NQR and X-ray investigation of the structure of Na$_{2/3}$CoO$_2$ compound

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We have synthesized various samples of the $x = 2/3$ phase of sodium cobaltate Na$_x$CoO$_2$ and performed X-ray powder diffractions spectra to compare the diffraction with the structure proposed previously from NMR/NQR experiments [H. Alloul $et$ $al.$, EPL 85, 47006 (2009)]. Rietveld analysis of the data are found in perfect agreement with those, and confirm the concentration $x$=2/3 obtained in the synthesis procedure. They even give indications on the atomic displacements of Na inside the unit cell. The detailed NQR data allow us to identify the NQR transitions and electric field gradient (EFG) parameters for 4 cobalt sites and 3 Na sites. The spin-lattice and spin-spin relaxation rates are found much smaller for the non-magnetic Co$^{3+}$ sites than for the magnetic sites on which the holes are delocalized. The atomic ordering of the Na layers is therefore at the source of this ordered distribution of cobalt charges. The method used here to resolve the Na ordering and the subsequent Co charge order can be used valuably for other concentrations of Na.

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I. INTRODUCTION

Since the discovery of high thermo-electric-power (TEP) and superconductivity in Na cobaltates, extended efforts have been done in order to understand their magnetic and electronic properties. Anomalous magnetic properties have been discovered in unexpected ranges of Na concentrations, with an abrupt change of magnetic correlations from AF for $x \leq 0.62$ to ferromagnetic for $x \geq 0.67$. However, a situation quite unusual in solid state physics prevailed so far, as very few experiments have allowed to correlate these magnetic properties with Na ordering, apart for the featureless band insulator for $x=1$, and the very peculiar $x=1/2$ phase$^2$. We have recently reported that a combination of nuclear magnetic resonance (NMR) and nuclear quadrupolar resonance (NQR) experiments did concur to let us determine the Na order in the $x=2/3$ phase$^2$, which is a nearly ferromagnetic metallic phase which does not order magnetically down to the lowest temperatures$^{18}$. For this particular phase the large set of NMR data obtained in the past allowed us, when complemented by NQR data, to demonstrate finally that the Na order is rather simple. It results in a differentiation of Co sites into non-magnetic Co$^{3+}$ sites in which the $t_{2g}$ subshell of electronic levels is filled, and a metallic Kagome network of Co sites on which the doped holes are delocalized$^9$.

We perform here a careful Rietveld analysis of the X-ray data which confirms the structure proposed from NMR and NQR and definitively establishes the $x=2/3$ Na content of this phase contrary to the $x=0.71$ value estimated by others from chemical analyzes of single crystal samples$^{14}$. Furthermore, we report in detail here the NQR data which, together with the approach developed in Ref. $^1$, will help in similar analyzes for other structurally more complicated cases detected for different $x$ values.

The paper is organized as follows. In section II we display the methods used to synthesize single phase samples for $x = 2/3$ and display the powder X-ray spectra in which the Bragg peaks associated with the Na ordered substructure are resolved. The best Rietveld fits allowed us to determine the slight atomic displacements of the Na atoms in the model unit cell deduced from NMR/NQR data. In section III we report the Na and Co NQR spectra and show that we could detect most of the NQR lines associated with 4 Co sites identified by the former combination of NQR and NMR data. Some of the low frequency lines were however difficult to detect owing to experimental limitations. At the end of section III we show that the accurate electric field gradient (EFG) parameters can be hardly described merely by a point charge model, even taking into account the site displacements determined by X-rays. This reveals the need for more sophisticated and accurate calculations taking fully into account the atomic and electronic band structure. The spin-spin and spin-lattice relaxation data reported in section IV for the four Co sites are studied and analyzed then, which allowed us to establish that both quantities can be used to distinguish the non-magnetic cobalts from those of the more magnetic Co sites which are organized in a Kagome sublattice in the $x=2/3$ phase.

II. SAMPLE PREPARATION AND LATTICE STRUCTURE

It has been established that the phase diagram of Na cobaltates is discontinuous and consists of a series of homogeneous phases extending over limited concentration ranges, separated by composition gaps$^{4,10}$. A homogeneous domain range is characterized by a specific Na ordering which one can monitor by powder X-ray diffraction experiments. These diffraction patterns were taken at 300 K in the range of 2$\theta$ angle 10$^\circ$–130$^\circ$ (Cu Kα radiations were used). X-ray spectra such as that displayed in Fig. I allow to determine the lattice parameters from the X-ray diffraction peaks of the hexagonal structure of the...
CoO$_2$ substructure. Also, as shown in the inset of Fig. 1, a set of satellite reflections associated with the specific Na ordered structure could be detected and were found quite distinct for the various stable phases.

**A. Sample synthesis**

We have evidenced that in pure oxygen atmosphere the compounds with $x = 2/3$ are stable in the temperature range 600-700°C. Phases with higher Na content are stabilized at higher temperatures, which for a nominal composition $x = 2/3$ releases some Co$_3$O$_4$. Conversely lower preparation temperatures favor phases with $x < 2/3$, and in such case the excess Na is somewhat difficult to detect by diffraction, although after treatment in air the characteristic diffractions of Na$_2$CoO$_3$ appear. So to retain the $x = 2/3$ phase in powders, the samples were directly introduced in a furnace stabilized at 700°C, and were then quenched at room temperature after treatment. Three different approaches have been used to synthesize single phase materials:

1) direct synthesis from a stoichiometric composition of Co$_3$O$_4$ and Na$_2$CO$_3$. However we found that the reaction is rather slow at such low temperatures and requires weeks of treatment with intermediate grindings to eliminate the last traces of unreacted Co$_3$O$_4$.

2) from a mixture of cobaltates with calibrated compositions synthesized previously (such as Na$_{1/2}$CoO$_2$ and Na$_{0.71}$CoO$_2$ taken in a proper ratio).

3) by de-intercalation of Na from Na$_{0.71}$CoO$_2$ by annealing it at 700°C - out of its own stability temperature range. Of course, in that case the composition $x = 2/3$ of the material prepared differs from its nominal composition $x = 0.71$, which remains unchanged and would be detected by chemical analysis. The released Na remains in excess and is not well crystallized (oxidized) and difficult to observe by X-rays.

Overall the second method was found the most reliable and was easily reproducible.

**B. Rietveld refinement of the structure**

As already indicated in a previous published report, the NMR and NQR data have allowed us to identify 3 Na and 4 Co sites, their occupancy and those with axial symmetry in the lattice. It has been then possible to establish the lattice cell of the structure displayed in Fig. 2. Such a structure ought to be recovered by X-ray scatter-
ing experiments and should explain the set of satellite diffractions detected, such as those displayed in the inset of Fig. 1

For the phases with \( x > 0.5 \) we have detected such sets of satellites, which in most cases can be described by a single incommensurate wave vector with component \( q_{b}^{*} \). Under these conditions the lattice loses the hexagonal symmetry and becomes generally orthorhombic with \( a_{ort} = a_{hex} \sqrt{3} \), \( b_{ort} = a_{hex}/q_{b}^{*} \), \( c_{ort} = c_{hex} \), as was noticed early by Zandbergen et al. from high resolution microscopy experiments. This has led to propose a phenomenological model in which an increase of Na content corresponded to the insertion of "stripes" of Na2 with increasing \( a_{ort} \) in the known structure of Na1/3CoO2. It is easy to evaluate that in such a model the empirical relation \( x = 1 - q_{b}^{*} \) applies.

In contrast only the particular composition \( x = 2/3 \) exhibits a commensurate locking leading to a conventional superstructure with a rhombohedral unit cell \( a_{rh} = 2a_{hex} \sqrt{3}, c_{rh} = 3c_{hex} \) which, in the phenomenological description, corresponds to \( q_{b}^{*} = 1/3 \), as expected. This structure, which corresponds to the spatial group R-3c (n°167) allowed excellent quality Rietveld fits of the X-ray diffraction pattern as can be seen in the expanded diagrams of Fig. 2. These Rietveld refinements lead to the distribution and occupancy of cobalt and sodium sites given in Table I in perfect agreement with the NMR-NQR results. Moreover, they definitively confirm the composition \( x = 2/3 \). Indeed, only the sodium sites mentioned in the Table I are fully occupied whereas the other sites deduced from the hexagonal substructure reveal themselves to be completely empty within the limits of standard deviations.

Most of the ionic coordinates are unchanged with respect to the substructure positions (see Table I). The most displaced are the Na2 ions. The displacement of Na2 sites already were mentioned in the Ref. 12,13 but it was attributed to the repulsion of randomly located neighboring Na ions, locally violating the hexagonal symmetry. But as one can see on Fig. 2 the relaxation of position of these sites corresponds to a dilatation of the Na2 triangles, which agrees with the interionic repulsion in this highly charged region. As might be expected, the displacements of Na along the honeycomb lattice (ionic conduction channel) of the outer Na2b triangle are nearly twice larger than those of the inner Na2a triangle.

In addition we would like to mention that we have calculated the diffraction spectra for eight distinct samples and found in all cases that the Coa position is slightly shifted along the c-axis direction towards the Na2 trimer, with the same offset \( \approx 0.06(1) \) Å. The oxygen ions are only found slightly displaced with respect to the ideal unit cell, which points the compactness of the CoO2 slabs between which are inserted the Na ions.

### III. NQR SPECTRA AND EFG PARAMETERS

A nucleus with nuclear spin \( I > 1/2 \) has an electric quadrupole moment in addition to its nuclear magnetic moment. The nucleus interacts with the electronic environment not only through magnetic hyperfine couplings due to its magnetic moment, but also through the interaction of its quadrupole moment with the local crystal electric field gradient (EFG), either static or dynamic. The EFG arises from a non-symmetric distribution of electric charge around the nucleus. This charge can originate from non-bonding electrons, electrons in the bonds and

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**TABLE I: X-ray determination of the structure of Na2/3CoO2, data collection 2θ = 10-130°, Cu Kα, \( a = 9.8007(1) \) Å; 3c = 32.8151(4) Å; spatial group R-3c (n°167), hexagonal axes, Z = 72, R = 5.41%, \( R_{w} = 7.16\% \).**

| Site       | Position | x     | y     | z     | B   |
|------------|----------|-------|-------|-------|-----|
| Co1b       | 7 b      | 0     | 0     | 0     | 0.34(2) |
| Co1a       | 12 c     | 0     | 0     | 0     | 0.3315(3) |
| Co2a       | 18 d     | 1/2   | 0     | 0     | " |
| Co2b       | 36 f     | 1/3b  | 1/6b  | 0b    | " |
| Na1        | 12 c     | 0     | 0     | 0     | 1/12b 0.52(7) |
| Na2a       | 18 e     | 0.632(2)| 0    | 1/4   | " |
| Na2b       | 18 e     | 0.187(2)| 0    | 1/4   | " |
| Ox-1       | 36 f     | 1/6b  | 0b    | 0.0298(5)| 1.3(2) |
| Ox-2       | 36 f     | 2/3b  | 0b    | 0.0290(4)| " |
| Ox-3       | 36 f     | 1/2b  | 1/6b  | 0.0320(5)| " |
| Ox-4       | 36 f     | 1/6b  | 1/2b  | 0.0295(5)| " |

\( ^{a} \)Number of sites and Wyckoff notation for position. All sites are found to be fully occupied (see text).

\( ^{b} \)Those coordinates have been left free but the positions deduced from the fits did not deviate significantly within experimental accuracy with respect to the mean unit cell positions.
charges of neighboring atoms or ions. Therefore NQR is a sensitive tool for studying solids as it provides detailed information on the static and the dynamic properties of the structure on the scale of a few interatomic spacings. Thus, NQR may be regarded as a powerful tool for investigating the local order in solids whereas the interpretation of the data on disordered (or complex-ordered) materials from usual scattering experiments, such as X-ray or neutron scattering, is complicated by the absence of the long-range order translational symmetry or large and complicated unit cell.

Therefore to demonstrate these advantages of NQR to the non-NMR specialist we start this section by a brief NQR background introduction (A) and describe in (B) the basic features of the experimental techniques used. Next we show the $^{23}\text{Na}$ NQR spectrum (C) and compare it to the $^{23}\text{Na}$ NMR data\textsuperscript{12}. We present then (D) the $^{59}\text{Co}$ NQR spectrum and show how fast and slow relaxing cobalt sites can be separated in the spectrum. Finally in (E) we show that the accurate EFG parameters can hardly be described merely by a point charge model, even taking into account the site displacements determined by X-rays.

**A. NQR Background**

If the crystal field symmetry is lower than cubic, the Hamiltonian of the quadrupolar interaction can be written\textsuperscript{15}:

$$\mathcal{H}_Q = \frac{\hbar \nu_Q}{6} \left( 3I_Z^2 - I(I-1) + \eta(I_X^2 - I_Y^2) \right), \quad (1)$$

where the quadrupole frequency 

$$\nu_Q = \frac{3eQV_{ZZ}}{2I(2I-1)\hbar}$$

is defined by the nuclear quadrupole moment $Q$ and the largest principal axis component $V_{ZZ}$ of the EFG tensor and $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ is the asymmetry parameter (here the principal axis of EFG tensor are selected such that $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$). In NQR experiments the magnetic transitions between energy levels with $\Delta m = \pm 1$ are observed.

**B. Experimental techniques**

The NQR measurements were done using a home-built coherent pulsed NMR/NQR spectrometer. NQR spectra were taken “point by point” with a $\pi/2 - \tau - \pi$ radio frequency (RF) pulse sequence by varying the spectrometer frequency in equal frequency steps in the range 1.5-15 MHz at 4.2 K. The detailed NQR spectra were then constructed using a Fourier mapping algorithm\textsuperscript{16,17}.

The change of tuning frequency of the NQR spectrum has been done with a variable capacitor. However the Q-factor of the probe (and the sensitivity of the spectrometer) varies considerably with frequency. This limits seriously the accuracy of absolute intensity measurements of NQR signals. Relative intensity measurements could only be done accurately for lines occurring in a narrow frequency range.

Due to the spin-spin relaxation process (which will be discussed in detail later) the intensity of the observed spin echo NQR signal decreases with increasing delay $\tau$ between the RF pulses. It is usually impossible to reduce this time to zero, as the receiver is overloaded by the RF pulse and only recovers after a minimum time $\tau_R$. Furthermore, for short values of $\tau$ the detected signal is heavily distorted by residual oscillations (called "ringing") of the probe components and contains artifacts. To reduce the probe ringing time a low Q-factor NQR probe has been used with $Q$= 10-20. So, the signal can only be detected after a minimum time $\tau_D$ ("dead time") which usually increases markedly with decreasing frequency. In our experiments the minimum practical $\tau$ values varied from 70 $\mu$s at 1.5 MHz to 40 $\mu$s at 9 MHz.

**C. $^{23}\text{Na}$ NQR spectrum**

The nuclear spin energy levels split by the EFG are doubly degenerate (see Eq. (1)). So for $^{23}\text{Na}$ for which $I = 3/2$ a single resonance line which corresponds to the $\pm 1/2 \leftrightarrow \pm 3/2$ transition can be observed at the frequency:

$$\nu = \nu_Q \sqrt{1 + \frac{1}{3} \eta^2}. \quad (2)$$

The NQR spectrum of $^{23}\text{Na}$ in the Na$_2$CoO$_2$ compound measured at 4.2 K is shown in Fig. 3. It consists of three well resolved narrow lines which correspond to three Na sites with distinct local environment. Such a spectrum with resolved narrow lines undoubtedly confirms that this phase is well ordered, as was pointed out in the earlier NMR study which has established that a characteristic signature of the $x = 2/3$ phase\textsuperscript{14} is to exhibit three distinct sodium sites. The shape of the $^{23}\text{Na}$ NQR lines has been fitted by a Lorentzian function and their positions and linewidths (which were taken as a full width at half maximum - FWHM) are collected in Table I.

As for $I = 3/2$ the NQR frequency determined by Eq. (2) depends on both $\nu_Q$ and $\eta$, it is impossible to determine both parameters from the NQR spectrum. However, these parameters were determined by NMR for each sodium site and are also listed in Table I. Using these values and following Eq. (2) one can calculate the expected frequencies $f_{cal}$ of $^{23}\text{Na}$ NQR lines (Table III). As one can see the calculated and experimental values are in perfect agreement - therefore the notation proposed in Ref. 14 for different sodium sites have been used in
The tiny (<1.3%) difference in the experimental and calculated frequencies for the Na2b site can be easily explained by a small deviation (not more than 5°) of the Z principal axis of the EFG tensor and the c crystallographic axis for this site. The relative intensities of sodium lines will be discussed later in section IV of this paper.

D. 59Co NQR spectrum

Former 59Co NMR data18 taken on this phase have already allowed us to evidence distinct Co NMR lines, but the NMR spectra were somewhat difficult to analyze fully, as one needs to determine altogether the EFG parameters and NMR shifts of the various sites. The experiments were furthermore complicated by the need of a quasi perfect alignment of the powder sample with respect to the applied magnetic field. They however allowed us to determine some of the EFG parameters, which allowed us to know beforehand the range of expected νQ values. After a presentation of the spectra, we explain in some detail how the various transitions pertaining to the same sites can be identified. The identification of the Co NQR lines is explained in some details, and allow us then to determine the EFG values.

1. Experimental results

Typical NQR spectra of 59Co in the Na2/3CoO2 compound are shown in Fig. 4. We found that the number of lines and their intensities in the observed spectrum depend strongly on the delay τ between pulses. This corresponds to the fact that the experimental spin-echo intensity depends on the rate of the spin-spin relaxation process. Consequently the fast relaxing nuclei are not observable at long enough delay τ between pulses, as will be detailed in section IV. In the spectrum observed with the shortest possible τS = 45 μs there are 6 narrow intense lines and several lines with weaker intensity (Fig. 4). At the same time in the spectrum measured with τL = 100 μs the intensities of the high frequency lines greatly decrease, while the intensities of 4 low frequency narrow lines does not change a lot. So, it is obvious that in this phase with x = 2/3 two different types of Co sites - fast and slow relaxing - coexist, as was established already by NMR18.

As was shown earlier18 for the high sodium content range (x > 0.5) of the sodium cobaltates phase diagram, a cobalt charge disproportionation into Co3+ and Co3+5+ is a quite common picture. Cobalt ions in sodium cobaltates are in low spin configurations, so Co3+ has an electronic spin S = 0 and relax rather slowly in comparison with the cobalts with higher charge state on which holes delocalize (formally Co4+ should have S = 1/2).

2. Identification of the NQR lines

As the 59Co nuclei have I = 7/2, for a single crystallographic site one should observe up to 3 lines in the NQR spectrum. The positions of these lines depends on both νQ and η. Figure 5a shows the theoretical dependence of NQR frequencies of the allowed transitions on the asymmetry parameter of the EFG tensor for nuclear spin 7/2. These data were obtained by numerical diagonalization of the main Hamiltonian recalled in Eq. (1).

One can see that the frequencies of the ±3/2 ↔ ±1/2 and ±3/2 ↔ ±1/2 transitions weakly depend on the asymmetry parameter η, contrary to that of the ±1/2 ↔ ±1/2 transition (Fig. 5b). For η = 1 only two resonance lines in the spectrum should be observed. Measuring experimentally the resonance frequencies for different transitions should allow then to determine both νQ and η for I = 7/2.

Since the number of lines in the experimental 59Co NQR spectrum (Fig. 4) is much larger than 3 (number of the observable NQR lines for I = 7/2), an analysis has to be done to determine the triplet of lines which are associated with a given cobalt site in the unit cell of this x = 2/3 compound. The basic data which can be used for such an analysis are the theoretical ratios of frequencies.

### Table II: Comparison of 23Na NQR and NMR results.

| Site  | ν(MHz) | Δν(kHz) | νQ(MHz) | η  | νcalc(MHz) |
|-------|--------|---------|---------|----|------------|
| Na1   | 1.645(1)| 8.2(1)  | 1.645(5)| 0.01(1)| 1.645      |
| Na2a  | 1.928(2)| 8.2(1)  | 1.74(1) | 0.84(2)| 1.93       |
| Na2b  | 2.117(1)| 9.0(1)  | 1.86(1) | 0.89(2)| 2.09       |

FIG. 3: 23Na NQR spectrum in the Na2/3CoO2 compound measured at 4.2 K. The fully resolved quadrupole structure for the three Na sites is discussed in the text.
of different transitions for a single cobalt site which are restricted as established from Fig. 5b.

Let us consider as an example the two intense lines at \( \approx 7.52 \) MHz and \( \approx 6.47 \) MHz (Fig. 4) which corresponds to an an experimental frequency ratio \( \approx 1.16 \). Although we know from NMR experiments that those EFG values correspond to distinct Co sites, we want to show here that a simple analysis of the NQR spectra does confirm that point. In theory such a ratio could be found for a single site with EFG’s with \( \eta = 0.47 \) or \( \eta = 0.85 \) (see Fig. 1b).

As \( \eta = 0.47 \) corresponds to the ratio of frequencies of \( \pm \frac{3}{2} \leftrightarrow \pm \frac{3}{2} \) and \( \pm \frac{1}{2} \leftrightarrow \pm \frac{1}{2} \) transitions, then one should find in the spectrum a line corresponding to the \( \pm \frac{5}{2} \leftrightarrow \pm \frac{5}{2} \) transition at a frequency \( \approx 7.52 \pm 1.578 \approx 11.87 \) MHz. We indeed didn’t find such a line in our experiment. Also we know from NMR that such large EFG values do not exist. Similarly for \( \eta = 0.85 \) one should find a line for the \( \pm \frac{1}{2} \leftrightarrow \pm \frac{1}{2} \) transition at \( 7.52/1.51 \approx 4.98 \) MHz which does not exist either. Therefore the \( \approx 7.52 \) MHz and \( \approx 6.47 \) MHz lines cannot be attributed to the same cobalt site and correspond to two different fast relaxing cobalt sites Co2b and Co2a.

Then one has to consider the next pair of lines, e.g. at \( \approx 7.52 \) MHz and \( \approx 4.83 \) MHz. The frequency ratio is equal \( \approx 1.56 \) and 3 possible values of \( \eta \) should be considered. However only one value of \( \eta \approx 0.36 \) gives the right 3rd line position in the spectrum, a weak and broad line at \( \approx 3.52 \) MHz which completes the spectrum of the Co2a site. We found this line by observing the slight asymmetry of the shape of the intense and narrow slow relaxing line at \( 3.581 \) MHz decreases with increasing \( \tau \). To better resolve this line we used the fact that slow and fast-relaxing cobalts can be separated also by the large difference in their spin-lattice relaxation rates, as seen by NMR and as detailed later in section IV. To saturate the signal an additional \( \pi/2 \) pulse with 100 \( \mu s \) delay was used before the \( \pi/2 - \pi \) pulse sequence. In the spectrum obtained after such a pulse sequence (“saturated” in the insert of Fig. 4), the intensities of the slow-relaxing cobalt lines decrease and the lines of the fast-relaxing cobalts can be better resolved. This method allowed us to detect one more fast relaxing line at 4.145 MHz which completes the three line spectrum for the 2nd fast relaxing Co2a site, with the two other lines at 6.473 MHz and 3.03 MHz.

Such an analysis allowed us also to determine that the two slow-relaxing lines at 3.581 and 4.178 MHz are the \( \pm \frac{5}{2} \leftrightarrow \pm \frac{5}{2} \) transitions of two different sites of cobalt, Co1a and Co1b, as could already be anticipated from the Co NMR data. The corresponding \( \pm \frac{3}{2} \leftrightarrow \pm \frac{3}{2} \) transitions are at 2.387 and 2.785 MHz. We did not attempt to observe the \( \pm \frac{1}{2} \leftrightarrow \pm \frac{1}{2} \) transitions for these slow-relaxing cobalts which should appear at low frequencies \( \approx 1.19 \) and \( \approx 1.39 \) MHz, outside of the frequency range of our spectrometer.

FIG. 4: Main panel: \(^{59}\text{Co} \) NQR spectra taken at 4.2 K for short (\( \tau_s = 45 \mu s \)) and long (\( \tau_L = 100 \mu s \)) delay between pulses. Insert: the two weak intensity lines of the \( \pm 3/2 \leftrightarrow \pm 5/2 \) Co2a and Co2b sites are revealed by saturation of the high intensity slow relaxing lines.

\[ \text{Na}_2\text{CoO}_2 \quad T=4.2K \]

Spin-echo intensity (arb. units)
The broadening of the Co1 and Co2 groups of lines were found to display different behaviours likely linked with their different magnetic properties. Figure 4 shows the linewidth variation with resonance frequency of the various transitions for each of the cobalt NQR lines. Two different behaviors appear clearly: the linewidths increase with increasing frequency for Co1 sites while the opposite holds for the Co2 sites. The Co1a and Co1b sites are non-magnetic with localized holes and one expects essentially a broadening due to a distribution of EFG values. Indeed for a spin $\frac{7}{2}$ system with zero asymmetry parameter (Co1 case), a spread $\epsilon \Delta \eta$ of EFG values induces broadenings of the different NQR transitions such that $\Delta \nu_i / \nu_i \propto \Delta \eta / \eta$, so that the linewidth increases linearly with the frequency of the transition as found in the data of Figure 6. One would expect then a linewidth of $\approx 6$ kHz for the lowest ($\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$) transitions of the Co1a,b sites. Extrapolating the linear fits for Co1a,b sites to zero frequency gives a very small residual value $\approx 1$ kHz, which could be attributed to dipole dipole coupling as will be detailed in section IV.

As Co2a and Co2b are magnetic sites, a broadening due to magnetic interactions might take place and apparently increases with decreasing index of the quadrupole transition. This will be discussed in section IV after considering the spin spin $T_2$ processes.

E. Rough estimates of the EFG values

We have calculated the EFG tensors and the corresponding parameters of the quadrupole Hamiltonian ($\nu_Q$ and $\eta$) for all sites of the $^{23}$Na and $^{59}$Co in the simplest point charge model assuming charges $1^+$ on Na, $3^+$ on Co1, $3.44^+$ on Co2 and $2^-$ on O (see Table IV). Of course one does not expect such point charge calculations to fit perfectly the data as similar calculations do not even explain the simple case of Na$\text{II}$CoO$_2$ for which all Co are Co$^{3+}$ (Ref. 8 and references therein). Such an approach does not take into account correctly the cobalt-oxygen covalency. We do however clearly see in the results displayed in the Table IV that for the NaI and Co1 sites the asymmetry parameter is of course that expected from the site symmetry, that is $\eta = 0$. We also find that

All the observed $^{59}$Co NQR lines were fitted by Lorentzian functions and their positions and linewidths are collected in Table III and Table VI respectively. The values of $\nu_Q$ and $\eta$ found in this work are in perfect agreement with those quoted in the Ref. 18. The fact that we observe a limited number of narrow and well-resolved $^{59}$Co NQR lines (Fig. 3) confirms the existence of long-range order in this $x = 2/3$ phase of sodium cobaltates. Moreover NQR is clearly able to distinguish the charge segregation between the slow relaxing non-magnetic Co$^{3+}$ (sites Co1a and Co1b), and the fast relaxing cobalt sites Co2a and Co2b, on which holes are delocalized. Despite all our efforts we have not found in the $^{59}$Co NQR spectrum any traces of the Co3 site anticipated from NMR (see Ref. 18). As explained in the Ref. 1 we did conclude that this apparent ”site” was an experimental artifact due to imperfect alignment of the NMR sample. This point will be detailed in an extensive experimental report of the Co NMR spectra. The intensities of the $^{59}$Co NQR lines will be discussed later in section IV after the analysis of the spin-spin relaxation of these cobalt NQR signals.
the asymmetry of the structure yields rather large asymmetries for the EFG values on the Na2 and Co2 sites as found experimentally. However the magnitudes of the EFG computed do not agree quantitatively with the experimental values. We did however find that the displacement of the Na atoms found in the X-ray structure analysis yields significant changes in the calculated EFG values. This reveals that more sophisticated calculations taking into account the atomic displacements and the band structure at least in the local density approximation (LDA) are required to explain the EFG parameters.

IV. SPIN-LATTICE RELAXATION AND SPIN-SPIN RELAXATION

When thermal equilibrium of the nuclear spins is disturbed by RF pulses, their equilibrium magnetization is recovered by the nuclear nuclear spin-lattice relaxation (NSLR) process which corresponds to the relaxation of the longitudinal component of the magnetization. The decay of the transverse component of the magnetization, the nuclear spin-spin relaxation (NSSR) process is connected with the loss of coherence inside the spin system due to spin-spin interactions. Generally both relaxation processes could have different origins which reflect magnetic and electronic properties of the materials, the inner arrangement, the interactions in the spin system, the different motion and diffusion processes. In this section we report and discuss first in (A) the $^{59}$Co spin-lattice relaxation for all four cobalt sites. Next we consider in (B) the spin-spin relaxation starting from $^{23}$Na as a simple case of NSSR. Then we analyze the $^{59}$Co spin-spin relaxation. We demonstrate that both NSLR and NSSR allow to differentiate the two types of Co sites - nonmagnetic $^{3+}$ ions on 25% of the cobalt sites and a metallic Kagome network of Co sites on which the doped holes are delocalized.

| Site      | Experiment | Non-shifted | shifted |
|-----------|------------|-------------|---------|
| Na1       | $\nu_Q=1.645(5)$ | $\nu_Q=0.61$ | $\nu_Q=0.28$ |
|           | $\eta=0$  | $\eta=0$   | $\eta=0$  |
| Na2a      | $\nu_Q=1.74(1)$ | $\nu_Q=0.93$ | $\nu_Q=0.94$ |
|           | $\eta=0.84(2)$ | $\eta=0.88$ | $\eta=0.19$ |
| Na2b      | $\nu_Q=1.86(1)$ | $\nu_Q=0.93$ | $\nu_Q=1.15$ |
|           | $\eta=0.89(2)$ | $\eta=0.31$ | $\eta=0.36$ |
| Co1a      | $\nu_Q=1.193(1)$ | $\nu_Q=1.06$ | $\nu_Q=1.71$ |
|           | $\eta\leq0.017$ | $\eta=0$   | $\eta=0$   |
| Co1b      | $\nu_Q=1.392(1)$ | $\nu_Q=1.18$ | $\nu_Q=0.94$ |
|           | $\eta\leq0.01b$ | $\eta=0$   | $\eta=0$   |
| Co2a      | $\nu_Q=2.187(1)$ | $\nu_Q=1.42$ | $\nu_Q=1.55$ |
|           | $\eta=0.362(5)$ | $\eta=0.26$ | $\eta=0.56$ |
| Co2b      | $\nu_Q=2.541(1)$ | $\nu_Q=1.55$ | $\nu_Q=1.37$ |
|           | $\eta=0.358(4)$ | $\eta=0.56$ | $\eta=0.40$ |

A. $^{59}$Co spin - lattice relaxation

To study the NSLR process we have used the magnetization inversion recovery method which uses three pulses: $\pi - t - \pi/2 - \tau - \pi$, where $t$ and $\tau$ are the time intervals between pulses. In this sequence the first pulse rotates the magnetization by 180 degree, the second and third pulses gives a spin-echo, and the dependence of the spin-echo intensity on delay time $t$ allows to monitor the recovery of the nuclear magnetization associated with a given NQR transition:

$$M(t) = M_0(1 - B \cdot R(t)).$$

Here $M_0$ is the thermal equilibrium value of magnetization and the parameter $B$ characterizes the actual magnetization after the first pulse at $t = 0$ (the imperfection of the experimental conditions gave typical values $B \approx 1.8$ rather than $B = 2$ expected for a perfect $\pi$ pulse). The shape of the relaxation function $R(t)$ depends on the nuclear transition sampled. For a two-level nuclear system (like the $I = 3/2$ NQR case) this process is exponential $R(t) = \exp(-t/T_1)$, with a characteristic time constant $T_1$, the spin-lattice relaxation time. But generally for $I > 1/2$ the nuclear energy levels are differentiated by the quadrupole interaction with the crystalline electric field (Eq. II). As a consequence the difference in population between adjacent levels which are probed by the RF
pulses depends on the populations of the levels which are not hit by the RF pulses. Therefore the magnetization recovery becomes multi-exponential

\[ R(t) = \sum_i a_i \exp \left( -\frac{\lambda_i t}{T_1} \right), \]

but is still characterized by a single \( T_1 \) value.

The spin-lattice relaxation could be driven either by magnetic or quadrupolar fluctuations. However in the sodium cobaltates, which exhibits unusual magnetic properties, the magnetic relaxation mechanism dominates at least at low \( T \). Following Ref. [21] we obtained the parameters for the theoretical relaxation functions \( R(t) \) for the case of magnetic relaxation by weak isotropic fluctuating magnetic fields for different transitions of different Co sites - see Table V.

![Graph showing spin-lattice relaxation curves for Co2b site measured at 7.52 MHz and 4.83 MHz (\( \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2} \) and \( \pm \frac{5}{2} \leftrightarrow \pm \frac{7}{2} \) transitions correspondingly) at 4.2 K. Solid lines are the fits of experimental points by the magnetization relaxation functions with parameters from the Table V.](image1)

**TABLE V:** Theoretical spin-lattice relaxation function [21] parameters for different \(^{59}\)Co sites for the case of magnetic relaxation by weak isotropic fluctuating magnetic fields (based on Ref. [21]).

| Site | \( \eta \) | Transition | \( a_1 \) | \( \lambda_1 \) | \( a_2 \) | \( \lambda_2 \) | \( a_3 \) | \( \lambda_3 \) |
|------|------|-------------|------|------|------|------|------|------|
| Co1  | 0    | \( \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2} \) | 0.14 | 21   | 0.65 | 10   | 0.21 | 3    |
|      |      | \( \pm \frac{5}{2} \leftrightarrow \pm \frac{7}{2} \) | 0.74 | 21   | 0.16 | 10   | 0.1  | 3    |
| Co2  | 0.36 | \( \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2} \) | 0.27 | 17.7 | 0.53 | 8.96 | 0.2  | 3    |
|      |      | \( \pm \frac{5}{2} \leftrightarrow \pm \frac{7}{2} \) | 0.88 | 17.7 | 0.038| 8.96 | 0.082| 3    |

papera, Similarly the spin-lattice relaxation measurements for \(^{23}\)Na were technically challenging and have therefore not been performed here as they have been studied in great detail by NMR in Ref. [10] for various \( Na_xCoO_2 \) phases including the \( x = 2/3 \) phase.

**B. Spin-spin relaxation and signal intensities**

NSSR is a complex phenomenon, but at its most fundamental level the random fluctuations of the local magnetic field leads to a loss of the initial phase coherence

![Graph showing temperature dependence of nuclear spin-lattice relaxation rates \( 1/T_1 \) for all four cobalt sites in the \( Na_{2/3}CoO_2 \) compound. For Co1a and Co1b measurements were done on the \( \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2} \) transitions and for Co2a and Co2b measurements were done on the \( \pm \frac{5}{2} \leftrightarrow \pm \frac{7}{2} \) transitions. Linear fits shown by dotted lines are guides to the eyes.](image2)
of the nuclear spins and therefore to the decrease of the transverse nuclear spin magnetization. In the Redfield theory, the transverse relaxation arises from two mechanisms: (1) nuclear spin-spin coupling (via magnetic dipolar or indirect interactions) and (2) the spin-lattice relaxation.

The NSSR is studied by monitoring the spin-echo intensity as a function of the time delay \( \tau \) between \( \pi/2 \) and \( \pi \) pulses. In general the decay of transverse magnetization \( M(t) \) as a function of time \( t = 2\tau \) can be fitted by the equation:

\[
M(t) = M(0) \exp \left( - \left( \frac{t}{T_2} \right)^n \right). \tag{5}
\]

The NSSR process is characterized by the relaxation time \( T_2 \) and the exponent \( n \), which characterizes the decay shape which usually varies between Lorentzian \((n = 1)\) and Gaussian \((n = 2)\).

1. \( ^{23}\text{Na} \) spin-spin relaxation

The spin-spin relaxation decays for sodium sites are shown in Fig. 9. The shortest \( \tau \) value used was only \( \approx 65 \mu\text{s} \) due to the long 'dead time' \( \tau_D \) of the spectrometer (see section III). Then the beginning of the relaxation decays were lost and only tails were measured. Therefore it was impossible to determine reliably the transverse magnetization decay shape. Nevertheless the experimental data were fitted by a Lorentzian \((n = 1)\) function (see Eq. 5) in order to obtain estimates of the spin-spin relaxation times and of the NQR lines intensities. The \( T_1 \) values of \( ^{23}\text{Na} \) known from the data of Ref. [11] for the same phase of sodium cobaltates were long enough to ascertain that they do not contribute significantly to the transverse magnetization decay. So the values obtained by fitting the relaxation decays for the sodium sites given in Table VII can be associated with spin-spin processes.

The values of magnetization at zero time \( M(0) \) after \( \nu^2 \) frequency correction allowed us to estimate the relative intensities of sodium lines (sites) which are also reported in Table VII. These data are in good agreement with the more accurate ones obtained by NMR. Here the accuracy is indeed limited primarily by the extrapolation required from \( \tau_D \) to \( \tau = 0 \), and also by the variation of spectrometer sensitivity with frequency.

Due to the NSSR process the linewidth of an NQR signal at half-height should be equal \( \Delta \nu_{\text{calc}} = 1/(\pi \cdot T_2 \cdot \tau) \). Such \( \Delta \nu_{\text{calc}} \) for different Na sites are also collected in Table VII. And it is easy to see that they are approximately three times smaller than the experimentally measured linewidths for all sodium sites (Table VII). This clearly shows that the experimentally observable Na lines are inhomogeneously broadened by a weak distribution of EFG such that \( \Delta \nu_{Q}/\nu_Q \approx 4 \cdot 10^{-3} \). Such a small value found indeed imply a very well ordered structure in the sodium layers of this Na\(_2/3\)CoO\(_2\) compound.

![Spin-spin relaxation curves of \( ^{23}\text{Na} \) sites](image)

**FIG. 9:** Spin-spin relaxation curves of \( ^{23}\text{Na} \) sites and fits by the Eq. 5.

| Site | \( T_1 \) (\( \mu\text{s} \)) | \( T_2 \) (\( \mu\text{s} \)) | \( \Delta \nu_{\text{calc}} \) (kHz) | \( \Delta \nu \) (kHz) |
|------|----------------------|----------------------|-----------------------|-----------------------|
| Na1  | 23(5)                | 125(2)               | 2.5(1)                | 8.2(1)                |
| Na2a | 46(8)                | 82.3(7)              | 3.8(2)                | 8.21(5)               |
| Na2b | 31(7)                | 97(1)                | 3.3(2)                | 9.02(6)               |

| Site | \( I \) (%) | \( T_2 \) (\( \mu\text{s} \)) | \( \Delta \nu_{\text{calc}} \) (kHz) | \( \Delta \nu \) (kHz) |
|------|-------------|----------------------|-----------------------|-----------------------|
| Na1  | 23(5)       | 125(2)               | 2.5(1)                | 8.2(1)                |
| Na2a | 46(8)       | 82.3(7)              | 3.8(2)                | 8.21(5)               |
| Na2b | 31(7)       | 97(1)                | 3.3(2)                | 9.02(6)               |

**TABLE VI:** \(^{59}\text{Co} \) relaxation and NQR linewidth parameters (see text for details).

**TABLE VII:** \(^{23}\text{Na} \) relaxation and NQR linewidth parameters.
the Table V can be written, at short enough times for the ± transitions. For example, the Eq. 4 with the parameters from Table VI for the Co2 site. So we conclude that for Co2 sites the measured T2 values are determined by spin-lattice relaxation process. This explains as well the difference in the transverse magnetization decay shape for Co1 and Co2 sites.

This influence of spin-lattice relaxation on the spin-spin relaxation explains why the intensity of the low frequency transitions of Co2a and Co2b sites are found so weak experimentally (see Fig. 4). As one can see from the Table VI for the Co2b site, the measured T2 =30(2) µs for the ± transition is smaller than that (49(2) µs) for the ± transition. Also as was already stated in section III, the minimum usable time T between RF pulses increases with decreasing frequency. So both factors reduce the intensities of the observed low frequency Co2 NQR lines.

As has been noticed previously in section III, the signal intensities observed at different frequencies are affected by the variation of spectrometer sensitivity, so careful determination of the relative site occupancies of Co1 and Co2 could not be done directly from our experiments. But we could estimate the fractional occupancies inside each group of cobalt (Co1 and Co2) separately, as their resonance frequencies are close. After correcting for the spin-spin relaxation T2 and for the frequency dependence of the signal intensity we obtained: Co1a/Co1b=1.95(0.1) and Co2b/Co2a=1.9(0.2), in agreement with similar determinations from 59Co NMR, which allowed as well better determinations of the Co1/Co2 ratio.

Spectral lines of cobalt are inhomogeneously broadened (see Table VI) and this is clear if one compares the experimental linewidth with the calculated one. Notice that the ratio ∆ν/∆νcalc is ≈ 4.0(0.4) for both ± and ± transitions of Co2b and ≈ 5.0(0.3) for Co2a, which confirms that these broadenings have the same origin.

V. CONCLUSION

In summary, we have reported detailed powder X ray and NQR data for the Na2/3Co2O4 compound supporting the recent paper in which we proposed a detailed structural model for this material from NMR/NQR results. The NQR spectrum of 23Na and 59Co consists of several narrow lines, which could be associated with 3 sodium and 4 cobalt sites, in a 2D unit cell comprising 8 Na sites over 12 Co. The finite number of unequivalent site positions confirms that the simple 3D ordering of the Na layers leads to a differentiation of cobalt sites. We have performed as well a careful Rietveld analysis of the
X-ray data which confirms the atomic 3D unit cell proposed from NMR/NQR. The best Rietveld fits allowed us to determine the slight atomic displacements of the Na atoms in the model unit cell. Also the quality of the fit allows us to ascertain the x=2/3 value of the Na content.

Others have also detected this phase and identified it with the present one from its large spin susceptibility at low temperatures.\(^1\) They have performed single crystal diffraction experiments in which they also find a 12 Co 2D unit cell. Using chemical analyses of their single crystals they proposed that x = 0.71, and have elaborated then a structural model in which the concentration of Na alternates between planes with x = 2/3 with 8 Na per 2D cell and x = 3/4, with 9 Na per 2D cell. In these Na layers the Na vacancies would be alternatively organized in divacancies and trivacancies. One can immediately see that such a structure would never explain the present NMR/NQR data as it corresponds to a larger number of distinct Na sites (3 in each Na plane) than found experimentally. Furthermore the only sites exhibiting the threefold symmetry and η = 0 would then be the NaI sites of the x = 2/3 planes. The fraction of such sites would be x = 2/17, nearly twice smaller than the 25% = 2/8 found experimentally.

The spin-spin and spin-lattice relaxation of the NQR lines were studied for all Co sites, and the data analysis has allowed us to demonstrate that both T\(_1\) and T\(_2\) data do allow to establish the difference of magnetic properties of the two types of Co sites. As indicated in Ref.\(^1\) they constitute two sublattices: a Kagome structure for the magnetic sites and the complementary triangular lattice of non-magnetic Co sites involving 25% of the Co.

Beyond the simple results obtained for this Na\(_{2/3}\)CoO\(_2\) compound, the approach developed here will be certainly useful to perform structural determinations for pure phases with different Na contents. We have indeed isolated some of them, which display quite distinct ground state physical properties.\(^10\)

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