Spin-State Change of Co atoms of $La_4Co_3O_{10+\delta}$

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Abstract

Samples of $La_4Co_3O_{10+\delta}$ with $\delta \sim 0.1$, 0.3 and 0.6 have been prepared and studied mainly by NMR for $\delta \sim 0.1$. The NMR spectra exhibit the very large broadening at low temperatures due to the antiferromagnetic ordering. The NMR spectra of the sample with $\delta \sim 0.6$ consist of two components. The intensity of one of the two with the larger relaxation rate $1/T_2$ decreases, while that of the other with the smaller $1/T_2$ increases, with decreasing T below 100 K. The result indicates that the spectra of the latter are from the Co^{3+} in the low spin state. Detailed studies of the longitudinal relaxation rate shows the existence of the energy difference between the low spin (spin S=0) and intermediate spin (S=1) states of the order of 100 K.

Key words: NMR; $La_4Co_3O_{10+\delta}$; spin state transition

The spin-state change of $LaCoO_3$ with the perovskite structure has been studied by several authors [1–5]. With decreasing temperature T, the magnetic susceptibility χ exhibits, anomalous behavior at ~ 550 K and after having a peak at about 100 K, it decreases very rapidly. The behavior is considered to be due to the changes or crossovers of the Co^{3+} ions among three spin states, the high spin (HS; spin $S = 2$) state above ~ 550 K, the intermediate spin (IS; $S = 1$) state in the region ~ 100 K $< T <\sim 550$ K and the low spin (LS; $S = 0$) state below ~ 100 K.

The Co^{3+} ions of $La_4Co_3O_{10+\delta}$ exhibit the similar spin state changes. The system has the so-called triple layered perovskite structure. In the previous work carried out by Hansteen *et al.* [6], samples with the δ values between 0 and 0.3 were prepared and anomalous T dependences of χ at about 100 K and 550 K were found. Although the anomalies indicate the spin state change of the system, we cannot observe the decrease of χ, even when T approaches zero, or the Co^{3+} ions go into the LS state, because the system has Co^{2+} ions with $S = 3/2$, too. Moreover, these spins exhibit the antiferromagnetic (AF) ordering at about 13 K. Then, we have tried, in the atmosphere of high O_2 pressure, to prepare samples with larger δ values, in which almost all Co atoms have the valency of +3. We have obtained samples which do not exhibit the AF transition and carried out the NMR studies on the spin-state change.

Polycrystalline samples with $\delta \sim 0.1$ and $\delta \sim 0.3$ were prepared by the method described in ref. [6]. Samples with $\delta \sim 0.6$ were obtained by annealing the samples with $\delta \sim 0.1$ at 500 °C for 12 h in the oxygen pressure of 50 MPa. The δ value of the obtained samples were determined by the Thermo Gravimetric Analysis (TGA). The ^{59}Co-NMR measurements were carried out by a $\pi/2$-τ-π phase-cycled pulse sequence with fixed τ.

We measured χ of the samples with $\delta \sim 0.1$, 0.3 and 0.6. For $\delta \sim 0.1$, the temperature dependence of the inverse of the susceptibility, $1/\chi$ has the slope changes at ~ 100 K and ~ 550 K, indicating the spin state transitions. The Curie constants estimated above 550 K, in the region of 110 K $< T <$ 550 K and below 100 K are consistent with the S values reported previously [6] in the corresponding T regions. For $\delta \sim 0.1$, the T-dependence of χ shows the AF order at 10 K. This ordering vanishes with increasing δ, possibly because the number of Co^{2+} ions decreases.

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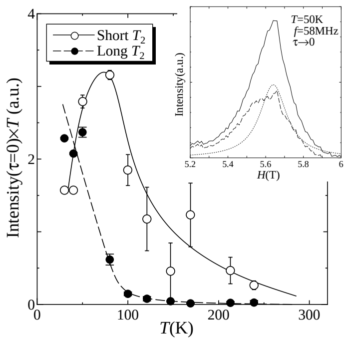

Fig. 1. T-dependences of the integrated intensities of the two components of the ^{59}Co-NMR signal. The inset shows an example of the decompositions, where the total ^{59}Co-NMR signal(solid line) obtained at 50 K for $\tau \rightarrow 0$ is divided into two components with the smaller and the larger $1/T_2$ values shown by the short and long broken lines, respectively.

The NMR measurements were carried out for $\delta \sim 0.1$ and $\delta \sim 0.6$. The width of the spectra for $\delta \sim 0.1$ begins to increase with decreasing T below 120K. At 10K, the broadening becomes very large, indicating the existence of the AF order. This kind of broadening is hardly observed for $\delta \sim 0.6$, which is consistent with the observed behavior of χ. Then, for the latter sample, we have carried out the ^{59}Co-NMR study in rather detail.

The nuclear spin-spin relaxation rate $1/T_2$ has been measured for $\delta \sim 0.6$ at the peak position of the spectra, first, where the observed relaxation curves are found to be well decomposed into components with different values of $1/T_2$. Then, this type of decomposition has been carried out at many H points to obtain the integrated intensities of the two components at $\tau \rightarrow 0$. The results of decomposition are shown in the inset of Fig. 1 at 50 K, for example. The integrated intensities of the two components are shown in Fig. 1 against T. Because the component with smaller $1/T_2$ increases with decreasing T below 100 K, it can be considered to be the contribution of the Co^{3+} ions in the LS state. However, because the large $1/T_2$ component has a significant fraction of the intensity even at the temperature as low as 30 K, we think that Co ions with different valence(s) also contribute to the intensity.

In Fig. 2, the longitudinal relaxation rate $1/T_1$ of ^{59}Co nuclei is plotted against T, where $1/T_1$ was estimated at temperatures $T \leq 20$ K by using the slope of the slow decay component in the large t region shown, for example, by the solid line in the inset. The data can be considered for the nuclei of Co^{3+} ions in the LS state, because at these ion sites, the spin fluctuations which contribute to the nuclear relaxation, is expected to be much weaker than at other sites. If the relaxation rate is solely determined by the number of the Co^{3+} ions in the IS state, $1/T_1$ should have the exponential-type decrease, which has not been observed here. Instead, the rate has the tendency to approach a finite constant value, which is possibly contributed from the magnetic fluctuations of Co atoms with different valences and therefore with finite spin values. Then, we express the rate $1/T_1$ by the relation, $1/T_1 \sim \alpha\exp(-\Delta/T)+\beta$. In the figure, the curve fitted to the data by using Δ=100 K is shown, which roughly reproduces the observed results. We do not carry out further detailed fitting, because the data is not very accurate to determine the energy difference Δ between the LS and IS states. The Δ value roughly estimated here($\sim$ 100 K) is slightly smaller than that($\sim$ 180 K) of $LaCoO_3$ [5].

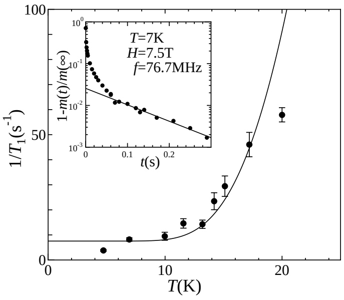

Fig. 2. T-dependence of $1/T_1$ is plotted against T, where the slope in the large t region is used for the estimation of the value of $1/T_1$(See the inset which shows the logarithm of [1-$m(t)/m(\infty)$] against t.). The solid line shows the fitted result for $\Delta = 100$ K, where the relation $1/T_1 \sim \alpha\exp(-\Delta/T)+\beta$ is used.

In summary, we prepared the samples of $La_4Co_3O_{10+\delta}$ with $\delta \sim 0.1$ and 0.6 and performed NMR measurements. The NMR spectra observed for $\delta \sim 0.1$ exhibit the very large broadening at low temperatures due to the antiferromagnetic ordering. For $\delta \sim 0.6$, the NMR spectra have been studied in rather detail and the results show that there exist two kinds of Co atoms: The NMR spectra with the smaller $1/T_2$ are from the Co^{3+} in the LS state. The T-dependence of $1/T_1$ shows the existence of the energy difference between the LS and IS states of the order of 100 K.

References

[1] R. R. Heikes, R. C. Miller and R. Mazelsky, Physica **30** (1964) 1600.

[2] M. A. Korotin, S. Y. Ezhov, I. V. Solovyev and V. I. Anisimov, Phys. Rev. B **54** (1996) 5309.

[3] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda and M. Takano, Phys. Rev. B **55** (1997) 4257.

[4] K. Asai, A. Yoneda, O. Yokokura, J. M. Tranquada, G. Shirane and K. Kohn, J. Phys. Soc. Jpn. **67** (1998) 290.

[5] Y. Kobayashi, N. Fujiwara, S. Murata, K. Asai and H. Yasuoka, Phys. Rev. B **62** (2000) 410.

[6] O. H. Hansteen and H. Fjellvåg, J. Solid State Chem. **141** (1998) 212.