Structural polymorphism and magnetic behavior of $Li_3Co_2SbO_6$

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Introduction

- Layered oxides with the general formula $A_3M_2XO_6$ (A = Li, Na; M = transition metals such as Co, Cu, Ni; X = Bi, Sb, Te; $0 \leq x \leq 3$) can form a crystallographic 'honeycomb' structure where one third of the transition metal sites are doped with high charge cations such as Sb^{5+} and Te^{6+}.[1-4]
- Layered-honeycomb oxides are materials that exhibit an array of interesting properties, including use as electrodes for Li-ion batteries, high electrical conductivity, low temperature magnetic phases, and spin-glass properties.[1]
- The compound $Li_3Co_2SbO_6$ had been relatively under-represented in the literature on the $Li_3M_2SbO_6$ honeycomb-type phases. It has been described with a less crystalline ion-exchange synthesis from the Na analogue $Na_3Co_2SbO_6$ but not solid-state synthesis.[3] Here, we report the solid-state synthesis, crystal structures and magnetism of $Li_3Co_2SbO_6$ in two polymorphs.[4]

Experimental Methods

- Samples were synthesized by high temperature solid-state reactions, with the most crystalline samples of $Li_3Co_2SbO_6$ achieved by using the precursor Li_3SbO_4 in the following reaction:

$$Li_3SbO_4 + 2\,CoO \xrightarrow{900\ ^\circ C,\ \text{flowing Ar}} Li_3Co_2SbO_6$$

- X-ray (XRD) and neutron powder diffraction (NPD) were collected at RT to determine crystal structures. NPD measurements below T_N and in-field were also performed to determine magnetic structures.
- Magnetometry and heat capacity data collected on a PPMS down to 2 K.

References

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2. Nalbandyan, V. *et al., Phys. Rev. B* . 2017, 96
3. Stratan, M.I. *et al., New J. Chem.* 2019, 43, 13545-13553
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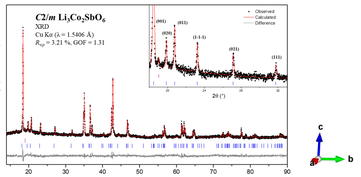
Crystal Structures and Rietveld Refinement

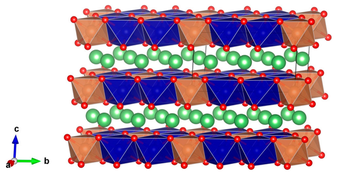
- $Li_3Co_2SbO_6$ is found to adopt two highly distinct structural forms depending on slight changes to synthesis conditions (namely Li stoichiometry, particle size and reaction temperatures)[4]:

1. A pseudohexagonal (monoclinic *C*2/*m*) layered O3-$LiCoO_2$ type phase with "honeycomb" 2:1 ordering of Co and Sb.
2. An orthorhombic (*Fddd)* rocksalt phase, isostructural with $Li_3Co_2TaO_6$ but with the addition of significant Li/Co ordering.[5]

C2/*m* O3-type honeycomb phase

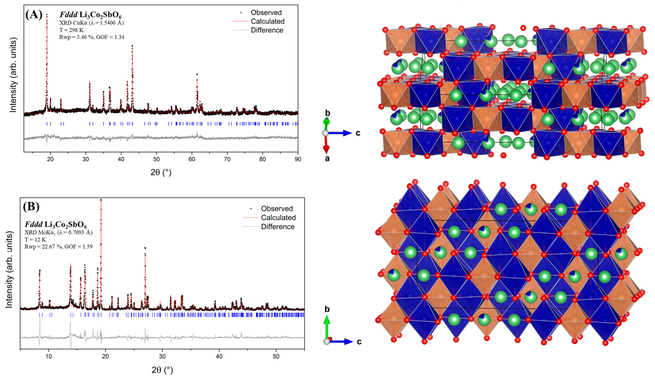


Rietveld refinement against XRD data (λ = 1.5406 Å)



CoO_6 octahedra are blue, SbO_6 octahedra are bronze, O atoms are red, and Li atoms are green

Orthorhombic (*Fddd*) rocksalt phase

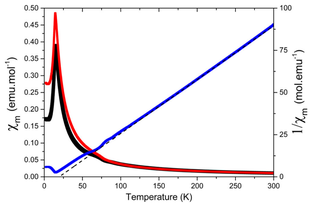


Rietveld refinement of the orthorhombic Fddd phase against XRD data from (A) a Cu Kα source (λ = 1.5418 Å) at 298 K and (B) a Mo $Kα_1$ source (λ = 0.7093 Å) at 12 K under a vacuum.

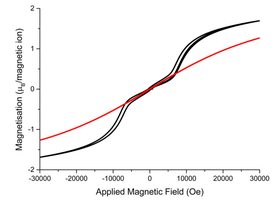
Colored wedges show mixed occupancies.

Magnetic Properties

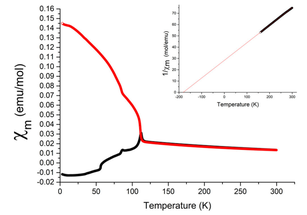
- Both phases show long range antiferromagnetic (AFM) order at low temperatures.
- The honeycomb phase undergoes a transition to AFM order below T_N = 14 K. Isothermal magnetisation below T_N shows hysteresis with clear evidence for a metamagnetic transition at H ≈ 0.7 T
- The orthorhombic phase orders antiferromagnetically below T_N = 112 K and then undergoes two more transitions at 80 and 60K.



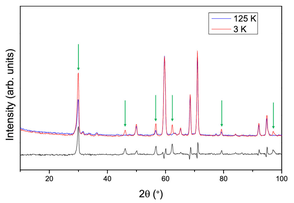
Temperature-dependent DC magnetic susceptibility (χ_m) and inverse magnetic susceptibility ($1/\chi_m$) for the honeycomb phase of $Li_3Co_2SbO_6$, using an applied field of 0.1 T. The ZFC curve is black, the FC curve is red, and the inverse susceptibility is blue.



Isothermal field-dependent magnetization of the honeycomb phase of $Li_3Co_2SbO_6$ at 2 K (black) and 20 K (red), below and above T_N = 14.5 K, respectively.



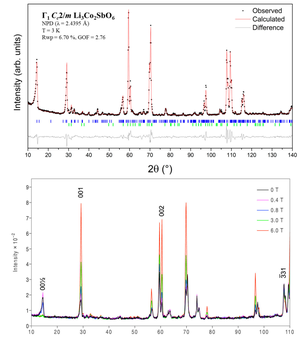
Magnetic susceptibility as a function of temperature for the orthorhombic phase of $Li_3Co_2SbO_6$ in an applied field of 0.1 T. ZFC data are black and FC data are red. The inset shows the Curie–Weiss fit to ZFC inverse susceptibility above 160 K.

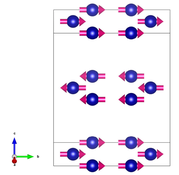


NPD data (λ = 2.4395 Å) of rocksalt (Fddd) phase $Li_3Co_2SbO_6$ at 3 K (red) and 125 K (blue). The difference curve (black) shows the possible magnetic Bragg peaks, highlighted with green arrows, indicating long-range magnetic order. The magnetic peaks were unable to be indexed with a rational k-vector indicating that the ground-state is incommensurate.

Magnetic Structure from Neutron Diffraction

- The magnetic structure of the honeycomb phase below T_N was able to be determined from NPD. The associated magnetic peaks were able to be indexed unambiguously with a k-vector of (0 0 ½), with the order determined to be A-type (ferromagnetic planes, antiferromagnetically coupled).
- This is the first honeycomb oxide to show A-type AFM order with most others showing Zig-Zag order of the spins in the plane. In-field neutron diffraction below T_N also shows clear evidence for a metamagnetic transition at H ≈ 0.7 T to three-dimensional ferromagnetic order.





A-type AFM structure of the honeycomb phase with a refined magnetic moment of 2.53(3) μ_B/Co along b at 3K.

- *AFM coupling between layers implies that there are considerable interplane magnetic interactions.*
- *In-field NPD below T_N reveal a metamagnetic "spin-flop" transition to a 3-D FM phase above H ≈ 0.7 T.*

Conclusions

- $Li_3Co_2SbO_6$ is found to adopt two distinct structural forms depending on synthesis conditions.
- Both the polymorphs show long-range AFM order at low temperatures
- The honeycomb phase is the first of its type to show A-type antiferromagnetic order below T_N and undergoes a metamagnetic transition at H ≈ 0.7 T to three-dimensional ferromagnetic order.
- The rocksalt phase displays multiple AFM transitions. Neutron diffraction data show that the ground state is incommensurate.

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