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Phase Separation in Oxygen Doped $La_2CoO_{4+\delta}$

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The oxygen doping effects on the magnetic and structural properties in $La_2CoO_{4+\delta}$ were studied by a neutron scattering experiment. Oxygen doping in terms of the heat treatment under the fixed oxygen partial pressure, $\log P_{O_2}$=-13, -8.5, -7, -6 at 950 °C induces at least 3 phases successively. All measured crystals show the phase separation, as it is observed in La_2NiO_4 and La_2CuO_4.

KEYWORDS: La_2CoO_4, oxygen doping, phase separation, neutron scattering

§1. Introduction

Hole doping into the transition metal oxides triggers various exotic phenomena, which have attracted both theoretical and experimental interests. One of the ways to introduce holes is to load excessive oxygen atoms into the system. In the oxygen doped system, the excessive oxygen atoms themselves also cause interesting phenomena. Thus oxygen doping effects have been extensively investigated in $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$.[1–4] In $La_2NiO_{4+\delta}$, in the range of the doping concentration, $\delta < 0.11$, the oxygen atoms are regularly intercalated,[2] which is called 'staging,' while ordering becomes rather three dimensional (3D) in high doping region, $\delta > 0.11$.[3] Staging of the excessive oxygen atoms is also found in $La_2CuO_{4+\delta}$.[4] In a low doping region in both $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$, oxygen doping successively induces different phases and phase separation is observed in wide range of δ.[1,2,4] Staging of excessive oxygen atoms is considered to be responsible to the phase separation observed in these systems.

La_2CoO_4 is another La 2-1-4 transition metal oxide, which shares large similarities with La_2CuO_4 and La_2NiO_4. Structural and magnetic properties in non-doped La_2CoO_4 were studied previously.[5] $La_2CoO_{4.00}$ has orthorhombic crystal structure at the room temperature (RT). On cooling, the system shows a 3D antiferromagnetic (AF) long range order, in which the magnetic structure is so-called La_2NiO_4-type (τ[100], $\boldsymbol{S}$[100]), where τ and $\boldsymbol{S}$ denote the AF propagation vector and spin direction. At 135 K, the crystal structure changes to tetragonal accompanied with change of magnetic structure to La_2CuO_4-type (τ[100], $\boldsymbol{S}$[010]). As observed in La_2CuO_4 and La_2NiO_4, strong oxygen doping effects are expected also in La_2CoO_4. In contrast to the cuprates and the nickelates, the doping effects in the cobalate are not well investigated so far.

In the present work, we have studied the oxygen doping dependence of the magnetic and structural properties of single crystals of oxygen doped $La_2CoO_{4+\delta}$ by means of neutron scattering experiments.

§2. Experiment

Single crystals of La_2CoO_4 were prepared by a traveling-solvent floating zone method. As grown single crystals were annealed in $CO+CO_2$ gas flow at 950 °C to tune the amount of the excessive oxygen. The partial pressure of oxygen (P_{O_2}) was controlled at $\log P_{O_2}$=-13, -8.5, -7 and -6 at the maximum temperature of annealing. In the annealing, with increasing $\log P_{O_2}$, the amount of the excessive oxygen is expected to increase in the resulted crystals.[1]

Neutron scattering experiments were carried out on a triple-axis spectrometer PONTA (5G) installed at JRR-3M at Tokai establishment of Japan Atomic Energy Research Institute. The (002) reflection of pyrolytic graphite (PG) crystals were used for the monochromator and the analyzer. In the part of the measurements, the spectrometer was operated in the double-axis mode, without an analyzer. A PG filter was employed to remove higher order neutron components. Appropriate sets of horizontal collimators were employed to optimize the resolution. The crystals ($\log P_{O_2}$=-13, -8.5, -7: 0.5 cm^3; $\log P_{O_2}$=-6: 0.1 cm^3) were set independently into a ^{4}He closed-cycle refrigerator so as the scattering plane contains a*- (or b*-, due to the crystal twining) and c*-axes.

§3. Results

In the present experiment, in addition to the stoichiometric (δ=0) phase, we observed 2 extra phases induced by oxygen doping. All crystals show a phase separation behavior, and, therefore, observed results can be accounted by the superposition of each phases.

3.1 $\log P_{O_2}$=-13, -8.5 and -7

The diffraction patterns of nuclear Bragg reflections at (2, 0, 0)/(0, 2, 0) from $\log P_{O_2}$=-13, -8.5 and -7 crystals are shown in Figs. 1 (a)-(c). Due to the twining, reflections at (2, 0, 0) and (0, 2, 0) are observed by a scan along [100]/[010] simultaneously. At RT, 3 crystals shows triple peaks, which indicates that crystals contains different phase with different set of lattice parameters. In lightly doped La_2CoO_4, it is reported that basal plane

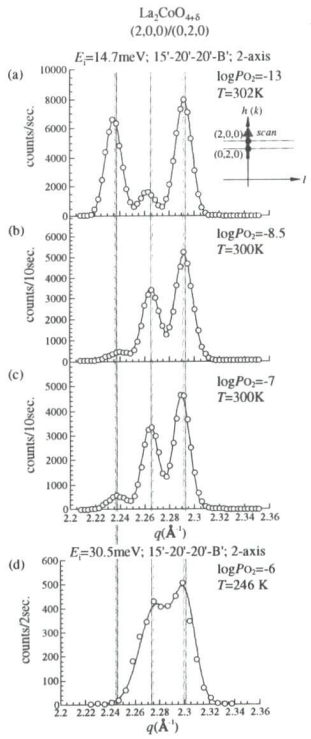

Fig. 1. Diffraction profiles of nuclear Bragg reflections at (2, 0, 0)/(0, 2, 0) from the crystals annealed at (a) logP_{O_2}=-13, (b) logP_{O_2}=-7, (c) logP_{O_2}=-8.5 and (d) logP_{O_2}=-6.

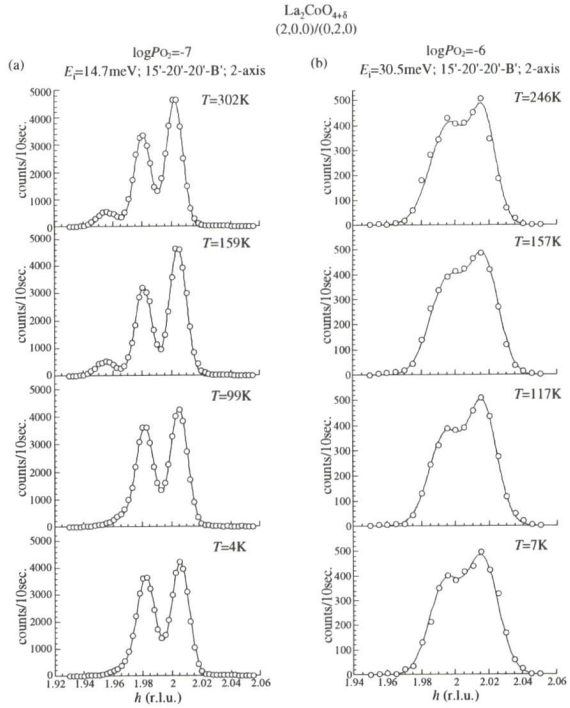

Fig. 2. Temperature dependence of diffraction profiles of nuclear Bragg reflections at (2, 0, 0)/(0, 2, 0) from the crystals annealed at (a) logP_{O_2}=-7 and (b) logP_{O_2}=-6.

lattice parameters take two of three values, a_1=5.47 Å, a_2=5.53 Å and a_3=5.60 Å.[6,7] a_1, a_2 and a_3 correspond to Q values at (2, 0, 0) (or (0, 2, 0)), $Q_{(2,0)_1}$=2.30 Å^{-1}, $Q_{(2,0)_2}$=2.27 Å^{-1} and $Q_{(2,0)_3}$=2.24 Å^{-1}. Observed peak positions roughly coincide to these three Qs. (Since we did not calibrate the neutron wavelengths, absolute values of the lattice parameters are not reliable. But relative values of same experimental conditions are reliable.) The δ=0 phase (Phase I) takes the lattice parameters of a_1 and a_3.[5] Hole doping induces the new phase (Phase II), which takes the basal-plane lattice parameters of a_1 and a_2 in 3 crystals. With increasing P_{O_2}, the portion of Phase II increases. ($Q_{(2,0)_1}$ peak in logP_{O_2}=-7 crystal is relatively smaller than that in logP_{O_2}=-8.5 one, which is considered to be come from the reliability of our annealing process, or is caused by fluctuation of volume portion of twining.) The temperature dependence of the (2, 0, 0)/(0, 2, 0) profile of logP_{O_2}=-7 crystal shows change of the crystal structure, which is expected in Phase I (Fig. 2(a)). We consider that there is no structural transition in Phase II in observed temperature range.

In Figs. 3 (a) and (b), temperature dependence of the peak intensities of 3D AF Bragg reflections from crystals of logP_{O_2}=-13 and -7 are shown respectively. Since the large part of logP_{O_2}=-13 crystal is Phase I, the result is nearly the same as that of $La_2CoO_{4.00}$. In the crystals of logP_{O_2}=-7, intensity appears at T_{N_1} = 275K at (0, 1, 1), which indicates that the magnetic structure just bellow T_{N_1} is La_2NiO_4-type. Upon cooling, (1, 0, 0) and (0, 1, 1) intensities change at T_{N_2} = 158K but the reduction of (0, 1, 1) intensity is much less than that expected in the δ=0 system. We consider that Phase II has La_2NiO_4-type magnetic structure and remains unchanged in an observed temperature range. Then, the observed temperature dependence of magnetic Bragg intensity can be explained as superposition of that of Phase I and Phase II (Fig. 3 (d)). Actually, at 166 K > T_{N_2}, integrated intensities at (1, 0, 0), (0, 1, 1), (1, 0, 2) and (0, 1, 3) are consistent to the pure La_2NiO_4-type magnetic structure. Estimated magnetic moment averaged over the crystal is $1.27 \pm 0.06 \mu_B$. From (2, 0, 0)/(0, 2, 0) scan profile at RT, volume of Phase I and Phase II are estimated to be 14% and 86%. Using the magnetic moment in $La_2CoO_{4.00}$, 2.9 μ_B,[5] the magnetic moment in Phase II is estimated to be roughly 1 μ_B. At 50 K < T_{N_2}, measured intensities at (1, 0, 0), (0, 1, 1), (1, 0, 2), (0, 1, 3) and (3, 0, 0) indicate the ratio of the intensities from the La_2NiO_4-type structure (Phase II) and La_2CuO_4-type one (Phase I) is 1.5:1, which is roughly consistent to the estimated values of volume and magnitude of moment from 166 K data, $86\% \times 1\mu_B : 14\% \times 2.9\mu_B \approx 2 : 1$.

3.2 logP_{O_2}=-6

No trace of Phase I is observed in Bragg reflection profiles at (2, 0, 0)/(0, 2, 0) from logP_{O_2}=-6 crystal (Fig. 1 (d)). Temperature dependence of 3D AF Bragg reflections from logP_{O_2}=-6 crystal is shown in Fig. 3 (c). Phase II contributes to the intensity at (0, 1, 1) appears at T_{N_1} = 280 K. Additional intensities of magnetic Bragg reflections appear at (1, 0, 0) and (0, 1, 1) at T_{N_2} = 103 K. We consider that these reflections come from another phase, Phase III. Positions of reflections indicate that Phase III has La_2CuO_4-type magnetic structure. Again temperature dependence of (1, 0, 0) and (0, 1, 1) intensities can be accounted by sum of those from Phase II and Phase III as depicted in Fig. 3 (e). Since there is no structural change in the basal plane (Fig. 2 (b)), we consider there is no magnetic structural change in Phase III, as in Phase II.

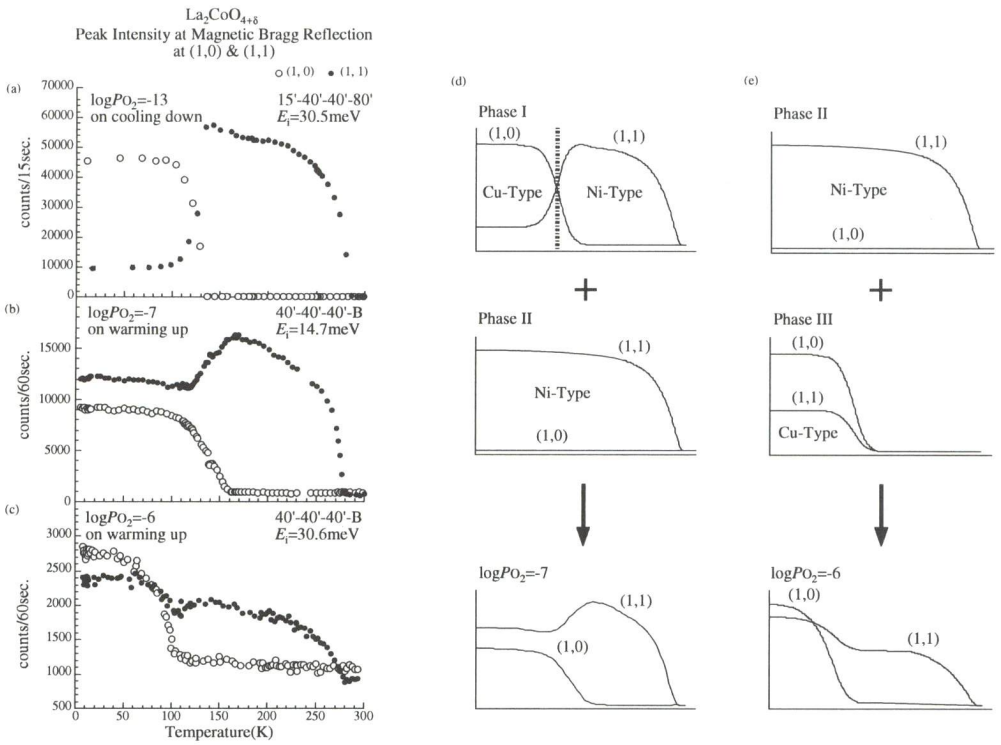

Fig. 3. Temperature dependence of the antiferromagnetic Bragg reflections from the crystals annealed at (a) $\log P_{O_2}$=-13, (b) $\log P_{O_2}$=-7 and (c) $\log P_{O_2}$=-6. (d) and (e) Schematic views of the accounting obtained results in the context of the phase separation.

No indications of phase separation are observed in (2, 0, 0)/(0, 2, 0) profiles. There are 3 possibilities of the basal plane lattice parameters of Phase III, i) $a = a_1$ and $b = a_2$ (orthorhombic), ii) $a = b = a_1$ (tetragonal) and iii) $a = b = a_2$ (tetragonal). Oxidized phase with $a = b = a_1$ is found previously,[8] and the La_2CuO_4-type magnetic structure appears in tetragonal phase in Phase I. Therefore, we speculate that $a = b = a_1$ is the most probable, although further study on single phase crystal is required to make a definitive conclusion.

§4. Summary

Oxygen doping induces different phases with different crystal and magnetic structures successively. Up to $\log P_{O_2}$=-6, we have observed at least 3 phases, Phase I : undoped phase, which has the La_2NiO_4-type (285 K $\geq T \geq$ 135 K) and La_2CuO_4-type ($T \leq$ 135 K) magnetic structures and takes an orthorhombic ($T \geq$ 135K) and a tetragonal ($T \leq$ 135K) crystal structures; Phase II : the first oxidized phase, which has the La_2NiO_4-type magnetic structure and an orthorhombic crystal structure; Phase III : the second oxidized phase, which has the magnetic structure of La_2CuO_4-type and a tetragonal or an orthorhombic crystal structure. All measured crystals show phase separation as observed in $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$. Thus, phase separation is considered to be generic in the oxygen doped La 2-1-4 transition metal oxides. Phase separation is considered to be caused by primarily the oxygen staging. The superlattice structure caused by oxygen staging should be studied in future experiments.

Detailed properties of Phase II and III are not clear yet. Thus, further experiments, especially studies on the single phase crystal are important. Here we could not determine the precise oxygen concentration. Since the same annealing condition of $\log P_{O_2}$=-6 in La_2NiO_4 gives rise to δ=0.03, we can expect similar value of δ. Now we undertake the determination of oxygen concentration.

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1) S. Hosoya, T. Omata, K. Nakajima, K. Yamada and Y. Endoh: Physica C **202** (1992) 188.
2) J. M. Tranquada, Y. Kong, J. E. Lorenzo, D. J. Buttrey, D. E. Rice and V. Sachan: Phys. Rev. B **50** (1994) 6340.
3) J. M. Tranquada, J. E. Lorenzo, D. J. Buttrey and V. Sachan: Phys. Rev. B**52** (1995) 3581.
4) B. O. Wells, Y. S. Lee, M. A. Kastner, R. J. Christianson, R. J. Birgeneau, K. Yamada, Y. Endoh and G. Shirane: Science **277** (1997) 1067.
5) K. Yamada, M. Matsuda, Y. Endoh, B. Keimer, R. J. Birgeneau, S. Onodera, J. Mizusaki, T. Matsuura and G. Shirane: Phys. Rev. B **39** (1989) 2336.
6) J. J. Janecek and G. P. Writz: J. Am. Ceram. Soc. **61** (1978) 242.
7) T. Matsuura, J. Tabuchi, J. Mizusaki, S. Yamauchi and K. Fueki: J. Phys. Chem. Solids **49** (1988) 1403.
8) U. Lehmann and H. K. Muller-Buschbaum: Z. Anorg. Allg. Chem. **59** (1980) 470.