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Identifying the distribution of Al³⁺ in LiNi_{0.8}Co_{0.15}Al_{0.05}O₂

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ABSTRACT: The doping of Al into layered Li transition metal (TM) oxide cathode materials, LiTMO₂, is known to improve the structural and thermal stability, although the origin of the enhanced properties is not well understood. The effect of aluminum doping on layer stabilization has been investigated using a combination of techniques to measure the aluminum distribution in layered LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) over multiple length scales with ²⁷Al and ⁷Li MAS NMR, local electrode atom probe (APT) tomography, X-ray and neutron diffraction, DFT, and SQUID magnetic susceptibility measurements. APT ion maps show a homogenous distribution of Ni, Co, Al and O₂ throughout the structure at the single particle level in agreement with the high-temperature phase diagram. ⁷Li and ²⁷Al NMR indicates that the Ni³⁺ ions undergo a dynamic Jahn-Teller (JT) distortion. ²⁷Al NMR spectra indicate that the Al reduces the strain associated with the JT distortion, by preferential electronic ordering of the JT long bonds directed toward the Al³⁺ ion. The ability to understand the complex atomic and orbital ordering around Al³⁺ demonstrated in the current method will be useful for studying the local environment of Al³⁺ in a range of transition metal oxide battery materials.

INTRODUCTION

Layered Ni rich mixed transition metal oxides have generated significant interest as lower cost and higher capacity Li ion battery cathode materials to replace LiCoO₂.¹ Layered LiNiO₂ (*R* $\bar{3}m$) was originally studied as a potential cathode material, however it was found that stoichiometric LiNiO₂ could not be synthesized as a result of the tendency of Ni³⁺ to reduce to Ni²⁺.² The presence of Ni²⁺ in the Li layers was found to hinder Li migration.³ LiNiO₂ was also found to have poor thermal stability in the delithiated state causing safety concerns for functional commercialization.⁴ The structure of LiNiO₂ has been debated due to the complex orbital ordering found for Ni³⁺.⁵ Ni³⁺ occupy octahedral sites in the structure of LiNiO₂ and have a low spin d⁷ (t_{2g}⁶e_g^{*1}) configuration.⁴⁻⁶ EXAFS studies identified that, each Ni³⁺ undergoes a positive Jahn Teller (JT) distortion in which two of the Ni-O bonds are elongated and four shortened.⁴ Unlike in other compounds, such as NaNiO₂⁷ and LiMnO₂,^{8,9} a cooperative ordering of the JT distortions is not observed in LiNiO₂. The lack of a cooperative ordering has been suggested in a number of studies to be due to a dynamic JT process, in which the distortion on each Ni³⁺ center fluctuates due to thermal vibrations.^{4,6,10,11} EPR studies of LiNiO₂ observed a dynamic JT distortion and only showed static behavior below 30K.⁶ For delithiated Li_xNiO₂, there is a transformation from a dynamic to a static JT distortion as a result of the coupling between the Li vacancy ordering and the JT distortion on the Ni³⁺ centers that leads to a cooperatively distorted monoclinic cell.⁴

Doping of other cations into the parent LiNiO₂ structure has lead to increased thermal stability, stabilization of the layered structure and improved electrochemical performance. One of the most widely studied Ni-rich materials, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, which will be referred to as NCA, has even been commercialized. NCA adopts the same (*R* $\bar{3}m$) layered structure as LiNiO₂, in which Co³⁺ and Al³⁺ are substituted for Ni³⁺ in octahedral sites. The substitution of Co³⁺ was found to stabilize the layered structure and improve the electrochemical performance in LiNi_{1-y}Co_yO₂.¹² although other studies suggest that Co³⁺ may lead to a strained TM layer. TM with different ionic radii have different M-O bond lengths causing a strain of the edge sharing MO₆ octahedra. In Al-doped LiNi_{0.45}Mn_{0.45}Co_{1-y}Al_yO₂ (NMC), it has been suggested that the doping of Al reduces this strain due to its smaller ionic radii leading to a more ordered TM structure.^{13,14}

Even though it is electrochemically inactive, the substitution of Al³⁺ in the structure has been found to improve the thermal stability and capacity retention even at low doping levels (5%).¹⁵ Although the addition of Al³⁺ is essential in order to improve the thermal stability of NCA, the exact mechanism of stabilization or ordering of Al within the TM layer is not fully understood. It was proposed by Guilnard *et al.*^{16,17} that the enhanced thermal stability was due to the stability of Al³⁺ tetrahedral sites within the structure that hinders the migration of Ni³⁺ required to transform the structure from the layered (*R* $\bar{3}m$) to a spinel-like structure. In a series of Li_{1+x}(Ni_{0.40}Mn_{0.40}Co_{0.2-z}Al_z)_{1-x}O₂, it was found that by increasing the Al³⁺ content and decreasing the amount of unstable Ni⁴⁺ and Co⁴⁺

formed in the delithiated state, an increased thermal stability was observed.¹⁸ For $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Al}_z\text{O}_2$ it was found that the structural stability imparted by Al was sensitive to how Al^{3+} was distributed in the structure.^{19,20} Samples in which the Al^{3+} was distributed homogeneously throughout the material were found to be less reactive in the presence of electrolyte. It has also been observed in $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ there is a tendency for Ni and Al segregation into nano domains.²¹ Developing techniques that probe the local structure and distribution of Al within the structure of NCA is therefore essential in order to understand the role that Al plays in enhancing the structural stability.

Proper characterization of the transition metal (TM) layer is required to understand the mechanisms of increased performance and to further the development of new materials with increased capacity. There are many methods employed to investigate the structure of layered metal oxides. Neutron and X-ray techniques provide a detailed analysis of long-range order. TEM provides a measure of local order but is only a surface sensitive technique. Recently, APT (atom probe tomography) has been used to probe the cation distribution in layered materials.²² This technique employs a large (~kV) DC bias and a pulsed UV laser to induce field evaporation of ions from a sample prepared in the form of a needle. A position sensitive detector and time of flight measurements enable identification of atomic positions at the nanoscale coupled with chemical composition, providing unparalleled three-dimensional (3D) maps of the system under investigation. They were able to identify Li-rich and Li-poor regions in Li-excess $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$.

The application of ^6Li solid state NMR to the study of lithium batteries has been fundamental to the study of the changes in the local structure as a function of charge in batteries.²³⁻³² The diamagnetic NMR shift region of Li is extremely narrow (0 ± 5 ppm). Although, Li is a quadrupolar nucleus (^7Li $I=1/2$ and ^6Li $I=1$) it has a small quadrupole moment and typically does not experience a large quadrupolar broadening compared to other quadrupolar nuclei. In paramagnetic materials, the unpaired electrons on the TM lead to the Fermi contact shift that can shift resonances thousands of ppm and to a paramagnetic broadening of the spectrum due to the electron-nuclear dipolar coupling. The assignment of the ^6Li NMR shift near paramagnetic centers has mainly been the focus of NMR studies on battery materials to date.^{25, 29, 31, 33, 34} Although NMR of other nuclei has been performed to investigate changes in local structure by observing the transition metals, such as ^{27}Al and ^{59}Co in dilute Ni^{3+} structures,²⁴⁻²⁸ and ^{51}V in vanadium phosphates²³, sulfides³⁵ and oxides^{23, 36-39}.

The development of ^6Li NMR as a probe of the Li local structure near paramagnetic TMs, specifically in layered metal oxides, has been based primarily on two methods: experimental NMR of materials with dilute TM concentration and assignment using DFT calculations, the later being limited until recent years due to computationally expensive calculations. Marichal *et al.* observed the static and MAS ^6Li NMR shift in a series of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ for increasing Ni content.³¹ Although, the high Ni content structures gave broad resonances, they developed a correlation between the isotropic NMR shift and Ni^{3+} content. It was observed that the isotropic shift was dependent on the number of Ni^{3+} neighbors. Further experimental and computational work by Carlier³³ and the

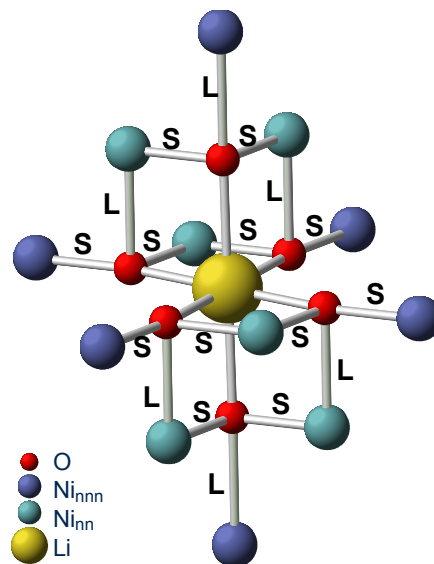


Figure 1. Local structure around a Li atom in a Jahn-Teller distorted layered LiNiO_2 . S and L represent JT short and long bonds, respectively. Blue and purple atoms represent Ni_{nn} and Ni_{nnn} , respectively.

groups of Grey and Delmas developed a direct correlation between the orbital overlap of the M-O-Li bonds to the NMR shift that followed the Goodenough-Kanamori rules.^{23, 33} In dilute paramagnetic samples, they showed that the contribution to the NMR shift was additive, the total shift was a sum of contributions from all the 90° and 180° M-O-Li nearest neighbors. Only nuclei within the first metal coordination sphere contribute to the overall shift due to the orbital overlap with the paramagnetic center (M) with Li through a M-O-Li bond.

Although the NMR shift for ^6Li and ^7Li is identical for the same Li environment. Many of the previous Li NMR studies have been performed using the ^6Li isotope, even though it is only 7.5% naturally abundant (N.A.) compared to ^7Li (92.5% N.A.) requiring isotopic enrichment or long experiment times to signal average. ^6Li has the advantage of having a smaller quadrupole moment and a smaller gyromagnetic ratio than ^7Li . The greater advantage comes from the smaller gyromagnetic ratio ($\gamma(^6\text{Li}) / \gamma(^7\text{Li}) = 0.38$) which leads to greater Hz/ppm resolution in the frequency domain allowing the isotropic peaks to be sufficiently separated from each other and spinning side-bands. With recent developments of fast MAS (magic-angle spinning) NMR techniques to obtain isotropic spectra, such as aMAT²⁹ or pj-MATPASS⁴⁰, high-resolution ^7Li NMR spectra of paramagnetically broadened materials is now achievable in a reduced experimental time with greater signal to noise compared to ^6Li .

Recently, Middlemiss *et al.*³⁴ applied a spin-flipping approach on an optimized structure of LiNiO_2 with a collinear JT distortion to calculate the individual DFT bond pathway contributions to the ^6Li Fermi-contact (FC) NMR shift. This method confirmed the additive nature of the FC shift observed experimentally. In layered materials, the nearest neighbor M (M_{nn}) atoms interact with the Li through two $\sim 90^\circ$ M-O-Li bond pathways and the next nearest neighbors (M_{nnn}) interact with the Li with one $\sim 180^\circ$ M-O-Li bond pathway as depicted in Figure 1, leading to bond pathway contribution to the NMR

1 shift of $\delta_{nn,i}$ and $\delta_{nnn,i}$, respectively. Each M-O-Li bond
 2 pathway contribution is proportional to the difference in the
 3 unpaired spin density at the Li site when the M spins are
 4 aligned ferromagnetically and when one is flipped, i.e.
 5 ferrimagnetic. The 4 different M environments in Figure 1
 6 lead to 4 different shift contributions for the Li^+ in the LiNiO_2
 7 structure. There are two M_{nn} environments, one contains 2
 8 short Ni-O bonds and the other contains a long and short Ni-O
 9 bond with shift contribution of δ_{SS} and δ_{SL} , respectively,
 10 where the subscript denotes each Ni-O bond. The two M_{nnn}
 11 environments only have contributions from one Ni-O bond;
 12 one short and one long with shift contributions of δ_S and δ_L ,
 13 respectively. The overall FC shift, δ_{FC} , is a sum of all the
 14 individual bond pathways between the observed NMR nucleus
 15 and each M, $\delta_{FC} = \sum \delta_{nn,i} + \delta_{nnn,i}$. It was found that the shifts
 16 predicted with hybrid DFT calculations were sensitive to the
 17 amount of Hartree Fock exchange in the hybrid functional,
 18 with most experimental values falling within the range of
 19 values calculated with 20 to 35% HF exchange.^{34, 41} Their
 20 calculated ^7Li shift contributions using the B3LYP functional
 21 with 20% HF exchange are $\delta_{SS} = 6.9$, $\delta_{SL} = -29.6$, $\delta_S = 44.4$,
 22 and $\delta_L = 325.6$.³⁴ They also assigned the observed
 23 experimental shift in dilute Ni mixed metal oxides to a
 24 dynamic JT distortion. In a dynamic JT structure, the Li
 25 nucleus experiences an axially averaged shift during the NMR
 26 experiment, $\delta_{nn} = (\delta_{SS} + 2\delta_{SL})/3$ and $\delta_{nnn} = (2\delta_S + \delta_L)/3$
 27 assuming rapid fluctuation of the JT axis on the NMR
 28 timescale.³⁴ For LiNiO_2 , their calculated axially averaged
 29 contributions to the shift are $\delta_{nn,dJT} = -17.4$ ppm and $\delta_{nnn,dJT} =$
 30 138.13 ppm, yielding an overall shift of 724 ppm, which
 31 agreed well with reported experimental values.³⁴

32 ^{27}Al NMR is very sensitive to the Al local environment and
 33 its coordination and it has been readily used in the study of
 34 materials, but only a few studies have been reported on battery
 35 materials.²⁴⁻²⁸ ^{27}Al is also a quadrupolar nucleus ($I=5/2$), but
 36 has a larger quadrupole moment than ^6Li or ^7Li and can
 37 experience a large quadrupolar shift and broadening. In
 38 diamagnetic materials, octahedral AlO_6 environments are
 39 observed near 0 ppm, whereas, tetrahedral AlO_4 environments
 40 are observed near 70 ppm. Previously, only one study reported
 41 ^{27}Al NMR of Al-doped into the transition metal layer of a
 42 paramagnetic material. In this study, a very broad Al signal
 43 was observed for delithiated Al-doped LiNiO_2 .²⁵ Based upon
 44 the NMR shifts of diamagnetic Al, they observed that
 45 increased levels of Al doping (greater than 20%) resulting in
 46 the observation of pseudo-tetrahedral Al. Just prior to the
 47 submission of this manuscript, Dogan et al.⁴² analyzed the ^6Li
 48 and ^{27}Al NMR spectra of NCA and NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$)
 49 with varying Al content. They found that increasing Al content
 50 above 5% in NCA led to the presence of diamagnetic peaks
 51 indicating aluminate phase segregation.

52 In non-paramagnetic materials, ^{27}Al NMR has also been
 53 used to study the structure in $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$.^{24, 28} They found
 54 that with increased Co content the Al resonance shifts to
 55 greater frequencies, giving shifts that could be incorrectly
 56 assigned to tetrahedral environments. This increasing shift was
 57 ascribed to a +7 ppm shift per Co neighbor. The use of ^{27}Al
 58 NMR has also been applied to studying the effectiveness of
 59 coating on layered battery materials, such as Al_2O_3 coated
 60 LiCoO_2 ²⁶ and AlF_3 coated $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$.²⁷ In all the
 previous ^{27}Al NMR studies of layered oxide materials, the

spectra of high Ni^{3+} content with Al in the bulk material have
 yet to be assigned or analyzed.

Here we have developed a method of using ^{27}Al NMR as a
 probe of the local structure in high Ni content Al-doped
 LiNiO_2 paramagnetic materials using DFT NMR shift
 calculations. We also show that APT provides a method to
 determine the bulk distribution of ions within a material. By
 combining ^{27}Al and ^7Li NMR, SQUID magnetic susceptibility
 measurements, APT, neutron and X-ray diffraction coupled
 with first-principles structural and NMR shift calculations we
 show that the Al distribution is homogenous throughout the
 bulk material in the dynamic JT distorted layered NCA.

EXPERIMENTAL METHODS

Materials

$\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ was used as purchased (NAT1050, TODA
 America).

NMR

^{27}Al MAS (magic-angle spinning) NMR spectra were acquired on a
 Bruker Avance II (4.7T) and a Bruker Avance III (7T) using a Bruker
 1.3mm MAS probe. A Hahn-echo pulse sequence with $\pi/2=1.5\mu\text{s}$
 optimized on solid AlF_3 was used. Solid AlF_3 was used as a secondary
 reference at -17 ppm (with respect to aqueous $\text{Al}(\text{NO}_3)_3$ at 0 ppm).²⁷

^7Li MAS NMR spectra were acquired on a Bruker Avance II (4.7T)
 using a Bruker 1.3mm MAS probe. Spectra were referenced to solid
 Li_2CO_3 at 0 ppm using a $\pi/2 = 1.02\mu\text{s}$. The pj-MATPASS sequence⁴⁰
 was used to obtain the isotropic ^7Li spectrum.

Neutron and X-ray Diffraction

Time of flight (TOF) powder neutron diffraction data was collected
 on the POWGEN instrument at the Spallation Neutron Source (SNS)
 in the Oak Ridge National Lab (ORNL). Around 3 g of powder was
 filled into a vanadium sample can, and sent via the mail-in service to
 the SNS. Data were collected at a wavelength of 1.066 Å to cover a d-
 spacing range of 0.3–3.0 Å.

Synchrotron X-ray powder diffraction was taken at the Advanced
 Photon Source (APS) at Argonne National Laboratory (ANL) on
 beamline 11-BM ($\lambda = 0.45999$ Å). The beamline uses a sagittally
 focused X-ray beam with a high precision diffractometer circle and
 perfect $\text{Si}(111)$ crystal analyzer detection for high sensitivity and
 resolution.

Full pattern joint X-ray and neutron Rietveld refinement was
 performed to extract the structure parameters using GSAS software
 with EXPGUI interface.^{43, 44}

Atom Probe Tomography (APT)

Samples were prepared using FEI Helios focused ion beam at
 Pacific Northwest National Laboratory, from pristine powders
 scattered onto a Si substrate. A pick and place technique was used to
 affix particles onto a Si microtip array followed by Pt deposition to
 protect the particle from Ga ions during the milling process.
 Subsequently an annular mill with Ga ions gave the final needle
 shaped specimen. The needle specimens were then analyzed using a
 CAMECA LEAP 4000 XHR APT system at Pacific Northwest
 National Laboratory.

The fabrication procedure and preparation conditions are provided
 in detail in the supplementary information.

SQUID Magnetic Susceptibility

The temperature dependence of the dc magnetization was measured
 using a Quantum Design SQUID magnetometer (MPMS XL-5) on
 cooling the samples from 350 to 2 K in a magnetic field of 1000 Oe.

Structure Optimization and Phase Diagram Calculations

DFT calculations to find optimized structures were performed with
 the Vienna ab initio Simulation Package (VASP)⁴⁵⁻⁴⁸ with the on-site
 Coulomb correction of Dudarev et al.⁴⁹ and PAW pseudopotentials.⁵⁰
⁵¹ These DFT calculations were used to parameterize cluster
 expansions using the Clusters Approach to Statistical Mechanics
 (CASM) code.⁵²⁻⁵⁵ The effect of vibrational contributions to the free
 energy on the relative stability of $\gamma\text{-LiAlO}_2$ and the layered phases

was accounted for using the method of Ref. [56]. Additional calculation details can be found in the Supplementary Information.

First Principle Calculations of NMR Shifts

Calculations of the ^{27}Al hyperfine shifts were done using methods described previously^{29, 34, 41, 57}. Periodic spin polarized DFT calculations were performed in CRYSTAL⁵⁸. Previous studies^{34, 41, 59} have shown that the use of hybrid functionals in the DFT description of the electronic structure is necessary to get an accurate description of hyperfine shifts and furthermore, the spin transfer mechanism is sensitive to the amount of Hartree Fock exchange included in the functionals construction. We therefore adopt the approach outlined in Refs [29, 34, 41] in which the hyperfine parameters are calculated with two B3LYP^{60, 61} hybrid functionals containing 20% and 35% Hartree Fock exchange, which will be referred to as HYB20 and HYB35 respectively.

The extended basis sets (BSII) from Ref. [41] for Li (TZDP⁶²) and O (IGLOIII⁶³) were used for the computation of the hyperfine shift parameters. The Ni basis set (Ahlrichs DZP⁶²) was taken from Ref. [34] and the Al set (IGLOIII⁶³) from Ref. [57]. The number of Gaussian primitives and the contraction scheme used for each basis set, along with details of the convergence criteria used for the calculations are provided in the Supporting Information.

The DFT+U optimized $\text{Li}_{32}\text{Ni}_{31}\text{Al}_1\text{O}_{64}$ structure was used for all of the hyperfine calculations without further optimization. Single point energy calculations were performed in the ferromagnetic state in order to calculate the unpaired spin density transferred to the Al nuclear position from the neighboring Ni^{3+} centers through an intervening O. The amount of unpaired spin density transferred can be directly related to the Fermi contact shift that would be expected in the zero temperature regime. The zero temperature shift is scaled into the paramagnetic temperature regime under which the NMR experiment is performed. Using the approach in Ref. [57] the scaling factor, Φ , can be expressed as $B_0\mu_{\text{eff}}^2/3k_Bg_e\mu_B S(T-\Theta)$ where B_0 is the applied magnetic field, μ_{eff} is the effective magnetic moment, k_B is Boltzmann's constant, g_e is the free electron g value, μ_B is the Bohr magneton, S is the formal spin of Ni ($S_{\text{Ni}^{3+}}=1/2$), T is the experimental temperature and Θ is the Weiss constant. The values of μ_{eff} and Θ were taken from the fits to experimental magnetic data and the NMR temperature was taken as 320 K account for frictional heating during MAS.

The electron-nuclear dipolar and quadrupolar tensors were also calculated and are given in the Supporting Information along with further details of the calculations.

RESULTS AND DISCUSSION

In order to test the hypothesis that Al is uniformly distributed in NCA, the $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ phase diagram was calculated using cluster expansions parameterized by density functional theory (DFT) calculations. These phase diagrams were constructed from the free energy landscape of layered $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$, as well as the line compound $\gamma\text{-LiAlO}_2$

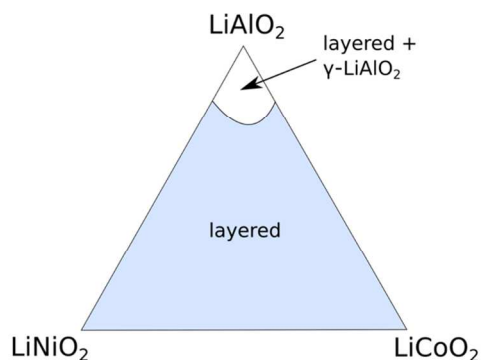


Figure 2. NCA phase diagram calculated at 1000 K using DFT + U with $U_{\text{Ni}} = 5$ eV and $U_{\text{Co}} = 0$ eV.

which is more stable than layered LiAlO_2 at high temperatures⁵⁶.

The calculated NCA phase diagram at 1000 K (representative of synthesis temperatures) shows that Al has a high solubility in layered NCA (Figure 2). For Al concentrations in the TM layer below $\sim 80\%$, the system consists of a single layered phase. At high Al concentrations ($>80\%$) phase separation occurs, with a two-phase equilibrium between the layered phase and $\gamma\text{-LiAlO}_2$. Additional phase diagrams using different values of U on the Ni and Co confirm the high solubility of Al regardless of the choice of U (Figure S1).

The long-range order, structure and Li/M/O occupancy of NCA was confirmed using both X-ray and neutron diffraction. In this refinement, the occupancy of O was fixed at 2, the occupancy of 3a and 3b sites were fixed at 1, and the content of Ni + Al + Co was constrained to 1. The isotropic atomic displacement parameter (ADP) model was used in this study, with constraints of $U_{\text{iso}}(\text{Li1}) = U_{\text{iso}}(\text{Li2})$, and $U_{\text{iso}}(\text{Ni1}) = U_{\text{iso}}(\text{Ni2}) = U_{\text{iso}}(\text{Al}) = U_{\text{iso}}(\text{Co})$. The Li/Ni mixing, Co, Al occupancy, lattice parameters, oxygen coordinates, and ADPs

Table 1: Rietveld refinement results. Conventional Rietveld reliability factors: overall R_{wp} : 0.0778.

Atoms	Site	Wyckoff positions			Occupancy	100×Uiso
Li1	3a	0	0	0	0.001(1)	1.02(2)
Ni1	3a	0	0	0	0.812(4)	0.262(5)
Co	3a	0	0	0	0.138(4)	0.262(5)
Al	3a	0	0	0	0.050(3)	0.262(5)
Li2	3b	0	0	0.5	0.999(1)	1.02(2)
Ni2	3b	0	0	0.5	0.001(1)	0.262(5)
O	6c	0	0	0.25920(2)	2	0.67(1)

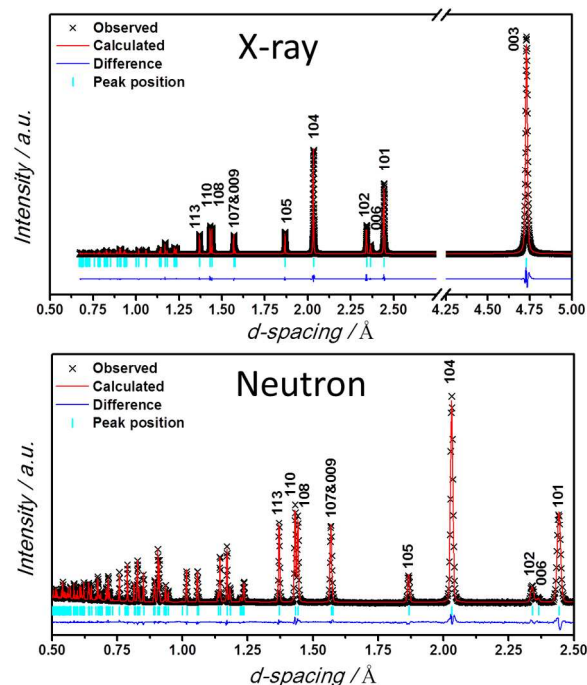


Figure 3. a) X-ray diffraction and b) neutron diffraction patterns of NCA.

were allowed to be refined. Figure 3 shows the joint Rietveld refinement of both X-ray and neutron diffraction patterns. All peaks for the NCA sample could be indexed to a single phase with the $R\bar{3}m$ space group.^{64,65} The patterns indicate that NCA adopts a well-layered structure with little Li/Ni mixing, 0.1%, as evidenced by the existence of doublets at (006)/(102) and (108)/(110).⁶⁶ Table 1 lists the summary of Rietveld refinement results. The refined lattice parameters of NCA are $a = 2.86415(1)$ Å and $c = 14.19052(4)$ Å. The refined oxygen position of the NCA material is (0, 0, 0.25920(2)). The occupancy of Al has also been refined, which is 5.0(3)%.

The distribution of atoms was measured using APT. APT ion maps provide unique insight into the nanoscale distribution of elements in battery materials. The 3D atom probe maps for Al, Ni, Co and O₂ maps show a uniform distribution (Figure 4a-e). Maps for Ga, CoO, Ni and O are also shown in the supplementary information (Figure S7). The presence of Ga arises from the annular milling process to form the needle specimen. The map for Li shows a slightly decreased concentration at the surface, which coincides directly with the Ga enriched region of the needle apex; indicating surface damage due to Ga as the cause for the observed loss of Li near the top surface of the specimen (Figure S7). The mass spectrum shows the peaks assigned for various ions evaporated (Figure 4f). Strong signals for Li, Ni, Co and O₂

Table 2: Bulk composition analysis of NCA as obtained from neutron diffraction and atom probe tomography. The Ni composition is taken as the reference. With the exception of Li, the results show a strong agreement. *Average composition determined from three specimens.

Stoichiometric composition		
	Expected from diffraction data (%)	Obtained from atom probe tomography* (%)
Li	1.000	0.410
Al	0.052	0.058
Ni	0.813	0.800
Co	0.135	0.164
O	2.000	1.825

indicate high concentrations of these species. With the exception of Li, the elemental compositions show good agreement with the stoichiometric composition as obtained by neutron diffraction (Table 2). Currently, an effort is underway to study the effect of laser pulse energy on the observed deviation in Li concentration, which will be the subject of a future publication.

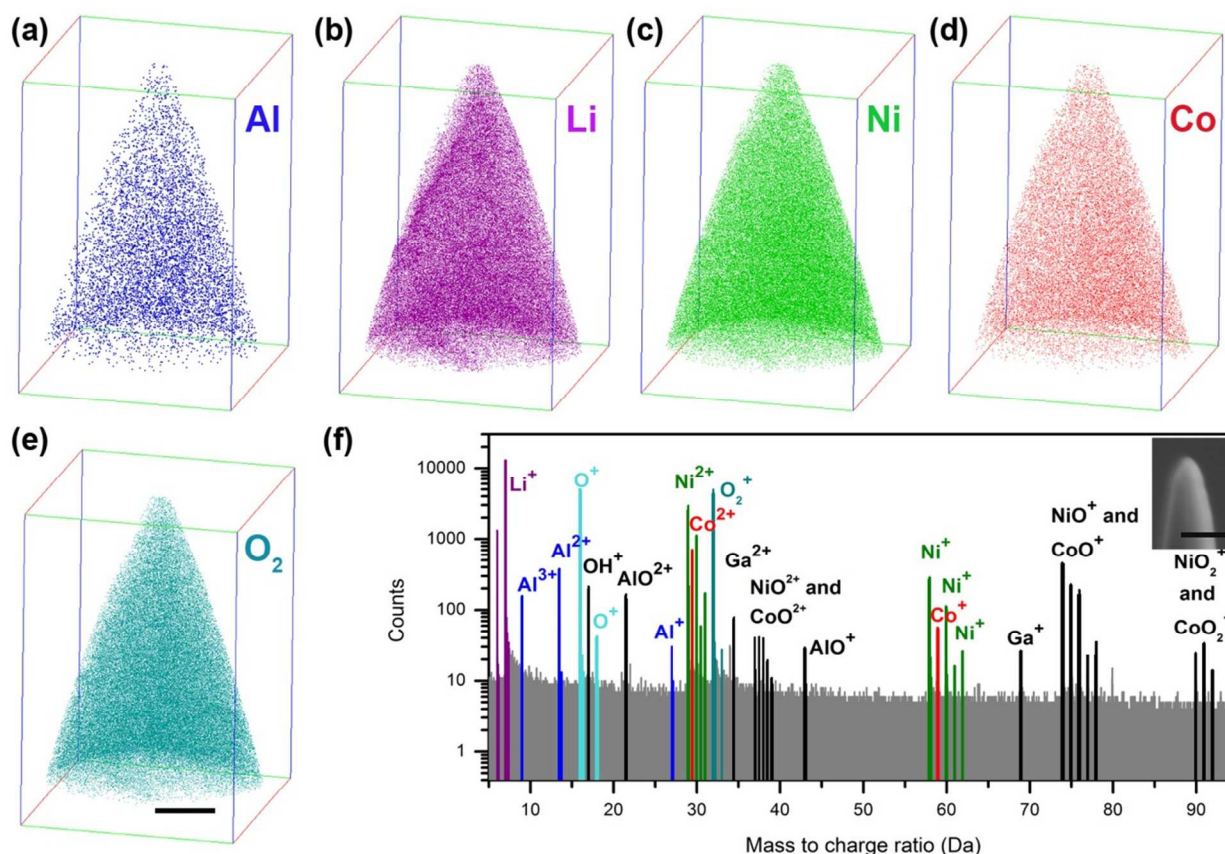


Figure 4: (a-e) Individual atom probe maps for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) showing the spatial distribution of Al, Li, Ni, Co and O₂ ions. The maps clearly show a uniform distribution of the elements. The Al distribution in the pristine powdered sample is uniform and not segregated on grain boundaries as previously believed. (Scale bar is 10 nm) (f) Mass spectrum for chemical identification of ions present in the analyzed volume. Peaks associated with each ion count are color coded to the respective chemical species. The color coding does not represent the actual mass ranging process followed to identify chemical species. Inset shows the final shape of the sample tip before atom probe tomography. (Scale bar is 300 nm).

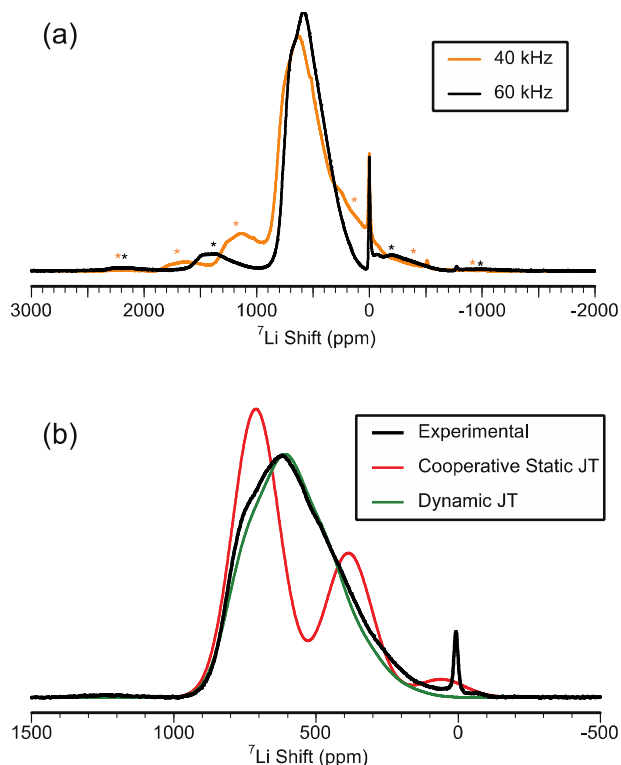


Figure 5. Experimental ${}^7\text{Li}$ NMR spectra of NCA acquired at 7T. a) Hahn-echo spectra obtained at two different ν_r , 40 kHz (orange) and 60 kHz (black). b) Experimental 1D slices obtained from the 2D pj-MATPASS spectrum (blue) compared to the calculated dynamic JT (red) and static JT (green) spectra. The calculated dynamic JT spectrum indicates a better fit. The peak at 0 ppm is attributed to diamagnetic surface species.

${}^7\text{Li}$ NMR spectra were obtained to probe the local order near the Li. The ${}^7\text{Li}$ NMR Hahn-echo spectra of NCA shown in Figure 5a were acquired at two different spinning speeds, ν_r , of 40 and 60 kHz. Even at a low magnetic field of 4.7 T and ν_r of 60 kHz, the electron nuclear dipolar interaction significantly broadens the spectrum, resulting in spinning sidebands overlapping slightly with the isotropic resonances. To accurately assign the shifts, a ${}^7\text{Li}$ pj-MATPASS NMR spectrum was acquired, this 2D NMR sequence suppresses the spinning sidebands and a 1D spectrum containing only the isotropic resonances is observed (Figure 5b). The full 2D pj-MATPASS spectrum is given in the Supporting Information. This allows accurate deconvolution, fitting, and assignment of the NMR lineshape. The sharp resonance at 0 ppm is attributed to diamagnetic impurities on the surface and to Li with 0 Ni^{3+} neighbors, as Al^{3+} and Co^{3+} are both diamagnetic. The broad resonance arises due to the distribution of Li near Ni^{3+} in the layers. As discussed in the introduction, the Li shift depends on the number of Ni^{3+} neighbors in 90° and 180° Li-O-Ni bond pathway configurations, but also on the orientation of the JT axis in each of the Li-O-Ni pathways, as JT lengthened and shortened bonds result in different shifts. Using the calculated bond pathway contributions of Middlemiss *et al.*³⁴ the shifts of different JT orderings were considered to rationalize the Li spectrum, in which Al, Ni and Co were assumed to be randomly distributed on the octahedral sites based on the APT results. The static JT (assuming there is a cooperative JT ordering, such as in the C2/m or zigzag structures) and dynamic JT ${}^7\text{Li}$ NMR spectra were calculated

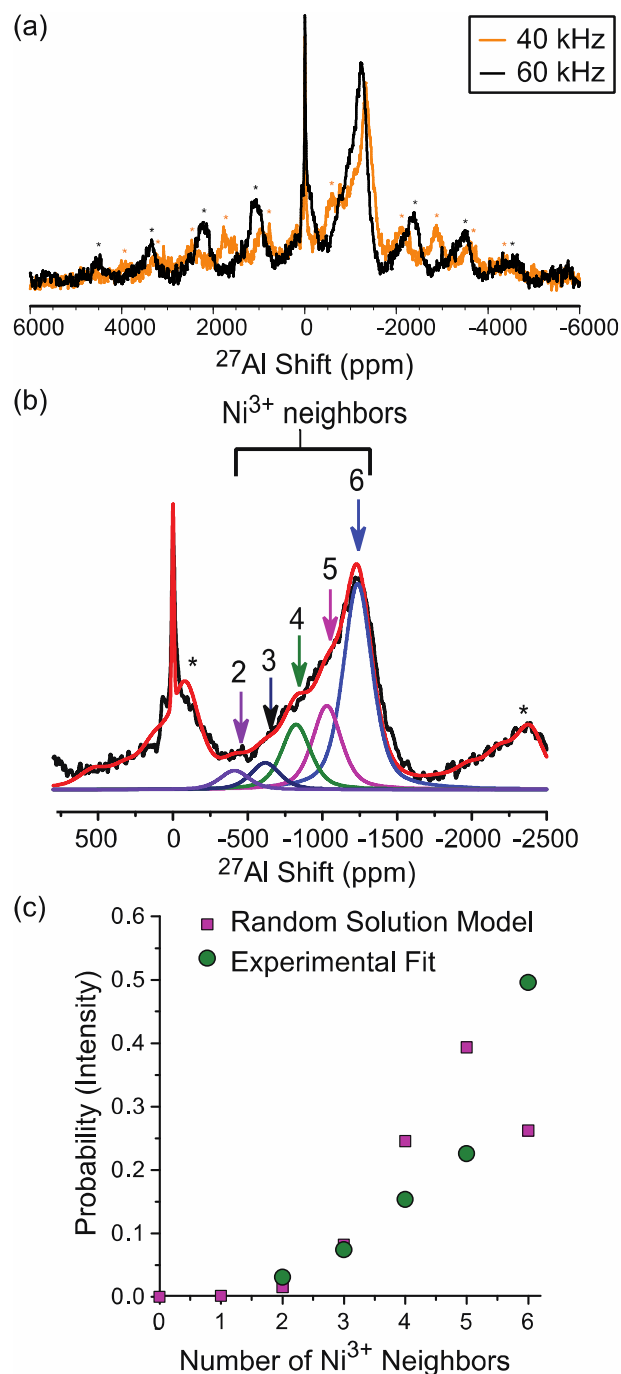


Figure 6. ${}^{27}\text{Al}$ NMR spectra of NCA acquired at 4.7T. a) Spectra at two different spinning speeds, ν_r , 40 kHz (orange) and 60 kHz (black). The spinning sidebands are denoted by *. b) Fit (red) of the experimental (black) 60 kHz spectrum using shifts calculated from bond pathways. The individual peaks indicate the number of Ni^{3+} neighbors to Al. c) Comparison of the experimental intensity and the intensity predicted from a random solution model for Al, indicating a preference for Al to be next to Ni. Details of how the random solution model is calculated are given in the Supplementary information.

using a random solution model (further details are given Supporting Information). The calculated NMR spectra for a static JT distortion gives three broad peaks centered at 700, 400 and 50 ppm, whereas, the dynamic spectrum has a unique lineshape distributed from 1000 to 0 ppm, with the greatest

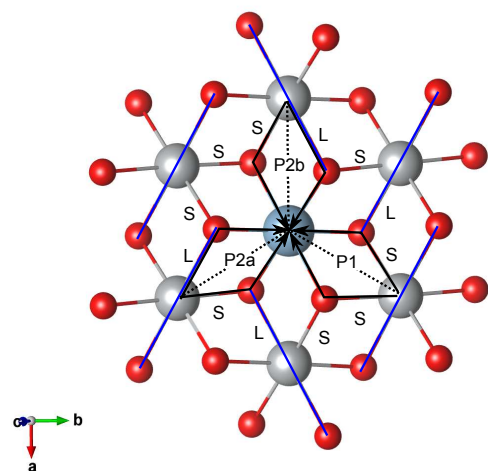


Figure 7. Bond pathway contributions to the Al in the ‘zigzag’ JT distorted layered NCA. (Ni: Grey, O: Red, Al: Light blue, the blue line indicates the JT lengthened axis.)

intensity at 724 ppm. Comparison of the calculated spectra with experimental spectra (Figure 5b), indicate there is superb agreement between the experimental and the calculated dynamic JT spectrum. Our analysis of the ^7Li NMR spectrum differs slightly from that recently reported by Murakami *et al.*⁶⁷. In their analysis of a NCA spectrum obtained at 14 T, they utilized the correlation of Delmas and co-workers³¹ where they assigned 3 isotropic resonances, two dominant peaks associated with 6 and 5 Ni^{3+} nearest neighbors and another broad peak associated with 1 to 4 Ni^{3+} nearest neighbors. The deviation of intensity of the sites from a random solution model was attributed to Ni-rich and Ni-poor domains. Even though their spectrum was acquired with a very fast spinning speed of 100 kHz, at such a high magnetic field (14 T) the paramagnetic dipolar broadening still caused overlap of the isotropic resonances and spinning sideband manifold at such a high magnetic field strength making it difficult to identify and quantify the isotropic resonances. Dogan *et al.*⁴² also recently assigned the ^6Li NMR spectrum of NCA to two broad resonances attributed to Ni-Co clusters differing from our interpretation. Our results show the importance of accounting for the dynamic JT distortion and using a statistical distribution when assigning ^6Li NMR spectra of high Ni content materials.

To further investigate the local structure, ^{27}Al NMR spectra of pristine NCA were obtained at 4.7 T at multiple spinning speeds to determine the isotropic resonances and are given in Figure 6a. The broad signals from -200 to -1500 ppm are the main isotropic resonances; the spinning sidebands are marked with asterisks occurring at multiples of the spinning speed. The isotropic resonances are separated from the spinning sidebands only in the spectrum obtained with a ν_r of 60 kHz at 4.7 T. The sharp resonance at 0 ppm in the ^{27}Al spectra (Figure 6) is attributed to diamagnetic impurities on the surface of the material arising from exposure to air and is less than 0.2% of the material. Thus, greater than 97% of the Al experiences a NMR shift and broadening induced by its proximity to the unpaired electrons on Ni^{3+} , indicating the Al is homogeneously distributed throughout the Ni matrix. This agrees well with the atom probe Al distribution and the high temperature calculated $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ phase diagram.

Table 3: Calculated bond pathway contributions for the Al center in a ‘zigzag’ JT distorted layered NCA supercell as depicted in Figure 4. δ_{SL} is the average of the P2a and P2b pathways.

Pathway	^{27}Al NMR Shift (ppm)	
	HYB20	HYB35
P1 (δ_{SS})	11	114
P2a	-339	-290
P2b	-333	-254
δ_{SL}	-336	-277
Dynamic Shift	-220	-143

To assign the paramagnetically broadened ^{27}Al NMR shift, DFT calculations were performed on a $\text{Li}_{32}\text{Ni}_{31}\text{Al}_1\text{O}_{64}$ super cell, formed by doping an Al atom into an optimized LiNiO_2 super cell structure. Further details on generating the super cell are given in the Supporting Information. Contributions to the NMR shift were calculated by using the ‘spin-flip’ procedure using both HYB20 and HYB35 functionals, using $\mu_{\text{eff}} = 1.98$ and $\Theta = 16$ K derived from fits to the magnetic data obtained for NCA. In the $\text{Li}_{32}\text{Ni}_{31}\text{Al}_1\text{O}_{64}$ model structure, the Al site has six possible Ni^{3+} nearest neighbors within the transition metal plane with four long JT Ni^{3+} -O bond orientated towards the Al. The Al is connected to each Ni^{3+} neighbor through two 90° Ni^{3+} -O-Al spin transfer pathways. Thus the contribution to the Fermi contact shift is only a sum over the nearest neighbor bond pathways, $\delta_{\text{FC}} = \sum \delta_{\text{nn},i}(90^\circ)$. Three bond pathways from the neighboring Ni^{3+} to the Al are observed in the ‘zigzag’ JT structure (Figure 7). The two P1 (δ_{SS}) pathways consist of 2 Al-O-Ni 90° interactions along the short JT axes, and the four P2 (δ_{SL}) pathways consist of 2 Al-O-Ni interactions, one with a short and the other with a long JT Ni-O bond. Al^{3+} is not JT active and it behaves as a defect site in the JT distorted matrix, leading to a slight increase and decrease in the length of the JT short and long bonds, respectively, at the Al center. This defect results in the small differences in the bond lengths, splitting the P2 pathway into the P2a and P2b pathways, yielded bond pathway contributions of -339 and -333 ppm, respectively, using the values computed with HYB20. Taking the average of the P2a and P2b pathways, δ_{SL} , the calculated contributions to the shift are $\delta_{\text{SS}} = 11$ and $\delta_{\text{SL}} = -335$ ppm, giving an axially averaged dynamic JT bond pathway contribution for each Ni^{3+} of $\delta_{\text{nn,dJT}} = -220$ ppm for HYB20. A summary of the bond pathway shifts calculated using both HYB20 and HYB35 is shown in Table 3. Although it has been experimentally observed that each Co^{3+} neighbor will contribute a +7 ppm shift to the ^{27}Al NMR resonance²⁴, we have not included this in our model as negligible compare to the predicted -220 ppm contribution from Ni^{3+} .

The spectra in Figure 6 were deconvoluted yielding five isotropic resonances attributed to the number of nearest Ni^{3+} neighbors. The experimental shift for Al with 6, 5, 4, 3, and 2 Ni^{3+} neighbors occurs at -1243, -1030, -827, -620, and -413 ppm, respectively, in the $\nu_r = 60$ kHz spectra and at -1346, -1113, -891, -668, and -445 ppm, respectively, in the $\nu_r = 40$ kHz spectra. Since the overall NMR shift is additive of each of the Ni^{3+} -O-Al pathways, the experimental derived contribution to the dynamic JT NMR shift for each Ni^{3+} is -207 ppm and

–223 ppm for $\nu_r = 60$ kHz and 40 kHz, respectively. The difference in the shift obtained at different spinning speeds arises from the dependence of the Fermi-contact shift on the temperature dependent susceptibility. These values agree exceptionally well with the HYB20 calculated bond pathway contribution of –220 ppm for each Ni^{3+} neighbor.

In Figure 5c, a comparison of the experimental NMR intensity is made with the calculated intensity using a random solution model. Assuming that each experimental peak is associated with Al coordinated by n Ni^{3+} , there are significantly more Al sites with a NMR shift corresponding to 6 Ni^{3+} nearest neighbors (~40%) than predicted by a random solution model. This would imply that Al has a strong preference to be surrounded by Ni^{3+} , indicative of either Co-deficient nano-domains or strong short-range ordering. Indeed, nano-domains have been observed in high Al content $\text{LiNi}_x\text{Al}_{1-x}\text{O}_2$.²¹ EPR studies have indicated that Ni^{3+} experiences a JT stabilization with increasing Al coordination reaching a maximum stabilization with 6 Al neighbors.⁶ This stabilization could lead to an increased coordination of Al by Ni. However, the presence of nano-domains is in contrast to the DFT derived high temperature phase diagram (Figure 2) and the homogenous distribution of all ions observed in the atom probe maps. Furthermore, Monte Carlo calculations based on our cluster expansion predict that there is essentially no short-range ordering of Ni, Co, and Al at synthesis temperatures.

One possible way to reconcile the ^{27}Al NMR spectrum with the cluster expansion and atom-probe results is that the dynamic JT ordering at the Al atom could be quasistatic, i.e., on average more long JT Ni^{3+} -O bonds are orientated towards the Al atom than short bonds. The preference for the JT axis to be directed toward the dopant ions is observed in the DFT optimized structure of $\text{LiNi}_{0.5}\text{Co}_{0.25}\text{Al}_{0.25}\text{O}_2$ with a linear ordering of Ni and dopant cations. This linear ordering of cations has also been observed to be more energetically favorable in $\text{LiNi}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$.⁶⁸ In $\text{LiNi}_{0.5}\text{Co}_{0.25}\text{Al}_{0.25}\text{O}_2$, each Al is coordinated by 2 Co^{3+} and 4 Ni^{3+} and has four long JT Ni^{3+} -O bonds directed towards it (Figure S2). A pairwise coupling of the JT long bonds on two Ni atoms was predicted to be energetically favorable in LiNiO_2 using a spin-orbit model.⁵ Assuming a pairwise coupling, an Al coordinated by 5 Ni^{3+} with 4 long and 1 short JT Ni^{3+} -O bonds would only break the coupled distortion on one pair of Ni atoms. An ordering with 3 long and 2 short bonds would break the coupling for two pairs of Ni atoms thus increasing the energy, suggesting that the 4 long and 1 short JT Ni^{3+} -O bond ordering is more energetically favorable. This preferential ordering of the JT long axis towards the Al would increase the dynamic shift experienced by the Al. An Al with only 5 Ni^{3+} neighbors but has on average 4 long and 1 short JT Ni^{3+} -O bonds directed towards it, will have a shift of –1333 ppm similar to that of dynamic 6- Ni^{3+} coordinated Al (–1320 ppm). This would lead to an increase in the expected intensity for 6 Ni^{3+} neighbors in the dynamic JT model. A comparison of the static and dynamic shifts for $n = 6, 5,$ and 4 Ni^{3+} neighbors is given in Table 4 (a full table is available in the Supporting Information). A preferential ordering of the JT long Ni^{3+} -O bond towards the Al atom would increase the expected intensity of NMR resonances associated with $n=6, 5,$ and 4 Ni^{3+} in agreement with the experimental ^{27}Al NMR spectrum. Our assignment differs from the recent work of Dogan et al.⁴² who suggest that there is a preference for Al to

Table 4: Calculated dynamic and “quasi-static” ^{27}Al NMR shifts for $n=6, 5,$ and 4 Ni^{3+} neighbors. The shaded configurations indicate the most probable number of short and long bonds.

# Ni^{3+} nn	^{27}Al Shifts (HYB20)			Dynamic Shift (ppm)
	JT ordering of Ni^{3+} -O bonds		Total Shift (ppm)	
	SL	SS		
6	4	2	–1322	–1320
5	4	1	–1333	–1100
	3	2	–966	
4	4	0	–1344	–880
	3	1	–997	
	2	2	–650	

have 6 Ni^{3+} neighbors. In their study, they did not take into account the shift dependence of long or short Ni^{3+} -O bonds or assign the dynamic JT shift.

That the shape of the ^{27}Al NMR spectrum is controlled by the energy preference for JT distortions rather than energetic preference for chemical ordering, can be understood in terms of thermodynamics. The energetic preference for chemical ordering must compete with the thermal energy at synthesis temperatures because ion mobility is low at room temperature. However, the energetic preference for JT orientation need only compete with the room-temperature thermal energy because the reorientation of distortions is facile. Thus we ascribe the observed ^{27}Al NMR derived distribution to a preference of the JT ordering to be directed towards the Al atom and not a preferential coordination of Al by Ni^{3+} . However, given the limitations of the cluster-expansion model of NCA, we cannot rule out the possibility that some degree of short-range ordering occurs.

CONCLUSIONS

To properly characterize the distribution of Al in doped metal oxides, multiple characterization methods are necessary. The DFT calculated high-temperature phase diagram of $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ indicates a single layered phase with Al doping up to 80% in NCA. We have confirmed that NCA adopts a well ordered layered ($R\bar{3}m$) structure with little Li/M layer mixing <0.1% in agreement with the calculated phase diagram. The 3D APT ion maps of elemental distributions allowed us to observe the homogeneous Al distribution at a scale never seen before. Atom probe tomography is an exciting new frontier in understanding the relationship between chemical composition and cycling performance in battery materials.

The combination of DFT structure and NMR shift calculations is essential to assign and interpret paramagnetically broadened NMR spectra. Using the “spin-flip” procedure we have calculated the contribution to the ^{27}Al Fermi-contact NMR shift of an Al coordinated by Ni^{3+} . Both the ^7Li and ^{27}Al NMR indicate that NCA experiences a dynamic JT distortion on the NMR timescale. The distribution of ^{27}Al NMR shifts indicates a preferential ordering of long JT Ni^{3+} -O bonds near the Al^{3+} ion, instead of a preference for Al^{3+}

to be coordinated by Ni^{3+} . DFT calculations support that the JT axis has a preferential ordering toward the dopant ions. The local JT ordering increases the number of long JT Ni^{3+} -O bonds directed towards Al, accommodating the strain of the dynamic JT distortion. Proper characterization of the Al environment in the initial metal oxide structure is essential to understanding the role of Al in structural stability and surface phase reconstruction during electrochemical cycling. The techniques outlined in this work will be used to investigate the structural changes occurring in NCA and will be the focus of a future publication.

ASSOCIATED CONTENT

Supporting Information

Additional details of the NCA phase diagram, structural and NMR shift calculations, atom probe tomography experimental details and additional maps, calculated NMR spectra, 2D ^7Li pJ-MATPASS spectra, full deconvolution of ^{27}Al NMR spectra and static ^{27}Al NMR shifts are given in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

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The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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