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## **Research** articles

# Impact of temperature dependent octahedra distortions on magnetic properties of Co-containing double layered hydroxides



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<i>Keywords:</i> LDH Structural distortions Magnetic susceptibility	Distortions of hydroxide octahedral complexes in the $\text{Co}^{II}{}_{n}\text{Al}^{III}$ layered double hydroxides (LDHs) ( $n = \text{Co}^{II}/\text{Al}^{III} = 2$ and 3) were studied as a function of the ratio of divalent-to-trivalent cations and temperature. A method for calculation the magnetic susceptibility of polycrystalline samples taking into account the statistical distribution of divalent and trivalent cations, and their effect on the distortions of the original structure is proposed. It is shown that the presence of a local maximum on the magnetic susceptibility curve of Co <sub>n</sub> Al LDHs compounds near $T \sim 160 \text{ K}$ is due to freezing of the lattice parameters and, as a consequence, freezing of the tilting fluctuations of the O–H bonds.				

# 1. Introduction

The general formula of the layered double hydroxides (LDHs) under study can be represented as  $[M_{1-x}^{II}M_{-x}^{III}(OH)_2]^{x+}(A^{y-})_{x/y}zH_2O$  [1] (hereafter  $M_n^{II}M_{-x}^{III}A$ , where n = (1 - x)/x is the cations ratio, A – anions, e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>2</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> etc.). The metal cations in the hydroxide layers are coordinated by six hydroxyl ions in such a way that O–H bonds are perpendicular to the plane of the layers (Fig. 1). A great majority of LDHs is rhombohedral (space group  $R\bar{3}m$ ).

Although some LDHs occur naturally as minerals, the absolute majority of layered double hydroxides are synthetic. The main areas of their application are catalysis and anion exchange [1]. In the latter, the anion-exchange ability of LDHs is usually considered regardless the cation content, while specific cations in the hydroxide layer can induce new effects and even novel functionalities in these materials.

In the LDHs with  $M^{\rm II} = {\rm Co}^{\rm II}$  or Ni<sup>II</sup>, onset of spontaneous magnetization and a peak of magnetic susceptibility were observed at 4–15 K [2–4]. Position of the susceptibility peak was found to depend on the interlayer gallery height rather than on nature (Fe<sup>III</sup>, Cr<sup>III</sup>, Mn<sup>III</sup> or Al<sup>III</sup>) of the trivalent cation and the  $M^{\rm II}/M^{\rm III}$  ratio. Moreover, it was shown that temperature of onset of the magnetic order in those LDHs is a function of the interlayer height regardless of the magnetic or non-magnetic nature of the intercalated anion [5].

Very recently, we have revealed an unusual kink of susceptibility of

 $Co_nAl$  LDHs with  $A = NO_3^-$  (n = 2, 3) in the range of 75–175 K [6]. The same behaviour was then observed in other  $Co_nAl$  compositions intercalated with other inorganic anions of different size and charge. This phenomenon appears to have a structural origin and certainly deserves a particular investigation.

Although it is not recognized yet, LDHs are of potential interest as convenient and unique objects for the experimental modelling of the 2-D quantum magnets. Provided the  $M^{II}$  and  $M^{III}$  cations are ordered, an atomic framework known as *kagome lattice* can be formed. Such a structure is the main prerequisite for the rarely observed *spin-liquid state* with the fully frustrated interactions between magnetic ions [7]. Because of the considerable size difference between Co<sup>II</sup> and Al<sup>III</sup>, some specific distortions of the cobalt environment can appear.

To the best of our knowledge, no detail study of the oxygen octahedra distortions, the cation ordering nor temperature evolution of the LDH structures below room temperature have been undertaken so far. The objectives of this work were to study structural changes in hydroxide layers and to correlate them with the magnetic phenomena in the  $Co^{II}$ -containing LDHs. The following compositions with the rhombohedral structure were prepared and characterized (the chemical formulas are presented in an anhydride form):  $Co_{0.67}Al_{0.33}$  (OH)<sub>6</sub>(NO<sub>3</sub>)<sub>0.33</sub> (Co<sub>2</sub>Al-NO<sub>3</sub>),  $Co_{0.75}Al_{0.25}$ (OH)<sub>6</sub>(NO<sub>3</sub>)<sub>0.25</sub> (Co<sub>3</sub>Al-NO<sub>3</sub>),  $Co_{0.67}Al_{0.33}$ (OH)<sub>6</sub>(CO<sub>3</sub>)<sub>0.17</sub> (Co<sub>2</sub>Al-CO<sub>3</sub>), and  $Co_{0.75}Al_{0.25}$ (OH)<sub>6</sub>(CO<sub>3</sub>)<sub>0.13</sub> (Co<sub>3</sub>Al-CO<sub>3</sub>).

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Fig. 1. Structure of (a) hydroxide layers and (b) oxygen octahedra of LDH.

### 2. Experimental details

 $Co_nAl-NO_3$  LDHs with n = 2 and 3 were synthesized via the conventional co-precipitation method as described in Ref. [8] using cobalt (II) nitrate hexahydrate ( $\geq$ 98%) and aluminium nitrate nonahydrate ( $\geq$ 98.5%) as the main reagents. A nitrate-to carbonate anion exchange in the  $Co_nAl-NO_3$  LDHs was carried out in a 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution at pH 8 under continuous stirring at room temperature for 1 week.

Chemical composition (in terms of the molar Co/Al ratio) of the obtained samples was characterized using a Hitachi 9100 transmission electron microscope (TEM) equipped with a Bruker energy dispersive spectroscopy (EDS) detector.

Phase content and crystallinity of the samples were monitored by methods of powder X-ray diffraction (XRD) using a Rigaku D/MAX-B diffractometer (Cu-radiation) at room temperature.

*In situ* T-XRD study were performed using a DRON-4 diffractometer (Fe-radiation) equipped with a low-temperature chamber either in vacuum or at ambient pressure over the range of 100–300 K.

#### 3. Distortions analysis

# 3.1. Distortions caused by M<sup>III</sup> ions

Each octahedron in the plane is surrounded by six other octahedra. In the case of its uniform filling by divalent or trivalent metal ions, an oxygen octahedron has a  $D_{3d}$  symmetry.

The Co<sup>II</sup> and Al<sup>III</sup> radii difference  $(R(Co^{II}) = 0.75 \text{ Å} \text{ and } R (Al^{III}) = 0.57 \text{ Å})$  leads to the appearance of various distortions of oxygen complexes. Besides, these distortions are affected also by the cations ratio, *n*. A shift of the surrounding oxygen ions may achieve 0.2 Å.

When  $M^{\text{II}}$  in any of the six neighbouring octahedra is substituted by  $M^{\text{III}}$ , the oxygen complex becomes distorted and the symmetry is lowered. Such distortions are a set of shifts of oxygen ions (towards  $M^{\text{III}}$ ) and hydrogen ions (in the opposite direction). Thus, there is an additional "clamping" of the OH-connection closer to the plane to keep the bound length.

In total there are 7 possible options for filling the outer ring of octahedra by  $M^{III}$  ions (without taking into account a specific location):

Table 1 The probability of different  $M^{\text{III}}$ -filling numbers depending on the  $M^{\text{II}} / M^{\text{III}}$  molar ratio

n	Number of neighbour M <sup>III</sup> ions								
	0	1	2	3	4	5	6		
2/1	0.072	0.25	0.347	0.25	0.099	0.02	0.002		
3/1 4/1	0.164 0.235	0.363 0.383	0.308 0.239	0.133	0.03	0.003	0		

from 0 (no  $M^{III}$ ) to 6 (full filling). The probability of each of these cases depends on the initial  $M^{II}/M^{III}$  ratio *n*:

Ultimately, there are 13 types of placements, the likelihood of which also depends on the total concentration of  $M^{II}/M^{III}$ .

Fig. 3 schematically shows some possible types of such distortions.

#### 3.2. Distortions stimulated by temperature

In situ X-ray diffraction analysis carried out for the  $Co_3Al-CO_3$  compound in the temperature range of 100–293 K showed a non-linear dependence of the lattice parameters on the temperature. The obtained dependences of the lattice parameters a(T) and c(T) are characterized by a rather sharp drop in the region of 293–200 K followed by a much weaker *T*-dependence at lower temperatures (Fig. 4). According to the estimates made, the total relative change in the lattice parameters in the investigated temperature range are about 0.3% and 0.5% for *a* and *c*, respectively.

It can be seen that decreasing temperature leads to a decrease of both parameters indicating a comprehensive compression of the lattice. The value of *c*-parameter is contributed by both the octahedra size and the interlayer distance. As temperature decreases, the octahedra shrink and the distance decreases. As a result, the oscillating hydrogen ions press closer to the octahedra plane. The *a*-parameter decrease is caused by chiral distortions of the octahedra in the layer plane. Moreover, both the angle of "compression" of oxygen-hydrogen bonds and the magnitude of chiral distortions are functions of lattice parameters. When  $T \sim 200 \text{ K}$  is reached, the dynamics change and the grating stop shrinking.

### 4. Magnetic susceptibility calculations

Based on the previously obtained crystallographic data [7], taking into account the temperature dependences of the lattice parameters, the distortions corresponding to each of the 13 types of arrangements (Fig. 2), the energy spectra of the LDHs in the external magnetic field were calculated. The calculations were performed using the MCFT method [9,10]. The main parameter of MCFT is the effective nuclear charge  $Z_{eff}$  of the central ion which depends on the strength of crystal field.

The main contribution to the formation of the magnetic properties of Co<sup>II</sup>-based LDHs is made by four Kramers doublets ( $3d^7$ -configuration, <sup>4</sup>F basic term) with energies ~ kT. At room temperature, all four doublets are populated. As temperature is decreased, the population of the upper doublets decreases. At low temperatures only the lowest doublet remains populated. Distortions of the octahedral complexes change the distances between doublets, which affects their population and, as a consequence, the magnetic properties of the compound.

Each of the types of distortions mentioned above is taken into account by the corresponding shifts of the ions in the octahedron (taking into account the shifts of the hydrogen ions associated with them). For example, the chiral distortions associated with the temperature variation of the lattice parameter a are given by the following shifts of the



**Fig. 2.** 13 types of  $M^{III}$  and  $M^{II}$  ions placements around  $M^{II}$  ion in the center of hexagon. Dark circles are  $M^{II}$ , light –  $M^{III}$  ions.



Fig. 3. Examples of possible types of distortions: (a) with three  $M^{\rm III}$  ions, (b) with one  $M^{\rm III}$  ion, (c) chiral distortions.



**Fig. 4.** The temperature dependences of the *a* and *c* lattice parameters of  $Co_3$ Al- $CO_3^*$ . Different symbols correspond to results of independent measurements. The solid line is a guide to the eyes.

 $^* The Co_3Al-CO_3$  is taken as an example. Only qualitative behavior of the lattice constants is taken into account in this work. Therefore, the quantitative difference between the results for Co\_3Al-CO\_3 and Co\_3Al-NO\_3 in this case is neglected.

oxygen-hydrogen pairs (in the octahedral coordinate system according to Fig. 3c):

$$\begin{bmatrix} x_1^{OH} - \Delta x & y_1^{OH} - \Delta y & z_1^{OH} - \Delta z \\ x_2^{OH} - \Delta x & y_2^{OH} + \Delta y & z_2^{OH} - \Delta z \\ x_3^{OH} + \Delta x & y_3^{OH} - \Delta y & z_3^{OH} + \Delta z \\ x_4^{OH} - \Delta x & y_4^{OH} - \Delta y & z_4^{OH} + \Delta z \\ x_5^{OH} + \Delta x & y_5^{OH} + \Delta y & z_5^{OH} - \Delta z \\ x_6^{OH} + \Delta x & y_6^{OH} + \Delta y & z_6^{OH} + \Delta z \end{bmatrix}$$
(1)

Modelling of the powder spectrum was carried out for various directions of the external magnetic field uniformly distributed in space.



Fig. 5. One eighth of sphere with uniformly distributed directions of the magnetic field vectors.

In the general case, the magnetic susceptibility tensor  $\chi_{\rho\rho}$  reflects the relationship between the magnetization of matter M(T) and the external magnetic field **B**:

$$\chi_{\theta\rho} = \mu_B \frac{\partial M_{\theta}}{\partial B_{\rho}} \tag{2}$$

Considering the fact that the free energy  $F\,{\rm can}$  be represented in the form

$$F = -kT \cdot \ln\left(\sum_{i=1}^{N} e^{-\frac{\varepsilon_i}{kT}}\right)$$
(3)

The temperature dependence of the diagonal components susceptibility will have the following form:

$$\chi_{\sigma\sigma} = \mu_B \frac{\partial M_{\sigma}}{\partial B_{\sigma}} = -\mu_B \frac{\partial^2 F(T)}{\partial B_{\sigma}^2} = \frac{\mu_B \sum_{i=1}^{N} \left(\frac{\partial e_i}{\partial B_{\sigma}}\right)^2 e^{-\frac{e_i}{kT}}}{\sum_{i=1}^{N} e^{-\frac{e_i}{kT}}}$$
(4)

where  $\varepsilon_i$  is the energy of the *i*-th electronic level, and the summation is over the entire set of the energy levels *N* along one direction of the magnetic field  $\sigma$ . The equations (1) and (4) have been applied for susceptibility calculations of every 13 patterns shown in Fig. 2.

The total susceptibility of the powder will represent a weighted sum of susceptibilities calculated for all directions  $\sigma$  (Fig. 5) and all types of allocations  $\lambda$ :

$$\chi(T) = \sum_{\lambda=1}^{13} \omega_{\lambda} \sum_{\sigma} \chi_{\sigma\sigma}^{(\lambda)}(T)$$
(5)

where  $\omega_{\lambda}$  is the corresponding weight from Table 2.

Table 2

Particular type of placement occurrence probabilities, taking into account the  $M^{II}/M^{III}$  ratio and the probabilities from Table 1.

n	Type of placement							
	а	b	с	d	е	f	g	
2/1	0.072	0.25	0.14	0.14	0.07	0.075	0.15	
3/1	0.164	0.363	0.123	0.123	0.062	0.04	0.08	
4/1	0.235	0.383	0.096	0.096	0.048	0.024	0.048	
	h	i	j	k	1	m		
2/1	0.025	0.04	0.04	0.02	0.02	0.002		
3/1	0.013	0.012	0.012	0.006	0.003	0		
4/1	0.008	0.005	0.005	0.003	0.001	0		



Fig. 6. Calculated  $\chi T$  curves of Co<sub>n</sub>Al-NO<sub>3</sub> LDHs with (*a*) n = 2 and 3 with  $Z_{eff} = 6.5$  and (b) n = 2 with different  $Z_{eff}$  in comparison to the experimental Co<sub>2</sub>Al-NO<sub>3</sub> curve (black line).

Using the procedure described above, the temperature dependences of the magnetic susceptibility  $\chi$  were calculated for three different molar ratios,  $n = M^{II}/M^{III} = 2$ , 3, and 4 (at a constant  $Z_{eff}$  parameter, with increasing  $Z_{eff}$  with increasing T and with decreasing  $Z_{eff}$  with increasing T for Co<sub>n</sub>Al-NO<sub>3</sub> LDHs. The results are shown in Fig. 6. The black line shows the experimental curve obtained for the Co<sub>2</sub>Al-NO<sub>3</sub> compound.

The experimental curve demonstrates the local maximum at  $T \sim 160$  K. Such a maximum arises due to the termination of the sharp contraction of lattice parameters and, consequently, freezing of the angle between the oxygen-hydrogen bond and the plane of the octahedra and freezing of distortions in the plane of the octahedra. The change of the effective nuclear charge makes it possible to vary the depth and slope of the curve, and the position of a maximum.

The experimental line in Fig. 6a is located between the lines calculated for  $Co_2Al-NO_3$  and  $Co_3Al-NO_3$ . It suggests some inhomogeneity in distribution of  $Al^{III}$  ions in the sample: there are local areas with a reduced content of  $Al^{III}$  ions, i.e., the regions corresponding to the  $Co_3Al-NO_3$  composition.

## 5. Conclusions

Distortions of oxygen octahedra in hydroxide layers of  $\text{Co}^{II}_{n}\text{Al}^{III}$ LDHs with different Co/Al molar ratio and the non-linear temperature dependence of the lattice parameters were studied.

Due to significant difference of radii, the non-equivalent locations of  $M^{\rm II}$  depending on the  $M^{\rm II}/M^{\rm III}$  ratio lead to the appearance of a large number of additional distortions that lower the initial symmetry of the octahedra.

The magnetic properties of cobalt-based LDHs strongly depend on the four lowest Kramers doublets. The energy spectra of  $Co_nAl-NO_3$ (n = 2 and 3) were calculated by the method of a modified crystal field theory with allowance of the spin-orbit interaction for all possible distortions and directions of the magnetic field.

It is assumed that the appearance of a local maximum of the magnetic susceptibility at  $T \sim 160$  K is due to the freezing of the lattice parameters, and the behaviour of the curve itself can be described by a non-linear change of the Co<sup>II</sup> effective nuclear charge. Besides, the presence of a contribution of the non-uniform distribution of Al<sup>III</sup> ions

and the appearance of regions with a reduced  $M^{II}/M^{III}$  ratio is shown on the example of the experimental  $\chi T$  curve of Co<sub>2</sub>Al-NO<sub>3</sub>.

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