

Influence of the cation substitution on the magnetic properties of LiCo_2O_4 and $\text{Li}(\text{Me},\text{Co})_2\text{O}_4$ spinels

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Lithium-based cells LiCo_2O_4 have been characterized by magnetic techniques, looking at the influence of the partial substitution of cobalt by 3d or 4d transition metal elements (Fe, Ni, Cu, Cr, Mo). The non-substituted compound LiCo_2O_4 behaves as an antiferromagnet, with a Néel temperature T_N of 30 K, although antiferromagnetic interactions are much more important, as suggested by a Weiss parameter Θ of the order of -225 K. In the solid solution $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$ the Weiss parameter Θ changes with $x(\text{Ni})$, reaching large positive values (e.g., $\Theta \sim +230$ K, for $x = 0.5$). This phenomenon suggests the existence of a canted-antiferromagnetic or ferrimagnetic structures with large ferromagnetic components. Substitution of cobalt by other 3d or 4d transition metals in the $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ series shows dramatic effects with respect to the non-substituted LiCo_2O_4 compound: copper completely suppresses the magnetic order, while iron increases T_N to almost room temperature. No modifications are observed when molybdenum substitutes cobalt, while chromium transforms the AF order in a ferromagnetic one, with T_c of about 90 K.

Keywords: magnetic oxides, spinels, magnetic exchange, lithium-based batteries

Influencia de la sustitución catiónica sobre las propiedades magnéticas de las espinelas LiCo_2O_4 Y $\text{Li}(\text{Me},\text{Co})_2\text{O}_4$

Se ha caracterizado por técnicas magnéticas, el efecto de la sustitución parcial de Co por elementos de transición 3d o 4d (Fe, Ni, Cu, Cr, Mo) en celdas LiCo_2O_4 a base de litio. El compuesto no sustituido LiCo_2O_4 se comporta como un antiferromagneto de temperatura de Néel T_N de 30 K, aunque existen interacciones antiferromagnéticas mucho más importantes, como lo indica un parámetro de Weiss Θ del orden de -225K. En la solución sólida $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$ el parámetro de Weiss Θ cambia con $x(\text{Ni})$, alcanzando valores positivos altos (e.g., $\Theta \sim +230\text{K}$, para $x=0.5$). Este fenómeno sugiere la existencia de una estructura antiferromagnética inclinada ("AF-canted") o de una estructura ferrimagnética, donde predominan componentes ferromagnéticas importantes. La sustitución del cobalto por otros elementos de transición 3d o 4d en la serie $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ muestra un efecto dramático con respecto al compuesto no sustituido LiCo_2O_4 : el cobre suprime completamente el orden magnético, mientras que el hierro incrementa su T_N hasta alcanzar prácticamente la temperatura ambiente. La sustitución del cobalto por el molibdeno no produce modificaciones, mientras que el cromo transforma el orden antiferromagnético en un orden ferromagnético, con una T_c de alrededor 90 K.

Palabras clave: óxidos magnéticos, espinelas, interacciones de canje, baterías a base de litio

1. INTRODUCTION

Lithium-based cells represent an important technological challenge due to the ever-growing miniaturization processes, low-cost fabrication and high-safety demands [1]. The search for new cathode components is presently oriented toward metallic oxides, in which different oxidation states play an important role during electrochemical processes. Well-known materials are LiCoO_2 and LiNiO_2 of layered structure (S.G. $R3m$) and the Li-Mn oxide of spinel structure (LiMn_2O_4 , S.G. $Fd3m$) [2,3]. More recently, the synthesis of the cobalt-based spinel LiCo_2O_4 has been reported [4]. It became then interesting to investigate the $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$ solid solution in which the cobalt ions were partially substituted by nickel. In addition, other 3d or 4d transition-metal elements were investigated for their influence on the magnetic properties of the parent compound. For this, a given composition $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ was chosen, using different Me ions (Mn, Ni, Cu, Cr, Mo). We report herein the magnetic properties of such spinel compounds prepared by soft-chemistry routes.

2. EXPERIMENTAL PROCEDURE

The $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$ oxides were prepared by a sol-gel method. We first prepared pure cobalt carbonate by addition of sodium carbonate to a concentrated aqueous solution of cobalt chloride at 60 C. After

precipitation, filtration and washing with hot water, the CoCO_3 carbonate was dried at 100 C. This powder was mixed with nickel carbonate in adequate molar amounts and dissolved in excess of propionic acid. The solution was heated at 140 C so that most excess of propionic acid was evaporated until a gel was formed. Liquid nitrogen was then immediately added, thus powdering the gel into solid state of mixed nickel cobalt propionate. This metal propionate salts mixture was then heated at 200 C for 2h in order to remove the excess of propionic acid. Chemical analysis by atomic absorption and EDX confirmed the stoichiometry. Oxides (Fe_2O_3 , CuO, Mn_3O_4 , MoO_3) and nitrates ($\text{Cr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were also used to prepare the intermediate composition $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ by a modified Pechini method, using a 1:4 / ethilenglicol : citric-acid molar solution.

Calcination of the as-prepared precursors was performed between 600 and 700 C, depending on the concentration of the substituent. This temperature was chosen after verification of the samples' stability (see §3.1., below). X-ray diffraction (XRD) was performed on the calcined powder using a D-5000 Siemens diffractometer and a Philips PW 3710 diffractometer with $\text{CuK}\alpha$ wavelength ($\lambda = 0.154060$ nm). Peak positions were determined through the X'Pert Graphics-&-Utility software. The XRD data showed pure samples of the solid solution $\text{Li}(\text{Ni},\text{Co})_2\text{O}_4$ for the range $[0.0 \leq x \leq 1.0]$, which could be indexed in the

spinel structure (S.G. $O_h^- Fd3m$). Faint peaks appearing for the $x(\text{Ni}) = 1.0$ composition could be due to the presence of NiO , thus defining the limits of the solid solution. Table I gives the lattice parameters for the series $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ ($0.0 \leq x \leq 1.0$). XRD patterns of the $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ series show no presence of impurity phases, except in the case of $\text{Me} = \text{Mo}$, for which two crystallographic phases coexisted (see below). The crystallites' dimensions were estimated from the width of the diffraction lines and by independent SEM observations, to about 2-3 μm , which confirms that the synthesis technique yields highly-reactive nanoparticles.

Magnetic properties were measured between 2 and 300 K on powder specimens, using a SHE VTS-906 susceptometer. Orientation effects of the crystallites under the presence of the external field was avoided by pressing the powder into thick tablets, these latter being placed on gelatin capsules and hold against the walls using cotton pellets. Correction of the sample holder was made in each case.

TABLE I. LATTICE PARAMETERS OF THE SOLID SOLUTION $\text{LiNi}_x\text{Co}_{2-x}\text{O}_4$ ($0.0 \leq x \leq 1.0$)

compound	lattice constant <i>S.G. Fd3m</i>
LiCo_2O_4	8.046 ± 0.008
$\text{LiNi}_{0.25}\text{Co}_{1.75}\text{O}_4$	8.070 ± 0.008
$\text{LiNi}_{0.50}\text{Co}_{1.50}\text{O}_4$	8.078 ± 0.005
$\text{LiNi}_{0.75}\text{Co}_{1.25}\text{O}_4$	8.099 ± 0.027
LiNiCoO_4	8.111 ± 0.027

3. RESULTS AND DISCUSSION

3.1. Influence of the annealing temperature

Preliminary measurements were made on the influence of the annealing temperature on the physico-chemical properties of these compounds. For this, samples of nominal composition $\text{LiMo}_{0.5}\text{Co}_{1.5}\text{O}_4$ were annealed at various temperatures and during different times. This specific composition was chosen because it is characteristic of a biphasic domain of existence between a hexagonal-rhombohedral phase mixed to a cubic $Fd3m$ spinel phase. The relative proportion between these two crystallographic phases is relative independent of the annealing temperature, but rapidly changes with the annealing

time (from 50 % spinel phase after 24 h at 680 C, up to 75 %, after 3 days of heat treatment, stabilizing afterwards) [5]. Also, the microstructure is relatively not modified with time and temperature, since the crystallites' size decreases by about half, after 3 days at 680 C. We then performed magnetic measurements under identical conditions of applied field and following a ZFC-mode procedure, on $\text{LiMo}_{0.5}\text{Co}_{1.5}\text{O}_4$ samples annealed for 24 h at temperatures comprised between 400 C and 680 C (Fig. 1). The anomaly occurring at $T_{\text{max}} \sim 30\text{-}35$ K, which we can assimilate to a magnetic transition towards an antiferromagnetic state ($T_{\text{max}} = T_N$), stays strictly constant, within experimental error, after different heat treatments. Only the slight increase of the magnetization at low temperatures, indicative of some impurity phases or unreacted cobalt salts, becomes less pronounced at the highest annealing temperatures. For this reason, the final annealing temperatures chosen for all compounds reported in this work was kept in the range [600 C - 700 C]. It was then assumed that, if any influence of such heat treatment on the magnetic properties, this would be even less noticeable for all other compounds, since all of them showed a pure monophasic domain of existence for the spinel phase.

3.2. The LiCo_2O_4 parent compound

Figure 2 shows the magnetic properties of the non-substituted spinel compound LiCo_2O_4 . The magnetic susceptibility presents a maximum at $T_N \sim 30$ K and a Weiss parameter Θ of the order of -225 K. The magnetic moment deduced from a linear fit of the inverse magnetic susceptibility in the range [180 K $\leq T \leq 300$ K] is equal to $2.90 \mu_B/\text{Co-atom}$, much lower than the moments expected for Co^{2+} , Co^{3+} or Co^{4+} , suggesting a decrease of the magnetic moment due to incipient antiferromagnetic or ferrimagnetic interactions. This experimental fact suggests the presence of unbalanced moments at the tetrahedral and octahedral sites, similar to NiCo_2O_4 [6]. However, the fact that the susceptibility data shown in figure 2 is strictly reversible during a ZFC/FC cycle performed under 300 Oe (not shown) and that the magnetization curve is highly linear in field (insert, Fig. 2) let us think of a predominant antiferromagnetic character for this compound, rather than the ferrimagnetic-like behavior usually reported for spinels [7]. Neutron diffraction techniques should be able to determine the magnetic structure and the local moment at each given site of the crystalline structure.

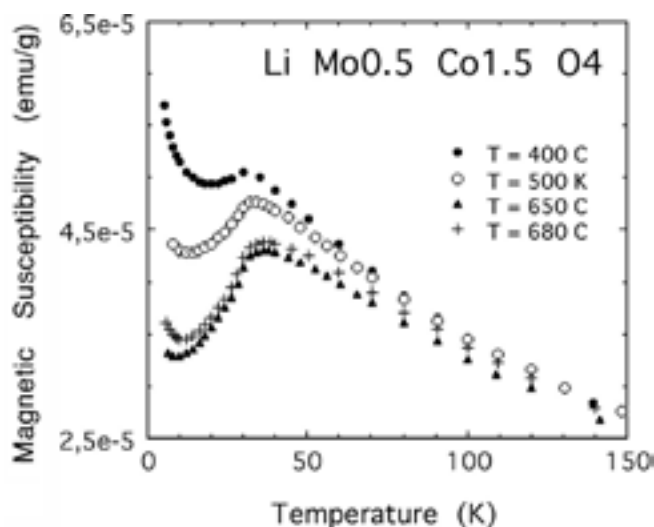


Fig. 1. Temperature dependence of the magnetic susceptibility of $\text{LiMo}_{0.5}\text{Co}_{1.5}\text{O}_4$ as a function of the heat treatment (see text)

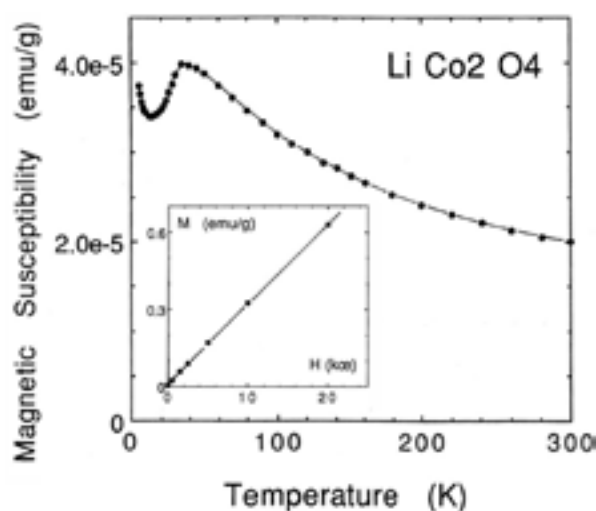


Fig. 2. Magnetic susceptibility of the parent compound LiCo_2O_4 , measured under a 1-kOe applied field. Insert shows the field dependence of the magnetization, measured at 5 K.

3.3. The solid solution $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$, $0.0 \leq x \leq 1.0$

Partial substitution of cobalt by nickel in the $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$ solid solution radically changes the magnetic behavior of LiCo_2O_4 (figure 3). A large ferromagnetic component appears, even at the lowest substitution rate ($x = 0.25$). Extrapolation of the high temperature data yields positive Θ values of +200 K or more, indicating strong ferromagnetic interactions or highly unbalanced antiferromagnetic networks. The temperature of the maximum susceptibility T_{max} stays more or less constant, changing from 30 to 38 K, with lower values of 22 and 25 K for $x = 0.25$ and 0.50, respectively. No attempts have been made to estimate the effective magnetic moment, since experiments should be performed at a much higher temperature range. Present work is aimed to complete these data under new experimental conditions of field and temperature.

3.4. Substitution of Co by transition metals $\text{Me} = \text{Fe}, \text{Ni}, \text{Cu}, \text{Cr}, \text{Mo}$

We have looked for the influence of the partial substitution of cobalt by other transition metal elements on the magnetic properties of the LiCo_2O_4 spinel. For this, nominal composition $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ samples were prepared and annealed at 600 - 700 C. Figure 4 shows the magnetic susceptibility measured between 5 and 300 K, under a 1-koe applied field. For comparison, we consider the magnetic behavior of the pure compound LiCo_2O_4 and its solid solution $\text{Li}(\text{Ni},\text{Co})_2\text{O}_4$ discussed above. Indeed, the characteristic temperature T_{max} of the $\text{Li}(\text{Ni},\text{Co})_2\text{O}_4$ series stays relative constant with the partial substitution, and constitutes then a good reference point to compare with the other $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ compounds.

Little or no influence is observed when the 4d element Mo partly replaces cobalt, as already concluded in §.3.1, above. To be noticed, in particular, that the value of the susceptibility at T_{max} , $\chi(T_{\text{max}})$, is almost identical to the one observed for the non-substituted spinel LiCo_2O_4 (compare Figs. 1 and 2), in contrast to the observations in the nickel-based solution, where $\chi(T_{\text{max}})$ is almost one order of magnitude higher for equivalent substitution rate. Presence of Cu, however, completely destroys the magnetic order, with no hints of anomalies at 30-35 K and a magnetic susceptibility dominated by a temperature-independent paramagnetism mainly coming from the Cu^{2+} ions.

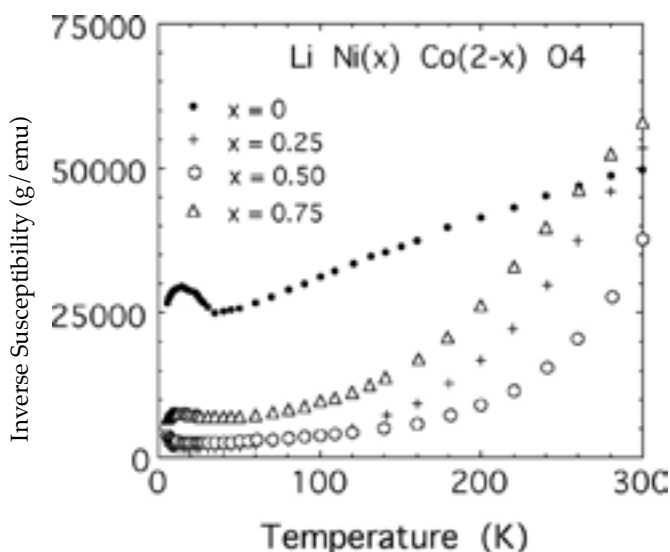


Fig. 3. Inverse susceptibility of the solid solution $\text{Li}(\text{Ni}_x\text{Co}_{2-x})\text{O}_4$, measured under 1 kOe.

The situation differs when Cr ions partly substitute cobalt (Fig. 4.b). The magnetic moment progressively increases with the chromium content [5], while T_{max} rapidly reaches 78 K at $x(\text{Cr}) = 0.5$. A sudden increase of the magnetization occurs at $T_c \sim 90$ K, indicative of a transition from a high-temperature paramagnetic state towards a ferro(ferri)magnetic state at low temperature. A ZFC/FC cycle performed under low field shows a large irreversibility of the magnetization, tending towards a plateau during the FC branch (figure 5). The fact that a constant magnetization is not reached at low temperatures may indicate that we are in presence of a ferrimagnetic-like state rather than a ferromagnetic one.

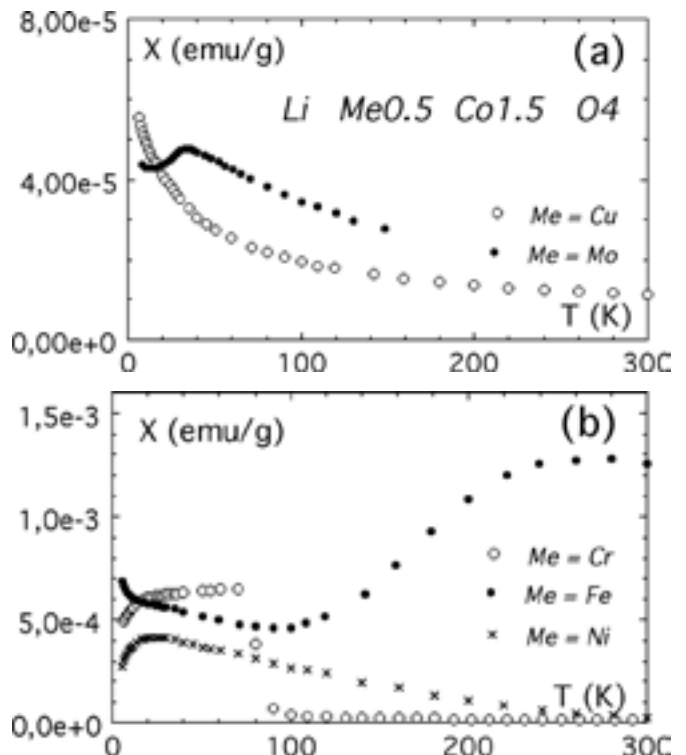


Fig. 4. Magnetic susceptibility of several $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$ compounds, measured at 1 kOe. (a) $\text{Me} = \text{Cu}$ and Mo ; (b) $\text{Me} = \text{Cr}, \text{Ni}$ and Fe

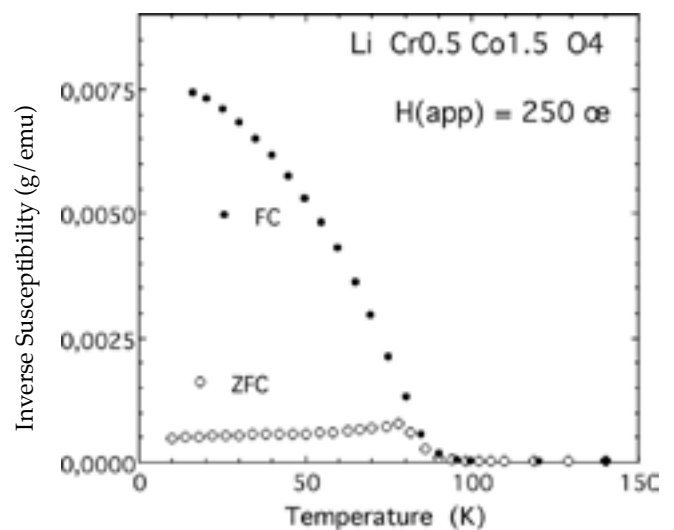


Fig 5. Thermal variation of the ZFC/FC cycle measured at 250 Oe on the $\text{LiCr}_{0.5}\text{Co}_{1.5}\text{O}_4$ compound

Finally, the most striking case appears to be the $\text{LiFe}_{0.5}\text{Co}_{1.5}\text{O}_4$ compound, for which the characteristic temperature T_{max} reaches room temperature or above (Fig. 4.b). Complementary experiments should be performed at higher temperatures in order to reach the paramagnetic state. In this compound, a small increase of the magnetization occurs at low temperatures, together with the presence of a faint shoulder at about 35 K. It may be that some traces of the parent compound LiCo_2O_4 are still present in the final product, leading to some unreacted traces of iron or iron oxides, responsible of the Curie upturn at low temperatures. Both impurity phases, if present, were undetected by classical XRD techniques. Nevertheless, this compound is worth to be further investigated due to the very high value of its ordering temperature. Work is being taken along this direction.

4. CONCLUSIONS

Magnetic measurements performed on two series of lithium-based spinel samples ($\text{Li}(\text{Ni},\text{Co})_2\text{O}_4$ and $\text{LiMe}_{0.5}\text{Co}_{1.5}\text{O}_4$), as a function of composition and of the nature of the transition-metal substituent element Me , showed dramatic effects on the physico-chemical properties of the parent compound LiCo_2O_4 . Ferromagnetic components appear when $Me = \text{Ni}$ and Cr , while the characteristic temperature of the AF or ferrimagnetic state is enhanced in the case of $Me = \text{Fe}$. Presence of Mo does not have any influence on the magnetic properties of LiCo_2O_4 , while $Me = \text{Cu}$ destroys any magnetic ordering. A thorough study of the influence of the annealing temperature in the case of $Me = \text{Mo}$ allowed us to establish the best conditions for synthesis, microstructural aspects and enhanced magnetic properties. Further studies using neutron diffraction techniques should allow

the characterization of the magnetic structure of these interesting compounds, in particular, the case of $\text{LiFe}_{0.5}\text{Co}_{1.5}\text{O}_4$, which presents a magnetic transition at or above room temperature.

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