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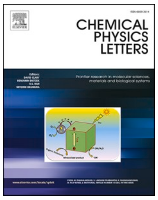

Research paper

Cluster spin glass behaviour of Co^{2+}–Al^{3+} layered double hydroxides

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ABSTRACT

Frequency-dependent magnetic behaviour of cobalt-aluminium layered double hydroxides (LDH) with the Co/Al ratio of 2 and 3, was studied between 2 and 300 K. It was found from analysis of the temperature-dependent *ac* magnetic susceptibility that these LDH exhibit a magnetic cluster spin glass behaviour regardless of their basal spacing value and the Co/Al ratio as evidenced by $E_A/k_BT_0 > 1$ relation obtained using Vogel-Fulcher law. The obtained values of Mydosh parameters in the range of 0.017–0.052 suggest that some of these materials are not far from the canonical spin glasses, implying a rather small size of the magnetic clusters.

1. Introduction

Layered double hydroxides (LDH) are 2-D materials with an incredible flexibility of chemical composition. The general chemical formula of the most numerous group of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][(A^{y-})_{x/y}\cdot zH_2O]$, where the layer part and the interlayer part are within the first and the second square brackets, respectively. The divalent-to-trivalent cation ratio, $n=(1-x)/x$, can be continuously changed from about 1 to 5 [1]. A wide variety of metal cations are capable of serving as M^{2+} and M^{3+} in the mixed-metal hydroxide layer formed of edge-shared OH octahedra. Anions A^{y-} of different charge, shape, and size can be intercalated into the interlayer [1–3]. Water molecules screen the anions from each other and contribute to the chemical bonding layer-interlayer. The relative amount of molecular water (z) generally depends on the nature of the anion species and their arrangement in the interlayer but it can vary in some range. Another characteristic feature of LDH is their ability to exchange (permanently) the anion species without destruction of the crystal structure. The basal spacing (d) value, which is a sum of the hydroxide layer thickness and the interlayer gallery height, can be changed in some cases as much as by a factor of 5. Such a chemical flexibility both in the mixed-metal hydroxide layers and in the interlayer offers a unique opportunity for fine composition control, which is a key factor in unveiling the *composition-property* relations and, thereby, a way to tune many important properties of LDH.

Many current applications of LDH are linked to functionalities of the intercalated anion species: corrosion inhibitors [4,5], drugs [6], DNA [7,8], barrier agents for food packaging [9], and many others. LDH are widely used as (nano)containers for capture, storage, and controllable release of such species. Manipulation of the chemical composition of the mixed metal hydroxide layers is another way to add new properties to LDH materials. The use of metal cations with individual or cooperative properties (e.g., luminescent or magnetic) was shown to extend the functionalities of LDH [10–15].

Magnetic properties of LDH containing transition metal cations M^{2+}= Co, Ni, and/or M^{3+}= Fe, Cr, Mn were studied as functions of the cations' composition, ratio, and basal spacing [16–22]. The peaks of the χT product *versus* temperature were observed in the typical range of about 3–20 K, indicating a long-range magnetic ordering in those LDH. The temperature of the spontaneous magnetisation onset was found to be dependent on basal spacing only at relatively small d-values [14,19,23]. It has been shown that the magnetic properties of Co-Al and Ni-Fe LDH are influenced by the size and morphology of their crystallites [24]. Due to the hexagonal crystal symmetry and layered nature, the LDH crystallites are flake-like shaped. It was found that crystallites of Co^{2+}-containing LDH are magnetically anisotropic at room temperature and, in a magnetic field oriented along the precipitation direction, can

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form dense and homogeneous layers [25,26]. To describe the phenomenon, we considered all thirteen types of possible coordinations of Co^{2+} by the nearest-neighbouring cations (Co^{2+} or Al^{3+}); their probabilities and the specific distortions of the oxygen octahedra were estimated and used for calculations of the energy spectra [23,27,28]. We explained the magnetic anisotropy of the LDH crystallites in terms of clusters with the ideal honeycomb-like 2:1 cation ordering of Co^{2+} and Al^{3+} cations, which corresponds to the configuration when each Co^{2+} is coordinated by three cobalt ions and three aluminium ions forming a hexagon Co-Al-Co-Al-Co-Al- [27,28].

The non-random distribution of Ni^{2+} and Fe^{3+} (clustering) was indirectly confirmed in nickel–iron LDH from the Mössbauer spectroscopy measurements [12]. The nature of such atomic clusters and even their characteristic size are still unclear. Since formation of bulk M^{2+}-rich/M^{3+}-poor zones as well as M^{2+}-poor/M^{3+}-rich zones is unfavourable because of violation in local electroneutrality, one can assume that the clusters are the regions with divalent-trivalent cation ordering in a cation-disordered matrix. Combinations of numerous atomic coordinations, orderings as well as local distortions impact magnetic behaviour of LDH, which cannot be considered in terms of ideal long-range interaction. Therefore, when analysing the physical properties of LDH, the possible effects induced by combinations of cation-ordered and cation-disordered zones in hydroxide layers should be taken into account.

Measurements of the dynamic (*ac*) magnetic properties of LDH in the temperature vicinity of the onset of their spontaneous magnetisation revealed a frequency-dependent behaviour typical of spin glasses [12,18,19]. Based on analysis of the *ac* susceptibility data on the carbonate-intercalated Co-Al LDH prepared in two different morphological forms, Carrasco *et al.* concluded on the cluster glass behaviour of these materials [24]. We have recently reported a combined experimental and theoretical study of low-temperature heat capacity and magnetisation of Co^{2+}-Al^{3+} LDH (with the cobalt-to-aluminium ratio of 2 and 3) intercalated with different anions [23]. Theoretical modelling of the heat capacity in increasing magnetic field unambiguously indicated a cluster glass state in the cobalt-aluminium LDH regardless of the type of the intercalated anion. Nevertheless, the nature of the low-temperature magnetic phenomena in those LDHs is still not completely clear. In particular, questions arise about whether there is true long-range ferromagnetic ordering and how magnetic ordering and glass behaviour coexist.

In this paper, we considered the peculiarities of the dynamic magnetic properties of Co^{2+}-Al^{3+} LDH (Co/Al = 2 and 3) LDH in the vicinity of the peak of their magnetic susceptibility. We show that these LDH exhibit a cluster spin glass (spin glass-like) behaviour. The features of such behaviour are analysed and discussed.

2. Materials and methods

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, $M^{2+}{}_nM^{3+}$-A) were prepared using two conventional routes. Co_nAl-NO_3 LDH were obtained by co-precipitation from nitrate salts of the respective metals as described in Ref [26]. For more detail on the preparation procedure see Suppl. Mater. The compositions with n = 2 and 3 were synthesised at the same conditions. The nitrate-intercalated compounds were then used to obtain LDH intercalated with different anion species such as hydroxide, carbonate, gluconate (GNT), and mercaptobenzothiazolate (MBT) *via* the respective anion exchange reactions in the solution containing these species (Table S1 in Suppl. Mater.). In such a way, the compositions mentioned hereafter as Co_nAl-OH, Co_nAl-CO_3, Co_nAl-GNT, and Co_nAl-MBT, were prepared. 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.

Phase purity and crystal structure of the obtained LDH powders were monitored using a PANalytical X'Pert Powder diffractometer in Cu Kα radiation with the exposition corresponding to about 1 s per step of 0.02° at room temperature. In the case of cobalt-containing samples, a diffracted beam monochromator was used to suppress the fluorescence contribution. The lattice parameters of the LDH compositions and their basal spacings were calculated from the angular positions of the diffraction reflections (0 0 l) and (1 1 0) and compared with the previously reported values [23] (see Suppl. Mater. for more detail).

For measurements of magnetic properties, the LDH powders were compacted into discs of about 3 mm in diameter and about 0.3 mm thick. Complex *ac* susceptibility, $\chi(T) = \chi'(T) - i\chi''(T)$ (where χ' and χ'' are in-phase and out-of-phase components, respectively), was measured at different constant frequencies up to 1 kHz at a fixed *ac* field of 1.5 Oe using an MPMS3 magnetometer (Quantum Design).

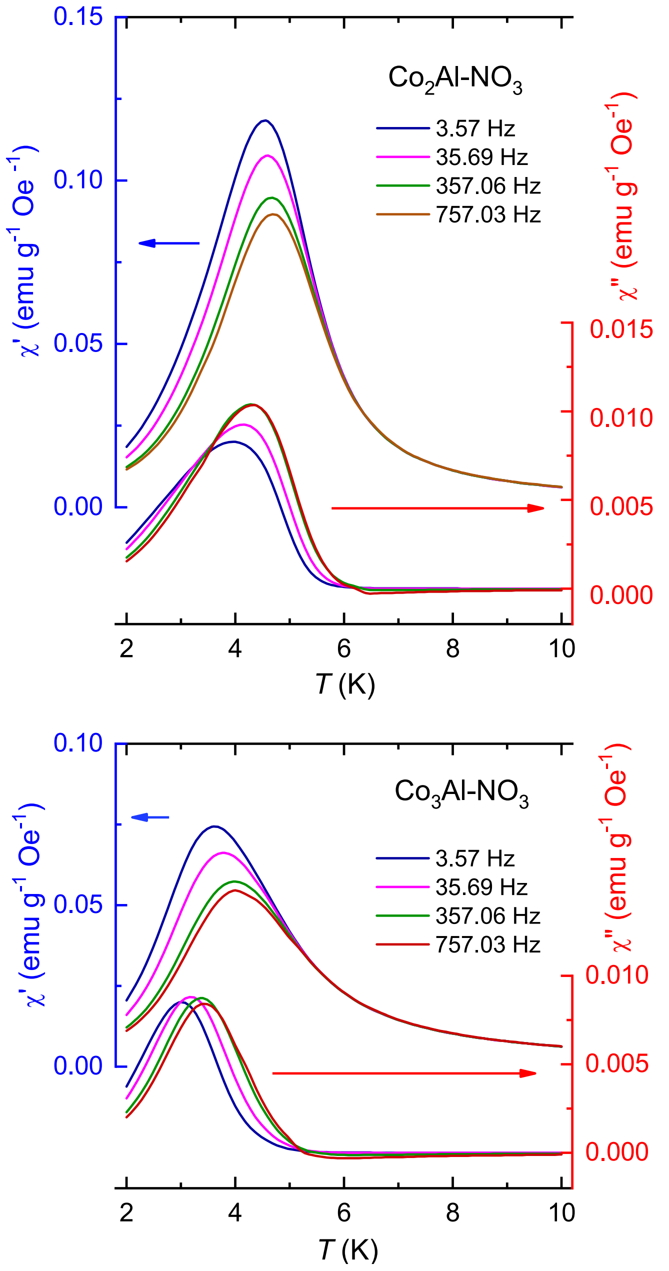

Fig. 1. The temperature-dependent in-phase (χ') and out-of-phase (χ'') parts of the complex *ac* susceptibility of Co_2Al-NO_3 (top panel) and Co_3Al-NO_3 (bottom panel) measured at different frequencies.

3. Results and discussion

Fig. 1 shows both the in-phase and out-of-phase parts of the *ac* susceptibility of $Co_nAl\text{-}NO_3$ LDH ($n = 2$ and 3) as a function of temperature. The dynamic susceptibility is strongly frequency-dependent, indicating a glassy magnetic state of these materials at low temperatures.

The frequency-dependent shift of the cusp temperature T_f (freezing temperature) of the $\chi'(T)$ curves, also known as the Mydosh parameter ϕ [29], can be estimated as

$$\phi = \frac{\Delta T_f}{T_f \cdot \Delta \log_{10} f} \tag{1}$$

A graphical representation of the procedure for a case of Co_2Al-GNT LDH is shown in Fig. 2 (top panel). The calculated ϕ values are listed in Table 1.

The ϕ values obtained for all studied Co_nAl LDH in this study are typical of cluster glass, e.g., (EuSr)S ($\phi = 0.06$) [29], $PrRhSn_3$ (0.086) [30]. They are in good agreement with the respective values (within the range of 0.013–0.085) reported for other magnetic LDH with M^{2+}=Co, Ni and M^{3+}=Fe, Cr, Al [15]. These ϕ values are higher than those characteristic of the canonical spin glasses ($\phi = 0.005$ for CuMn) [29] and lower than the reported for noninteracting superparamagnetic systems (0.28 for a-(Ho_2O_3)(B_2O_3) glass) [29].

In the studied LDH with small *d*-spacings, the temperature dependence of χ'' displays a frequency-dependent maximum with another frequency-dependent shoulder at lower temperatures. Those two relaxation components in the $\chi'(T)$ curve merge in a single broad maximum with no possibility of the relaxation analysis, as shown in Fig. 3 (see also Figs. S3 and S4 in Suppl. Mater.). Therefore, the χ'' part of the *ac* susceptibility was used for fitting, similarly to that done in the study of the relaxation behaviour of Ni_2Fe LDH in Ref. [24] analyzing a more pronounced higher temperature maximum in χ'' part of the *ac* susceptibility. We also attempted to subtract the position of the maxima by fitting them to two Gaussian lineshapes; for $Co_2Al\text{-}CO_3$ we were able to analyze the relaxation behaviour of the low-temperature maximum as well.

The net magnetism in LDH is contributed by both intralayer and interlayer interactions [15,16]. It was found experimentally that the magnetic interactions *via* intralayer coupling of the metal cations are much stronger than the interlayer dipolar interactions [14,23,31]. The latter decreases as the interlayer distance is increasing. In particular, Co_2Al and Co_3Al LDH with the *d*-spacing value above about 0.89 nm can be considered as solely 2-D magnets [23]. We suppose that the observed complex behaviour of $\chi''(T)$ and $\chi'(T)$ in Co_2Al-OH (Fig. 3), $Co_2Al\text{-}CO_3$ (Fig. S3) and $Co_3Al\text{-}CO_3$ (Fig. S4) reflect two relaxation processes associated with intralayer and interlayer interactions, respectively.

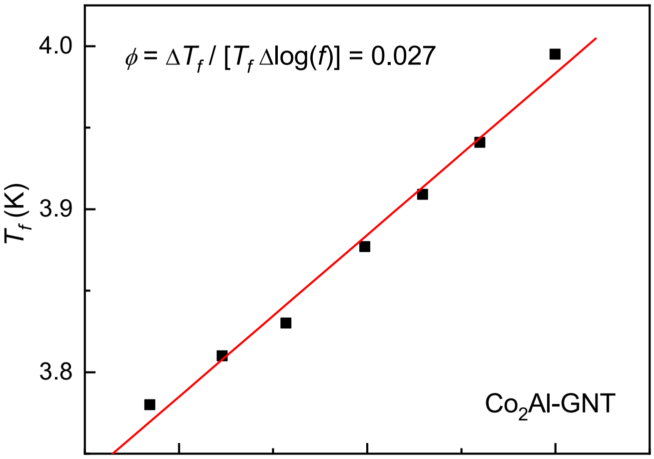

Fig. 2. The fitting procedures of the dynamic susceptibility data of Co_2Al-GNT LDH. Estimation of a Mydosh parameter according to Eq. (1) from the slope of the linear fit.

Table 1
The Mydosh parameter (ϕ) of the magnetic LDH under study estimated using Eq. (1).

Composition	ϕ parameter
$Co_2Al\text{-}NO_3$	0.017
$Co_3Al\text{-}NO_3$	0.052
$Co_2Al\text{-}CO_3$	0.043
$Co_3Al\text{-}CO_3$	0.031
Co_2Al-OH	0.030
Co_2Al-GNT	0.027
Co_2Al-MBT	0.018

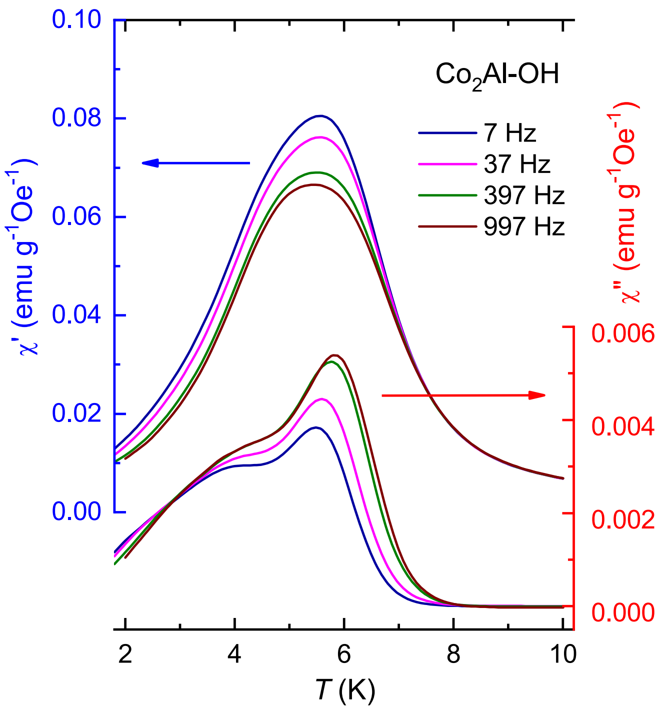

Fig. 3. The temperature-dependent in-phase (χ') and out-of-phase (χ'') parts of the complex *ac* susceptibility of Co_2Al-OH measured at different frequencies.

The analysis of the frequency-dependent T_f values extracted from the *ac* susceptibility of studied LDH failed to be appropriately described by a simple Arrhenius law because an unphysical energy barrier and characteristic relaxation time $\tau_0 = 1/f_0$ were obtained. Therefore, the dynamics of the glassy state was analysed by the empirical Vogel-Fulcher law [32]:

$$f = f_0 exp\left(-\frac{E_A}{k_B(T_f - T_0)}\right) \tag{2}$$

where k_B is the Boltzmann constant, f_0 is the characteristic frequency, and E_A is the activation energy, assuming the interaction between relaxing spins. The non-zero T_0 value is associated with the interaction between the relaxing species, thus allowing us to estimate the correlation between the frozen magnetic moments. Provided that $T_0 = 0$, one obtains the well-known Arrhenius law. The procedure of the estimation of T_0, which is used to plot the Vogel-Fulcher law on a logarithmic scale, as shown in the top panel of Fig. 4, is not straightforward, and we first used the method outlined in Ref. [33]. The linear fit of the Vogel-Fulcher law on a logarithmic scale then yields the energy barrier and characteristic relaxation time. The results of the analysis are summarised in Table S3. An alternative method was proposed [34,35], in which the

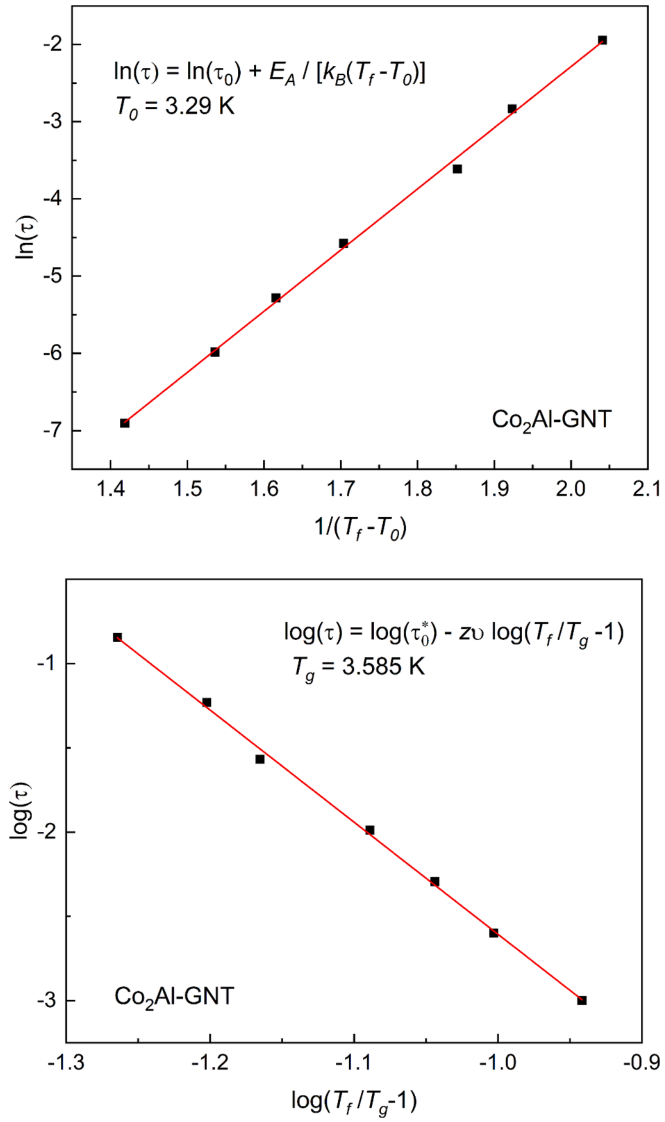

Fig. 4. Analysis of the *ac* susceptibility using the Vogel-Fulcher law (Eq. (2) (top panel) and the power law (Eq. (3) (bottom panel).

adjusted R^2 parameter of the fit is evaluated for a wide range of T_0, and the one with the best adjusted R^2 is selected to estimate τ_0 and E_A reported in Table 2. In the case of a larger scatter in the data and a relatively small experimental frequency range, it seems to provide a better estimate of T_0. This method was further used also in the analysis of the temperature dependence of the relaxation time by the power law

$$f = f_0^* \left(\frac{T_f}{T_g} - 1\right)^{z\upsilon} \tag{3}$$

in which υ represents the critical exponent for the correlation length and z critical index involved in the dynamical-scaling theory used in describing three-dimensional (3-D) spin glasses [36]. The magnetic correlation length and the energy barrier in 3-D spin glasses become a function of time and temperature when approaching glassy temperature T_g in systems with magnetic interaction between freezing magnetic moments (as suggested by non-zero T_0 temperature obtained from the analysis using Vogel-Fulcher law).

Using Eq. (2), the activation energy E_A/k_B in the range of 6.85–38.6 K, the Vogel-Fulcher temperature, T_0, between 2.15 and 4.57 K, and the characteristic relaxation time in the range of 10^{-15}-10^{-7} s were obtained. The extracted parameters using the method from Ref [33] seem more reasonable for Co_3Al-CO_3, which can be explained by a very flat dependence of the adjusted R^2 parameter on T_0, yielding a quite large range of possible T_0. The values are compatible with those reported for magnetic cluster glass materials [30], although some shorter τ_0 seem to be compatible with canonical spin glass. As discussed in Ref. [34], the characteristic relaxation time may span a larger range in other cluster spin glass systems, and another parameter, E_A/k_BT_0, is suggested to be more appropriate for classifying glassy systems. For all presented LDH, this parameter is greater than 1, which is typical value for cluster spin glass systems (see Table 2). The analysis of the temperature dependence of the relaxation time using the power law (Eq. (3) as shown in the bottom panel of Fig. 4 and summarized in Table 3 yields similar characteristic relaxation times ($\tau_0^* = 1/f_0^*$) as obtained from the Vogel-Fulcher law. The power law exponent $z\upsilon$ for most studied LDH falls within the 4–12 range typical for most spin glass systems [34]. Note that for Co_2Al-CO_3, where two maxima in χ'' part of the *ac* susceptibility were quite well resolved, we obtained a similar parameter set for both of the maxima, but with different energy barriers suggesting the presence of two sets of clusters with different average sizes.

The analysis of temperature and frequency-dependent *ac* susceptibility of the Co_nAl LDH can be understood within the picture of long-range magnetic order occurring in separate areas (clusters) whose magnetic moments are randomly oriented. The random correlations between magnetic moments of clusters lead to cluster glass behaviour. Although the Mydosh and the E_A/k_BT_0 parameters for all studied LDH fall within the typical range of value for cluster glass, the characteristic relaxation time for Co_2Al-NO_3 and Co_2Al-MBT with the smallest Mydosh parameter from studied LHD is already close to the range typical for canonical spin glass (although the power law exponent $z\upsilon$ extends beyond the typical range for spin glasses). Such an observation might suggest a more complicated mechanism of spin freezing in the case of small Mydosh parameter for Co_2Al-NO_3 and Co_2Al-MBT. This may indicate a crossover between spin glass and cluster glass with very small magnetic clusters. We associate these magnetic clusters with spatial domains with a long-range Co-Al ordering. A 2:1 cation ordering was

Table 2
Parameters obtained from analysis of the ac magnetic susceptibility of the LDH under study using the Vogel-Fulcher law (Eq. (2) using the method from Refs [34,35]. The analysis was performed also on low-temperature* or high-temperature** maximum obtained from the χ''(T) data.

Composition	T_0 (K)	E_A/k_B (K)	τ_0 (s)	E_A/k_BT_0	
Co_2Al-NO_3	3.40	31.67	9.19×10^{-16}	9.31	
Co_3Al-NO_3	2.15	35.92	1.59×10^{-11}	16.71	
Co_2Al-CO_3	2.88	6.85	2.25×10^{-7}	3.38	*
	4.185	18.55	4.57×10^{-9}	4.43	**
Co_3Al-CO_3	1.51	200.32	2.26×10^{-24}	132.66	**
Co_2Al-OH	4.57	20.6	3.35×10^{-10}	4.51	**
Co_2Al-GNT	3.295	7.78	1.5×10^{-8}	2.36	
Co_2Al-MBT	3.33	19.075	2.76×10^{-13}	5.73	

Table 3
Parameters obtained from analysis of the ac magnetic susceptibility of the LDH under study using the power law (Eq. (3) using the method from Refs [34,35]. The analysis was performed also on low-temperature* or high-temperature** maximum obtained from the χ''(T) data.

Composition	T_g (K)	$z\upsilon$	τ_0 (s)	
Co_2Al-NO_3	3.90	15.95	3.63×10^{-16}	
Co_3Al-NO_3	3.035	10.1	4.05×10^{-8}	
Co_2Al-CO_3	3.185	5.46	4.54×10^{-8}	*
	4.77	7.82	2.60×10^{-9}	**
Co_3Al-CO_3	3.48	25.39	1.45×10^{-8}	**
Co_2Al-OH	5.13	9.10	5.7×10^{-11}	**
Co_2Al-GNT	3.585	6.65	5.52×10^{-10}	
Co_2Al-MBT	3.725	12.04	1.57×10^{-14}	

indirectly revealed in Co_2Al LDH [23]. The same type of regular arrangement and/or a 3:1 one can occur in Co_3Al LDH as well, although probabilities of these ordering are smaller than those in the case of $n = 2$ [27].

We have recently studied a low-temperature heat capacity of Co_nAl LDH and extracted a lattice contribution (C_{lat}) to the total heat capacity [31]. The results demonstrate that the observed behaviour of the C_{lat} versus T is affected by a disorder of the intercalated species, which can be considered as a structural glassy state. Therefore, Co-Al layered double hydroxides demonstrate the properties of both structural glass and magnetic glass with independent origin related to the peculiarities of the arrangement of anions in the interlayer and cations in the layer, respectively.

4. Conclusions

The *ac* magnetic susceptibility of all the Co_nAl LDH studied is frequency dependent. The Mydosh parameter values (0.017–0.052) estimated from the obtained data are within the range typical for magnetic cluster glass (spin glass-like) materials. Due to interactions between the magnetic clusters, the characteristic relaxation parameters could be estimated using the Vogel-Fulcher law instead of the Arrhenius law to analyse the temperature dependence of the relaxation time. The obtained values of the activation energy, Vogel-Fulcher temperature, and characteristic relaxation time are generally compatible with those reported for magnetic cluster glass materials, and especially $E_A/k_BT_0 > 1$ relation for all studied LDH strongly supports their classification as cluster spin glasses. However, the relaxation time values for $Co_2Al\text{-}NO_3$ and Co_2Al-MBT LDH, which revealed the lowest Mydosh parameters, 0.017 and 0.018, respectively, are close to those for canonical spin glass. This feature might suggest a crossover between spin glass and cluster glass with small-sized magnetic clusters. Our results indicate that with a large set of different intercalated anions in LDH, one can reveal subtle differences in spin-glass formation due to the underlying structural and magnetic changes in LDH layers. It is suggested that the microscopic nature of a possible structural clusterisation needs to be studied in detail by advanced X-ray diffraction or other methods.

CRediT authorship contribution statement

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2024.141745.

Data availability

Data will be made available on request.

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