

Crystal growth, defect structure and magnetism of new Li_3N -derived lithium nitridocobaltates

Alexandra G. Gordon,^a Ronald I. Smith,^b Claire Wilson,^a Zlatka Stoeva^a and Duncan H. Gregory^{*a}

^a School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD.

E-mail: Duncan.Gregory@Nottingham.ac.uk; Fax: +44 (0)115 9513563; Tel: +44 (0)115 9514594

^b ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, UK OX11 0QX

Received (in Cambridge, UK) 24th August 2004, Accepted 8th October 2004

First published as an Advance Article on the web 16th November 2004

New nitridocobaltates $\text{Li}_{3-x-y}\text{Co}_x\text{N}$ are revealed to contain significant Li^+ vacancies ($y \approx 0.45$) disordered within lithium–nitrogen planes and to exist as partially delocalised spin systems as a result of increased covalency through infinite $-\text{N}(\text{Li},\text{Co})-\text{N}-$ chains.

Lithium cobalt nitrides, $\text{Li}_{3-x}\text{Co}_x\text{N}$, were first reported by Juza and Sachsze over 50 years ago.¹ Juza speculated on the oxidation state of the Co as it entered these compounds, but attempts to study the magnetic susceptibility of powders were hampered by metallic Co contamination. Similar problems affected later electrical and magnetic measurements,² although Li^+ ion conduction was revealed in the system. More recently teams led by Takeda and Shodai have demonstrated fast ion Li^+ conduction, electrochemically deintercalating and reintercalating Li^+ for $\text{Li}_{3-x-z}\text{Co}_x\text{N}$, $0 \leq z \leq 1.0$ between 0 and 1.1 V.^{3,4} Nitridocobaltates such as $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ are, to date, the most promising candidates from the emerging group of nitridometallate anode materials for use in lithium secondary batteries. Nitridocobaltates exhibit capacities far exceeding those of graphite (e.g. 900 mAh g^{-1} vs. 372 mAh g^{-1}), with good cyclability and high energy densities for a variety of trial cells.⁵ Yet, despite the unequivocal potential of these materials, little is known regarding crystal chemistry, electronic structure or mechanisms of ion transport.

Here we report new nitridocobaltates with the highest transition metal substitution levels (x) reported to date. Growth of single crystals has enabled structure determination and magnetic property measurements of pure $\text{Li}-\text{Co}-\text{N}$ materials to be performed for the first time. Further, powder neutron diffraction (PND) investigations of bulk powders confirm structures with significantly enhanced Li^+ vacancy levels compared to Li_3N .

Single crystals of $\text{Li}_{1.99}\text{Co}_{0.53}\text{N}$ (**1**) were grown by the reaction of Li_3N with Co metal foil.⁶ Li_3N was first prepared by the reaction of Li metal with nitrogen using a liquid sodium solvent⁷ and Co foil was pre-treated under flowing N_2-H_2 (80% : 20%) at 873 K to reduce surface oxide. Only after three 144 h heating cycles under N_2 at 923 K was crystal growth observed on the Co foil. Bulk $\text{Li}_{1.95}\text{Co}_{0.6}\text{N}$ (**2**) was prepared by reaction of Li_3N with Co powder at similar reaction temperatures.⁸

Structure solution from single crystal data yields a structure isotopic to the parent compound, Li_3N in which Co partially replaces Li at the interlayer Li(1) site (Fig. 1).⁹ This structural description corroborates previous room temperature powder diffraction evidence where patterns could be indexed within the $P6/mmm$ space group with increased a parameters and decreased c parameters relative to Li_3N .¹ The refined model of **1** describes a nitridocobaltate containing Co in excess of the previously reported solubility limit.¹ Furthermore, the refined occupancy of the in-plane Li(2) site reveals appreciable Li^+ vacancies within the $[\text{Li}_2\text{N}]$ planes of the ternary nitride. X-Ray diffraction evidence thus suggests that, as in the equivalent $\text{Li}-\text{Ni}-\text{N}$ system,⁷ as the transition metal replaces Li at the interplanar site, vacancies are generated within $[\text{Li}_2\text{N}]$ planes (24% Li^+ vacancies as compared to 1–2% in Li_3N). The composition of the ternary nitridometallate approaches $\text{Li}_{3-2x}\text{Co}_x\text{N}$ and hence the substitution is predominantly aliovalent.

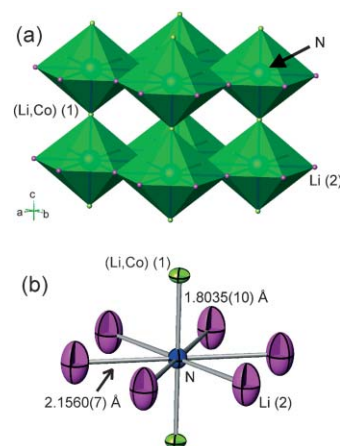


Fig. 1 Structure of **1** as (a) a polyhedral representation, and (b) an ORTEP plot detailing the $\text{NLi}_6(\text{Li},\text{Co})_2$ unit (thermal ellipsoids are drawn at the 50% probability level).

Time-of-flight PND data were collected for **2** on the POLARIS medium resolution diffractometer at ISIS, RAL, to obtain a more accurate quantification of the lithium vacancies in the nitridocobaltates and hence a more complete model of the defect structure.¹⁰ Rietveld refinements against neutron data at 298 K and 3 K using GSAS^{11,12} (Fig. 2) reveal disordered Li_3N -type structures essentially invariant with temperature (allowing for thermal expansion). The cobalt content in the bulk material, **2**, further surpasses the previously reported solubility limit in the $\text{Li}-\text{Co}-\text{N}$ system.¹ Moreover PND data for **2** confirm the results observed for **1** in that significant vacancies (>20%) are disordered on the Li(2) site within the $[\text{Li}_2\text{N}]$ planes. Selected structural parameters for **1** and **2** are summarised in Table 1.

In accord with the changes in cell parameters observed as transition metals replace lithium in Li_3N -derived $\text{Li}-\text{M}-\text{N}$ ($\text{M} = \text{Mn}-\text{Cu}$) systems, Li(2)–N bond lengths increase and (Li,Co)(1)–N distances decrease relative to Li_3N .¹³ These changes are commensurate with ideas of the decreasing population of the Li(2) site and

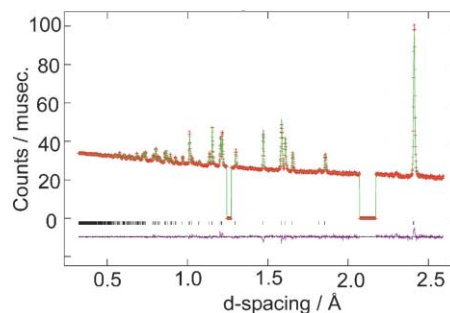
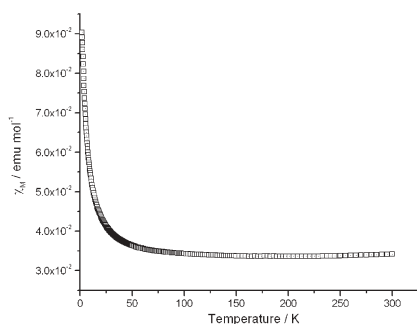


Fig. 2 Profile plots for the refinement of the structure of **2** against PND data at 3 K. The data shown are from the backscattering detector bank at $\langle 2\theta \rangle = 145^\circ$. Cryostat peaks are excluded.

Table 1 Selected structural parameters for $\text{Li}_{3-x-y}\text{Co}_x\text{N}$ nitrides

Sample	$a/\text{\AA}$	$c/\text{\AA}$	(Li,Co)		x	y
			Li(2)–N/ \AA	(1)–N/ \AA		
1 ^a	3.734(1)	3.607(2)	2.1560(7)	1.804(1)	0.53(2)	0.48(9)
2 ^b	3.7300(2)	3.6483(2)	2.1535(1)	1.8241(1)	0.598(2)	0.45(1)
2 ^c	3.7111(2)	3.6401(2)	2.1426(1)	1.8201(1)	0.602(2)	0.42(1)

^a XRD at 150 K. ^b PND at 298 K. ^c PND at 3 K.

**Fig. 3** Plot of molar susceptibility vs. temperature for **1**.

the likely increased covalency of the (Li,M)(1)–N bond as less electropositive Co ($\chi = 1.8$) replaces Li ($\chi = 1.0$).¹⁴

Variable temperature magnetic susceptibility measurements were performed on crystals of **1**.¹⁵ The susceptibility data were only weakly temperature dependent between ca. 100 and 300 K. A sharp Curie tail was observed below 100 K (Fig. 3). The data were fitted to a modified Curie–Weiss expression with $\chi_0 = 0.0331(2)$ emu mol⁻¹, $C_M = 0.202(2)$ emu mol⁻¹ K and $\theta = 1.000(9)$ K. No evidence of magnetic ordering transitions was observed in agreement with the absence of magnetic peaks in the PND patterns of **2**. The value of χ_0 suggests a significant Pauli paramagnetic component and probable delocalisation through the –N(Li,Co)1–N– linkages forming $[\text{Li,CoN}_{2/2}]_{\infty}$ infinite chains in the c direction. Similar magnetic behaviour is seen in the Li–Ni–N system, where delocalisation increases with increasing x until with the formation of $[\text{NiN}_{2/2}]_{\infty}$ chains, the system is almost completely delocalised.^{16,17} Interestingly in the Co system, however, the localised moment is much larger than the Li–Ni–N value for equivalent x (1.86 μ_B per Co in **1**). In fact, **1** is intermediate between nitridonickelates and nitridoferrates, $\text{Li}_{3-x-y}\text{Fe}_x\text{N}$ in which spin-orbit coupling is proposed to be responsible for the unexpectedly high moments observed.^{18,19}

Shodai *et al.* proposed a semi-quantitative band structure for $\text{Li}_{2.6-y}\text{Co}_{0.4}\text{N}$ in which the Fermi level lies within a conduction band dominated by N 2p and Co 3d states.²⁰ The original interpretation of EELS results was that as Li^+ was electrochemically extracted, holes were created predominantly within N 2p orbitals as opposed to their localisation on Co (to form Co^{2+}).²¹ DFT calculations performed for the ordered nitridonickelate, LiNiN , describe a band structure where the Fermi level lies in a partially filled N 2p–Ni 3d band and clearly portray the Ni–N linkages along c as covalent π bonds.²² Similarly, we would thus expect the Li–Co–N materials to become low dimensional metals as x approaches 1.²³ Our ⁷Li NMR studies have demonstrated a low E_a and fast Li^+ diffusion in LiNiN .¹⁷ Initial experiments to measure chemical shifts and Li^+ diffusion dynamics in the nitridocobaltates by ⁷Li NMR have been dominated by the magnitude of the localised moments yielding spectra consisting of a broad and featureless line (60–80 kHz wide) preventing further analysis. The high level of Li^+ vacancies and covalency of the (Li,Co)–N bond in **1** and **2** should engender rapid Li^+ diffusion as suggested by electrochemical studies of $\text{Li}_{3-x-y}\text{Co}_x\text{N}$ compounds with lower x (and y).^{3–5} It is pertinent to highlight the probable

importance of reaction temperature (and heating/cooling rates) in the generation (and ordering) of Li vacancies in the $M = \text{Co}$ and Ni systems. Higher temperatures appear to lead to Li loss and potential control (enhancement) of both y and x (*cf.* nitridocobaltates prepared here and nitridonickelates synthesised between 773–873 K¹⁶). In principle, it should thus be possible to modify systematically magnetism and the DOS at the Fermi level in addition to the ionic transport properties.

DHG thanks the EPSRC for supporting this work and for the provision of a diffractometer, the CCLRC for beamtime and the University of Nottingham for a studentship for AGG.

Notes and references

- W. Sachsze and R. Juza, *Z. Anorg. Chem.*, 1949, **259**, 278.
- N. A. Martem'yanov, V. Kh. Tamm, V. P. Obrosof and Z. S. Martem'yanova, *Inorg. Mater.*, 1995, **31**, 72.
- M. Nishijima, T. Kagohashi, M. Imanishi, Y. Takeda, O. Yamamoto and S. Kondo, *Solid State Ionics*, 1996, **83**, 107.
- T. Shodai, S. Okada, S. Tobishima and J. Yamaki, *J. Power Sources*, 1997, **68**, 515.
- Y. Takeda, M. Nishijima, M. Yamahata, K. Takeda, N. Imanishi and O. Yamamoto, *Solid State Ionics*, 2000, **130**, 61.
- Single crystals of **1** were grown by the reaction of Li_3N with Co foil ($5 \times 30 \times 0.1$ mm) in a steel reaction vessel under $\text{N}_2(\text{g})$ heated to 923 K for 6 days. The reaction was cooled by switching off the furnace. After 3 such cycles, lustrous silver crystals grew on the foil surface.
- D. H. Gregory, P. M. O'Meara, A. G. Gordon, J. P. Hodges, S. Short and J. D. Jorgensen, *Chem. Mater.*, 2002, **14**, 2063.
- Li_3N and Co powder were sealed in a stainless steel reaction vessel under $\text{N}_2(\text{g})$ and heated to 923 K for 144 h.
- 1**: Hexagonal space group $P6/mmm$, $Z = 1$, $V = 43.56(3) \text{\AA}^3$, $\rho_{\text{calc}} = 2.267 \text{ g cm}^{-3}$, $\mu = 4.935 \text{ mm}^{-1}$. 205 reflections at 150(1) K, 35 independent ($R_{\text{int}} = 0.019$). The structure was solved by direct methods with SIR 97 and refined by least squares within SHELXL-97, $R1 = 0.0278$, $wR2 = 0.0669$. CCDC 249196. See <http://www.rsc.org/suppdata/cc/b4/b413022g/> for crystallographic data in .cif or other electronic format. (a) A. Altomare, M. C. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115; (b) G. M. Sheldrick, *SHELXL97-Program for Crystal Structure Refinement (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- Samples were loaded into V cans with In seals in a N_2 -filled glovebox before data collection. Data were collected at the 145°, 90° and 35° detector banks. **2** crystallises in hexagonal space group $P6/mmm$ with $Z = 1$. **2** (298 K): $V = 43.959(1) \text{\AA}^3$, 11614 observations, 71 parameters, $R_{\text{wp}} = 0.0243$, $R_p = 0.0360$, $\chi^2 = 3.51$; **2** (3 K): $V = 43.417(5) \text{\AA}^3$, 10637 observations, 85 parameters, $R_{\text{wp}} = 0.0091$, $R_p = 0.0142$, $\chi^2 = 1.78$.
- A. C. Larson and R. B. von Dreele, *The General Structure Analysis System*, Report LAUR 086-748, Los Alamos National Laboratories, LANL, Los Alamos, NM, 2000.
- B. H. Toby, *J. Appl. Crystallogr.*, 2001, **34**, 210.
- A. Rabenau and H. Schulz, *J. Less-Common Met.*, 1976, **50**, 155.
- L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 3rd edn., 1960.
- Magnetic susceptibility measurements were made using a Quantum Design MPMS XL 5 T SQUID susceptometer between 2 and 300 K.
- R. Niewa, Z.-L. Huang, W. Schnelle, Z. Hu and R. Kniep, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1778.
- Z. Stoeva, R. Gomez, A. G. Gordon, M. Allan, D. H. Gregory, G. Hix and J. J. Titman, *J. Am. Chem. Soc.*, 2004, **126**, 4066.
- J. Klatyk, W. Schnelle, F. R. Wagner, R. Niewa, P. Novák, R. Kniep, M. Waldeck, V. Ksenofontov and P. Gütlich, *Phys. Rev. Lett.*, 2002, **88**, 207202.
- P. Novák and F. R. Wagner, *Phys. Rev. B*, 2002, **66**, 184434.
- T. Shodai, Y. Sakurai and T. Suzuki, *Solid State Ionics*, 1999, **122**, 85.
- S. Suzuki, T. Shodai and J. Yamaki, *J. Phys. Chem. Solids*, 1998, **59**, 331.
- B. Jäger, P. Herzig, W. Wolf, R. Gautier, Z. Stoeva, G. B. Hix, J. J. Titman and D. H. Gregory, manuscript in preparation.
- Pellets of **2** yield resistivity values of $11.8 \times 10^3 \Omega \text{ cm}$ at 293 K.