

# Magnetic anisotropy in the Co<sup>II</sup>-Al<sup>III</sup>-nitrate layered double hydroxides with the Co/Al ratios 2, 3, and 4

Yurii Pashkevich, Roman Babkin  
*Department of theory of dynamic properties of complex systems*  
*O. O. Galkin Donetsk Institute for Physics and Engineering of NAS of Ukraine*  
Kharkiv-Kyiv, Ukraine  
[yu.pashkevich@gmail.com](mailto:yu.pashkevich@gmail.com)  
[r.yu.babkin@gmail.com](mailto:r.yu.babkin@gmail.com)

Vasili Rubanik Jr., Vasili Rubanik,  
Aleksandr D. Shilin  
*Institute of Technical Acoustics of NAS of Belarus,*  
*General Lyudnikov Ave. 13, 210023*  
Vitebsk, Belarus  
[ita@vitebsk.by](mailto:ita@vitebsk.by)

Daniel E.L. Vieira, Andrei N. Salak,  
*Department of Materials and Ceramics Engineering and CICECO-Aveiro*  
*Institute of Materials, University of Aveiro, 3810-193*  
Aveiro, Portugal  
[salak@ua.pt](mailto:salak@ua.pt)

Jūras Banys  
*Faculty of Physics, Vilnius University,*  
*Sauletekio Ave. 9, LT-10222*  
Vilnius, Lithuania  
[juras.banys@ff.vu.lt](mailto:juras.banys@ff.vu.lt)

**Abstract**—It is shown that the difference in the Co<sup>II</sup> and the Al<sup>III</sup> ionic radii and a random distribution of the Co ions in the metal hydroxide layers of layered double hydroxides (LDHs) result in a series of highly distorted Co(OH)<sub>6</sub> octahedral complexes. The distortions have been modelled by accounting for the Shannon ionic radii of metals and ligands. The energy of the four low lying Kramers doublets and its g-factors were calculated for all the Co-complexes. The statistical distribution of the distorted octahedra types has been shown to vary with cations content. It was found that the g-factors of the lowest Kramers doublets are highly anisotropic with different orientations of their main axes. The calculated broad range of the g-factor distribution is illustrated by the observed anomalies of the low temperature electron paramagnetic resonance response. The impact of the relative cations content  $n = (1-x)/x = \text{Co}^{\text{II}}/\text{Al}^{\text{III}}$  on the nanoparticles aspect ratio of the [Co<sup>II</sup><sub>1-x</sub>Al<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(NO<sub>3</sub>)<sub>x</sub>·zH<sub>2</sub>O LDHs has been considered.

**Keywords** — layered double hydroxides, oxygen octahedra, magnetic anisotropy, electron paramagnetic resonance

## I. INTRODUCTION

New effects and features that are discovered in 2-D nanomaterials make them very attractive as objects of fundamental studies. Owing to unique combination of functionalities, they find a variety of important applications, such as optoelectronics, catalysis, energy storage and conversion, sensing, and biomedicine [1].

Layered double hydroxides (LDHs) known also as anionic clays represent a numerous family of promising 2-D materials. In the majority of LDHs, the double metal cations are of the M<sup>II</sup>-M<sup>III</sup> type. Such compounds are composed of parallel layers of the [M<sup>II</sup><sub>1-x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> hydroxides, in which the oxygen octahedra MO<sub>6</sub> are edge-linked. Thickness of the hydroxide layer does not exceed 0.5 nm, while the interlayer height can be changed from about 0.3 nm to few nanometres depending on size, charge and arrangement of the intercalated anions [2].

Owing to the relative stability in air and the capacity to adapt various chemical compositions and the layer charge (which is a function of the M<sup>II</sup>/M<sup>III</sup> ratio), LDHs demonstrate unique features that make them very promising for new

applications beyond the conventional areas such as catalysis and anion-exchange.

Magnetic properties of LDHs that contain divalent cations of Co, Ni and/or trivalent cations of Mn, Cr, Fe in the hydroxide layers have been reported [3-7]. Magnetic ordering was found to occur in those LDHs at very low temperatures that makes unlikely a direct practical exploration of their magnetic transition. However, the dependence of their magnetic behaviour on the cation content and ratio as well as on the interlayer distance can be used in development of hybrid magnets and other functional materials [8-10]. Because of the layered nature of LDHs and a rhombohedral symmetry of the hydroxide layers, their crystallites are flake-like hexagons with the *c*-axis perpendicular to the flake face and large aspect ratio (i.e., the diameter-to-thickness ratio). Crystallites of the cobalt based layered double hydroxides are magnetically anisotropic. Such a property allows alignment of the crystallites in external magnetic field [11]. We have recently reported a magnetic field assisted formation of dense layers of the Co<sup>II</sup>Al LDH crystallites [12].

This work is a part of our systematic experimental and theoretical study of magnetic properties of Co<sup>II</sup>Al LDHs [13,14]. Here we report on a comparative study of magnetic anisotropy features of the Co<sup>II</sup>Al layered double hydroxides with the cobalt-to-aluminium molar ratio,  $n = (1-x)/x = 2, 3,$  and 4, and intercalated with nitrate anion (hereafter, Co(*n*)Al-NO<sub>3</sub> LDHs). We demonstrate that the considerable difference in ionic radii of Co and Al and a random distribution of Al ions both lead to the formation of a set of variously distorted nearest neighbour hydroxyl octahedral configurations for Co ions with very different magnetic ground states and a variety of the g-factor values. We suppose that the almost continuous g-factor variation in the range of more than one order degree can be one of a reason for the observed anomalous electron spin resonance (ESR) response in the Co(*n*)Al-NO<sub>3</sub> ( $n=2, 3, 4$ ).

## II. THEORETICAL CONSIDERATION

The cations in the LDH hydroxide layers form a honeycomb lattice. The average space group symmetry in

which Co and Al ions are not distinguished is  $\bar{R}3m$  (#166) [15]. The X-ray diffraction studies of  $\text{Co}(n)\text{Al}$  LDH do not reveal any superstructure peaks that would be expected in the case of the long-range cations ordering. The most prominent example of a possible ideal order may arise in the  $\text{Co}(2)\text{Al}$  LDH where in the case of undisturbed translation symmetry every Al ion has six cobalt ions as nearest neighbours and every Co ion is surrounded by three Co and three Al. In this ideal case, the net of Co ions forms so called magnetic kagome lattice.

The absence of the long-range cation ordering implies some random statistical distribution of the Co-Al pairs. It has been shown that there are thirteen types (configurations) of Co-Al surroundings around given Co ion. The statistical weight of each configuration varies in accordance with the Co/Al ratio,  $n$  [14]. The considerable difference in the ionic radii of  $\text{Co}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  in sixfold coordination ( $R(\text{Co}^{\text{II}})=0.75\text{\AA}$  versus  $R(\text{Al}^{\text{III}})=0.54\text{\AA}$ ) as well difference in valence state must lead to highly distorted hydroxyl octahedral cage with specific for each configurations oxygen's shift and tilting of the O-H bonds.

The rate of the oxygen distortions can be roughly estimated from comparison of the  $M\text{-O}$  distances in the same octahedral oxygen cage. For instance, in  $\text{CoCO}_3$  and  $\text{LaAlO}_3$ , in which the  $M\text{-O}$  ionic radii nicely follow to the sum of metal and oxygen ionic radii with  $R(\text{O}^{2-})=1.38\text{\AA}$ ,  $R_n(\text{Co-O}) = 2.1096\text{\AA}$  and  $R_n(\text{Al-O}) = 1.8997\text{\AA}$ , respectively. In  $\text{Co}(2)\text{Al}$  LDH, the averaged  $M\text{-O}$  distance is  $R_s(\text{Co-O})=R_s(\text{Al-O})=2.0018\text{\AA}$  [15]. This comparison demonstrates that to fulfil equality of ionic radii in the  $\text{Co}(n)\text{Al}$  LDH, oxygen ions must shift up to  $0.2\text{\AA}$ . A very large oxygen shift strongly affects the magnetic anisotropy of Co ions, which can be very different for all thirteen possible Co-Al configurations.

To proceed with direct calculations of energy spectrum and g-factor values for  $\text{Co}^{\text{II}}$  ions in the possible Co-Al configurations, we used the Modified Crystal Field Theory (MCFT), the original semi-empirical approach for calculations of the electronic structure of paramagnetic ions in coordination complexes with arbitrary symmetry and numbers of ligands [16,17]. The spin-orbit coupling is incorporated into MCFT and the positions of ligands, the ligands charges and the effective nuclear charge of the metal ion are the input parameters.

To build a quantitative model of distorted oxygen cages (e.g. to find positions of ligands) we fixed the distances between cations in the octahedral layer and used the average oxygen positions from structural data on the  $\text{Co}(2)\text{Al}$  LDH intercalated  $\text{CO}_3^{2-}$  [15] at a starting point. Note that in the following analysis of the magnetic anisotropy of  $\text{Co}(n)\text{Al}$  LDHs, the type of the intercalated anion does not matter.

The oxygen distortion pattern in a given Co-Al configuration can be found if the condition of the real mentioned above distances  $R_n(\text{Co-O})$  and  $R_n(\text{Al-O})$  are satisfied. This request is fulfilled when 1) the common oxygen for three neighbouring Co ions shifts by  $0.213\text{\AA}$  perpendicular to the plane of the octahedral layer ( $ab$ -plane); 2) the common oxygen for two Co and one Al neighbouring ions shifts towards Al ion by  $0.158\text{\AA}$  with the displacement vector in the  $ab$ -plane; 3) the common oxygen for one Co and two Al neighbouring ions shifts in a middle of the Al-Al connecting line by  $0.158\text{\AA}$  and with the displacement vector

in the  $ab$ -plane. It is supposed that for the cases 2) and 3) the O-H bonds with length  $R_n(\text{O-H}) = 0.97\text{\AA}$  being perpendicular to the octahedral layer are tilted by the angle  $\theta=12^\circ$  in the direction opposite to the oxygen shift. An example of the oxygen shifts is shown in the Fig. 1.

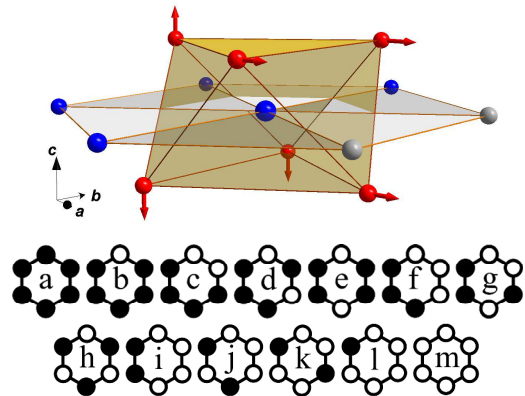


Fig. 1. The distortion of cage of oxygen ions (in red) around Co ion with four Co ions (in blue) and two Al ions (in grey) as cation's nearest neighbours. The hydrogen ions are not shown. This case corresponds to the type (c) of the thirteen possible Co-Al surrounding (a-m) [14] shown below. Dark circles are  $M^{\text{II}}$  ions, empty circles are  $M^{\text{III}}$  ions. The Co ions in the centres of hexagons are not shown.

The energy spectra of  $\text{Co}^{\text{II}}$  (configuration  $3d^7$ , basic term  $^4F$ ) for all 13 surroundings have been calculated using the distorted hydroxyls cages described above, the nominal valence charges of ligands and the  $\text{Co}^{\text{II}}$  effective nuclear charge of  $6.55|e|$ . The high spin state of  $\text{Co}^{\text{II}}$  has been detected for all surroundings. Only four lowest Kramers doublets with the energy lower than  $300\text{ cm}^{-1}$  are relevant for the LDH magnetic properties. For instance, the set of these energies in  $\text{cm}^{-1}$  for configurations (c) and (h) are: (0, 50.4, 159, 169.5) and (0, 18.9, 66.3, 206.3), respectively. The calculated g-factor values of the ground state doublets of (c)- and (h)-configurations are:

$$g_{xx}(c)=3.65; g_{yy}(c)=5.48; g_{zz}(c)=1.88;$$

$$g_{xx}(h)=0.27; g_{yy}(h)=0.25; g_{zz}(h)=6.61;$$

Here we chose Cartesian axes, where the z-axis is perpendicular to the octahedral layer and the x-axis is parallel to the  $a$ -lattice vector. The most symmetric (h)-configuration, which is the basic unit of an ideal Co-Al order in a  $\text{Co}(2)\text{Al}$  LDH, shows anomalously large g-factor anisotropy. Furthermore, in this configuration, the second Kramers doublet at  $18\text{ cm}^{-1}$ , which has the lowest energy among second doublets of all others configurations, also shows a highly anisotropic g-factor:  $g_{xx}(h,18) = 0.016$ ;  $g_{yy}(h,18) = 0.036$ ;  $g_{zz}(h,18)=3.198$ .

The full set of the g-factor xx- and zz -components distributed among all possible Co-Al configurations in the  $\text{Co}(2)\text{Al}$  LDH is shown in Fig. 2. We accounted for the statistical weight of each configuration for the particular Co/Al ratio,  $n=2$  [14].

The results of calculations based on our simplified structural model demonstrate that in  $\text{Co}(n)\text{Al}$  LDH, the g-factor of Co ions may vary by more than one order of magnitude, between 0.25 and 6.61. Our initial suggestion about fixed  $M\text{-M}$  distances can be violated in real LDH structures and the discrete g-factor distribution in Fig. 2 is replaced by a smoother one. Nevertheless, the range of variation should remain almost the same, since large and

multidirectional shifts of ligands is the main reason for this feature. In general, no magnetic anisotropy is expected for Co(2)Al LDH under  $g$ -factor distribution shown in Fig. 2.

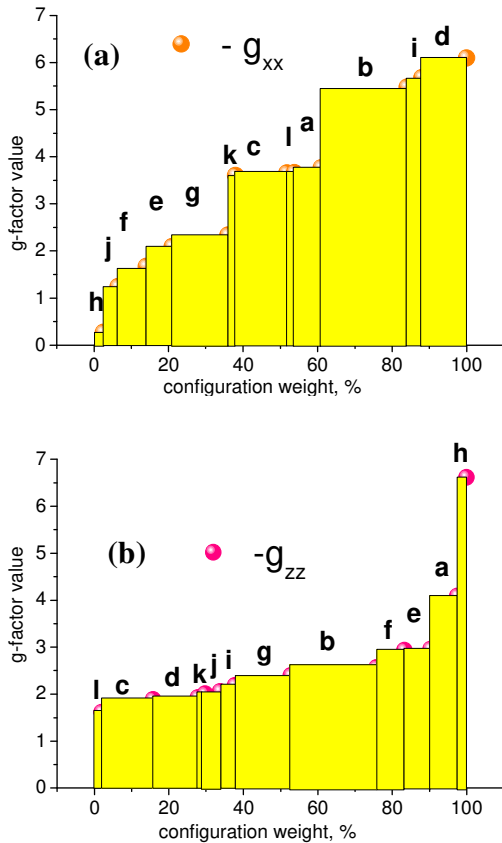


Fig. 2. The diversity of the  $g$ -factor's  $xx$ - (a) and  $zz$ - (b) components in Co(2)Al LDH. The letters above rectangles denote the type of the Co-Al configurations enumerated in Ref. [14] (see also Fig. 1). The width of rectangle reflects the statistical weight of the given configuration and the height of rectangle corresponds to the  $g$ -factor magnitude which is denoted by the colour spheres at the rectangle's right side.

The magnetic anisotropy of LDH nanoflakes may arise, if in the statistical limit of the Co-Al distribution, the weight of some configuration sufficiently prevails over others. We predict that for Co(4)Al LDH, the magnetic anisotropy lies in the **ab**-plane. In this case, the (b) configuration has the largest statistical weight of 0.383 [14] with the  $g$ -factor values  $g_{xx}(b)=5.47$ ;  $g_{yy}(b)=3.34$ ;  $g_{zz}(b)=2.56$ .

Another scenario can realize if the Co-Al distribution resides in between of two limiting cases, namely the fully random statistical distribution and the long-range order with perfect translational symmetry. A short-range order, which is not detectable in X-ray diffraction studies, may introduce some preferable configuration. In Co(2)Al LDH, a kagome

like short-range order forms within the (h)-type configuration. In accordance with the above calculations, a prevailing number of the (h) configuration in Co(2)Al LDH will induce magnetic anisotropy perpendicular to the octahedral layer.

### III. EXPERIMENTAL DETAILS AND SAMPLE PREPARATION

The experimental procedure of synthesis of the Co( $n$ )Al-NO<sub>3</sub> layered double hydroxides ( $n = 2, 3$  and 4) studied in this work was the same as that described in [11]. Phase content and crystal structure of the obtained LDH powders were monitored by X-ray diffraction (XRD) using a PANalytical X'Pert Powder diffractometer (CuK $\alpha$  radiation, 45 kV, 40 mA) at ambient conditions.

Size and morphology of the LDH nanoparticles were characterized using a Hitachi HD-2700 scanning transmission electron microscope (STEM) with an electron beam accelerating voltages of 80-200 kV. For a STEM study, the samples were prepared by dispersing 0.1 g of slurry into 5 ml of ethanol using an ultrasonic bath.

XRD study has confirmed that the obtained compositions are single-phase LDHs. It was found from analysis of the XRD patterns that the  $a$ -parameter of the Co( $n$ )Al-NO<sub>3</sub> LDHs appropriately increases with increasing  $n$  - value (i.e. with the Co content) as ionic size of cation Co<sup>II</sup> in octahedral coordination is bigger than that of cation Al<sup>III</sup>. In Co(2)Al-NO<sub>3</sub>, we observed no superlattice Bragg peaks that could arise as a result of long-range ordering of Co and Al ions. This is an indication of either a random distribution of Al ions or at least a short-range of kagome-like order with a few lattice constants length.

The STEM images of crystallites of the Co( $n$ )Al-NO<sub>3</sub> LDHs are shown in Fig. 3. It is seen that the diameter of the crystallites decreases as the Co/Al ratio increases.

Directional magnetic anisotropy that suggests a respective short range order in Co(2)Al-NO<sub>3</sub> is uncovered under application of static magnetic field during precipitation of dispersed flake-like nanocrystallites of this LDH [12]. It has been shown that the aligning action of magnetic field results in highly oriented dense layers of the Co(2)Al-NO<sub>3</sub> nanocrystallites with the flake surfaces perpendicular to the magnetic field (Fig. 4). Such anisotropy evidences the presence of kagome-lattice type of short-range order with the number of Co-Al (h)-configurations prevailing in the distribution expected for fully random Co-Al distribution.

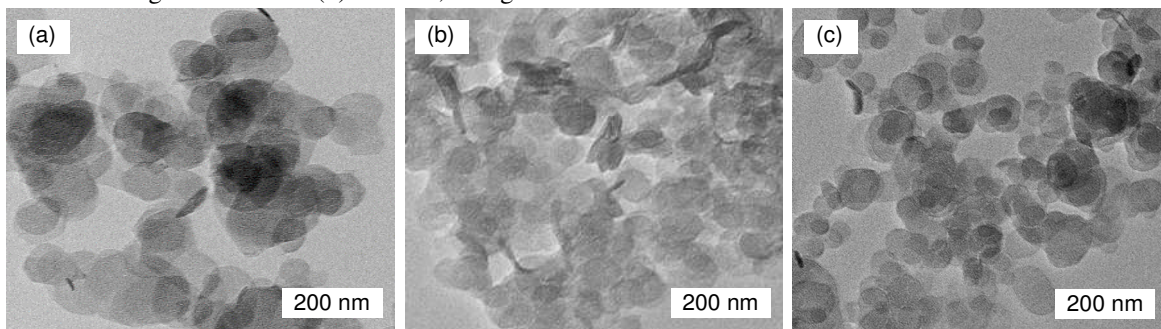


Fig.3 STEM images of the dispersed crystallites of Co(2)Al-NO<sub>3</sub> (a), Co(3)Al-NO<sub>3</sub> (b), and Co(4)Al-NO<sub>3</sub> (c).

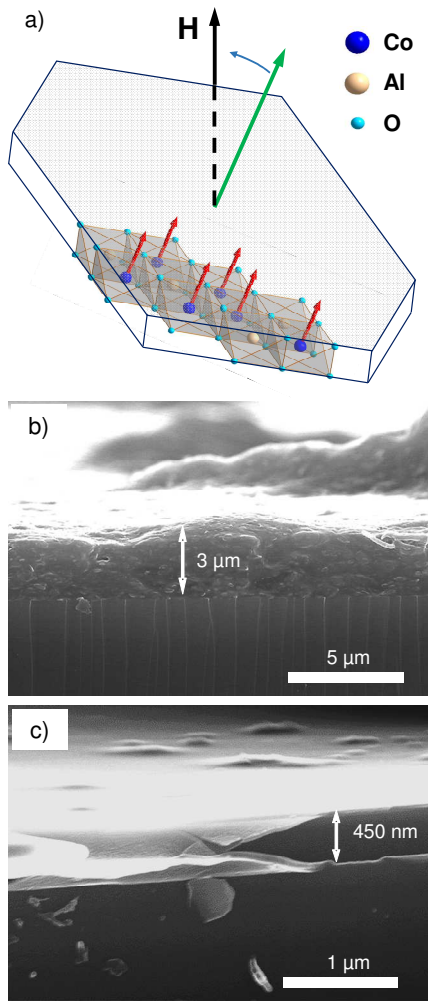


Fig.4 (a) Scheme of the magnetic field action on the precipitation process of a hexagonal crystallite of  $\text{Co}(2)\text{Al-NO}_3$ . A fragment of the octahedral layer is only shown. The red arrows represent magnetic moments of  $\text{Co}^{\text{II}}$  cations. The presence of the directional magnetic anisotropy due to  $g$ -factor anisotropy  $g_{zz} \gg g_{xx}, g_{yy}$  confirms by SEM images (cross section views) of layers of the  $\text{Co}(2)\text{Al-NO}_3$  crystallites deposited on glass substrates without (b) and with (c) application of magnetic field [12]. Magnetic field was applied perpendicular to the substrate surface.

#### IV. ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

The presence of Co-Al disorder in  $\text{Co}(n)\text{Al-NO}_3$  LDHs was analysed via electron paramagnetic resonance (EPR) study. For the EPR measurements, the LDH powders were compacted into discs of about 3 mm in diameter and about 0.3 mm thick. Continuous wave (CW) EPR measurements were performed at X-band microwave frequency ( $\sim 9.4$  GHz) using a conventional Bruker ELEXSYS E580 EPR spectrometer. A 1 mW microwave power was applied. The strength and frequency of the modulating field were set to 6 G and 100 kHz, respectively. The cooling of the samples was performed in a zero-field mode.

Temperature dependent CW EPR spectra of  $\text{Co}(n)\text{Al-NO}_3$  ( $n = 2, 3, 4$ ) are shown in Fig. 5. The significant changes and strong baseline distortions are observed in the spectra of  $\text{Co}(2)\text{Al-NO}_3$  and  $\text{Co}(3)\text{Al-NO}_3$  recorded below 70 K. A similar behaviour was detected in the spectra of  $\text{Co}(4)\text{-Al-NO}_3$  below 50 K. No EPR signals from the samples were obtained above these temperatures.

We relate the observed features of the EPR spectra to the large number of different  $\text{Co}(\text{OH})_6$  coordination complexes which induce a wide-range variation of the  $g$ -factor values. Our model calculations found a few excited Kramers doublets in the range of  $40\text{-}300\text{ cm}^{-1}$ , which should promote fast relaxation of the electron spin. Therefore EPR spectra are too broad to be observed at temperatures with  $k_B T$  comparable with energy of the lowest excited doublets. Such a situation is typical of the EPR data on high-spin  $\text{Co}^{\text{II}}$  complexes [18]. The exchange interactions may also contribute to anomalous broadening in spite of its quite low value of a few K in  $\text{Co}(n)\text{Al-NO}_3$  [13].

We also considered the observed low-field line at about 0.12 T labelled as " $\text{Co}^{2+}$ " in Fig. 5a with the  $g$ -factor value of about 5.7. A signal is clearly seen in the  $\text{Co}(2)\text{Al}$  EPR spectra but is absent for LDHs with  $n=3$  and 4 (Fig.5(b,c)). Since the  $g$ -factor value of this signal is rather high, it can be assigned to the EPR signal from the (h)-type Co-Al coordination. The absence of this signal in EPR spectra of  $\text{Co}(n)\text{Al}$  LDHs with  $n=3, 4$  can be explained by a relatively small number of the (h)-type configurations in these compounds. The signal is not seen at 5 K, which is the

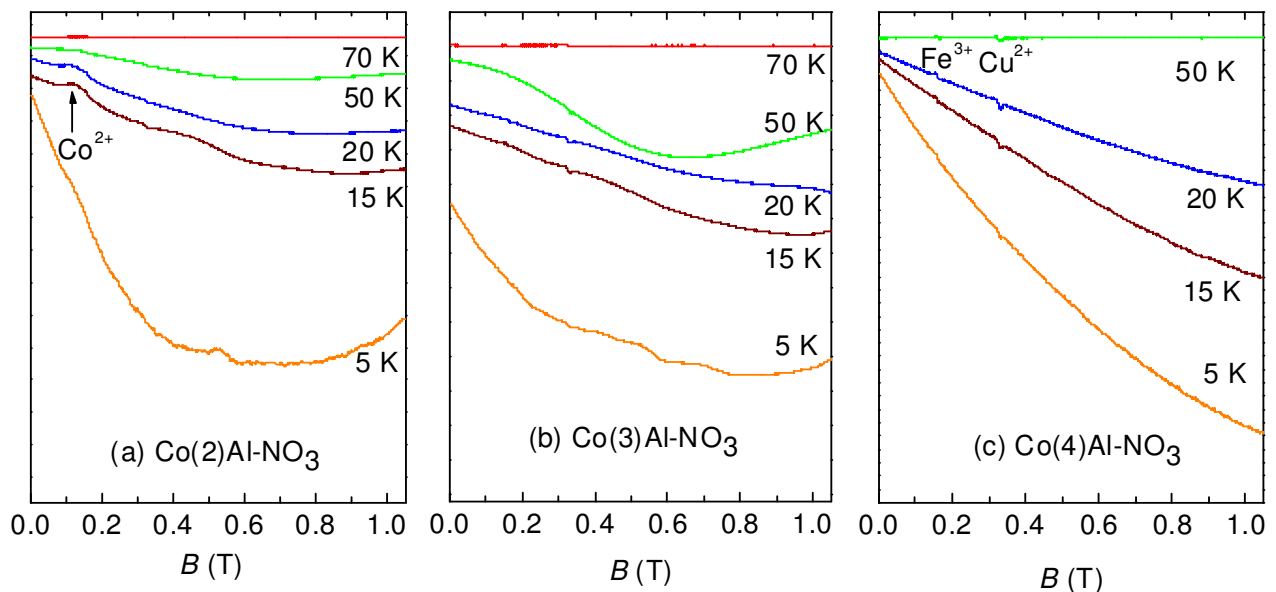


Fig. 5. X-band CW EPR spectra of  $\text{Co}(n)\text{Al-NO}_3$  ( $n = 2, 3$  and  $4$ ) recorded at different temperatures. Signal of  $\text{Co}^{2+}$  in distorted octahedral environment with  $g$ -factor around 5.7 is indicated by arrow in the panel (a). Impurity signals of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  of cryostat are marked in the panel (c).

temperature close to the onset of magnetic moment [13]. It is interesting that in [10], the highly anisotropic g-factors ratio  $g_{zz}/g_{xx} \sim 13 \div 20$  has been restored using a susceptibility fitting procedure for Co(2)Al LDH with various types of anions.

The EPR spectra of the Co(*n*)Al-NO<sub>3</sub> LDHs cannot determine the real composition of Co-Al configurations; however, a large diversity of them is clearly seen in every LDH compound under study.

#### CONCLUSION

We considered the microscopic origin of the magnetic anisotropy observed in Co(*n*)Al LDHs (*n*=2,3,4). The considerable difference in the Co and Al radii is the main cause of the highly anisotropic magnetic properties of various Co-Al surroundings. The random Co-Al distribution with short-range order results in very complex magnetic behaviour. Particularly, the direction of magnetic anisotropy depends on the Co/Al ratio.

#### ACKNOWLEDGMENT

The authors thank Dr. Mantas Šimenas (University College London) and Prof. Andreas Pöpl (University of Leipzig) for the EPR measurements and useful discussion. This work was supported by the Belarus-Ukraine grant "Effect of magnetic field and ultrasound on the anion-exchange properties of iron- and cobalt-containing layered double hydroxides" (2020-2021) N0120U000216, T20YKA-020. The authors also acknowledge the Slovakia-Portugal bilateral project FAST-LDH (2019-2020)/APVV-SK-PT-18-0019.

#### REFERENCES

1. C. Tan, X. Cao, X. J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. H. Nam, M. Sindoro, and H. Zhang, Recent advances in ultrathin two-dimensional nanomaterials, *Chem. Rev.* **117** (2017) 6225-6331.
2. D. E. Evans and R. C. T. Slade, Structural Aspects of Layered Double Hydroxides. In *Structure & Bonding* (Springer-Verlag, Berlin, Germany), **119** (2005), pp. 1-87.
3. M. Intissar, R. Segni, C. Payen, J. P. Besse, and F. Leroux, Trivalent cation substitution effect into layered double hydroxides Co<sub>2</sub>Fe<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>6</sub>Cl nH<sub>2</sub>O: study of the local order. Ionic conductivity and magnetic properties, *J. Solid State Chem.* **167** (2002) 508-516.
4. E. Coronado, J. R. Galan-Mascaros, C. Martí-Gastaldo, A. Ribera, E. Palacios, M. Castro, and R. Burriel, Spontaneous magnetization in Ni-Al and Ni-Fe layered double hydroxides, *Inorg. Chem.* **47** (2008) 9103-9110.
5. J. J. Almansa, E. Coronado, C. Martí-Gastaldo, and A. Ribera, Magnetic properties of Ni<sup>II</sup>Cr<sup>III</sup> layered double hydroxide materials. *Eur. J. Inorg. Chem.* (2008) 5642-5648.
6. E. Coronado, C. Martí-Gastaldo, E. Navarro-Moratalla, and A. Ribera, Intercalation of [M(ox)<sub>3</sub>]<sup>3-</sup> (M=Cr, Rh) complexes into Ni<sup>II</sup>Fe<sup>III</sup>-LDH. *Appl. Clay Sci.* **48** (2010) 228-234.
7. F. Giovannelli, M. Zaghrioui, C. Autret-Lambert, F. Delorme, A. Seron, T. Chartier, and B. Pignon, Magnetic properties of Ni(II)-Mn(III) LDHs. *Mater. Chem. Phys.* **137** (2012) 55-60.
8. Q. Wang and D. O'Hare, Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets, *Chem. Rev.* **112** (2012) 4124-4155.
9. G. Abellán, C. Martí-Gastaldo, A. Ribera, and E. Coronado, Hybrid materials based on magnetic layered double hydroxides: a molecular perspective. *Acc. Chem. Res.* **48** (2015) 1601-1611.
10. J. A. Carrasco, S. Cardona-Serra, J. M. Clemente-Juan, A. Gaita-Ariño, G. Abellán, and E. Coronado, Deciphering the role of dipolar interactions in magnetic layered double hydroxides. *Inorg. Chem.* **57** (2018) 2013-2022.
11. M. Shao, M. Wei, D. G. Evans, and X. Duan, Magnetic-field-assisted assembly of CoFe layered double hydroxide ultrathin films with enhanced electrochemical behavior and magnetic anisotropy, *Chem. Commun.* **47** (2011) 3171-3173.
12. A. N. Salak, D. E. L. Vieira, I. M. Lukienko, Yu. O. Shapovalov, A. V. Fedorchenko, E. L. Fertman, Yu. G. Pashkevich, R. Yu. Babkin, A. D. Shilin, V. V. Rubanik, M. G. S. Ferreira, and J. M. Vieira, High-power ultrasonic synthesis and magnetic-field-assisted arrangement of nanosized crystallites of cobalt-containing layered double hydroxides, *ChemEngineering*, **3** (2019) 00062.
13. D. E. L. Vieira, A. N. Salak, A. V. Fedorchenko, Yu. G. Pashkevich, E. L. Fertman, V. A. Desnenko, R. Yu. Babkin, E. Čížmár, A. Feher, A. B. Lopes, and M. G. S. Ferreira, Magnetic phenomena in Co-containing layered double hydroxides, *Low Temp. Phys.* **43** (2017) 977-981.
14. R. Yu. Babkin, Yu. G. Pashkevich, A. V. Fedorchenko, E. L. Fertman, V. A. Desnenko, A. I. Prokhvatilov, N. N. Galtsov, D. E. L. Vieira, and A. N. Salak, Impact of temperature dependent octahedra distortions on magnetic properties of Co-containing double layered hydroxides, *J. Magn. Magn. Mater.* **473** (2019) 501-504.
15. A. V. Radha, P. V. Kamath, and C. Shivakumara, Order and disorder among the layered double hydroxides: combined Rietveld and DIFFaX approach, *Acta Crystallogr. B.* **63** (2007) 243-250.
16. K. V. Lamonova, S. M. Orel, and Yu. G. Pashkevich, Modified Crystal Field Theory and its Applications, Kyiv: Akadempriodyka (2019) 226 p.
17. K. V. Lamonova, E. S. Zhitlukhina, R. Yu. Babkin, S. M. Orel, S. G. Ovchinnikov, and Yu. G. Pashkevich, Intermediate-spin state of a 3d ion in the octahedral environment and generalization of the Tanabe-Sugano diagrams. *J. Phys. Chem. A.* **115** (2011) 13596-13604
18. L. Banci, A. Bencini, C. Benelli, D. Gatteschi, and C. Zanchini, Spectral-structural correlations in high-spin cobalt(II) complexes. In: *Structures versus Special Properties. Structure and Bonding*, Springer, Berlin, Heidelberg, **52** (1982) 37-96.