Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 866–868

Formation of a single-ion magnet in the lanthanum calcium silicate apatite structure by the cobalt oxide doping

Timur Z. Sharifullin, Alexander V. Vasiliev, Artem A. Eliseev, Andrei A. Eliseev, Sebastian Bette, Robert E. Dinnebier, Reinhard K. Kremer and Pavel E. Kazin

Experimental

Chemically grade La_2O_3, $CaCO_3$, SiO_2, and $CoCO_3$ in stoichiometric amounts were ground and mixed in an agate mortar, pre-annealed at 900 °C for 24 h in air, reground, pressed in pellets, and annealed at 1400 °C for 3 h in flowing argon. The products were reground, pressed in pellets, and finally annealed at 1500 °C for 25 h in flowing argon. The obtained ceramic samples were of yellow-grey color (**1**) and dark-grey color (**2**).

X-ray diffraction was performed on a Brucker D8 Advance powder diffractometer in Bragg-Brentano geometry using $CuK_{\alpha 1}$ radiation in the 2θ range 5 – 120°. The crystal structure was refined by the Rietveld method using the Jana 2006 computer program.[S1] The peak's profile parameters, unit cell parameters, positional parameters, and metal site's occupancies were refined. Hydrogen atoms and Co atoms were not included in the refinement. Anisotropic atomic displacement parameters were refined for La and Ca. For all other atoms, isotropic atomic displacement parameters were refined. La and Ca occupancies (fractions) were refined admitting full occupancy of M1 and M2 sites. Berar's correction was applied to calculate more realistic (larger) statistical errors.

Scanning electron microscopy (SEM) with energy-dispersive analysis (EDX) was conducted using a Leo Supra 50 VP electron microscope.

Raman spectra were measured with a RENISHAW in Via Reflex spectrometer at a laser wavelength λ = 532 nm in the Raman shift range 100 – 4000 cm^{-1}.

Measurements of magnetic susceptibility were conducted on a Quantum Design MPMS-7XL magnetometer using a piece of a ceramic sample firmly fixed to a sample holder. The dc measurements were performed in the dc field range -50 – +50 kOe at a temperature of 2 K and in the temperature range 2 – 300 K under dc fields of 1, 4, and 10 kOe. The ac measurements were performed in the ac field frequency range of 0.1 – 1420 Hz at an ac field amplitude of 4 Oe under a dc field of 4 kOe at fixed temperatures in the range of 2 – 20 K. The sample magnetization and

susceptibility were corrected for the magnetization of the sample holder and for the core diamagnetism using Pascal's constants.

The real χ' and imaginary χ'' parts of susceptibility as a function of ac-field frequency (f and $\omega = 2\pi f$) were fitted simultaneously using the generalized Debye model:[S2]

$$\chi'(\omega) = \chi_S + \frac{(\chi_0 - \chi_S)\left[1+(\omega\tau)^{1-\alpha} sin(0.5\alpha\pi)\right]}{1+2(\omega\tau)^{1-\alpha} sin(0.5\alpha\pi)+(\omega\tau)^{2(1-\alpha)}}, \quad \text{(S1)}$$

$$\chi''(\omega) = \frac{(\chi_0 - \chi_S)\,(\omega\tau)^{1-\alpha} cos(0.5\alpha\pi)}{1+2(\omega\tau)^{1-\alpha} sin(0.5\alpha\pi)+(\omega\tau)^{2(1-\alpha)}}, \quad \text{(S2)}$$

where τ is a relaxation time, χ_0 and χ_S are equilibrium and adiabatic susceptibilities, α is the relaxation time distribution width. The simultaneous fitting helped to reduce correlations between τ, α, and $\chi_0 - \chi_S$. The more detailed description of the measurements and the data treatment can be found in ref. [S3,S4].

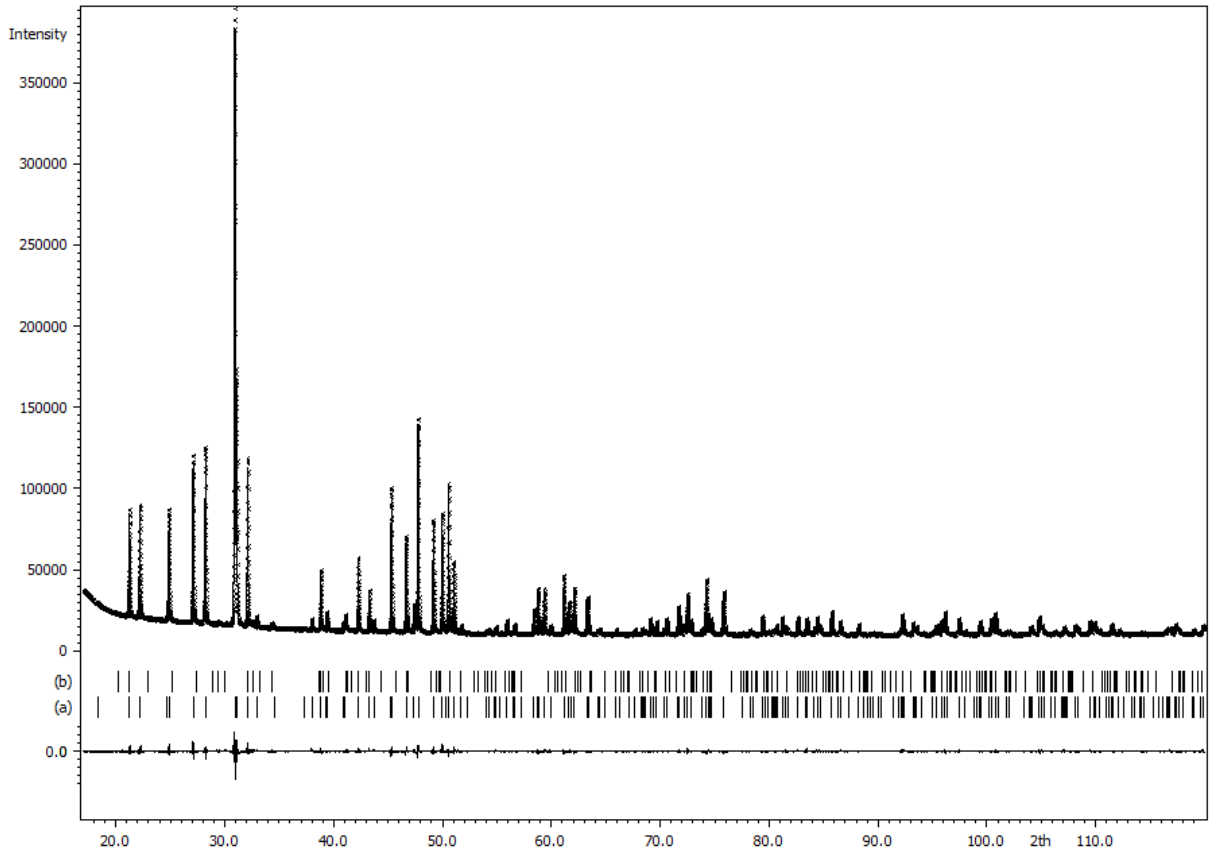


Figure S1 Powder X-ray diffraction pattern of **1**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown by vertical bars underneath. (a) main apatite phase; (b) admixture of Ca_3SiO_5, main peak intensity 0.9 %.

Table S1 Crystal structure refinement data for **1**.

Chemical composition	$La_{7.65}Ca_{2.35}(SiO_4)_6O_2[Co_{0.02}H_y]$
Temperature (K)	293 K
Wavelength (Å)	1.5406
Space group	$P6_3/m$
a (Å)	9.6510(1)
c (Å)	7.1529(1)
V (Å^3)	576.98(2)
Z	1
2θ range (deg.)	10 – 120
R_{wp}	0.017
R_{all}	0.013
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.48, -0.73

Table S2 Atom positional parameters and displacement parameters (Å^2) for **1** at ambient conditions.

Atom[a]	La1/ Ca1	La2/ Ca2	Si1	O1	O2	O3	O4
Site	4f	6h	6h	6h	6h	12i	2b
SOF	0.514(5)/ 0.486(5)	0.933(8)/ 0.067(8)	1	1	1	1	1
x	1/3	0.24624(9)	0.3724(5)	0.4913(9)	0.4703(17)	0.2557(6)	0
y	2/3	0.01464(13)	0.4028(4)	0.3289(9)	0.5994(16)	0.3394(5)	0
z	0.0024(4)	1/4	1/4	1/4	1/4	0.0701(6)	0.25
U_{eq}, U_{iso}	0.0098(5)	0.0085(5)	0.0110(12)	0.015(3)	0.015(2)	0.019(2)	0.012(3)
U_{11}	0.0090(6)	0.0076(7)					
U_{22}	0.0090(6)	0.0072(7)					
U_{33}	0.0114(10)	0.0076(5)					
U_{12}	0.0045(3)	0.0013(6)					
U_{13}	0	0					
U_{23}	0	0					

[a] Positions of hydrogen atoms were not determined in the structure. Co atoms were not included into refinement since their content in the compound was small, about 0.02 per formula unit.

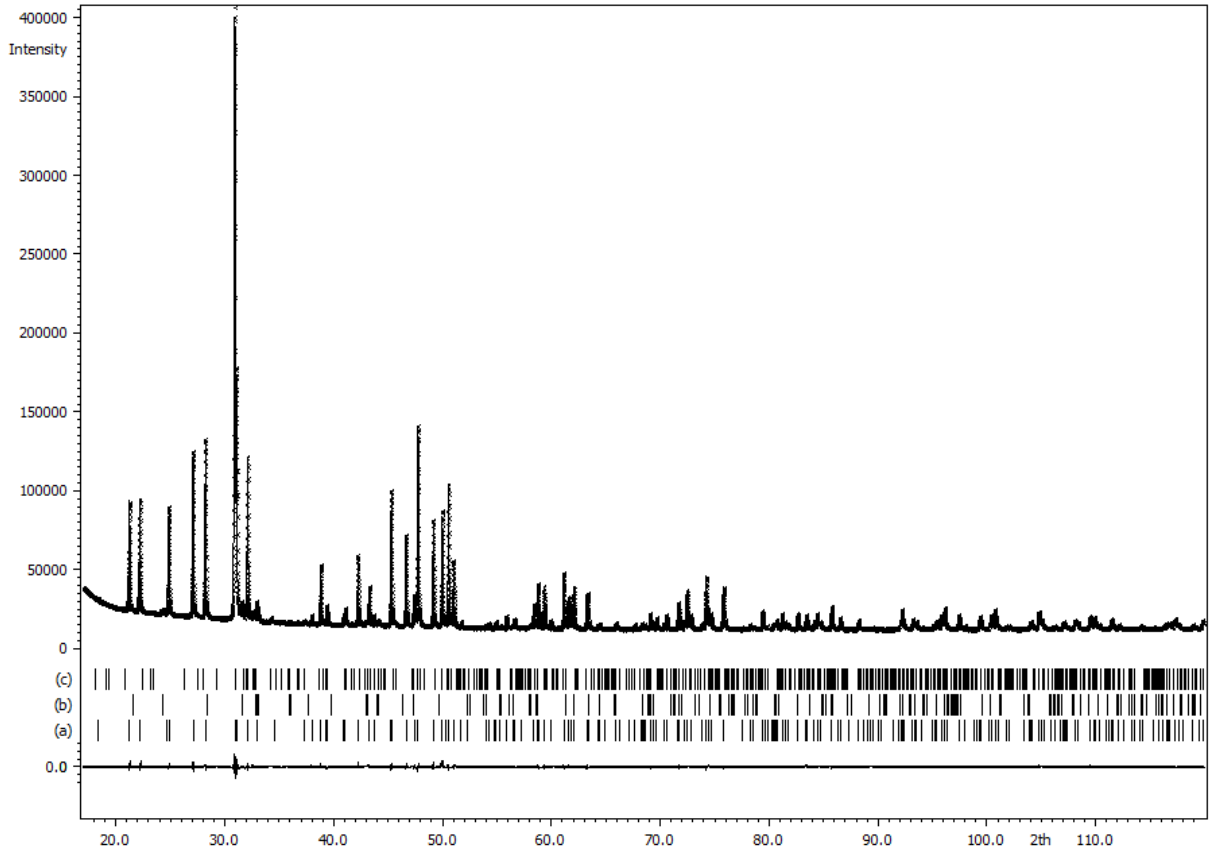


Figure S2 Powder X-ray diffraction pattern of **2**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown are shown by vertical bars underneath. (a) main apatite phase; (b) admixture of La_2CoO_4, main peak intensity 3 %; (c) admixture of Ca_2SiO_4, main peak intensity 1.7 %.

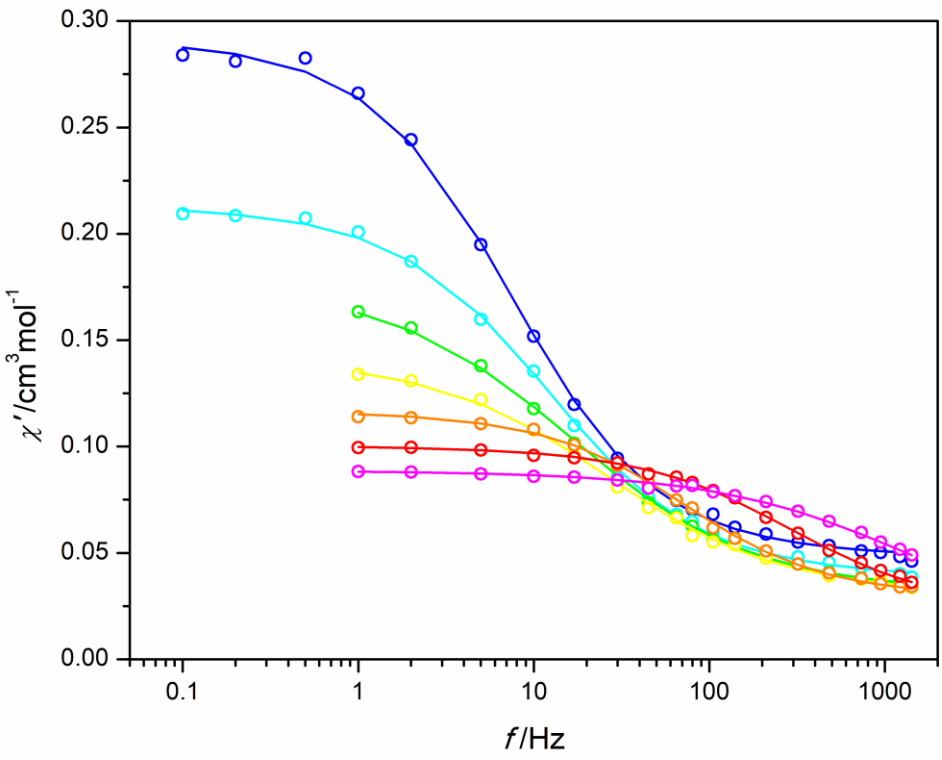
Table S3 Crystal structure refinement data for **2**.

Chemical composition	$La_{7.77}Ca_{2.23}(SiO_4)_6O_2[Co_{0.06}H_y]$
Temperature (K)	293 K
Wavelength (Å)	1.5406
Space group	$P6_3/m$
a (Å)	9.6511(1)
c (Å)	7.1553(1)
V (Å^3)	577.17(2)
Z	1
2θ range (deg.)	10 – 120
R_{wp}	0.013
R_{all}	0.011
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.42, -0.59

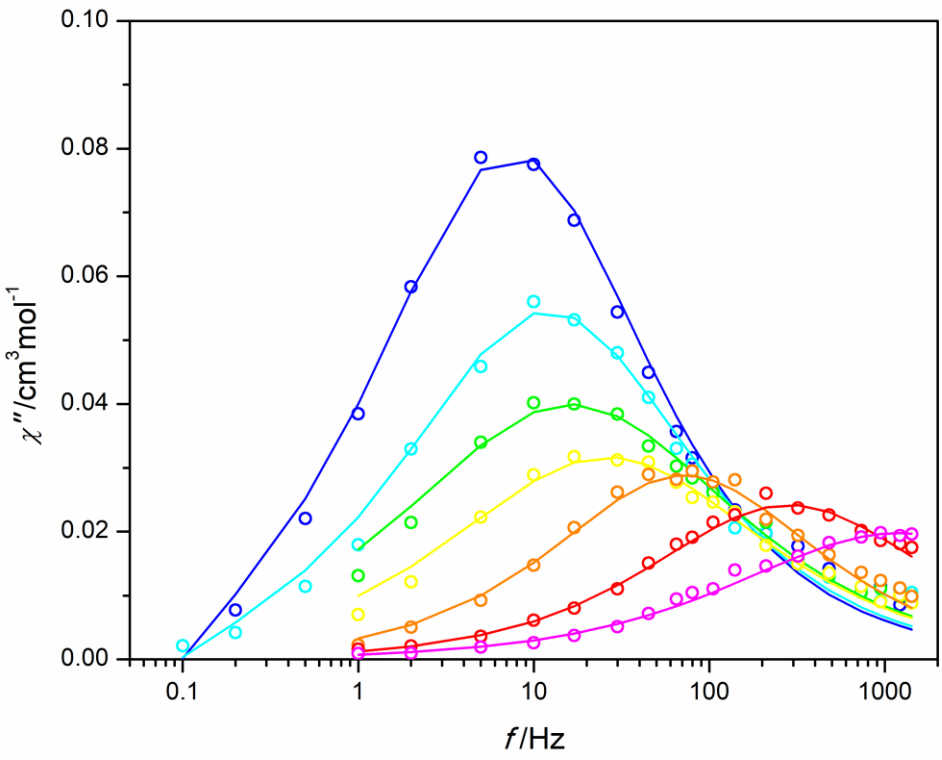
Table S4 Atom positional parameters and displacement parameters (Å^2) for **2** at ambient conditions.

Atom[a]	La1/ Ca1	La2/ Ca2	Si1	O1	O2	O3	O4
Site	4f	6h	6h	6h	6h	12i	2b
SOF	0.526(5)/ 0.474(5)	0.945(8)/ 0.055(8)	1	1	1	1	1
x	1/3	0.24633(9)	0.3717(4)	0.4927(8)	0.4696(9)	0.2548(6)	0
y	2/3	0.01499(12)	0.4030(4)	0.3312(8)	0.5986(9)	0.3404(5)	0
z	0.0023(3)	1/4	1/4	1/4	1/4	0.0708(6)	0.25
U_{eq}, U_{iso}	0.0095(5)	0.0074(5)	0.0088(11)	0.014(3)	0.018(2)	0.017(2)	0.011(3)
U_{11}	0.0088(6)	0.0061(7)					
U_{22}	0.0088(6)	0.0067(7)					
U_{33}	0.0108(10)	0.0064(5)					
U_{12}	0.0044(3)	0.0010(6)					
U_{13}	0	0					
U_{23}	0	0					

[a] Positions of hydrogen atoms were not determined in the structure. Co atoms were not included into refinement since their content in the compound was small, about 0.06 per formula unit.

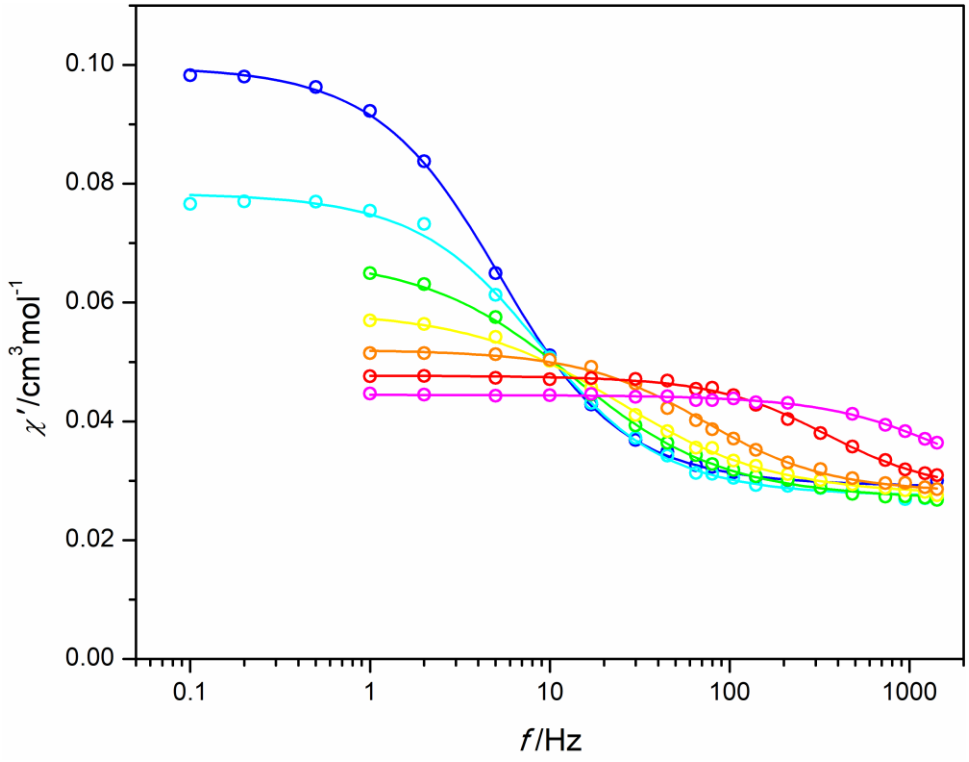


(a)

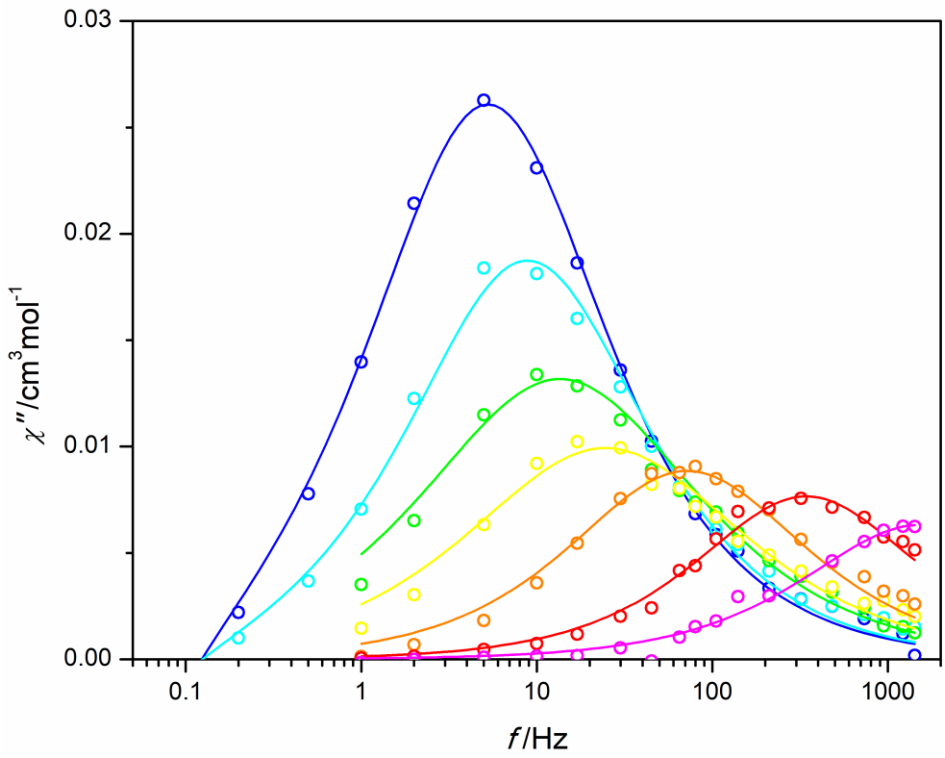


(b)

Figure S3 Frequency dependence of ac susceptibility per mol of Co in **1** at temperatures 2 – 8 K with the 1 K step (color codes from blue to magenta) under a dc magnetic field of 4 kOe. Symbols – experimental points, lines – fitting. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''.



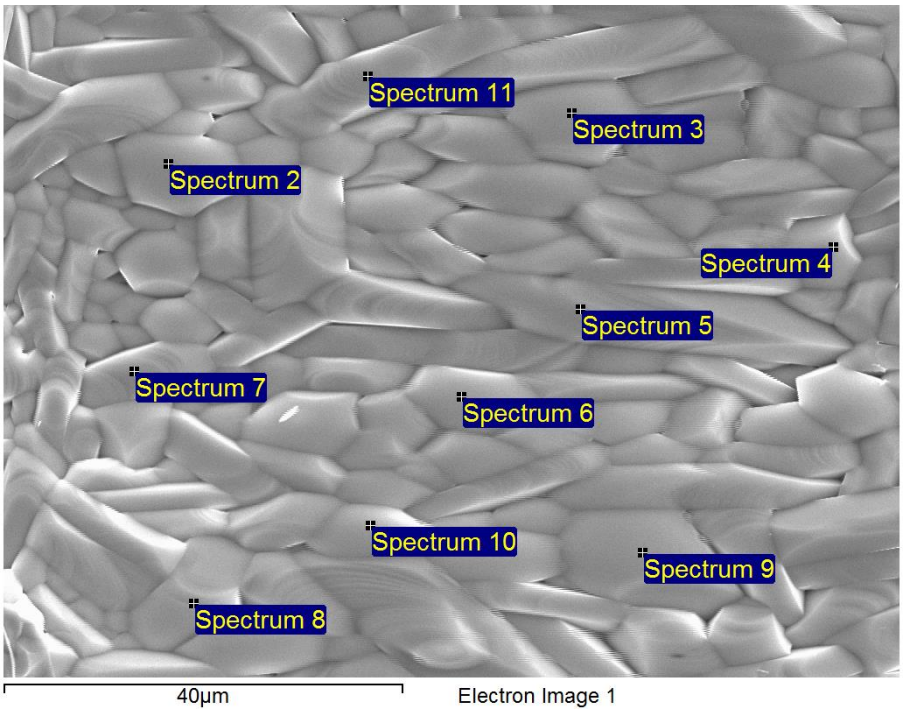
(a)



(b)

Figure S4 Frequency dependence of ac susceptibility per mol of Co in **2** at temperatures 2 – 8 K with the 1 K step (color codes from blue to magenta) under a dc magnetic field of 4 kOe. Symbols – experimental points, lines – fitting. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''.

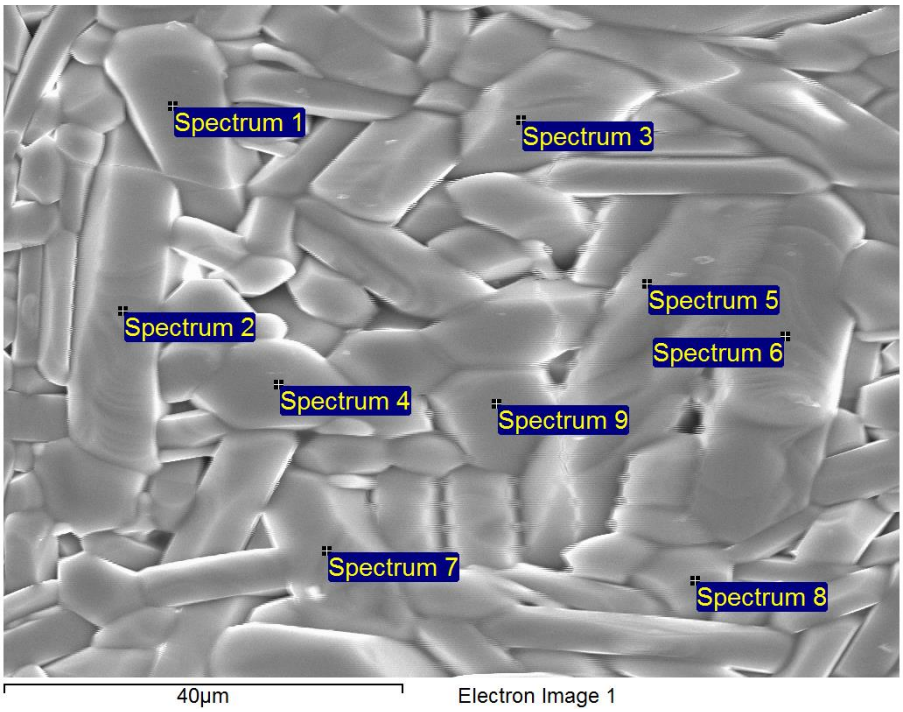
SEM with EDX analysis for sample 1



Processing option: All elements analyzed (Normalized). All results in atomic %

Spectrum	In stats.	Si	Ca	Co	La
Spectrum 2	Yes	40.14	12.38	0.11	47.37
Spectrum 3	Yes	33.89	13.23	0.15	52.74
Spectrum 4	Yes	43.97	12.46	0.24	43.34
Spectrum 5	Yes	37.66	12.56	0.19	49.59
Spectrum 6	Yes	33.84	13.27	0.08	52.81
Spectrum 7	Yes	34.30	13.27	0.00	52.43
Spectrum 8	Yes	42.08	12.27	0.12	45.52
Spectrum 9	Yes	39.37	12.59	0.07	47.97
Spectrum 10	Yes	32.94	13.68	0.05	53.33
Spectrum 11	Yes	36.00	12.90	0.21	50.88
Mean		37.41	12.86	0.12	49.60
Std. dev.		3.84	0.48	0.07	3.45

SEM with EDX analysis for sample 2



Processing option: All elements analyzed (Normalized). All results in atomic %.

Spectrum	In stats.	Si	Ca	Co	La
Spectrum 1	Yes	40.89	12.50	0.33	46.28
Spectrum 2	Yes	40.04	13.33	0.47	46.16
Spectrum 3	Yes	41.19	12.39	0.34	46.09
Spectrum 4	Yes	39.67	12.54	0.33	47.46
Spectrum 6	Yes	38.82	13.11	0.39	47.68
Spectrum 8	Yes	43.85	12.00	0.39	43.76
Spectrum 9	Yes	43.67	12.14	0.35	43.84
Mean		41.16	12.57	0.37	47.00
Std. dev.		1.93	0.49	0.05	1.56

References

S1. V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr.-Cryst. Mater.* 2014, **229**, 345.

S2. S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L. Brunel, A. L. Rheingold, G. Christou and D. N. Hendricson, *Inorg. Chem*., 1999, **38**, 5329.

S3. P. E. Kazin, M. A. Zykin, V. V. Utochnikova, O. V. Magdysyuk, A. A. Vasiliev, Y. V. Zubavichus, W. Schnelle, C. Felser and M. Jansen, *Angew. Chem. Int. Ed*., 2017, **56**, 13416.

S4. P. E. Kazin, M. A. Zykin, L. A. Trusov, A. V. Vasiliev, R. K. Kremer, R. E. Dinnebier and M. Jansen, *RSC Adv.*, 2020, **10**, 37588.