# Electronic Properties of 2D Alkali Cobalt Oxides

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**Abstract**

Selected recent results on $A_xCoO_2$ (A=Li, Na, K) layered cobaltites are reviewed. Potassium ordering was clearly evidenced in $K_4Co_7O_{14}$ using usual X-ray diffraction. Magnetic and transport properties reveal very different behaviors depending on the nature of the alkali element. These results are discussed taking into account an interplay between electronic correlations, spin entropy effects, alkali atom ordering, 2D character of the structure and the possible existence of oxygen vacancies that strongly influences the actual average oxidation state of cobalt.

**Introduction**

Although oxide based materials were for long identified as thermoelectric materials, industrial use of oxides in thermoelectric devices is still not achieved. The reason is that despite unique features required for high temperature power generation such as thermal stability and environmental issues compatibility, the ZT figure of merit should still be improved. This requires a better understanding of the electronic properties, which gave rise to a number of basic experimental and theoretical studies during the last years. One of the most studied thermoelectric oxide families is the alkali layered cobaltite series well known for its use in Li-ion secondary batteries. Their electronic properties including their metallic electrical conductivity as well as their large TEP values were first discovered about 25 years ago [1, 2], but their interest for thermoelectric generation was only recognized 10 years ago [3]. Despite a large number of experimental investigations and theoretical approaches that provided significant advances in the description of these complex systems some questions about the electronic properties of layered oxides remain open.

Instead of extensively reviewing the reported results on these systems, in the present paper we will rather focus on some recent results and on the main issues concerning the crystal structure and the electronic properties. A special attention will be paid to the influence of changing the nature of the alkali metal in the $A_xCoO_2$ (A=Li, NA, K) systems.

**Crystal structures**

The basic unit of the $A_xMO_2$ systems considered here is a closely packed oxygen double layer whose octahedral sites are completely occupied by a transition metal (M), thus resulting in a formulation $MO_2$. The possible structures can then be classified according to the packing of oxygen layers that can be labelized by letters *A*, *B* and *C*.

When the packing is of the *...AB-CA-BC...* type, the so-called α-NaFeO$_2$ structure is obtained: it actually consists in an oxygen arrangment similar to that of rocksalt, but with an ordering of the two types of cations located in plane triagular lattices alternating along the stacking direction. In this case the alkali site is octahedral and the structural type is denoted O3 (the figure refers to the number of MO$_2$ sheets within the corresponding hexagonal cell).

When the packing is of the *...AB-BA-AB...* type or of the *...AB-BA-AC-CA...* type the alkali site is prismatic and the structure type is denoted P2 or P3, respectively. These two possibilities of stacking also exist for the delafossite family (A=Cu, Ag, Pd, Pt), giving rise to the so-called 2H and 3R polytypes, respectively. The main difference with respect to alkali metallates is the linear twofold coordination of monovalent copper or silver and that non-stoichiometric occupancy of the A site has never been reported.

The prismatic sites are not exactly identical in the P2 and P3 structures. In P2 an alkali atom can have either two, or six M nearest neighbors depending whether the prism is sharing faces or edges with the closest MO$_6$ octahedra. In P3, a single possibility exists as the prism is sharing a face with an octaheron of one adjacent double layer and edges with three octahedra of the other adjacent layer.

**Sample composition**

Experimental conditions for sample preparation and characterization have been described elsewhere [4]. Normally, assuming a $A_xCoO_2$ formulation leads to a formal oxidation state of Co equal to (4-x). However, the presence of oxygen vacancies in $A_xCoO_{2-\delta}$ has been reported [5] and the actual oxidation state of Co should then be equal to (4-x-2δ). In order to overcome this difficulty an experimental value of the oxidation state of cobalt has been determined using iodometric titration. The cobalt oxidation state is compared to the Co-O distance in table 1. As expected the Co-O distance decreases as the oxidation state of cobalt increases and the comparison of the Li and K cobaltites shows that it does not significantly depends on the nature of the alkali element neither on the structural type (O3 or P2).

Table 1. Comparing Co oxidation state determined from iodometric titration with Co-O distances in $A_xCoO_{2-\delta}$.

| | Co average oxidation state | Co-O distance (Å) |
|---|---|---|
| P3-Na$_{0.6}$CoO$_{2-\delta}$ | 3.20 (5) | 1.907 |
| P2-K$_{0.6}$CoO$_{2-\delta}$ | 3.32 (5) | 1.899 |
| O3-Li$_{0.6}$CoO$_{2-\delta}$ | 3.35 (5) | 1.897 |
| P2-K$_4$Co$_7$O$_{14-\tau}$ | 3.35 (5) | 1.896 |
| P2-Na$_{0.31}$CoO$_{2-\delta}$ | 3.43 (5) | 1.886 |

## Potassium substitution

For fractional fillings of the A sites, the question of ordering of alkali atoms within the A plane has often been debated and – mainly theoretically – studied in the case of sodium cobaltites [6]. For x close to 0.6, replacing sodium by potassium provided an example of long range ordering that has been determined using conventional X-ray diffraction [7]. Potassium distribution is shown in Fig. 1. The overall atomic arrangement is of P2 type. The $\sqrt{7}a_H \times \sqrt{7}a_H$ supercell (where $a_H$ is the lattice constant of the hexagonal parent subcell) and the space group $P6_3/m$ lead to the formulation $K_4Co_7O_{14}$ for a full occupancy of appropriate atomic positions [7].
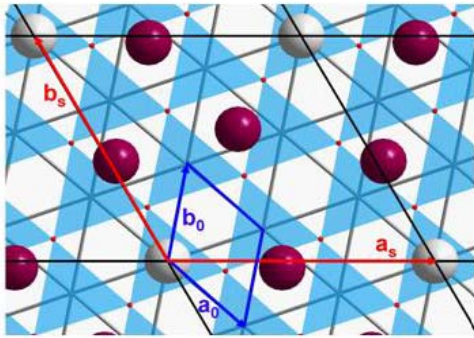


Fig. 1: Potassium ordering in $K_4Co_7O_{14}$ showing two sites for potassium ions: one sharing edges (dark or red spheres) and the other sharing a face (light or white spheres) with neighboring $CoO_6$ octahedra.

Only one quarter of the K-atoms occupies prism sharing bases with $CoO_6$ octahedra faces, the other three quarters occupying prisms sharing edges: actually, for the later, the electrostatic energy is smaller, but DFT calculations using the VASP code have shown that, for the whole system, the driving force for the observed potassium ordering is the $K^+$-$K^+$ electrostatic repulsion [7].
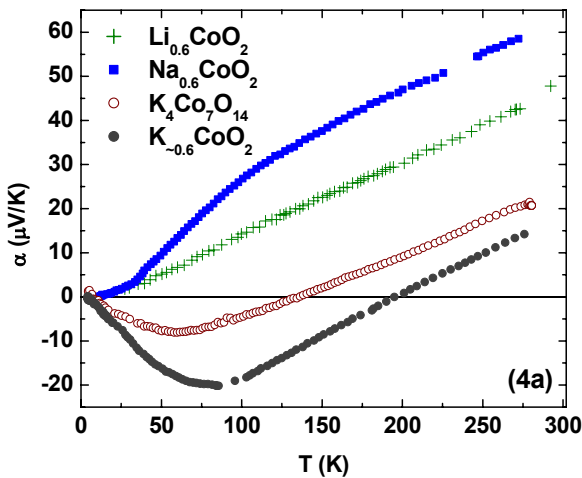
## Transport properties



Fig. 2 Temperature dependence of the thermoelectric power for selected alkali layered cobaltites with x=0.6. Data for $Li_{0.6}CoO_2$ are taken from ref 8.

Temperature dependence of Seebeck coefficient for Li, Na and K cobaltites with an x-value near 0.6 are compared in Fig. 2. The behavior of $Li_{0.6}CoO_2$ is close to the one expected for a metal from Mott formula [9]

$$\alpha = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \frac{\partial \log \sigma(E)}{\partial E} \right\}_{E=E_F}$$

when in the neighborhood of the Fermi level, one assumes $\sigma(E)=const. E^x$, which gives:

$$\alpha = \frac{\pi^2}{3} \frac{k_B^2 T}{eE_F} x .$$

For spherical Fermi surfaces (E=const.$\mathbf{k}^2$) and forgetting the wave vector ($\mathbf{k}$) dependency of the scattering process, x=3/2. Obviously, the slope $d\alpha/dT$ is strongly enhanced with respect to free electron gas, which can be attributed to electronic correlations with an effective mass of charge carriers much larger than the electron mass. Such a behavior is in agreement with specific heat measurements and magnetic susceptibility data [4]. It is also in agreement with the usual narrowness of d-bands in transition metal oxides and the 2D character of the crystal structure. The $d\alpha/dT$ slopes for the Na cobaltite and the two K cobaltites have values similar to that of $Li_{0.6}CoO_2$, at least for T>100K. However, the thermoelectric power values at room temperature are very different for the four samples. It is much larger in the case of sodium, which has been ascribed to spin entropy of the carriers, in agreement with the Curie-Weiss behavior of the oxide. It is much lower for the K cobaltites the thermopower of which becomes negative at low temperature. Such a behavior raises the question of the contribution of two types of carriers. Actually the $t_{2g}$ levels are split into two bands that could overlap at the Fermi level. Calculations of the band structure including accurately correlation effects are required to better understand the behavior. Another qualitative interpretation could be found in the already mentioned spin entropy contribution to the Seebeck coefficient. This contribution is not expected in the case of $K_{0.6}CoO_2$ as a Pauli type magnetic susceptibility is observed, suggesting that most of the electrons are paired. On the contrary, the effect should be strong for the Na compound that exhibits a Curie-Weiss paramagnetic behavior.

Electrical resistivity ($\rho$) measurements do not evidence any change of the scattering mechanism upon heating for the Li and Na cobaltites, as the T-dependence of the resistivity is more or less linear in the whole temperature range suggesting that phonon scattering dominates down to 4K or that much more complex effects whose discussion is out of the scope of the present paper are involved (Fig.3).

On the contrary both K cobaltites, ordered $K_4Co_7O_{14}$ and random $K_{0.6}CoO_2$, show a change from a temperature independent scattering mechanism to a classical phonon scattering as expected for any metallic phase in which a departure from the periodicity of the potential energy gives rise to a dominant elastic scattering at low temperature. For $K_4Co_7O_{14}$ it could originate from uncontrolled impurities, a

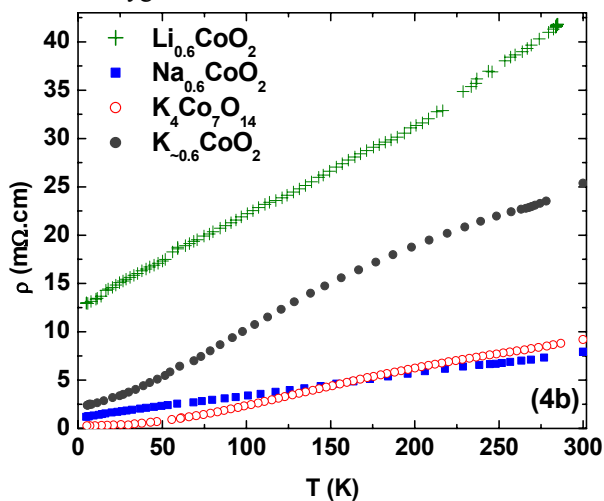residual disorder in K-atom distribution or randomly distributed oxygen vacancies.



Fig. 3. Temperature dependence of the electrical resistivity of alkali cobaltites with x=0.6.

However, the change in the $d\rho/dT$ slope at low temperature could also originate from electron-electron collisions expected in highly correlated systems according to the process known as Baber scattering [10] and reviewed by Mott [11] that predicts a $T^2$ dependence of $\rho$ at low temperature. The electrical resistivity of $K_4Co_7O_{14}$ is plotted against squared temperature in Fig. 4 showing a straight line at least up to 100K.
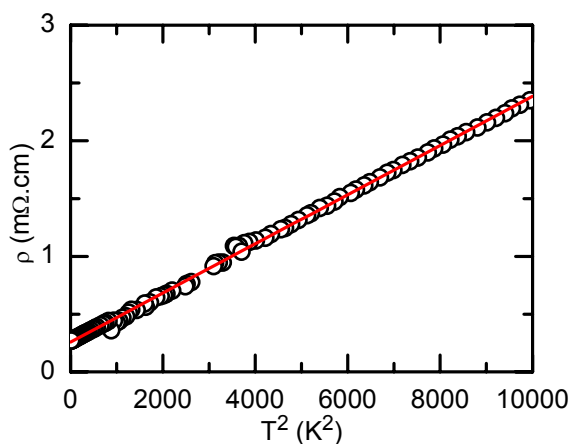


Fig. 4. Showing the $T^2$ dependence of the electrical resistivity of $K_4Co_7O_{14}$ for 4<T<100 K.

## Conclusions

Reviewing selected recent results on $A_xCoO_2$ (A=Li, Na, K) systems, enable us to draw the following conclusions.

The alkali atom ordering for x close to 0.6, already mentioned and theoretically investigated in the Na case has clearly been identified in $K_4Co_7O_{14}$ using conventional X-ray diffraction. Effect of potassium ordering is mainly sensed by electrical measurements: the electrical resistivity is larger for disordered $K_{0.6}CoO_2$ than for ordered $K_4Co_7O_{14}$ as, in addition to scattering by phonon, charge carriers are

further scattered by a random component to the potential energy. A $T^2$ dependence of the resistivity at low temperature suggests that electron-electron scattering expected in highly correlated system could play a role. The thermoelectric power differs strongly with the nature of the alkali element. No definite explanation can be provided for this tendency. Nevertheless regarding the contribution of spin entropy it can be simply correlated to the magnetic behavior that is either of enhanced Pauli type or including a Curie-Weiss contribution. For the potassium cobaltite two types of carriers seem involved.

Despite an increasing activity on these peculiar and fascinating materials a large part of their behavior is still not well understood and further investigations remain necessary.

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