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Phase segregation in Na$_x$CoO$_2$ for large Na contents

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We have investigated a set of sodium cobaltates (Na$_x$CoO$_2$) samples with various sodium content (0.67 $\leq$ x $\leq$ 0.75) using Nuclear Quadrupole Resonance (NQR). The four different stable phases and an intermediate one have been recognized. The NQR spectra of ^{59}Co allowed us to clearly differentiate the pure phase samples which could be easily distinguished from multi-phase samples. Moreover, we have found that keeping samples at room temperature in contact with humid air leads to destruction of the phase purity and loss of sodium content. The high sodium content sample evolves progressively into a mixture of the detected stable phases until it reaches the $x = 2/3$ composition which appears to be the most stable phase in this part of phase diagram.

Introduction. The family of sodium layered cobaltates Na$_x$CoO$_2$ ($0 < x \leq 1$) has a rich phase diagram [1], which includes most interesting scientific phenomena present in condensed matter physics, such as superconductivity [2], spin density wave [3], magnetic frustration in a triangular lattice, coexistence of metallic and magnetic properties, both Curie-Weiss and 2D metal, etc [4]. Moreover, high ionic mobility and high Seebeck coefficient [5, 6] allow to consider this compound for potential thermoelectric applications [7, 8].

The concentration x of sodium ions and their order/disorder in the Na plane play a fundamental role in the physical properties of cobaltates. The Co ions are in the large crystal field induced by their oxygen octahedral environment, so the 3d levels are split and the difference in energy between the lower t$_{2g}$ triplet and upper e$_g$ doublet is $\approx$ 2 eV, thus only the t$_{2g}$ triplet states are filled [1]. Therefore the electronic structure of the Co ions is expected to correspond to low spin configurations with total electron spin $S = 0$ or $S = 1/2$ with charge states Co^{3+}/Co^{4+}, respectively.

In the present work we have studied the cobaltates Na$_x$CoO$_2$ at large sodium content x range ($0.67 \leq x \leq$ ≤ 0.75). This concentration range bears our attention due to the occurrence of an A-type magnetic ordering at $x \simeq 0.75$ and its absence at lower sodium contents $x < 0.75$ [1, 9]. In Ref. [10] the existence of four stable phases in this Na concentration range has been established. These phases display a similar nearly ferromagnetic in-plane behavior above 100 K but exhibit significantly different ground states. The structure of one of these phases has been proposed recently using

NMR/NQR data and confirmed by x-ray Rietveld analysis [11, 12].

In NQR, nuclei with an electric quadrupole moment have their nuclear spin energies split by the electric field gradient (EFG) created by the electronic bonds in the local environment. So this technique is very sensitive to the nature of the bonding around the nucleus.

Samples. The reproducible preparation of single-phase samples with precise stoichiometries is not straightforward in cobaltates. The high ionic mobility of sodium and its chemical activity (for example, Na ions easily react with molecules present in the ambient atmosphere to form NaOH or sodium carbonates) make the control of Na content even more difficult.

However, the methods for reproducible synthesis of single-phase powder samples in the $0.67 \leq x \leq 0.75$ sodium range have been reported in Ref. [10, 12]. To protect the powders from the influence of water they were packed into protecting materials. Several protecting materials have been used in our experiments: the epoxy resin (Stycast 1266) and paraffin, which display distinct advantages and disadvantages. The Stycast perfectly protects the powder from *water influence*, however we have found that for samples packed in Stycast, the NQR spectra displayed resonance lines $\approx$1.9 times broader than pure powder or samples packed in paraffin (see Fig.1). Thus, the paraffin packed powder have been used for most further investigations. To eliminate diffusion processes in the Na layers the samples were kept in liquid nitrogen.

Experimental details. The NQR measurements were carried out with a home-built coherent pulsed NMR/NQR spectrometer. The NQR spectra of ^{59}Co were taken "point by point" with a $\pi/2 - \tau - \pi$ radio frequency pulse sequence by varying the spectrometer fre-
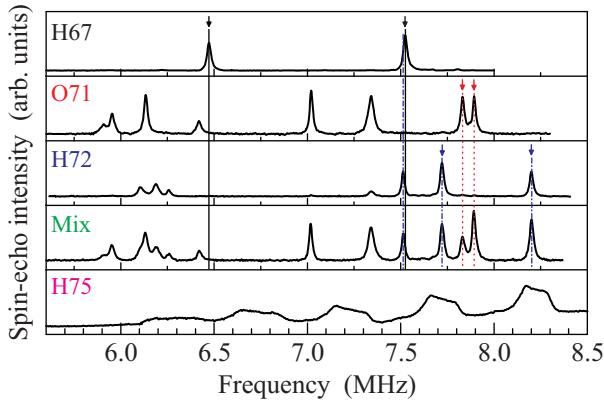
Fig.1. (Color online) Cobalt NQR lines of pure powder and powder packed in Stycast and paraffin: solid (red) line, dotted (black) line and dash-and-dot (blue) line, respectively

quency. These sweeps were done with equal frequency steps at 4.2 K. A Fourier mapping algorithm [13, 14] have been used for constructing the detailed NQR spectra.

NQR characterization of the phases. We have studied a series of samples with various sodium contents ($0.67 \leq x \leq 0.75$). The NQR spectra of ^{59}Co nuclei allowed us to clearly differentiate four stable phases (see Fig.2) marked as H67, O71, H72 and H75. This nota-
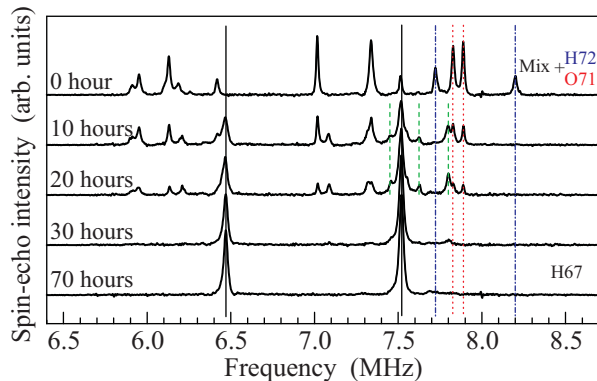

Fig.2. (Color online) NQR spectra for the four single phase samples studied in Ref. [10]. The difference in spectra is obvious – each spectrum has at least one line which does not appear in the other phases as shown by the coloured arrows and vertical lines (H67-solid (black) line, O71 – dotted line (red) and H72 – dash-dotted (blue) lines. The sample denoted as Mix, with a Na composition in between the O71 and H72 phases, is the mixture of those phases as its NQR signal is a weighted composition of the NQR signals of these two phases. H75 which is antiferromagnetically ordered at 4.2 K displays a broad ZFNMR signal due to the internal magnetic field

tion is the same as used in Ref. [10]. The number in the

phase label is an approximate sodium content ($x = 0.67$, 0.71, 0.72 and 0.75, respectively) and the letter is a type of unit cell (H-hexagonal, O-orthorhombic). The part of the ^{59}Co NQR spectra which correspond only to the ($\pm 7/2 - \pm 5/2$) transitions of ^{59}Co nuclei [10, 12] are shown in Fig.2. It is clearly seen that every phase has its own unique ^{59}Co NQR spectrum. The H67 phase has the simplest spectrum which consists of two lines at ≈ 6.5 MHz and ≈ 7.5 MHz in this frequency range. In the $5.5 \div 8.5$ MHz range the O71 has 8 and H72 has 6 resonance peaks. The doublet of lines at ≈ 7.8 MHz and the two resonance lines at ≈ 7.75 and ≈ 8.2 MHz are characteristic features of the O71 and H72 phases, respectively. These pairs of lines are labeled in Fig.2 by dotted lines and by dash-dotted lines. The spectrum of H75 phase differs considerably (Fig.2) and it will be discussed below.

Thus, the NQR spectrum is unique and characteristic for each single phase. This allows easily to distinguish samples which are a mixture of two or more phases. We show as an example in Fig.2 the ^{59}Co NQR spectrum of the sample (labeled as Mix) with a sodium content intermediate between O71 and H72 which contains both signals from these two phases. So the NQR is a sensitive method to distinguish single phase samples from a mixture of phases. This finding becomes very important as it will allow to characterize better freshly synthesized samples and clarify the phase diagram of the sodium cobaltates.

The spectral lines of H67, O71 and H72 phases are rather narrow (linewidths $\approx$30-50 kHz), which points out that the spread of EFG on the nuclear site positions is rather small. These phases have a finite number of cobalt non-equivalent sites indicating the existence of well defined local ordering in the Co and Na planes. The structural model of the H67 phase (Na$_{2/3}$CoO$_2$ compound) have been proposed recently in Ref. [11, 12]. One unit cell of this models contains four Co and three Na non equivalent sites which have been detected by NQR [11, 12] and by NMR [15, 16]. From the comparison of the NQR spectra it is obvious, that the H67 phase has the simplest structure in the $0.67 \leq x \leq 0.75$ sodium concentration range. The structural organization in the sodium planes is still an open question for the O71 and H72 phases.

The existence of the antiferromagnetic (AF) order with $T_N = 22$ K is the characteristic feature of the $x \simeq 0.75$ compound. Such AF order was detected by μSR in our samples [17], as well as by low field bulk susceptibility measurements. Neutron scattering study of the same phase established the A-type AF ordering (ferromagnetic in plane and AF between planes) [18, 19].

As our studies have been carried out at 4.2 K, the H75 phase sample was magnetically ordered at this temperature. Therefore the observed signal in the H75 phase corresponds to the so-called zero field NMR (ZFNMR). In this case, the nuclear energy levels are split by the internal magnetic field. Thus, the observed spectrum consists of seven lines, which correspond to the typical NMR spectrum for nuclear spin 7/2 (one central line and 6 satellites), but only five of them are shown on Fig.2. We have failed in detecting the NQR spectrum of the H75 phase above T_N, due to significant shortening of transverse relaxation time (T_2).

During the experiments we have found that the phase content of the samples packed in paraffin were changed. It should be noted that the paraffin packed samples between experiments were kept in liquid nitrogen. To perform the measurements we had to take out samples from liquid nitrogen, warm them to the room temperature and after that insert them in the probe of our spectrometer. In Fig.3 the evolution of phase content of one sample
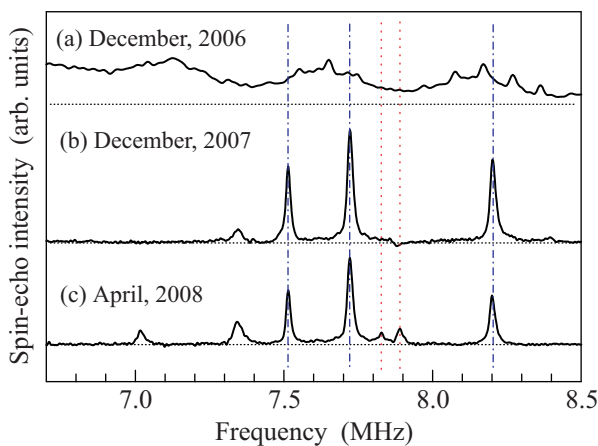

Fig.3. (Color online) Evolution of a paraffin packed sample from the H75 phase (a) to the H72 phase ((b), H72 phase lines are marked with dash-dotted (blue) lines) and, finally, to the mixture of H72 and O71 phases ((c), O71 phase lines are marked with dotted (red) lines). For details see text

after few tens such thermal cyclings to room temperature is shown. This sample was initially the H75 single-phase powder (upper spectrum in Fig.3 – broad ZFNMR lines). However, the powder transformed progressively into the H72 phase, and then the lines of the O71 phase appeared. Most probably, during repetitive fast changes of temperature, condensed water molecules were able to interact with the powder at room temperature.

Phase segregation. Therefore the phase composition of the samples could change due to non-perfect storage conditions at room temperature. To follow such

pocess a special experiment has been performed. A powder sample which initially was a mixture of H72 and O71 phases has been kept in humid atmosphere during 3 days at room temperature. The humidity was maintained $\simeq 75$ percent level in the closed half-filled bottle by saturated solution of NaCl in distilled water. Therefore the powder could easily interact with the water vapour in air.

We have measured the ^{59}Co NQR spectrum every 10 hours of exposure powder sample to humid air, and results are shown in Fig.4. There the NQR lines of the
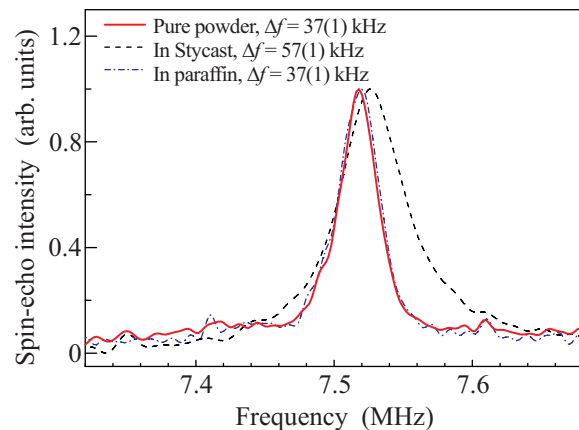

Fig.4. (Color online) NQR spectra of ^{59}Co reflect the evolution of the phase content of a powder sample versus the time of its exposure to humid air (see text for details). The sample was initially a mixture of O71 and H72 phases. The phase composition evolves after 10 and 20 hours to O71 + unknown + H67 phases, while only the H67 phase remains after 30 hours of treatment. This demonstrates that Na is progressively expelled from the Na_xCoO_2 sample

known phases are marked by the vertical lines similar to those in Fig.2. The H72 phase had almost disappeared after the first 10 hours of treatment. At the same time NQR lines in the spectrum corresponding to the H67 phase appeared, as well as NQR lines of another phase with intermediate sodium content between 0.71 and 0.67. This unknown and unstable phase persisted up to the 20th hour of treatment. Also a significant reduction of the O71 phase and clear increase of H67 phase content was observed in the 20th hours spectrum (Fig.2). After 30 hours of the sample exposure to humid air the O71 and H72 phases had almost disappeared and the only remaining phase was the H67 one with slight background of impurity phases. No significant changes in the ^{59}Co NQR spectra were detected during further treatment of the sample in humid air.

However, from our experience it is known that keeping cobaltates powder in air for a long time leads to

the destruction of H67 phase too. We had monitored such process observing the slow decrease of the H67 phase ^{59}Co NQR signal intensity and the appearance of a broad background signal from unknown phases – see 70 hours spectrum in the Fig.2. After such long exposure of the sample to the humid air white powder, most likely of sodium carbonates, appeared on the sample surface.

Thus, the powder samples evolve rapidly at room temperature in contact with humid air. The evolution process indicates a reduction of sodium content associated with a loss of Na ions. This statement is in a very good agreement with former work by Shu et al. [9] done at even higher Na content. These authors have investigated a single crystal $Na_{0.88}CoO_2$ and revealed a loss of sodium ions from the surface which were fixed in a white powder appearing on the crystal surface. Apparently, the water and/or CO_2 molecules react with Na ions from surface with formation of sodium hydroxide (NaOH) and sodium carbonates. So to avoid as much as possible the change of phase composition of the powder, we recommend to isolate cobaltates powders from interaction with humid air and to try to block the diffusion of Na ions. In some sense, the best way to store the cobaltates powders is to keep them at low temperature in hermetic ampoules with a small amount of helium gas as a heat exchanger. This arrangement isolates the powder from interaction with atmosphere and allows to perform experiments at low temperature.

Conclusion. Low temperature NQR is a very powerful method to investigate the phase content of sodium cobaltates. The four stable phases and an intermediate unstable one have been detected in the $0.67 \leq x \leq 0.75$ sodium range. The spectral lines of phases without magnetic ordering are rather narrow and non-overlapping, and the spectra could be described fully by finite set of Co non-equivalent sites. All these factors point out the existence of well defined orders in the Co and Na planes. These results are in good agreement with previous investigations [10]. So far, only the structure of the H67 phase has been determined [12], confirmed by x-rays [11] and agrees with LDA computations [20]. The present NQR results in combination with diffraction data should help to clarify the structures of the other phases. This should shed some light on the origin of the Curie-Weiss susceptibility behavior of studied phases and magnetic ordering of $x \simeq 0.75$ phase.

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