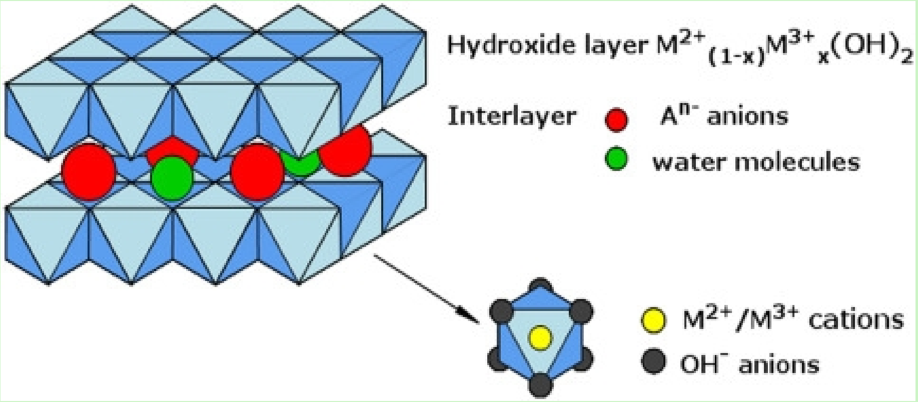
Low-temperature magnetism of Co-Al-based LDH

A. V. Fedorchenko[1], E. L. Fertman[1], I. P. Kobzar[1], Yu. G. Pashkevich[2,3], V. Tkáč[4], R. Tarasenko[4], E. Čižmár[4], A. Feher[4],
M. Holub[5], C. S. Neves[6], D. E. L. Vieira[6], A. N. Salak[6]

[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]Department of Physics and Fribourg Center for Nanomaterials, University of Fribourg, CH-1700 Fribourg, Switzerland
[4]Institute of Physics, Faculty of Science, P.J. Šafárik University in Košice, Košice, Slovakia
[5]AGH University of Krakow, al. Adama Mickiewicza 30, 30-059 Krakow, Poland
[6]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 quasi-two-dimensional materials with a general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}\cdot nH_2O]^{x-}$. Their unique structure consists of positively charged layers separated by an interlayer space containing anions and water molecules.

While the high-temperature properties and chemical applications of LDH are widely studied, their low-temperature physics remains poorly understood. In particular, the quasi-2D confinement and intrinsic structural disorder of the intercalated anions are expected to induce specific lattice dynamics (such as bending waves and glassy behavior) and strongly affect the low-temperature magnetism when transition metal cations (e.g., Co^{2+}) are introduced.

Objective

The primary objective of this work is to separate and comprehensively analyze the lattice and true magnetic contributions to the low-temperature heat capacity of Co-Al and Mg-Al layered double hydroxides. Specifically, we aim to probe the effects of structural and glassy disorder induced by different interlayer anions, validate a reliable method for lattice background subtraction using non-magnetic Mg-Al structural analogs, and determine the dimensionality and nature of magnetic correlations in Co-Al systems in zero field and under external magnetic fields up to 90 kOe.

Methods

Co-Al and Mg-Al samples with cation ratios of 2 and 3 intercalated with nitrate, carbonate, and hydroxide anions were prepared via co-precipitation and subsequent anion exchange methods. Structural quality, phase purity, and chemical composition were verified using X-ray diffraction, FT-IR spectroscopy, and elemental analysis. Total heat capacity was measured in the temperature range of 2–100 K using a commercial Physical Property Measurement System in zero magnetic field and under applied external fields up to 90 kOe using the standard relaxation technique.

Low-temperature heat capacity and lattice dynamics in zero magnetic field

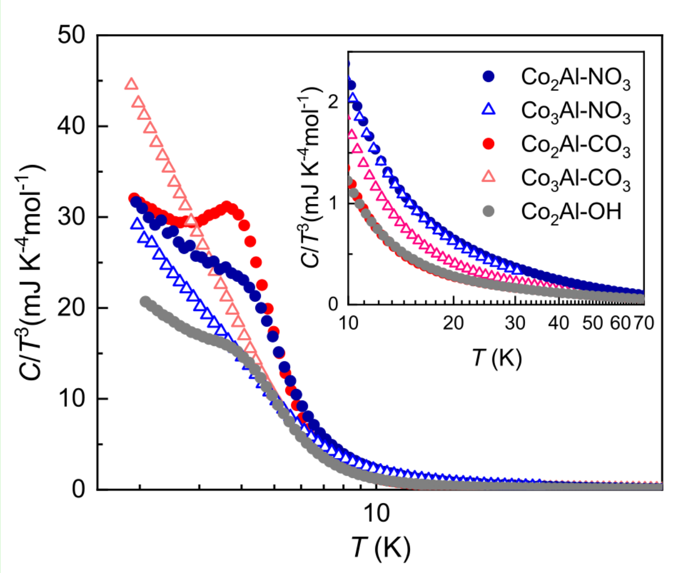


Fig. 1 Temperature dependence of the reduced heat capacity, C/T^3, of the Co(n)Al LDH studied. The inset shows a magnified high-temperature region of the graph.

The experimental low-temperature heat capacity plotted as C/T^3 versus T provides direct insight into the lattice dynamics and acoustic phonon deviations from the classical Debye behavior.

For the non-magnetic Mg(n)Al matrixes (Fig. 2), a pronounced asymmetric maximum is observed in the low-temperature region. This feature represents a boson peak, which is a characteristic signature of structural glass behavior. The glassy disorder originates from the random orientational and positional distribution of the intercalated anions and water molecules within the quasi-2D interlayer space. The experimental data for the matrixes are successfully described using the soft potential model (SPM), which accounts for both acoustic phonons and low-energy tunneling states.

The reduced heat capacity of the magnetic Co(n)Al systems (Fig. 1) exhibits a significantly higher magnitude at low temperatures, indicating a dominant magnetic contribution superimposed on the lattice background.

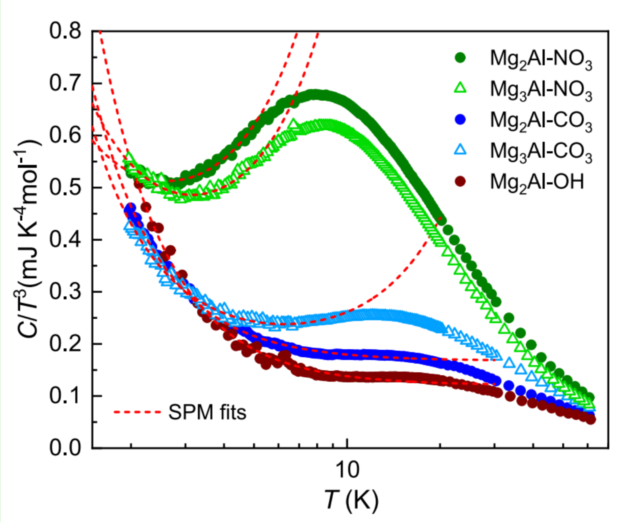


Fig. 2 Temperature dependence of the reduced heat capacity, C/T^3, of the Mg(n)Al LDH. Dashed lines represent the soft potential model (SPM) fits.

Isolation and analysis of the magnetic heat capacity for Co_2Al LDH

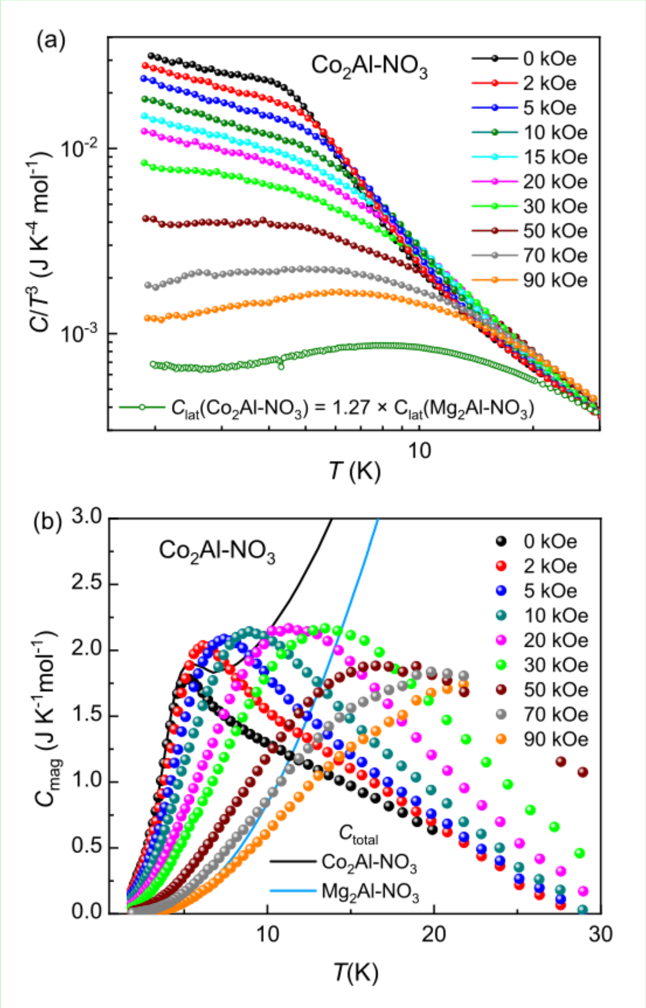


Fig. 3 (a) Temperature dependence of the reduced heat capacity of $Co_2Al\text{-}NO_3$ LDH. The lattice contribution to the heat capacity of $Co_2Al\text{-}NO_3$ is shown as green open circles. (b) Temperature dependence of the magnetic heat capacity of $Co_2Al\text{-}NO_3$ in different magnetic fields. The solid lines represent the total heat capacity of $Co_2Al\text{-}NO_3$ and $Mg_2Al\text{-}NO_3$ (for comparison).

To isolate the true magnetic contribution to the heat capacity of the $Co_2Al\text{-}NO_3$ system, the lattice background obtained from the non-magnetic Mg_2Al structural analog was successfully subtracted (Fig. 3a). In zero applied magnetic field, the resulting magnetic heat capacity C_{mag} exhibits a broad anomaly at low temperatures, which is associated with the onset of short-range magnetic correlations and long-range magnetic ordering. The application of an external magnetic field significantly modifies the low-temperature behavior (Fig. 3b), suppressing the low-temperature states and shifting the magnetic heat capacity maximum towards higher temperatures.

The field dependence of this peak position T_{max} (Fig. 4) reflects the redistribution of the magnetic entropy and demonstrates the transition from zero-field low-dimensional magnetic correlation regimes to a field-induced state.

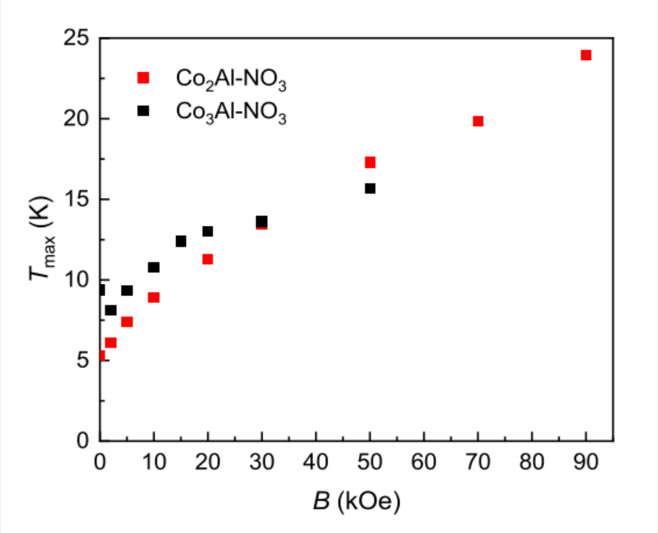


Fig. 4 Magnetic field dependence of the peak position (T_{max}) of the magnetic heat capacity of Co(n)Al-NO_3 (n = 2, 3).

Magnetic heat capacity of Co_3Al LDH and comparison of scaling behavior

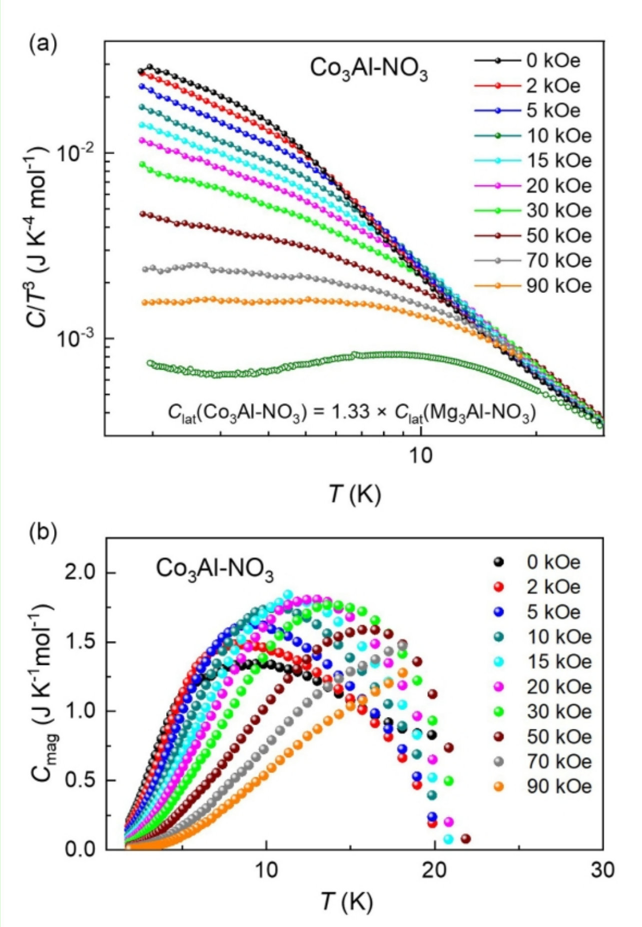


Fig. 6 (a) Temperature dependence of the reduced heat capacity of Co_3Al-NO_3 LDH. The lattice contribution to the heat capacity of Co_3Al-NO_3 is shown as green open circles. (b) Temperature dependence of the magnetic heat capacity of Co_3Al-NO_3 in different magnetic fields.

Similar to the previous system, the true magnetic heat capacity for Co_3Al-NO_3 was isolated by subtracting the lattice background of its non-magnetic Mg_3Al structural analog (Fig. 6a). In zero magnetic field, the magnetic contribution dominates at low temperatures, revealing a broad maximum shifted relative to the Co_2Al system due to different cation concentrations. The application of external magnetic fields up to 90 kOe systematically suppresses the low-temperature magnetic capacity and drives the anomaly toward higher temperatures (Fig. 6b), indicating a reorganization of the magnetic correlation network.

The log-log plots of the magnetic heat capacity (Fig. 5 and Fig. 7) allow a direct comparison of the magnon dimensionality and scaling behavior between the two systems. In zero magnetic field, the low-temperature magnetic heat capacity follows a power-law dependence C_{mag} proportional to T^{α}. The exponent α is sensitive to the Co/Al ratio, yielding $\alpha = 2.6$ for Co_2Al and $\alpha = 2.0$ for Co_3Al, which indicates a low-dimensional (quasi-2D) magnetic character. Under sufficiently strong applied magnetic fields, the scaling behavior of both systems undergoes a crossover and converges toward the conventional 3D magnon-like regime where C_{mag} is proportional to T^3, reflecting the suppression of low-dimensional magnetic fluctuations.

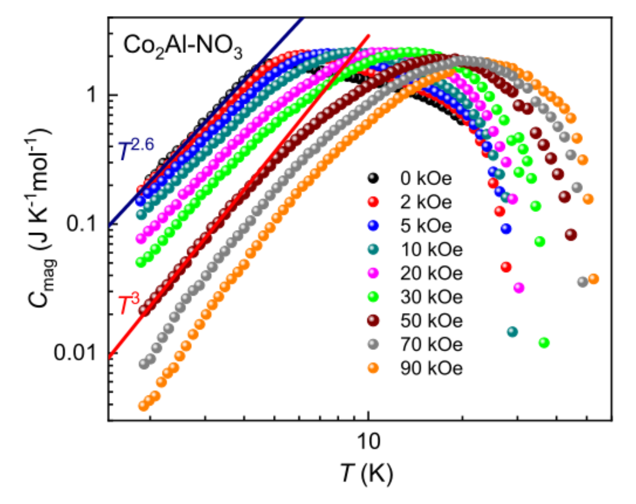


Fig. 5 Temperature dependence of the magnetic heat capacity of Co_2Al-NO_3 in different magnetic fields (log-log scale). See the main text for the details about the fitting models.

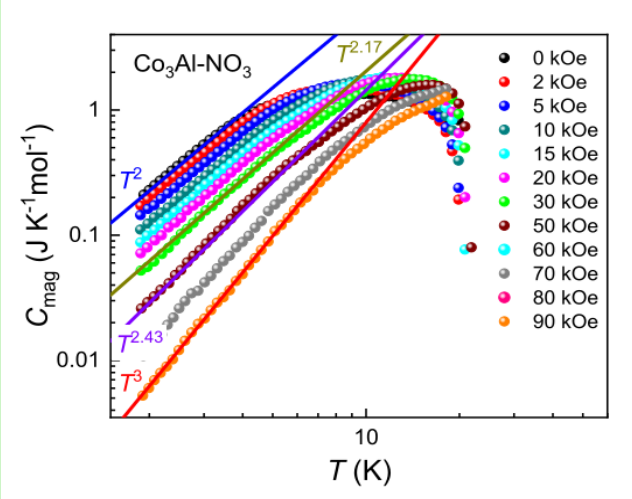


Fig. 7 Temperature dependence of the magnetic heat capacity of Co_3Al-NO_3 in different magnetic fields (log-log scale). See the main text for the details about the fitting models.

Conclusions and Acknowledgements

Conclusions

- Low-temperature heat capacity of non-magnetic Mg(n)Al (n = 2, 3) LDH matrixes reveals clear signatures of both two-dimensional lattice solids (bending modes) and structural glasses.
- The observed asymmetric maximum (boson peak) between 5 K and 15 K indicates intrinsic glassy disorder driven by the random positional and orientational distribution of intercalated anions and water molecules.
- A reliable method for lattice background isolation using non-magnetic structural analogs was validated, allowing the extraction of the true magnetic heat capacity contribution (C_{mag}) for Co(n)Al (n = 2, 3) systems.
- In zero applied magnetic field, C_{mag} dominates at low temperatures and follows a low-dimensional power-law dependence with exponents $\alpha = 2.6$ for Co_2Al and $\alpha = 2.0$ for Co_3Al.
- The application of strong external magnetic fields up to 90 kOe suppresses low-dimensional fluctuations and drives the magnon system toward a conventional 3D-like scaling regime with a cubic temperature dependence.

Acknowledgements

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