


(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

 MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012B0054 実験課題名 Title of experiment Novel Molecular Spin-State Polaron in Lightly Impurity-Doped LaCoO ₃ 実験責任者名 Name of principal investigator Keisuke Tomiyasu 所属 Affiliation Tohoku University	装置責任者 Name of responsible person Kenji Nakajima 装置名 Name of Instrument/(BL No.) AMATERAS (BL14) 実施日 Date of Experiment from night on 25 January, 2013 to morning on 30 January, 2013 (total 4.5 days)

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.
Perovskite LaCo _{0.99} Ni _{0.01} O ₃ , powder Perovskite LaCoO ₃ , powder

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.
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I. INTRODUCTION <p>The perovskite-type cobalt oxide LaCoO₃ (Co³⁺: d⁶) exhibits the characteristic degree of freedom: high, intermediate, and low spin states. This oxide is a nonmagnetic insulator with low-spin state (spin $S = 0$) below ~100 K. Interestingly, however, lightly hole-doped La_{1-x}Sr_xCoO₃ ($x = 0.002$) exhibits superparamagnetism with a colossal magnetic moment over 10 μ_B/hole [S. Yamaguchi <i>et al.</i>, PRB (1996)]. Recently, as its origin, powder inelastic neutron scattering suggested that nearest six Co³⁺ ions surrounding a Co⁴⁺ ion (hole) change from nonmagnetic low-spin state to magnetic intermediate-spin state ($S = 1$), probably caused by ferromagnetic double-exchange mechanism between Co³⁺ and Co⁴⁺ (molecular spin-state polaron heptamer) [A. Podlesnyak <i>et al.</i>, PRL (2008)]. This spin-state polaron is interpreted as a precursor of carriers, generating colossal magnetic resistivity, anomalous Hall effect, and thermopower in a semiconductor region and a ferromagnetic metal region with higher hole concentration.</p>

2. 実験方法及び結果(つづき) Experimental method and results (continued)

Very recently, we discovered an extended type of spin-state polarons in another doping system $\text{La}(\text{Co}_{0.99}\text{Ni}_{0.01})\text{O}_3$ [K. Tomiyasu *et al.* (submitted)]. In the magnetization curves measured at 1.8 K on single crystals of $(\text{La}_{0.99}\text{Sr}_{0.01})\text{CoO}_3$ and $\text{La}(\text{Co}_{0.99}\text{Ni}_{0.01})\text{O}_3$, they are clearly different in magnetic anisotropy, suggesting that Sr-induced polarons are nearly isotropic whereas Ni-induced polarons exhibit anisotropy with an easy axis of [100] direction. Ni ions are trivalent (Ni^{3+} : d^7 , low spin $S=1/2$ state) and Jahn-Teller active (probably e_g orbital), suggesting emergence of the novel anisotropic spin-state Jahn-Teller polarons that is sensitive to external magnetic field.

Thus, in this study, we measured an overall picture of spin excitations in $\text{La}(\text{Co}_{0.99}\text{Ni}_{0.01})\text{O}_3$ compared with non-substituted LaCoO_3 .

II. EXPERIMENTS

A high-resolution sophisticated chopper spectrometer with low background, AMATERAS, was used. The multi- E_i values were 3, 6, 10, and 23 meV. The two samples were adjusted with the completely same weight of 20.0 g in the same cylindrical form.

III. RESULTS

Figure shows the representative $S(Q,E)$ data, measured at 21 K. Surprisingly, many discrete spin-excitation levels were discovered for the first time, which strongly suggests not only that the spin-state polarons surely emerge in the Ni-substituted system but also that the polarons are identified to quantum molecular magnets, not classical spin short-range order with a molecular shape. This finding is expected to open the new insight as molecular magnets, which exhibit interesting phenomena of magnetization plateau with quantum tunneling and are tightly connected to quantum computing and magnetic memory applications.

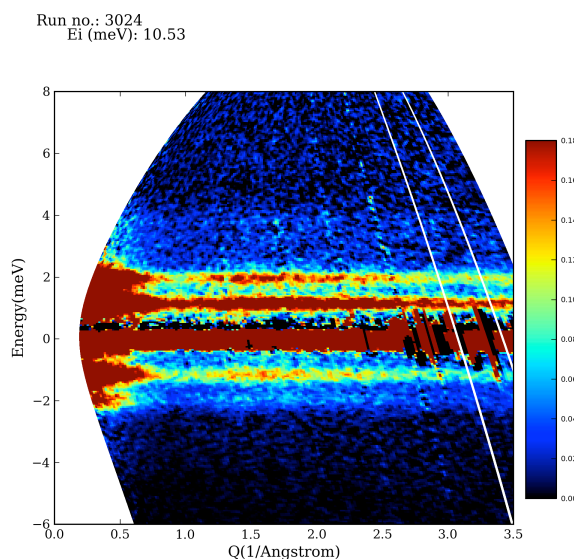


Figure: Inelastic neutron scattering data of $\text{LaCo}_{0.99}\text{Ni}_{0.01}\text{O}_3$. The data of LaCoO_3 was subtracted to extract only the contribution induced by the Ni substitution.