $YBaCo_2O_{5.5}$ is clearly concluded to be a magnetic site with the HS or IS state, whereas the others are considered to be in the LS state. Among the LS sites, the Co(2) and Co(3) sites with $H_{\rm n}$= 24 and 19 kOe, respectively, seem to be governed by the transferred hyperfine interaction from the magnetic Co(1) site. In some oxides such as $RCoO_3$ (R : rare earth) the Co^{3+} ion in an octahedron CoO_6 is known to have the LS ground state [5]. Therefore it is considered that the Co(2)-Co(4) sites are in the octahedra CoO_6 with the LS state. It is reasonable that the Co(1) site may be in the square pyramid CoO_5 with the HS or IS state.

In summary we made ^{59}Co NMR measurements to study the spin state and local magnetic properties of $YBaCo_2O_{5.5}$. The four NMR spectra coming from the four Co sites were observed in the antiferromagnteic state. This fact shows that the crystal structure at the antiferromagnetic state does not have the 2×1×1 superstructure observed at room temperature.

Acknowledgements

This study was supported by the Grant-in-Aid of Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] D. Akahosh, Y. Ueda, J. Phys. Soc. Jpn. **68** (1999) 736.

[2] D. Akahosh, Y. Ueda, J. Solid State Chem. **156** (2001) 355.

[3] M. Itoh *et al.*, J. Phys. Soc. Jpn. **64** (1995) 3967.

[4] M. A. Korotin *et al.*, Phys. Rev. B **54** (1996) 5309.

[5] M. Itoh *et al.*, Physica B **281-282** (2001) 510.