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Research Paper

Combined effect of 2D nature and structural glass behaviour and true magnetic contribution to the low-temperature heat capacity of layered double hydroxides

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ABSTRACT

Keywords: Layered double hydroxide Heat capacity Glassy state Boson peak Magnetic ordering Heat capacity of cobalt-aluminium and magnesium-aluminium layered double hydroxides (LDH) with the divalent-to-trivalent cations ratio (*n*) of 2 and 3, and intercalated with NO₃⁻, CO₃²⁻ and OH⁻, was measured as a function of temperature between 2 and 100 K. Magnetic contribution to the heat capacity (C_{mag}) of Co_nAl LDH was extracted from comparison of the *C*(*T*) dependences with the respective reduced dependences of their non-magnetic counterparts, Mg_nAl LDH. At the lowest measured temperatures, the magnetic contribution to the heat capacity (C_{mag}) of Co-containing LDH was found to be almost two orders of magnitude bigger than their lattice contribution. In a zero magnetic field, the low-temperature C_{mag} of Co₂Al LDH was measured to be proportional to $T^{2.6}$, while for Co₃Al LDH, $C_{mag} \sim T^2$ was observed. An application of an external magnetic field was revealed to converge these dependences to $C_{mag} \sim T^3$ in compounds with both n = 2 and 3. However, the conversion in Co₂Al LDH occurred at lower values of external magnetic field (50 kOe) than that in Co₃Al LDH (90 kOe).

It was revealed from the C(T) behaviour of the non-magnetic LDH at the lowest measured temperatures that they possess the features typical for both a 2D solid and a structural glass. The reduced $C(T)/T^3$ heat capacity of Mg_nAl LDH intercalated with nitrate was found to demonstrate a so-called boson peak, which is a manifestation of a glassy state. The observed low-temperature structural glassy state in LDH was associated with the disorder of the intercalated species.

1. Introduction

Layered double hydroxides (LDH) represent a large family of anionic clays. The characteristic feature of these materials is that their hydroxide layers contain metal cations of different charge, $M^{2+}-M^{3+}$ or M^+-M^{3+} [Evans and Slade, 2005] is such a ratio that each layer is positively charged: $M(OH)_{2}^{X+}$. The stability of the LDH structure results from the electrostatic interactions between the mixed metal hydroxide layers and the anionic species A^{y-} between them. Water molecules in the interlayer screen the electrostatic repulsion between the anion species and contribute to the hydrogen bonding [Evans and Slade, 2005]. The chemical composition of most LDH is described by the general formula

 $M_{(1-x)}^{2+}M_x^{3+}(OH)_2(A^y)_{x/y}zH_2O$. LDH are capable of non-destructive change of the chemical composition *via* anion exchange. Therefore, the ability to intercalate and exchange functional anionic species is the most explored feature of LDH [Li and Duan, 2006; Tian et al., 2015; Taviot-Guého et al., 2017; Mishra et al., 2018]. As a rule, in such applications of LDH, the features of electron configuration of the metal cations M^{2+} and M^{3+} are disregarded.

Layered hydroxides containing mixed metal cations with individual or cooperative properties (*e.g.*, luminescent or magnetic) were shown to extend the functionalities of LDH [Smalenskaite et al., 2017; Smalenskaite et al., 2018; Abellán et al., 2013; Abellán et al., 2015; Carrasco et al., 2018; Vieira et al., 2021; Carrasco et al., 2023]. Temperature- and

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field-dependent magnetic behaviours of LDH with $M^{2+} = Co$, Ni, and/or M^{3+} = Fe, Cr, Mn were studied. The onset of spontaneous magnetization and a peak of magnetic susceptibility in those LDH were observed at 4-16 K, depending on cation composition and the interlayer distance [Bujoli-Doeuff et al., 1991; Intissar et al., 2002; Almansa et al., 2008; Coronado et al., 2008; Coronado et al., 2010; Giovannelli et al., 2012; Vieira et al., 2017]. Such a low temperature of magnetic ordering makes direct exploitation difficult; nevertheless, LDH which contain magnetic cations offer unique opportunities for experimental modelling of cooperative phenomena in 2D magnets [Babkin et al., 2019; Oestreicher et al., 2021]. The features of magnetic LDH that make it possible to change the magnetic characteristics, such as the ordering temperature, the coercive field, and even the ferro- or antiferromagnetic nature of the system through variations in the cation content and ratio, as well as the interlayer distance, have been considered in detail in a very recent review [Carrasco et al., 2023]. Owing to these prominent features, the LDH containing magnetic cations find application in magnetic hybrids [Abellán et al., 2015; Silva et al., 2023].

A combined experimental and theoretical study of the lowtemperature heat capacity and the magnetization of $Co_n^{2+}AI^{3+}$ LDH (n = Co/AI = 2, 3) intercalated with different anions to provide a wide range of the interlayer distances has recently been reported [Pashkevich et al., 2023]. The theoretical calculations suggested that the observed distinctive features of the magnetic field-dependent behaviour of these LDH can be explained in terms of an excess of cobalt coordinations with a 2:1 Co—Al ordering (spatially organized as clusters) over the statistical distribution in the compositions with the cation ratio of 2, whereas the cation distribution in the LDH with n = 3 is rather random.

It was revealed that the temperature of the magnetization onset in Co_nAl LDH depends on the interlayer distance in the case of the low basal spacing (*d*) values only (below ~10 Å), which agrees with the previously drawn conclusion [Carrasco et al., 2018] that an increase in the interlayer distance in these LDH weakly affects the interlayer dipolar interactions. It was also found that the temperature of the Schottky-like anomaly in the heat capacity C(T) of Co_nAl LDH measured in a zero field is independent of the interlayer distance. The most exciting result of these studies is that the magnetic interactions *via* intralayer coupling of the metallic cations are much stronger than the interlayer dipolar interactions, which allows one to consider $Co_n^{2+}Al^{3+}$ LDH as the embodiments of the ideal 2D magnets.

One should note that the reported low-temperature C(T) studies in either magnetic LDH or non-magnetic ones are still very scarce [Coronado et al., 2008; Pashkevich et al., 2023; Jayanthi et al., 2023].

In this paper, the magnetic contribution to the low-temperature heat capacity of Co_nAl LDH (n = 2 and 3) intercalated with NO₃⁻, CO₃²⁻ and OH⁻ has been analysed to clarify the magnetic two-dimensional nature of these solids. To extract the magnetic contribution to the heat capacity of cobalt-aluminium layered hydroxides, the experimental C(T) data for Co_nAl LDH were compared with the respective reduced dependences of heat capacity for their non-magnetic counterparts, MgnAl LDH intercalated with the same anionic species. The low-temperature heat capacity of non-magnetic LDH was found to demonstrate some interesting features related to the fundamental properties of solids, which have not been experimentally observed before. The approach to extract the true magnetic contribution from the total heat capacity of magnetic materials using the heat capacity of their non-magnetic analogues [Liang et al., 2015; Somesh et al., 2023] has previously been reported. The novelty of this work is that such an approach was successfully applied to layered double hydroxides.

2. Experimental details

Cobalt (II) nitrate hexahydrate (\geq 98 %), magnesium nitrate hexahydrate (99 %), aluminium nitrate nonahydrate (\geq 98.5 %), sodium hydroxide (\geq 98 %), sodium nitrate (\geq 99.5 %), sodium carbonate (\geq 99.95 %) were purchased from Sigma-Aldrich, while nitric acid (65

%) was purchased from Merck. All the reagents were used as received.

The cobalt-aluminium and the magnesium-aluminium LDH with the cation ratio n = (1-x)/x of 2 and 3, and intercalated with anion A^{y} -(hereafter, $M_n^{2+}M^{3+}$ -A) were prepared using two conventional routes. Co_nAl-NO₃ and Mg_nAl-NO₃ LDH were obtained by conventional coprecipitation from nitrate salts of the respective metals as described in Refs. [Salak et al., 2019; Serdechnova et al., 2016] without any high-power mechanical activation. The compositions with n = 2 and 3 were synthesized at the same conditions. The nitrate-intercalated compounds in the form of slurry were then used to obtain LDH intercalated with either hydroxide or carbonate *via* the respective anion exchange reactions in the solution containing these species. Both the synthesis procedure and anion exchange reactions were conducted in nitrogen atmosphere in decarbonated water.

In such a way, the compositions mentioned hereafter as Mg_2 Al-OH, Mg_n Al-CO₃, and Co₂Al-OH, Co_nAl-CO₃ were prepared. (For more details on the exchange conditions see Table S1 in *Supplementary Material*). The resulting dense slurries were washed with deaerated water followed by centrifugation. The final product was dried at 330 K for 24 h in air.

The morphology of the LDH samples was investigated by scanning transmission electron microscopy (STEM) using a Hitachi HD-2700 microscope operated at 200 kV. Small amounts of the LDH slurries of each composition were dispersed in ethanol solution using an ultrasound bath and deposited on TEM grids.

For the purposes of the chemical and the phase analyses, the crystal structure characterization and magnetic measurements, the LDH slurries were dried at 330 K for 24 h.

An inductively coupled plasma spectrometer (Horiba Jobin Yvon Ultimata2CTM) was used for chemical analysis of the LDH compositions under study before and after the anion-exchange procedure. The samples were dissolved in a 0.1 mol L⁻¹ solution of HNO₃ and analysed with a solution flow of about 3 ml/min. The spectral lines of 167.02, 238.89 and 279.55 nm were used for estimation of Al, Co and Mg content, respectively. A crystal water content per formula unit was evaluated from thermogravimetric (TG) analysis using a Thermal Analysis System NEXTA STA300 (Hitachi). A weight loss of the powder samples was measured in air with heating rate of 5 K/min. The experimentally found chemical compositions of the obtained LDH are presented in Table S2 in *Suppl. Mater*.

Phase purity and crystal structure of the obtained LDH powders were monitored using a PANalytical X'Pert Powder diffractometer operated at 45 kV and 40 mA in Cu K α radiation with the exposition corresponding to about 1 s per step of 0.02° at room temperature. In the case of cobaltcontaining samples, a diffracted beam monochromator was used to suppress the fluorescence contribution. The lattice parameters of the LDH compositions and their basal spacings were preliminary calculated from the angular positions of the diffraction reflections (003), (006) and (110) and then refined using the FullProf suite [Rodriguez-Carvaja], 1993] in the profile matching mode (see Table S3 in *Suppl. Mater.*) and compared with the previously reported values [Baird et al., 1995; Radha et al., 2007; Johnsen et al., 2010; Serdechnova et al., 2016; Pashkevich et al., 2023].

For measurements of magnetic-field-dependent properties, the LDH powders were compacted into discs of about 3 mm in diameter and about 0.3 mm thick. The temperature dependence of heat capacity C(T) was measured using the Quantum Design Physical Properties Measurement System over the range of 1.9–60 K in a magnetic field up to 90 kOe.

3. Results and discussion

3.1. Comparative analysis of low-temperature heat capacity

The low-temperature heat capacity of Co_nAl LDH (n = 2,3) intercalated with anions of different chemical nature, size and charge was found to be strongly dependent on the external magnetic field [Pashkevich et al., 2023]. Results of the *C*(*T*) measurements conducted

in different magnetic fields indicate a magnetic contribution to the lowtemperature heat capacity, which is suppressed by an increasing field (as an example see Fig. S6 in *Supplementary Material*).

To analyse the contributions to the heat capacity of Co_nAl LDH at low temperatures, the C(T) behaviour of these compounds was compared with that of their non-magnetic counterparts, Mg_nAl LDH, intercalated with the same anions. Ionic radius of Mg²⁺ in octahedral coordination is very close to that of Co²⁺ [Shannon, 1976]. As a result, the lattice parameter values of the respective Mg_nAl and Co_nAl are similar (see Figs. S2-S4 and Table S3 in *Suppl. Mater.*). Moreover, the same method applied for preparation of Mg_nAl LDH and Co_nAl LDH can guarantee a similar morphology (shape and dimensions of the crystallites), which does not change in a course of anion exchange (Fig. S5). Therefore, Mg_nAl and Co_nAl LDH were chosen for comparative analysis. In contrast to cobalt-containing layered hydroxides, no magnetic contribution to the heat capacity is possible in magnesium-containing ones.

The temperature dependences of the heat capacity of Co_nAl LDH and their Mg_nAl counterparts are shown in Fig. 1 and Fig. 2, respectively. Notice the scale difference of the low-temperature reduced heat capacity, C/T^3 , for magnetic and non-magnetic LDH, while the temperature range is the same. This fact is in general agreement with the theoretical prediction that at low temperatures, the magnetic (spin) contribution to the heat capacity of non-metallic magnets is much larger than the lattice (phonon) one [Akhiezer et al., 1968].

In the case of non-magnetic solids, such as Mg_nAl LDH, only the lattice contribution, C_{lat} , to the heat capacity is expected. The low-temperature lattice heat capacity of a 3D perfect crystal is usually described by the Debye model as $C_{\text{D}}T^3$, assuming the contribution of solely acoustic phonons. The presence of any other vibrational states outside the Debye continuum can be revealed from deviations in the reduced thermal conductivity C/T^3 versus T.

In structurally quasi 2D objects, particularly layered solids such as LDH, which have metal hydroxide octahedral planes weakly connected by anions in the interlayer, C_{lat} is expected to demonstrate several temperature ranges with different $C_{\text{lat}}(T)$ dependences. The type of dependence in each range is determined by the relation between temperature and the Debye temperatures: Θ - for the in-plane and θ_{\perp} - for the out-of-plane (flexural) acoustic modes. According to general consideration [Landau and Lifshitz, 1980], interlayer interactions are neglected in the lowest temperature range and the resulting phonon dispersions yield the $C_{\text{lat}}(T)$ dependences in the following sequence: $C_{\text{lat}} \propto T^3$, then $\propto T^2$, and $\propto T$ with increasing temperature. C_{lat} is a linear function of *T* in the range of $\theta_{\perp} < T < < \Theta$. With further temperature rise, the increasing interlayer interactions result in *3D-merization*



Fig. 1. Temperature dependence of the reduced heat capacity, C/T^3 , of the Co_nAl LDH studied. The inset shows a magnified high-temperature region of the graph.



Fig. 2. Temperature dependence of the reduced heat capacity, C/T^3 , of the Mg_nAl LDH. Dashed lines represent the SPM fits using Eq. (2).

(whereas optical phonons still do not participate), and the $C_{lat}(T)$ dependence is restored into $\propto T^3$. One should note that the three aforementioned $C_{lat}(T)$ dependences cannot be presented together as a *T*-polynomial because the coefficients of the *T*, T^2 , and T^3 -containing terms are functions of temperature.

One of the characteristic features of $M^{2+}-M^{3+}$ LDH is that the divalent and trivalent cations in the metal position of the hydroxide layers, as well as the intercalated species in the interlayers, are typically disordered. Each intercalated anion can be arranged/oriented in many different ways without violating the LDH framework electroneutrality, and the energy necessary to switch between possible positions is very low. Both these features are expected to manifest themselves as a structural glassy state with the well-known linear *T* dependence of the low-temperature heat capacity [Zeller and Pohl, 1971; Anderson et al., 1972]. Thus, the unique situation of the LDH compounds is a possible coexistence of the temperature ranges in which two mechanisms, namely the 2D structure and the glassy state, contribute to the $C_{\text{lat}}(T) \sim T$ item.

As seen from Fig. 2, among the non-magnetic LDH under study, only Mg₂Al-OH and Mg₂Al-CO₃ demonstrate a $C_{\text{lat}} \sim C_{\text{D}}T^3$ behaviour (constant value of C/T^3) and solely in the range of 10 to 20 K. With decreasing temperature, a deviation from the 3D Debye model to the $C_{\text{lat}} \sim T$ dependence (increasing value of C/T^3) occurs. Such a linear C_{lat} versus *T* behaviour, indicative of both the 2D structural nature of LDH and a structural glassy state, was observed in all the non-magnetic LDH studied (Fig. 2). Notice that in this study, it was impossible to reach the extremely low temperatures where for 2D structures a T^3 -dependence of the heat capacity is expected due to undistinguished contribution of all three acoustic modes of the octahedral metal hydroxide layers into phonon density of states in this energy/temperature range. One can see below that it is also questionable whether the T^2 -dependences can be distinguished from the obtained experimental data.

3.2. The features of low-temperature heat capacity of the non-magnetic LDH. Manifestation of the structural glassy state

The temperature-dependent heat capacity of LDH exhibits a significant maximum at about 9 K (Fig. 2), the so-called boson peak (BP), which is also typical for highly disordered systems (glasses) [Zeller and Pohl, 1971]. The origin of this behaviour is associated with the intercalated nitrate anions, as the Mg_nAl LDH intercalated with other anions demonstrate no certain boson peak (Fig. 2). A hint of BP is only seen in Mg₃Al-CO₃ in a vicinity of 12 K. The observed differences in the lowtemperature *C*(*T*) dependences of the non-magnetic LDH under study is discussed in detail below.

The structural glassy state in the NO₃-intercalated LDH is suggested to result from the uncertainty of positions of this flat anion in the interlayer [Xu and Zeng, 2001; Salak et al., 2012]. A requirement of the layer-interlayer electroneutrality does not allow a "flat-lying" arrangement of nitrate in $M_n^{2+}M^{3+}$ LDH with n = 2 and 3. It was concluded from the combined diffraction and spectroscopic study that the most likely arrangement of nitrate anions in the interlayer is a "tilt-lying", at which the direction of the anion plane creates a tilting angle perpendicular to the hydroxide layers of an LDH [Salak et al., 2012] with the azimuthal angle unfixed. The numerous independent possible orientations of NO₃ result in high disorder in the arrangement of the species in the LDH interlayer. The shapes and positions of boson peaks of Mg2Al-NO3 and Mg₃Al-NO₃ LDH (Fig. 2) are essentially similar despite the difference in the content of the intercalated nitrate anions, which certainly points to a disorder-related origin of these peaks. The insensitivity of the BP position to the concentration of defects is a generally recognized feature of structural glassy states [Parshin, 1994].

Different positions of nitrate anions in the interlayer have the same binding energy (local minima), while to change orientation, an energy barrier *W* should be exceeded. Tunnelling between two energetically equivalent states and respective splitting of these energy levels provides an excess of the density of states in the case of a barrier with sufficiently low energy, which nevertheless must be strong enough to prevent resonance tunnelling [Anderson et al., 1972]. The so-called tunnel model (TM) operates with a double-well potential separating two level states (TLS), which are sources of additional low-energy vibrational density of states. A TLS-type contribution to the heat capacity is presented by the term $C_{TLS}T$ [Anderson et al., 1972]. The extension of the TM, the soft potential model (SPM), can be used to describe the temperature behaviour of the heat capacity right below BP [Vdovichenko et al., 2015; Ramos, 2004]:

$$C_{\rm lat} = C_{\rm TLS}T + C_{\rm D}T^3 + C_{\rm SM}T^5 \tag{1}$$

Where $C_{\rm SM}T^5$ is a contribution responsible for quasi-localized soft modes located in the single-well potential. However, for 2D structures in the temperature range below BP, one can also expect a contribution from the flexural layer vibrations. Therefore, the linear term Eq. (1) is composed of two components:

$$C_{\rm lat} = (C_{\rm TLS} + C_{\rm D\perp})T + C_{\rm D}T^3 + C_{\rm SM}T^5$$
(2)

Eq. (2) was used to fit the C/T^3 experimental data below 12 K for all the non-magnetic LDH studied. One can see from Fig. 2 that the fitting was successful, with an adequate description of the experimental data below the boson peaks. The fitting parameters (the coefficients in Eq. (2)) are presented in Table 1. At the fitting procedure, the values of coefficients C_{TLS} and $C_{\text{D}\perp}$ cannot be extracted independently from their sum; although estimation of C_{TLS} and $C_{\text{D}\perp}$ is possible through detailed comparison of heating capacity data of LDH with varying cation ratio while intercalated with the same anion.

Using the SPM approach, one can obtain some parameters characteristic of the structural glassy state in non-magnetic LDH under study. The energy barrier *W* represents the crossover energy from tunnelling states to the quasi-localized vibration states. The *W* value corresponds to the thermal energy of a few Kelvin and separate regions where the TLS and the SM contributions dominate. This parameter was determined from the minimum position in C/T^3 versus *T* as $W/k_B \approx 1.8 \bullet T_{min}$ [Ramos and Buchenau, 1997]. In turn, T_{min} can be calculated using the parameters from Eq. (2), namely $T_{min} = [(C_{TLS} + C_{D\perp})/C_{SM}]^{1/4}$. The boson peak energy was found via the relation $E_{BP} = 5 \bullet T_{BP}$ [Krivchikov et al., 2012]. The values obtained for T_{min} , W/k_B , T_{BP} , and E_{BP} are listed in Table 1. Note that the value *W* is overestimated due to the presence of the 2D structural component.

Let us discuss the values of the coefficients and other parameters obtained from fitting the experimental data using Eq. (2) with respect to the type of intercalated anion (Table 1).

The coefficients $C_{\rm D}$ demonstrate a general trend in accordance with the Debye model of the acoustic mode contribution. $C_{\rm D}$ can be described by the equation [Landau and Lifshitz, 1980]:

$$C_{\rm D} = const \cdot \left(s_{\parallel} s_{\perp}^{\rm in} s_{\perp}^{\rm out} \right)^{-1} = const \cdot \left(\frac{\rho_{\rm HL}^2 \rho}{E_{\parallel} E_{\perp}^{\rm in} E_{\perp}^{\rm out}} \right)^{1/2}$$
(3)

Here s_{\parallel} , s_{\perp}^{in} and s_{\perp}^{out} are the generalized sound velocities: for intralayer longitudinal sound, for intralayer transversal sound, and for out-of-layer transversal sound, respectively; E_{\parallel} , E_{\perp}^{in} and E_{\perp}^{out} are the rigidity modules along the corresponding directions; ρ is the density of the entire LDH and $\rho_{\rm HL}$ is the density of a single octahedral metal hydroxide layer (HL). The generalized sound velocities can be defined from the relation $k_{\rm B}\Theta_{\rm iD}a_i =$ hs_i , where $\Theta_{\rm iD}$ is the Debye temperature and $k_{\rm B}\Theta_{\rm iD}$ is the energy of acoustic phonon of branch *i* at the Brillouin zone boundary, a_i is the respective lattice parameter. Assuming that the intralayer modulus E_{\parallel} and E_{\perp}^{in} are the same for all LDH, as they consist of almost the same single octahedral hydroxide layers, one gets the following equation to estimate the coefficient $C_{\rm D}$ for $M_n^{2+}M^{3+}$ LDH intercalated with anion A_m :

$$C_D(A_m) = const \left(\frac{\rho(A_m)}{E_{\perp}^{out}(A_m)}\right)^{1/2}$$
(4)

According to Eq. (4), the $C_D(A_m)$ value lowers with the LDH density decreasing whereas a smaller anion content x in LDH with the cation ratio of 3 as compared to those with n = 2 (see the general formula of an LDH in Introduction) implies a lower transversal rigidity. It is reflected in the fitting parameters reported in Table 1 as an inequality $C_D(Mg_2Al-A_m) < C_D(Mg_3Al-A_m)$. One can conclude from a simple comparison of the $C_D(A_m)$ values that they obey the following inequality, in which the transversal rigidity of Mg_3Al-NO_3 LDH is the softest and the transversal rigidity of Mg_2Al-OH LDH is the hardest (for more detail see *Suppl. Mater.*):

$$E_{\perp}^{\text{out}}(\text{Mg}_{3}\text{Al} - \text{NO}_{3}) < E_{\perp}^{\text{out}}(\text{Mg}_{2}\text{Al} - \text{NO}_{3}) < < E_{\perp}^{\text{out}}(\text{Mg}_{3}\text{Al} - \text{CO}_{3}) < E_{\perp}^{\text{out}}(\text{Mg}_{2}\text{Al} - \text{CO}_{3}) < < F_{\perp}^{\text{out}}(\text{Mg}_{2}\text{Al} - \text{OH})$$
(5)

The peculiarities of the anion arrangement in the interlayer are also directly visible. The transverse stiffness of the carbonate-intercalated LDH, in which flat CO_3^{2-} anions are coplanar with the metal hydroxide layers [Evans and Slade, 2005; Sasai et al., 2019] is expectedly higher as compared to the LDH intercalated with "tilt-lying" nitrate anions. The differences in the spatial arrangement of the anions also manifest themselves in the differences in the lattice parameter along the *c*-axis (see Table S3 in *Suppl. Mater.*). The strongest lateral stiffness in Eq. (5) corresponds to the smallest *c*-parameter.

Table 1

The fitting parameters of the temperature-dependent heat capacity obtained using Eq. (2).

Composition	$C_{\text{TLS}} + C_{\text{D}\perp}$	$C_{\rm D}$	$C_{\rm SM}$	T _{min}	W/k _B	Т _{вр}	$E_{\rm BP}$
	(mJ mol ⁻¹ K ⁻²)	(mJ mol ⁻¹ K ⁻⁴)	(mJ mol ⁻¹ K ⁻⁶)	(K)	(K)	(К)	(cm ⁻¹)
Mg ₂ Al-NO ₃	0.84578	0.28609	0.00987	3.0425	4.7115	9.15	31.77
Mg ₃ Al-NO ₃	0.65775	0.35356	0.00668	3.1501	5.6701	8.80	30.56
Mg ₂ Al-CO ₃	1.18475	0.16791	0	-	-	-	-
Mg ₃ Al-CO ₃	0.95787	0.18917	6.26946•10 ⁻⁴	6.2520	11.2536	12.1	40.02
Mg ₂ Al-OH	1.70945	0.12119	0	-	-	-	-

The second component of the *T*-linear part of the lattice contribution to the heat capacity, $C_{D\perp}T$, arises from the cation layer flexural vibration density of states, in which the quadratic part of its dispersion curve dominates [Landau and Lifshitz, 1980]. The corresponding coefficients $C_{D\perp}$ depend only on the bending energy of the single octahedral metal hydroxide layer, and the interlayer interaction can be neglected due to the relatively weak connection with the anions. Besides, the bending energy of the layer is determined by the hydroxyl network and, therefore, does not depend much on the M^{2+}/M^{3+} cation ratio. Under this rough approximation, one can suppose that $C_{D\perp}$ coefficients are the same for all the Mg-Al LDH under study, and the variation of the sum $C_{TLS} + C_{D\perp}$ is only determined by the C_{TLS} coefficients.

Thus, the observed general trend of an increase in the $C_{\text{TLS}} + C_{\text{D}\perp}$ value (Table 1) when changing anions in the anion sequence NO₃⁻, CO₃²⁻, OH⁻ follows solely by a change in the C_{TLS} parameter and reflects a corresponding increase in the anion TLS density. One can also see in Table 1 the remarkable inequality $C_{\text{TLS}}(\text{Mg}_3\text{Al-}A_m) < C_{\text{TLS}}(\text{Mg}_2\text{Al-}A_m)$ for the same anions but different M^{2+}/M^{3+} ratio that simply corresponds to a decrease of the number of TLS per formula unit due to the relative reduction of the anion content (see the general formula of an LDH in Introduction).

The TLS density simply corresponds to the number of possible independent anion positions with equal energy in the interlayer space. The experimentally found values of the parameters (Table 1) suggest the following relations:

$$C_{\text{TLS}}(\text{Mg}_{3}\text{Al} - \text{NO}_{3}) < C_{\text{TLS}}(\text{Mg}_{2}\text{Al} - \text{NO}_{3}) < C_{\text{TLS}}(\text{Mg}_{3}\text{Al} - \text{CO}_{3}) < C_{\text{TLS}}(\text{Mg}_{2}\text{Al} - \text{CO}_{3}) < C_{\text{TLS}}(\text{Mg}_{3}\text{Al} - \text{OH})$$

$$(6)$$

thereby indicating that the number of possible positions increases from Mg_3Al - NO_3 (the smallest among the LDH under study) to Mg_2Al -OH (the largest).

Let us consider the observed BP features based on the modified soft potential model, the so-called soft-mode dynamic model (SMDM) [Klinger and Kosevich, 2001; Klinger and Kosevich, 2002]. According to SMDM, the boson peak arises due to an additional density of states caused by a crossover and following hybridization of an acoustic phonon branch with the localized soft optical phonon modes. The frequency range of the crossing point defines the BP position, T_{BP} . This mechanism can induce the heat capacity boson peak even in fully ordered compounds [Krivchikov et al., 2022].

In case of LDH, translational modes, in which neighbouring hydroxide layers undergo in-plane out-of-phase vibrations, play the role of those soft optic phonon modes. The localization of these modes is ensured by the violation of translational symmetry along the layers packing direction. The interlayer interaction defines the frequency of these modes and the lateral stiffness. This explains the correlation of the observed increase in the boson peak temperature ($T_{\rm BP}$ in Table 1) with the increase in lateral stiffness $E_1^{\rm out}$ shown in Eq. (5):

$$T_{\rm BP}(\rm Mg_3Al - \rm NO_3) < T_{\rm BP}(\rm Mg_2Al - \rm NO_3) < T_{\rm BP}(\rm Mg_3Al - \rm CO_3) \tag{7}$$

No boson peak in the Mg₂Al-CO₃ and Mg₂Al-OH LDH (with the highest lateral stiffness among studied LDH) has been detected in this study. A similar behaviour (without any BP in the low-temperature heat capacity *versus T*) was recently reported in Zn₂Al LDH intercalated with either carbonate, chloride or sulphate [Jayanthi et al., 2023]. In the frame of the suggested mechanism [Krivchikov et al., 2022], this indicates that the crossing point between optical mode and acoustic one in these LDH is considerably shifted due to sufficiently high frequency of the former.

The barrier energy value *W* also reflects the anion's features. The decrease of nitrate concentration with increasing *n* in Mg_nAl-NO₃ LDH implies a reduction of the average distance between its different positions that leads to a higher barrier for Mg₃Al-NO₃ as compared to Mg₂Al-NO₃. Accordingly, more than 100 % higher *W* value for Mg₃Al-CO₃ LDH

in comparison with those of any of Mg_nAl-NO_3 LDH (see Table 1) implies much stronger bonding energy of carbonate anions in the interlayer than that of the nitrate anions. This bonding is anticipated to be stronger for Mg_2Al-CO_3 .

The BP is a result of an excess in the vibrational density of states at low frequencies that arises due to crossover and hybridization of acoustic modes and some modes with frequencies lower than the acoustic ones at the Brillouin zone edge. It can be determined spectroscopically by inelastic neutron scattering, as well as using Fourier transform infrared spectroscopy and Raman spectroscopy techniques. The last two spectroscopies can give this information only if the translation symmetry is broken. This condition is realized in LDH due to anion disorder. Thermodynamically, the additional density of states is seen as a maximum of C/T^3 dependence. The combined FTIR and Raman measurements of the Mg₂Al-A ($A = CO_3$, NO₃, OH) revealed peaks at $60-70 \text{ cm}^{-1}$ that have the averaged energy lower than that of the acoustic modes at the Brillouin boundaries around 150-170 cm⁻¹ [Kagunya et al., 1998]. A similar peak in the vicinity of 60 cm^{-1} was detected in the vibrational spectra of Zn₂Al LDH intercalated with either pyrovanadate or nitrate and assigned to the translational lattice mode of the mixed-metal hydroxide layers [Salak et al., 2012]. All these experimental results indicate that the SMDM is an adequate model to describe the low-temperature heat capacity of the non-magnetic LDH.

One should note that from the SMDM point of view, cationic disorder by itself plays no role in the onset of the linear *T*-dependence of the heat capacity since the tunnel barrier is of the order of the metal-ligand binding energy, and TLS cannot occur. Besides, cation disorder has no impact on the BP formation as the vibration spectrum of a single hydroxide layer does not contain the optical phonons branches with frequencies lower than the acoustic ones. The optic-like phonons typical for cation vibrations in a hydroxyl octahedral cage of an LDH have energies of order 200–400 cm⁻¹ and cannot contribute to BP.

3.3. The features of the low-temperature heat capacity for magnetic LDH. Extraction of the true magnetic contribution

The temperature dependence of the reduced heat capacity of Co₂Al-NO₃ LDH and its non-magnetic counterpart Mg₂Al-NO₃ are shown in Fig. 3a. The total heat capacity of Co₂Al-NO₃ consists of magnetic and lattice contributions, $C_{\text{total}} = C_{\text{lat}} + C_{\text{mag}}$. To estimate the C_{lat} for Co₂Al-NO₃, the ratio of 1.27 between the molar weights of Co₂Al-NO₃ and Mg₂Al-NO₃ was used. Then the lattice contribution to the heat capacity of Co₂Al-NO₃ (Fig. 3a). A two-orders-of-magnitude difference between the C_{total} of Co₂Al-NO₃ in a zero field and the C_{lat} demonstrates the dominant role of the magnetic contribution to the heat capacity at the lowest temperatures. Even at 90 kOe, the maximum value of the reduced total heat capacity of Co₂Al-NO₃, C_{total}/T^3 is 16.8×10^{-4} J K⁻⁴ mol⁻¹, which is by a factor of two higher than that of the lattice contribution of this compound, $C_{\text{lat}}/T^3 = 8.62 \times 10^{-4}$ J K⁻⁴ mol⁻¹.

The estimated (using the data for Mg₂Al-NO₃) lattice contribution to the total heat capacity of Co₂Al-NO₃ allowed us to extract the net magnetic contribution (Fig. 3b). The temperature dependence of C_{mag} obtained in a zero magnetic field shows an explicit peak at about 5 K. An application of a small magnetic field of 2 kOe results in a shift of the peak to the higher temperature and an increase of the absolute value of C_{mag} . Further increase of the field up to 90 kOe shifts the C_{mag} peak to higher temperatures (Fig. 4). When the magnetic field value is between 2 and 30 kOe, the maximum value of C_{mag} is almost constant, while an increasing field above 50 kOe gradually suppresses the peak (Fig. 3b).

Analysis of the low-temperature behaviour of the magnetic heat capacity of Co₂Al-NO₃ revealed that $C_{mag} \sim T^{2.6}$ in a zero magnetic field and keeps this proportionality up to 30 kOe (Fig. 5). The change of the dependence to the $C_{mag} \sim T^3$ was found to occur between 50 and 90 kOe, in the same magnetic field range, where a decrease of the C_{mag} peak is observed (Fig. 3b).

V. Tkáč et al.



Fig. 3. (a) Temperature dependence of the reduced heat capacity of Co_2Al-NO_3 LDH. The lattice contribution to the heat capacity of Co_2Al-NO_3 is shown as green open circles. (b) Temperature dependence of the magnetic heat capacity of Co_2Al-NO_3 in different magnetic fields. The solid lines represent the total heat capacity of Co_2Al-NO_3 and Mg_2Al-NO_3 (for comparison). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Magnetic field dependence of the peak position (T_{max}) of the magnetic heat capacity of Co₂Al-NO₃.

The heat capacity of Co_3Al -NO₃ LDH was analysed in the same way as that of Co_2Al -NO₃ one. The temperature-dependent C_{total} of its nonmagnetic counterpart, Mg₃Al-NO₃, was used to modulate the $C_{lat}(T)$ of



Fig. 5. Temperature dependence of the magnetic heat capacity of Co_2AI -NO₃ in different magnetic fields (log-log scale). See the main text for the details about the fitting models.

 Co_3Al-NO_3 (Fig. 6a). The ratio of 1.33 between the molar weights of Co_3Al-NO_3 and Mg_3Al-NO_3 was applied.

Just as in the case of Co_2Al - NO_3 described above, the total heat capacity of Co_3Al - NO_3 at low temperatures is about two orders of magnitude higher than that of Mg_3Al - NO_3 , indicating the dominant



Fig. 6. (a) Temperature dependence of the reduced heat capacity of Co_3Al-NO_3 LDH. The lattice contribution to the heat capacity of Co_3Al-NO_3 is shown as green open circles. (b) Temperature dependence of the magnetic heat capacity of Co_3Al-NO_3 in different magnetic fields. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

magnetic contribution. One can see from Fig. 3a and Fig. 6a that the modelled $C_{\text{lat}}(T)$ coincides with the measured $C_{\text{total}}(T)$ data at high temperatures both for Co₂Al-NO₃ and Co₃Al-NO₃, which indicates that the approach to use the heat capacity dependences of the non-magnetic counterparts was correct.

The C_{mag} contribution to the heat capacity of Co₃Al-NO₃ is characterized by a broad maximum, as depicted in Fig. 6b. The T_{max} value for this compound at each magnitude of the applied magnetic field between zero and 90 Oe is lower than the respective value for Co₂Al-NO₃ (*cf*.: Fig. 3b and Fig. 6b). The C_{mag} peak gradually shifts to higher temperatures with an increasing magnetic field (Fig. 4). The peak value of C_{mag} demonstrates a non-monotonic dependence on the field, reaching the maximum at about 20 kOe (Fig. 6b). The $C_{mag}(T)$ measured in a zero magnetic field shows a round peak (Fig. 6b), without any sign of lambdatype shape observed in Co₂Al-NO₃ at the same conditions (Fig. 3b).

The C_{mag} versus T in the log-log scale shows a $C_{\text{mag}} \sim T^2$ proportionality at the lowest temperatures in a zero magnetic field (Fig. 7). The slope gradually rises with an increasing magnetic field, and at 90 kOe C_{mag} is proportional to T^3 . As compared to Co₃Al-NO₃, the $C_{\text{mag}} \sim T^3$ behaviour in Co₂Al-NO₃ LDH is observed in a smaller magnetic field, namely already at 50 kOe (Fig. 5).

In the recent study of Co₂Al-NO₃ and Co₃Al-NO₃ LDH, the observed magnetic field-dependent peak of Ctotal was identified as a Schottky-like anomaly caused by a set of ground-state Kramers doublets, which are split by the various internal exchange fields [Pashkevich et al., 2023]. Consequently, the width of the heat capacity peak is determined by the width of the splitting energy distribution of Kramers doublets, *i.e.*, by the density of states. One can see from Fig. 3b that the peak of magnetic heat capacity of Co₂Al-NO₃ in a zero magnetic field and at 2 kOe demonstrates weak lambda-type transition features, indicating a possible longrange magnetic ordering. Such field-dependent behaviour may indicate possible ferromagnetic ordering or spin-glass state formation in these compounds. Both mentioned magnetic states are characterized by C_{mag} $\sim T^{3/2}$ dependence [Anand et al., 2012]. On the other hand, the $C_{
m mag}$ \sim T^3 dependence is expected for the 3D spin wave excitations in the conventional gapless antiferromagnet, but the presence of a gap in the magnetic density of states yields the transformation of the temperature dependence in $C_{\text{mag}} \sim T^2$ form [Li et al., 2016]. Interestingly, the $C_{\text{mag}} \sim$ $T^{2.6}$ dependence in a zero magnetic field for the Co₂Al-NO₃ system and $C_{\rm mag} \sim T^2$ dependence for the Co₃Al-NO₃ system are close to those limiting predictions. In both Co2Al-NO3 and Co3Al-NO3 LDH, application of the external magnetic field converges their zero-field temperature dependences to $C_{\text{mag}} \sim T^3$, which is due to broadening of the energy range of the initial density of states [Pashkevich et al., 2023].



Fig. 7. Temperature dependence of the magnetic heat capacity of Co_3AI -NO₃ in different magnetic fields (log-log scale). See the main text for the details about the fitting models.

4. Conclusions

The heat capacity of Co_nAl LDH (n = 2,3) at low temperatures was analysed in comparison with the C(T) behaviour of their non-magnetic counterparts, Mg_nAl LDH, intercalated with the same anions.

In the LDH structure, the bending inside the octahedral metal hydroxide layer is much stronger than the bending between the layer and the intercalated species. The chemical nature of LDH allows the intercalated anions to be arranged in many possible positions with similar energies and small barriers between the positions, suggesting a structural glassy state in the interlayer. As a result, a coexistence of the temperature ranges in which two mechanisms, namely 2D structure and glassy state, contribute to the $C_{\text{lat}}(T) \sim T$ can be expected.

The observed temperature-dependent heat capacity of non-magnetic LDH was fitted using the modified Soft Potential Model (SPM). In comparison with a standard SPM, which includes three terms, namely the Debye term $(C_D T^3)$, two-level states (TLS) contribution $(C_{TLS}T)$, and a term (SM) responsible for quasi-localized soft modes located in the single well potential $(C_{SM}T^5)$, the modified model also includes a contribution from the flexural vibrations of the octahedral hydroxide layer (C_{D} , T). The C_{D} parameter is proportional to the reciprocal square root of the out-of-layer transversal rigidity module. The transversal rigidity decreases with an increase in both the divalent-to-trivalent cation ratio and the interlayer distance. In the LDH under study, the rigidity is the softest in Mg₃Al-NO₃ and the hardest in Mg₂Al-OH. The $C_{D\perp}$ parameter is roughly the same for all the Mg-Al LDH under study, and the C_{TLS} parameter determines the variation of the sum $C_{\text{TLS}} + C_{\text{D}\perp}$. The observed increase in the C_{TLS} value in the intercalated anion sequence NO_3^- , CO_3^{2-} , OH^- as well when the cation ratio changes from 3 to 2 corresponds to an increase in the anion TLS density. The lowtemperature heat capacity of Mg₂Al and Mg₃Al LDH demonstrate a socalled boson peak, which is typical for disordered systems. Onset on this peak and its position are adequately described by the soft-mode dynamic model, in which the cation ratio, anion nature, and content can be taken into account.

The magnetic contribution to the heat capacity of Co₂Al and Co₃Al layered hydroxides was estimated by subtracting the normalized lattice contributions measured in Mg₂Al and Mg₃Al LDH, respectively. The C_{lat} value of Co_nAl LDH is about two orders of magnitude lower than the C_{total} value measured in a zero field below 4 K, which demonstrates the dominant role of the magnetic part in the total heat capacity of these LDH at low temperatures. The peak of $C_{\text{mag}}(T)$ of Co₂Al LDH measured in a zero magnetic field looks like a lambda anomaly as opposed to that observed in Co₃Al LDH. With the increasing external magnetic field, the temperature-dependent magnetic heat capacity of Co₂Al and Co₃Al LDH demonstrates a round peak that behaves as a Schottky-like anomaly and gradually shifts to a high-temperature range.

Below about 4 K, the temperature dependence of the magnetic heat capacity of Co₂Al LDH in a zero magnetic field obeys the relation $C_{\text{mag}} \sim T^{2.6}$, which is changed by the increasing magnetic field and becomes $C_{\text{mag}} \sim T^3$ above 50 kOe. A zero-field C_{mag} of Co₃Al LDH is proportional T^2 in the same temperature range. The magnetic field value as high as 90 kOe is needed to change this relation to a T^3 proportionality.

The approach applied to extract the true magnetic contribution of Co-Al LDH allowed to reveal the fundamental differences in magnetic ordering of the LDH with the cation ratio Co/Al =2 and 3. The discovered features of low-temperature behaviour of non-magnetic LDH appear to be important and should be taken into account when designing LDH intercalated with molecular magnets for application as qubits in quantum information processing.

CRediT authorship contribution statement

V. Tkáč: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Yu.G. Pashkevich:** Writing – review & editing, Validation, Software, Methodology, Formal analysis, Conceptualization. E.L. Fertman: Writing – original draft, Investigation, Formal analysis, Data curation. R. Tarasenko: Validation, Investigation, Data curation. E. Čižmár: Writing – review & editing, Validation, Formal analysis, Data curation, Conceptualization. A. Feher: Validation, Resources, Project administration, Conceptualization. A.V. Fedorchenko: Validation, Investigation, Formal analysis, Data curation. C.S. Neves: Visualization, Investigation, Data curation. D.E.L. Vieira: Visualization, Methodology, Investigation. A.N. Salak: Writing – review & editing, Validation, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2024.107695.

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Applied Clay Science 266 (2025) 107695

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V. Tkáč et al.

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