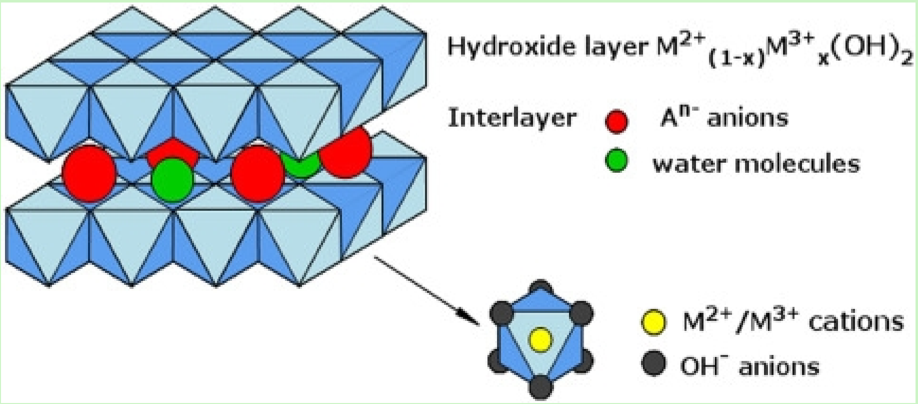
# Tunable Magnetic Properties of Layered Double Hydroxides: between Cluster Glass and Canonical Spin Glass


A. V. Fedorchenko[1], E. L. Fertman[1], I. P. Kobzar[1], Yu. G. Pashkevich[2], E. Čižmár[3], V. Tkáč[3], R. Tarasenko[3], A. Feher[3], M. Holub[4], A. N. Salak[5]

[1]B. Verkin Institute for Low Temperature Physics and Engineering of NASU, Kharkiv, Ukraine
[2]O. Galkin Donetsk Institute for Physics and Engineering of NASU, Kyiv, Ukraine
[3]Institute of Physics, Faculty of Science, P.J. Šafárik University in Košice, Košice, Slovakia
[4]Synchrotron SOLEIL, Gif sur Yvette Cedex, France
[5]Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal

e-mail: fedorchenko.alexey@gmail.com


## Introduction

Layered double hydroxides (LDH) are 2D materials with remarkable chemical flexibility, offering precise control over composition and properties. They consist of mixed-metal hydroxide layers intercalated with anions and water molecules. This tunability, including the divalent-to-trivalent cation ratio and interlayer anion species, makes LDH versatile for applications like magnetism. The interplay between hydroxide layer chemistry and intercalated anions affects structural organization and magnetic ordering, leading to complex magnetic behaviors in LDH containing transition metals. Magnetic properties of LDH containing cations of transition metal Co and post-transition metal Al have been studied as functions of composition and ratio.

## Objective

This study focuses on Co-Al LDH with varying cobalt-to-aluminum ratios to investigate their tunable magnetic properties. We analyzed the dynamic magnetic properties to understand the nature of the observed glassy magnetic state at low temperatures.

## Methods

Co-Al LDH with Co/Al ratios of 2 and 3 were prepared using conventional methods, including co-precipitation and anion exchange reactions to introduce various intercalated anions (e.g., $NO_3$, $CO_3$, OH, gluconate (GNT), and mercaptobenzothiazolate (MBT)). Phase purity and crystal structure were confirmed by powder X-ray diffraction. Magnetic properties were measured on compacted powder discs using complex *ac* susceptibility ($\chi = \chi' - i\chi''$) at different frequencies and temperatures.

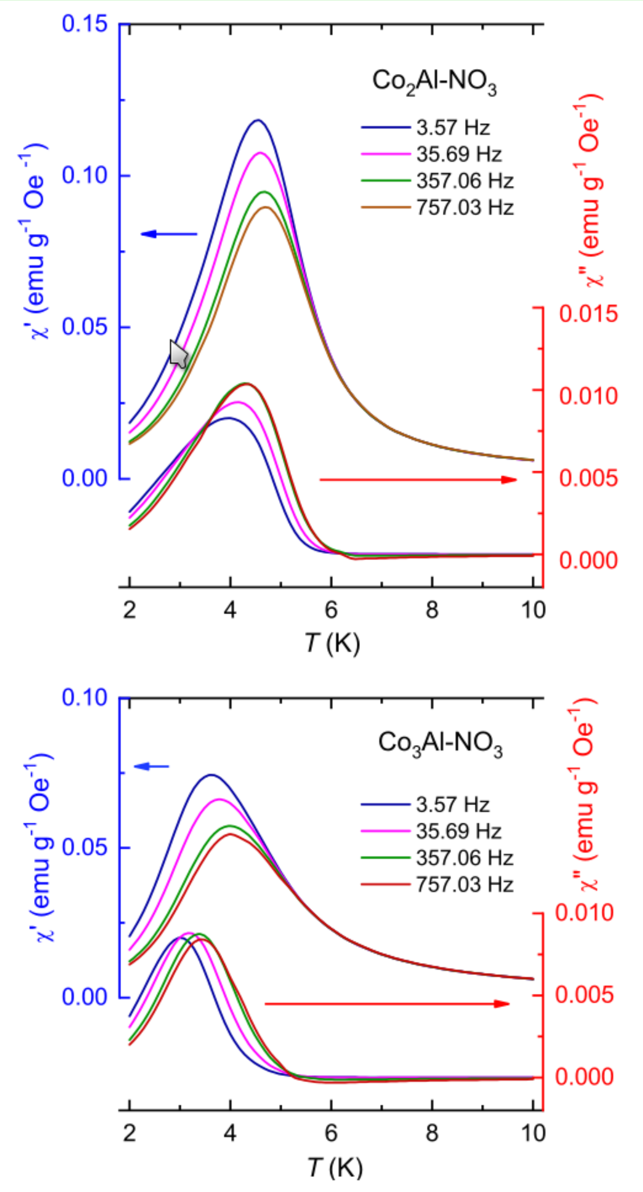



**Fig. 1** The temperature-dependent in-phase (χ′) and out-of-phase (χ″) parts of the complex *ac* susceptibility of Co2Al-$NO_3$ (top panel) and Co3Al-$NO_3$ (bottom panel) measured at different frequencies.

The temperature-dependent *ac* magnetic susceptibility of Co-Al LDH shows strong frequency dependence, indicating a **glassy magnetic state at low temperatures**.

**Fig. 1** shows the frequency-dependent in-phase (χ′) and out-of-phase (χ″) parts of the complex *ac* susceptibility for Co2Al-$NO_3$ and Co3Al-$NO_3$, illustrating this behavior.

The frequency-dependent shift of the freezing temperature ($T_f$) of the χ′(T) curves was used to estimate the Mydosh parameter φ using Eq. (1): $\varphi = \Delta T_f / (T_f \cdot \Delta \log_{10} f)$ **Fig. 2** illustrates the estimation procedure for Co2Al-GNT LDH.

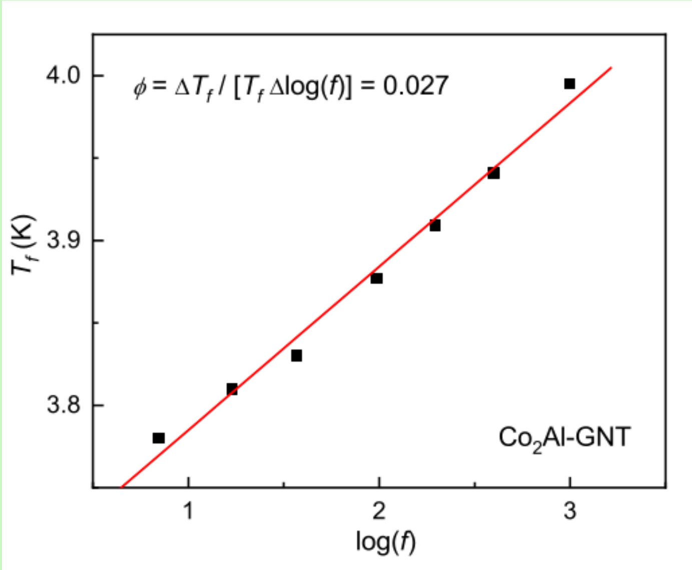



**Fig. 2** The fitting procedures of the dynamic susceptibility data of Co2Al-GNT LDH. Estimation of a Mydosh parameter according to Eq. (1) from the slope of the linear fit.

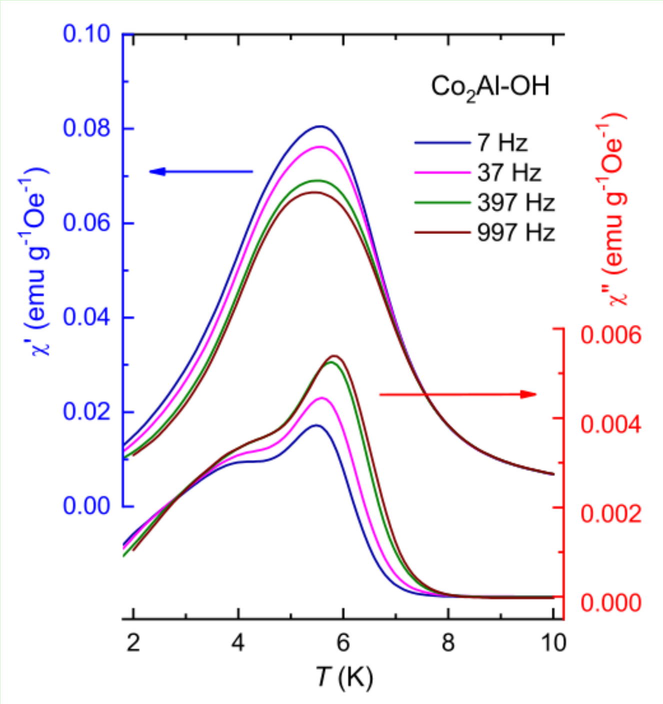



**Fig. 3** The temperature-dependent in-phase (χ′) and out-of-phase (χ″) parts of the complex *ac* susceptibility of Co2Al-OH measured at different frequencies.

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

| Composition | $\phi$ 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 |

For some compositions, the χ″(T) dependence exhibits a complex shape with a frequency-dependent maximum and a lower-temperature shoulder, suggesting two relaxation components. **Fig. 3** shows this complex behavior for Co2Al-OH. Intralayer magnetic interactions are experimentally found to be much stronger than interlayer interactions.

The frequency dependence of $T_f$ cannot be described by a simple Arrhenius law, indicating interactions between relaxing spins. The dynamics of the glassy state were analyzed using the **Vogel-Fulcher law:**

(Eq. 2): $f = f_0 \exp(- E_A / (k_B(T_f - T_0)))$

A non-zero $T_0$ value is associated with interactions between relaxing species. **Fig. 4 (top panel)** shows the Vogel-Fulcher analysis.

The calculated **φ values (listed in Table 1)** range from 0.017 to 0.052. These values are typical for **cluster glass materials**, higher than canonical spin glasses but lower than superparamagnetic systems.

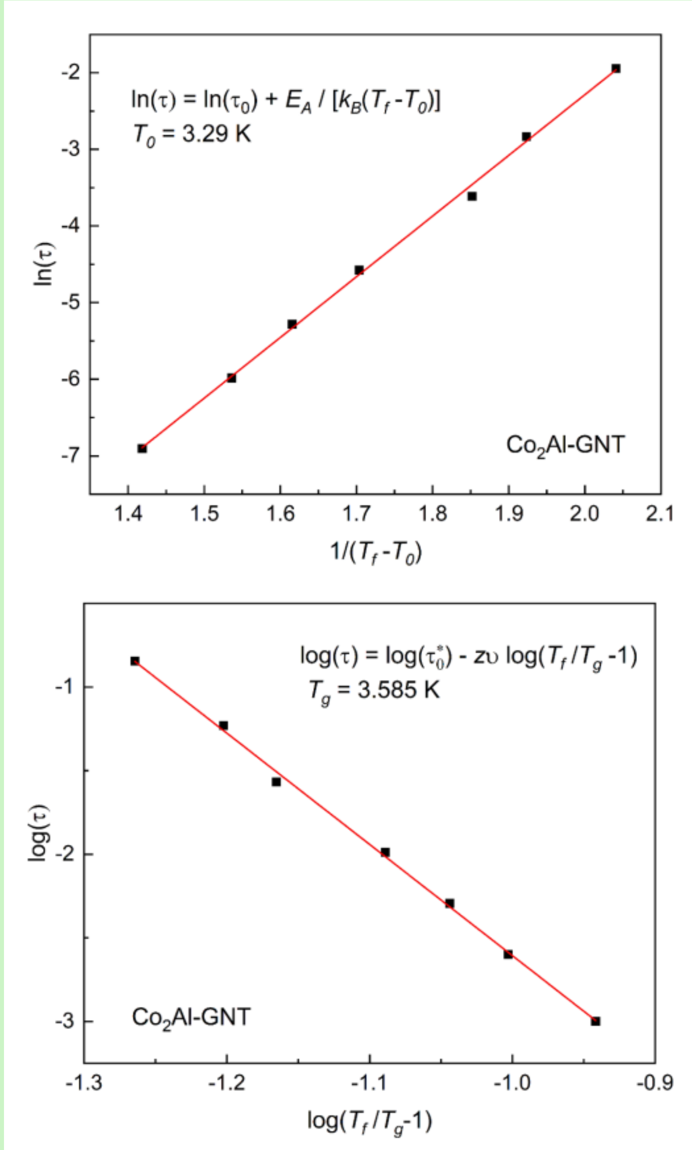



**Fig. 4** Analysis of the *ac* susceptibility using the Vogel-Fulcher law ( Eq. (2) (top panel) and the power law ( Eq. (3) (bottom panel) ).

**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 doi:10.1063/5.0169800 and doi:10.1088/1361-648X/acdbfa) 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) | $\tau_0$ (s) | $E_A/k_BT_0$ | |
|---|---|---|---|---|---|
| $Co_2Al\text{-}NO_3$ | 3.40 | 31.67 | $9.19 \times 10^{-16}$ | 9.31 | |
| $Co_3Al\text{-}NO_3$ | 2.15 | 35.92 | $1.59 \times 10^{-11}$ | 16.71 | |
| $Co_2Al\text{-}CO_3$ | 2.88 | 6.85 | $2.25 \times 10^{-7}$ | 3.38 | * |
| | 4.185 | 18.55 | $4.57 \times 10^{-9}$ | 4.43 | ** |
| $Co_3Al\text{-}CO_3$ | 1.51 | 200.32 | $2.26 \times 10^{-24}$ | 132.66 | ** |
| $Co_2Al\text{-}OH$ | 4.57 | 20.6 | $3.35 \times 10^{-10}$ | 4.51 | ** |
| $Co_2Al$-GNT | 3.295 | 7.78 | $1.5 \times 10^{-8}$ | 2.36 | |
| $Co_2Al$-MBT | 3.33 | 19.075 | $2.76 \times 10^{-13}$ | 5.73 | |

The parameters obtained from the Vogel-Fulcher analysis (summarized in **Table 2**) include activation energy $E_A/k_B$ (6.85–38.6 K), Vogel-Fulcher temperature $T_0$ (2.15–4.57 K), and characteristic relaxation time $\tau_0$ ($10^{-15}$–$10^{-7}$ s).

Crucially, the **$E_A/k_BT_0$ parameter is greater than 1 for all studied LDH**, which strongly supports their classification as **cluster spin glasses**.

An alternative analysis using a power law (Eq. 3): $f = f_0{}^*( T_f / T_g - 1)^{z\upsilon}$ also yielded characteristic relaxation times ($\tau_0$) and power law exponents $z\upsilon$ (4–12) typical for spin glass systems. **Table 3** presents these parameters.

**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 doi:10.1063/5.0169800 and doi:10.1088/1361-648X/acdbfa) The analysis was performed also on low-temperature* or high-temperature** maximum obtained from the χ″(T) data.

| Composition | $T_g$ (K) | $z\nu$ | $\tau_0$ (s) | |
|---|---|---|---|---|
| $Co_2Al\text{-}NO_3$ | 3.90 | 15.95 | $3.63 \times 10^{-16}$ | |
| $Co_3Al\text{-}NO_3$ | 3.035 | 10.1 | $4.05 \times 10^{-8}$ | |
| $Co_2Al\text{-}CO_3$ | 3.185 | 5.46 | $4.54 \times 10^{-8}$ | * |
| | 4.77 | 7.82 | $2.60 \times 10^{-9}$ | ** |
| $Co_3Al\text{-}CO_3$ | 3.48 | 25.39 | $1.45 \times 10^{-8}$ | ** |
| $Co_2Al\text{-}OH$ | 5.13 | 9.10 | $5.7 \times 10^{-11}$ | ** |
| $Co_2Al$-GNT | 3.585 | 6.65 | $5.52 \times 10^{-10}$ | |
| $Co_2Al$-MBT | 3.725 | 12.04 | $1.57 \times 10^{-14}$ | |

## Discussion

The observed magnetic behavior can be understood as a cluster spin glass state where the magnetic moments of separate areas (clusters) are randomly oriented, and random correlations exist between these cluster moments. The cluster glass behavior is influenced by both cation distribution within hydroxide layers and interlayer anion effects.

While the $E_A/k_BT_0$ parameter clearly indicates cluster glass behavior, the Mydosh parameter values and relaxation times for some compositions (Co2Al-$NO_3$ and Co2Al-MBT, which have the lowest φ values) are close to those typical for canonical spin glasses. This observation might suggest a **crossover between spin glass and cluster glass** with very small magnetic clusters. These magnetic clusters are associated with spatial domains exhibiting cation ordering, such as 2:1 ordering in Co2Al LDH.

Furthermore, Co-Al LDH demonstrate properties of both magnetic glass (related to cation arrangement) and **structural glass** (related to anion disorder in the interlayer) with independent origins.

## Conclusions

- Co-Al LDH exhibit **frequency-dependent *ac* magnetic susceptibility** characteristic of glassy systems.
- Mydosh parameters (0.017–0.052) fall within the range typical for **magnetic cluster glass (spin glass-like) materials**.
- Analysis using the Vogel-Fulcher law is appropriate due to interactions between magnetic clusters.
- Vogel-Fulcher parameters, particularly $\mathbf{E_A/k_BT_0 > 1}$, strongly support the classification as **cluster spin glasses**.
- Some compositions (Co2Al-$NO_3$, Co2Al-MBT) show Mydosh parameters and relaxation times close to those of canonical spin glasses, suggesting a potential **crossover or the presence of small-sized magnetic clusters**.
- The results highlight LDH as potential **tunable magnetic materials**, with spin-glass formation influenced by underlying structural and magnetic changes related to cation and anion arrangements.
- **Further advanced structural characterization is needed to elucidate the microscopic nature of cluster formation and its impact.**

## Acknowledgements

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