Electric and dielectric behavior of carbonate intercalated CoAl-Layered Double Hydroxide (LDH) investigated by impedance spectroscopy

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Abstract- Cobalt-based layered double hydroxides (LDH) have invoked a great deal of interest in the field of energy storage due to their unique properties and low cost. Herein, carbonate intercalated CoAl-LDH was prepared in order to investigate the electrical and dielectric properties of this material. This polycrystalline sample was synthesized by the conventional co-precipitation method, characterized by PXRD, FT-IR and TGA, and analyzed by ICP. Ac impedance was measured by the complex impedance spectroscopy (CIS) method using pressed pellet sample over a frequency range of (1Hz-1MHz) and room temperature, to separate contribution of grains and grain boundaries to capacitance, resistance and conductivity of the sample. The adjustment of conductivity parameters by the double power law allowed the determination of $\sigma_{dc}$. The relaxation mechanism is dominated by long range movement of charge carriers: carbonate ions and H$^+$ protons of water molecules in the interlayer space. This material exhibits high dielectric constant values and a low loss factor at high frequencies which makes the valorization of this material may be interesting in the area of dielectrics.

Keywords- Layered Double Hydroxide; Impedance Spectroscopy; Dielectric Properties; Equivalent Electrical Circuit; Ac Conductivity.

1. Introduction

LDH are a kind of (2D) anionic clays with positively charged brucite-like layers and intercalated charge balancing interlayer anions. LDH have the general formula $\left[\text{M}^{\text{II}}_{n}\text{M}^{\text{III}}_{n}(\text{OH})_{2n}\right]^{n}\text{An}^n_{2n}$, where M$^{\text{II}}$ ($\text{Mg}^{2+}$, $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Zn}^{2+}$…etc.) and M$^{\text{III}}$ ($\text{Al}^{3+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$…etc.) are respectively divalent and trivalent metal ions. $\text{An}^n$ is the exchangeable hydrated anions located in the interlayer gallery for charge balance [1, 2]. LDH have been intensively studied recently in various applications such as: environment [3], catalysis [4], medicine [5], supercapacitors [6], electrode modified materials [7], batteries [8], etc. Transition-metal-based LDH have been identified as efficient and stable with additional advantages, including composition flexibility, low cost, ease of preparation and light weight. Among them, the Co-based LDH has drawn much attention due to its electrochemical performances, not only in the layered form but they were regarded as ideal precursors to the preparation of the corresponding oxide nanoplates, and this by thermal transformation from the corresponding LDH precursors [9]. This kind of studies can be useful to designing functional nanodevices from spinel nanostructures. Indeed, many investigators have been attracted especially by CoAl-LDH. For example, CoAl-LDH nanosheets were in-situ incorporated with reduced graphene oxide to improve the electrochemical performance of lithium-oxygen battery
Also, Amperometric sensors were fabricated based on CoAl-LDH for hydrogen peroxide detection [11]. Since the CoAl-LDH has already been used as the active material for capacitors, electrochemical studies are reported on this compound. Although, so far the knowledge of the present author is concerned no significant reports are available on impedance spectroscopy study, dielectric study and ac conductivity.

In order to use LDH based materials in electric/dielectric fields, it is necessary to know their dynamic properties such as resistance, conductivity, time relaxation, permittivity, etc. by a technique which is used for simultaneous electric and dielectric characterization of samples. This is why complex impedance spectroscopy measurement was applied to LDH [12–15] and revealed interesting properties of these materials. Recent works interested to the study of electric and dielectric properties of LDH were focused on the effect of layer charge [16, 17], pH of the synthesis [5, 18], intercalated anions [19, 20], measurements conditions (humidity, temperature, pressure…) [21] on the ionic conductivity and the dielectric parameters.

In the present work, we describe the synthesis and characterization of carbonates intercalated CoAl-LDH by PXRD, FT-IR, TGA and ICP. We investigate the electric properties using modelization of the sample by equivalent electrical circuit. The ac conductivity, residual conductivity, and the dielectric parameters for the prepared sample were studied.

2. Experimental

2.1. Materials

The starting chemicals of cobalt nitrate (Co(NO$_3$)$_2$•6H$_2$O) and aluminum nitrate (Al(NO$_3$)$_3$•9H$_2$O) (Fluka Analytical ≥98%), sodium hydroxide (NaOH) (Fluka analytical > 97%) and sodium carbonate (Na$_2$CO$_3$) (Polysciences.INC, 99%) were used without further purification. Distilled water was used as solvent throughout this study.

2.2. Synthesis of sample

The preparation of the precursor at pH=9±0.5 with molar ratio of Co$^{2+}$/Al$^{3+}$ =1.5 has been done using the co-precipitation method [22]. The synthesis was carried out by mixing 8.43g and 7.56g respectively of Co(NO$_3$)$_2$•6H$_2$O and Al(NO$_3$)$_3$•9H$_2$O salts dissolved in 100 ml of distilled water. A volume of distilled water was placed in a reactor vessel heated to 70°C and adjusted with an excess of Na$_2$CO$_3$ solution to the desired pH. The two metal nitrates solutions were slowly added to the reactor with vigorous stirring. The pH value of the sample was controlled by dropwise addition of aqueous solution of NaOH (1.0M). The resulting slurry was aged at 70°C for 1h then at room temperature for 24h. The precipitate was washed with distilled water several times to remove sodium and nitrate ions, then filtered and dried in an oven at 50°C for 16h. The resultant nanostructure was ground into fine powder. The sample will be denoted as CoAl-CO$_3$-LDH.

2.3. Characterization

Powder X-ray Diffraction (PXRD) pattern of the samples was recorded on X-ray diffractometer (BRUKER-BINARY) using CuKα (λ = 1.54187Å). Fourier transform infrared spectroscopy (FT-IR) spectrum was carried out on a Thermo scientific NICOLET Is10. Thermogravimetric analysis (TGA) was carried out on instrument from Shimadzu model DTG 60H, air flow rate of 200cm$^3$/min. Inductively coupled plasma (ICP) analysis was recorded using VARIAN ms/13/35. The sample dissolution is carried out in nitric acid. The dielectric and electric measurements for the sample were recorded using a MTS Modulab (Solartron Analytical). The impedance was measured within a frequency range of 1Hz to 1MHz at room temperature with relative humidity of 74.1% and under low voltage (0.8V). The CoAl-CO$_3$ sample was prepared in pellet form (diameter = 10mm, thickness = 1.136mm).

3. Results and Discussion
3.1. Powder X-ray diffraction (PXRD) analysis

![Figure 1. Powder X-ray Diffraction pattern of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions showing the reflections indexed to a hexagonal lattice with rhombohedral symmetry.](image)

The PXRD pattern of CoAl-CO$_3$-LDH sample is represented in **Figure 1**. The intense diffraction lines located at $2\theta = 11.5^\circ; 24^\circ; 35^\circ; 60.5^\circ$ and $62^\circ$ can be indexed using the hexagonal cell with rhombohedral symmetry as (003), (006), (009), (110) et (113) respectively, which is a characteristic of a well-crystallized hydrotalcite-like phase with carbonate anions in the interlayer space. The lattice parameters $a=2d_{110}$ and $c=3d_{003}$ are calculated and seems to be in a good agreement with those reported in literature for the same phases and the same molar ratio (**Table 1**) [1, 22].

**Table 1.** Lattice parameters of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions.

| sample  | $d_{110}$ | $a$  | $d_{003}$ | $c$  |
|---------|-----------|------|-----------|------|
| CoAl-CO$_3$ | 1.52     | 3.04 | 7.57      | 22.72 |

3.2. Fourier transform-infrared spectroscopy (FT-IR)

In order to better study the different functional groups of precursor and intercalated anion, FT-IR measurement has been carried out. The FT-IR spectra represented in **Figure 2**, display a large band in the 3400 cm$^{-1}$ region, attributed to the water molecules and hydroxyl groups in the interlayer space. The band situated around 1630 cm$^{-1}$ can be attributed to the bending vibration $\delta$(H$_2$O) of water molecules. CoAl-CO$_3$-LDH displays a strong vibration around 1350 cm$^{-1}$ due to the presence of interlayer carbonate anions. It could also be seen that the band between 810 and 400 cm$^{-1}$ could be attributed to the stretching vibration of M–O and O–M–O bending vibration [23, 24].
Figure 2. Fourier Transform-Infrared spectrum of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions. (\%): Percent, (cm\(^{-1}\)): Centimeter\(^{-1}\).

3.3. Thermogravimetric analysis (TGA)

The thermal decomposition of the samples was monitored by thermogravimetric analysis. As seen in figure 3, the thermal decomposition of CoAl-CO\(_3\)-LDH sample occurs in three well-defined steps. Physisorbed and intercalated water are completely removed near 200\(^\circ\)C (about 3\% of mass loss below 100\(^\circ\)C representing physisorbed water and 13\% of mass loss between 100\(^\circ\)C and 200\(^\circ\)C representing interlayer water).

Figure 3. Thermogravimetric Analysis curve of layered double hydroxide based on cobalt and aluminum intercalated by carbonate ions, showing three steeps of thermal decomposition.(dehydration, dehydroxylation and departure of intercalated anions (carbonates in this case), (\(^\circ\)C): Celcius degree).
The second step which is in the temperature range of above 200°C and below 260°C is ascribed to the dehydroxylation of brucite-like layers and the beginning of decomposition of interlayer anions. The third process which is anions decomposition is finished at about 550°C [1].

3.4. **ICP**

The result of the elemental chemical analysis (Table 2) shows as expected that the experimental ratio $R_{ex} = \text{Co}^{2+}/\text{Al}^{3+}$ obtained is very close to the theoretical ratio $R_{th}$. The formula is determined using ICP and TGA results.

**Table 2. Chemical analysis and formula of the synthesized LDH**

| Sample     | % Co$^{2+}$ | % Al$^{3+}$ | % H$_2$O$^a$ | $R_{ex}$ | $R_{th}$ | Chemical formula                                      |
|------------|-------------|-------------|--------------|----------|----------|-------------------------------------------------------|
| CoAl-CO$_3$| 41.61       | 12.44       | 15.16        | 1.51     | 1.5      | Co$_{0.605}$Al$_{0.395}$ (OH)$_2$ (CO$_3^{2-}$)$_{0.197}$$^\cdot$0.913H$_2$O |

$^a$ % H$_2$O determined by TG analysis

3.5. **Electric and dielectric properties.**

3.5.1. **Complex impedance**

The electrical properties of the present sample have been investigated. The first and the most significant step in this regard is the Nyquist plot between the real and the imaginary part of impedance. Nyquist diagram allows the separation of the effect of grain, grain boundary and electrode interface on the relaxation process. Each contribution is represented by a semicircular arc, and the intersection of each arc with the ($Z'$) axis gives an estimation of the associated resistance value.

The Nyquist diagram (Figure 4) corresponding to CoAl-CO$_3$-LDH sample shows the adjustment of impedance data by an equivalent circuit consisting on three blocs serially arranged and describing grains, grain boundaries and electrode-LDH interface. Each bloc is a parallel arrangement of a resistor $R$ and a constant element phase CPE.

The arcs associated to the grains and the grain boundaries are confused and seem to be one semicircular arc, thing which is difficult to find out without the adjustment of impedance data and the modelization by an equivalent circuit. The low frequencies straight line forming a 45° angle with ($Z'$) axis represents the electrode blocking, which is a characteristic of ionic conductors [25]. The complex impedance in the case of three blocs equivalent circuit is given by:

$$Z^\prime\prime(\omega) = Z^\prime\prime_1(\omega) + Z^\prime\prime_2(\omega) + Z^\prime\prime_3(\omega)$$

(1)

$$Z^\prime(\omega) = \frac{R_g}{1 + \omega^2 \tau_g^2} + \frac{\sigma_0}{1 + \omega^2 \tau_{CPE}^2} + \frac{\sigma_0}{1 + \omega^2 \tau_{CPE}^2}$$

(2)

The real and the imaginary parts of complex impedance in this case are described as:

$$Z^\prime(\omega) = \frac{R_g}{1 + \omega^2 \tau_g^2} \cos(\omega \tau_g) + \frac{R_{g1}}{1 + \omega^2 \tau_{CPE1}^2} \cos(\omega \tau_{CPE1}) + \frac{R_{g2}}{1 + \omega^2 \tau_{CPE2}^2} \cos(\omega \tau_{CPE2}) + \frac{R_{g3}}{1 + \omega^2 \tau_{CPE3}^2} \cos(\omega \tau_{CPE3})$$

(3)

$$Z^\prime\prime(\omega) = \frac{R_g}{1 + \omega^2 \tau_g^2} \sin(\omega \tau_g) + \frac{R_{g1}}{1 + \omega^2 \tau_{CPE1}^2} \sin(\omega \tau_{CPE1}) + \frac{R_{g2}}{1 + \omega^2 \tau_{CPE2}^2} \sin(\omega \tau_{CPE2}) + \frac{R_{g3}}{1 + \omega^2 \tau_{CPE3}^2} \sin(\omega \tau_{CPE3})$$

(4)
Figure 4. Nyquist diagram of experimental and fitted impedance data of layered double hydroxide based on cobalt and aluminum and intercalated by carbonate ions, measured at room temperature, showing deconvolution of contributions and equivalent circuit used for the fitting.

The values of $R_i$, $T_i$, $P_i$ and $\tau_i$ are grouped in Table 3. Where $R_i$, $T_i$, $P_i$ and $\tau_i$ are respectively resistance, pseudo-capacitance, dispersion constant and relaxation time, and $i$ for electrode interface (ei), grain boundary (gb) or grain (g). Relaxation time can be confirmed by the following expression: $\tau_i = (R_i/\omega P_i)^{1/2}$.

Table 3. Fitting parameters of the equivalent circuit for layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions.

|                  | Resistance $(R)$ (Ohm) | Pseudo-capacitance $(T)$ (Farad) | Dispersion Constant $(P)$ | Relaxation time $(\tau)$ (second) | Relaxation frequency (Hertz) |
|------------------|------------------------|----------------------------------|---------------------------|-----------------------------------|-----------------------------|
| Interface (ei)   | $2.40 \times 10^7$     | $1.27 \times 10^{-8}$            | 0.67                      | 0.17                              | 0.93                        |
| Grain boundary (gb) | $9.50 \times 10^6$    | $3.06 \times 10^{-10}$           | 0.76                      | 4.60 $\times 10^4$               | 345.95                      |
| Grain (g)        | $6.27 \times 10^5$     | $3.21 \times 10^{-10}$           | 0.76                      | 1.37 $\times 10^5$               | 11612.06                    |

The grain boundaries are found to be more insulating owing to their high resistance. It acts as thin traps for charge carriers with high capacitance. Since the grain resistance is smaller compared to the grain boundaries, the predominant contribution to the sample conduction comes from the grains. This is confirmed in the case of the present sample.

In the case of an ideal behavior, the polarization mechanism exhibits a Debye relaxation consisting on equation with a single relaxation time. In polycrystalline materials case, the electrical response confirms the non-ideal behavior proved by the existence of a distribution of relaxation times. The frequency dependence of imaginary part $Z''$ (Figure 5) shows the existence of two relaxation frequencies, one for the electrode interface and another for the grain boundaries, while the grain relaxation is masked. Then, CoAl-CO$_3$-LDH exhibits a non-Debye type relaxation characterized by a distribution of relaxation times [26]. The two relaxations are found at 1Hz and 345.08 Hz respectively for electrode-LDH interface and grain boundaries, which confirms the previous results.
3.5.2. Electric modulus

In order to magnify any other contribution present in the sample and maybe masked or unidentifiable on the CIS formalisms, it is important to adopt an alternative approach which can discriminate against extrinsic relaxation effect. Hence the necessity of applying complex modulus analysis. It suppresses the unwanted contributions of electrode polarization and grain boundaries and highlights the intrinsic properties.

Figure 5. Frequency dependence of imaginary part of complex impedance of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions, showing two relaxation peaks.

Figure 6. Frequency dependence of imaginary part of complex modulus of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions, showing one relaxation peak related to the grain contribution. (m/F): meter per Farad, (Hz): Hertz.

Figure 6 shows the frequency dependence of imaginary part of complex modulus $M''$. The asymmetry of the curve is a consequence of the non-Debye type relaxation in the CoAl-CO$_3$-LDH sample, and the clear peak at high frequencies confirms the presence of grain contribution which was hidden in
complex impedance formalism. This contribution is previously found to be the predominant one in the material conduction.

According to the representation of imaginary part of modulus $M''$, probably a dispersion of grain relaxation time occurs at high frequencies causing an enlargement of the peak over a frequency range of 11052 Hz to 251190 Hz. The relaxation in this frequency range confirms the results of grains relaxation time obtained previously by the three blocs equivalent circuit. The nature of modulus spectrum suggests the existence of hopping mechanism of electrical conduction in the material [27].

### 3.5.3. Ac conductivity study

In polycrystalline materials, Ac conductivity analysis is the best way to understand conduction mechanism. For that, the frequency-dependent Ac electrical conductivity ($\sigma_{ac}$) of the CoAl-CO$_3$-LDH sample was investigated and obtained from the following equation: $\sigma_{ac} = \frac{Y'}{k}$. Where $Y'$ is the real part of complex admittance, $k$ is the cell constant ($k = \frac{e}{s}$ with $e$ is the sample pellet thickness and $s$ is the electrode surface).

![Figure 7](image_url)  
**Figure 7.** Frequency dependence of alternative current conductivity of layered double hydroxide based on cobalt and aluminum, intercalated by carbonate, showing the best fit of curve to a double power law by Origin 8 software. (S/m): Siemens per meter. (Hz): Hertz.

As shown in Figure 7, the Ac conductivity increases with increasing frequency, which is attributed to the gradual decrease of the sample resistance. It is also worth mentioning that a frequency independent region appears at low frequencies which smoothly relaxes to a strong dispersive region situated at high frequencies.

In order to analyze the Ac conductivity, experimental data has been fitted with Origin software using nonlinear curve fitting. A convenient formalism to investigate the frequency dependence of conductivity at constant temperature is based on the double power law: $\sigma_{ac} = \sigma_{dc} + A\omega^n + B\omega^m$. Where $\sigma_{dc}$ is the Dc conductivity for a particular temperature, the terms $A\omega^n$ and $B\omega^m$ denotes the frequency dependence and characterize dispersion phenomenon [28–30], and $n$ and $m$ are the power law exponents which generally vary between 0 and 2 it represents the degree of interaction between mobile ions and the lattices around them [31]. The obtained values of $\sigma_{dc}$, $A$, $B$, $n$ and $m$ are grouped in Table 3.

**Table 4.** Fitting parameters values of alternative current conductivity ($\sigma_{ac}$) for layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions. (R$^2$): correlation coefficient, ($\sigma_{dc}$):direct current conductivity, (S/m): (siemens per meter), (A) and (B): polarizability strength , (n) and (m) : the fractional exponents.
The value of $\sigma_{dc}$ determined by the Jonscher law was verified and compared to the one calculated using data obtained from the fitting by the equivalent electrical circuit. For this, $\sigma_{dc}$ was calculated using the following equation:

$$\sigma_{dc} = \frac{A}{R_s} \left( \frac{k}{\varepsilon} \right)^m$$

with $A$ (m$^{-1}$) ($k$: cell constant; $\varepsilon$: The thickness of sample pellet; $s$ is the contact surface between the sample and the electrode and $R_s$ is sample resistance). The $\sigma_{dc}$ obtained in some other works dealing with the same kind of materials is varying between $10^{-6}$ S/m and $10^{-8}$ S/m [12, 13, 15, 32]. So the value found in the present work is included in this range. The exponent $n$ and $m$ give an idea about the kind of hopping motion in the corresponding region, and this according to its value. Indeed, $n < 1$ means that the hopping movement of charge carriers involves long-range movement with a sudden hopping (a translational motion), whereas $n \geq 1$ means that the movement involves localized hopping [33, 34].

In this work, the obtained values of $n$ and $m$ are lower than 1 (Table 3). It means that the charge carriers undergo the same hopping process in both frequency-independent region and dispersive region which is hopping through translational motion. Since the cluster formed by the intercalated species (carbonate ions and $H^+$ protons of water molecules) is the only origin of charge carriers responsible of the hopping process, the conduction within the present material is of ionic type [12, 15].

### 3.5.4. Dielectric constant

The dielectric relaxation can be analyzed in terms of dipolar and conductivity mechanisms. In the case of CoAl-CO$_3$-LDH sample, Figure 8 is showing the logarithmic frequency dependence of real part of dielectric constant. A relaxation is observed as a gradual decrease in $\varepsilon_r'$. This can be explained by the frequency dependent orientational polarization. In fact, permanent dipoles can align themselves following the applied field when frequencies are low. In this case they contribute fully to the total polarization. But with the increase of frequencies, dipoles are not able to follow the field because its variation is too rapid, so their contribution to the dielectric constant becomes negligible causing the decrease of $\varepsilon_r'$ with the increasing frequency. CoAl-CO$_3$-LDH exhibits interesting values of dielectric constant for low and medium frequencies then decreases gradually to attain 6.88 at high frequencies.

**Figure 9** shows the value of tan$\delta$ with frequency, measured at room temperature and calculated according to the following formula: $\tan\delta = \varepsilon_r'' / \varepsilon_r'$. Maximum of dispersion in the loss tangent is observed at low frequencies (10Hz to 100Hz) due to polarization phenomenon, leading to a maximum of energy dissipation. Then loss tangent decreases as the frequency of the alternating field increases. Beyond a frequency of 10$^4$Hz, the tangent of dielectric loss decreases to attain a value of 0.09 where the loss is minimal.

| Sample    | $\sigma_{dc}$ (S/m) | A        | B        | $n$ | $m$ | $R^2$ |
|-----------|---------------------|----------|----------|-----|-----|-------|
| CoAl-Co$_3$ | $6.75 \times 10^{-7}$ | $1.15 \times 10^{-7}$ | $2.61 \times 10^{-8}$ | 0.12 | 0.57 | 0.99 |

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Figure 8. Frequency dependence of real dielectric constant of layered double hydroxide based on cobalt and aluminum, and intercalated by carbonate ions. (Hz): Hertz.

Figure 9. Frequency dependence of tangent of dielectric loss of layered double hydroxide based on cobalt and aluminum, intercalated by carbonate ions.

4. Conclusion

Carbonate intercalated CoAl-LDH sample was prepared by the conventional co-precipitation method. According to the PXRD pattern, the sample exhibit a well crystalized hydrotalcite-like phase with carbonate ions in the interlayer space. FT-IR analysis was carried out to confirm the presence of gallery anions and the forming of LDH layers. Using TG analysis coupled to ICP analysis the chemical formula of the sample was determined.

Electric and dielectric properties of the LDH phase were systematically investigated by the complex impedance spectroscopy. The Nyquist diagram corresponding to CoAl-CO$_3$-LDH sample was adjusted by an equivalent electrical circuit consisting on three blocs serially arranged. Each bloc is a parallel arrangement of resistor (R) and constant phase element (CPE), allowing the determination of the
resistance and the relaxation time of each contribution. The imaginary parts of impedance and Modulus analysis magnified all contributions and confirmed relaxation times calculated previously. To have an idea about the conduction mechanism within the present material, $\sigma_{dc}$ was investigated by the adjustment by the double power law. The adjustment parameters allowed the determination of $\sigma_{dc}$ and gave an idea about the movement of charge carriers ($H^+$ protons of water molecules and gallery anions) under the applied field, which is found to be a long-range movement according to the value of the fractional exponents of the double power law. The movement of charge carriers is similar in both frequency independent region and dispersive region of $\sigma_{ac}$. The representation of frequency dependence of $\varepsilon'$ showed an interesting dielectric constant value at low frequencies with a gradual decrease at high frequencies. Moreover, the maximum of energy dissipation was observed at low frequencies, and then $\tan \delta$ decreased to attain 0.09 beyond $10^8$ Hz. According to these results, this material may be promising in the field of dielectrics and energy storage, especially for the assembly of nanocomposites and hybrid materials with interesting properties.

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