Electronic Supplementary Information

Electronic and magnetic states of Fe ions in the Co$_2$FeBO$_5$

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Details of the calculations of the probabilities of the quadrupole splittings (*P(QS)*) and hyperfine fields (*P(H*$_{hf}$*)*).

The interpretation of the spectra was performed in two stages. At the first stage, the probability distribution of the quadrupole splitting *P(QS)* was determined. Such calculation gives possible nonequivalent iron positions in the samples.

To perform the *P(QS)*/*P(H$_{hf}$)* calculation, the experimental spectrum was filled by a number of doublets/sextets with Lorentzian line-form and natural line-width (*W* = 0.24 mm/s for ^{57}Co(Rh) source) and *QS*/*H$_{hf}$* with the step Δ = 0.01 mm/s (1.3 kOe) (in our case, from 0.00 mm/s to 2.2 mm/s and from 200 to 560 kOe). Then, the isomer shift and intensity of Mössbauer lines were varied. As a result, we obtained the set of the intensities corresponding to each doublet/sextet in our series. These data conform to the probability of each doublet/sextet existence in the experimental spectrum.

Then, based on these calculations, we formed a preliminary spectrum. It contained a set of Mössbauer doublets, corresponding to possible non-equivalent positions and modelling as a group of the analytical functions. This group was fitted to the experimental spectrum by varying the entire set of hyperfine parameters using the least-squares method in the linear approximation (χ^2 criterion). Mössbauer absorption lines were represented by the pseudo-Voight function, following the equation

$$I = I\left(\frac{k}{(1 + x_i)^2} + (1 - k) \cdot e^{-\ln 2 \cdot x_i^2}\right).$$

Here, $x_i = 2 \cdot \left(\frac{IS - i}{W}\right)$, i – is a channel number. *I*, *IS* and *W* are hyperfine parameters (line intensity, isomer shift, and line-width, respectively), nominated in channels, k – is the Lorentz-Gauss parameter, which determines the absorption line form. In our case the approximation of the Lorentz form was used, i.e. $k = 1$.
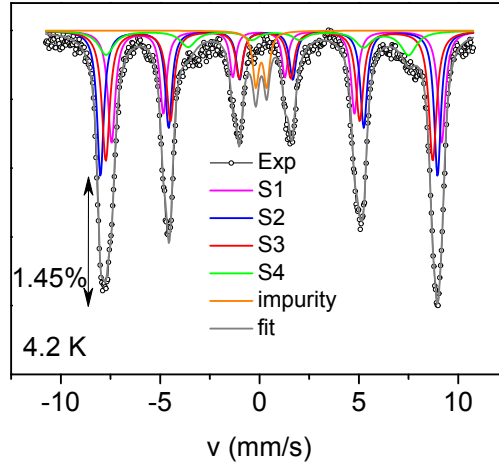
Fig. 1S. The original Mössbauer spectrum measured at T=4.2 K. The solid lines S1, S2, S3, and S4 indicate the calculated spectrum components corresponding to high-spin Fe^{3+} ions in the Co_2FeBO_5 ludwigite, the orange line corresponds to an accident impurity as a result of grinding. The absorption scale is shown in the %.

Table S1. The hyperfine structure parameters for Co_2FeBO_5 obtained at intermediate temperatures: IS – isomer chemical shift with respect to αFe (± 0.01 mm/s), $H_{hf.}$ –hyperfine field (± 10 kOe), QS, 2ε – quadruple splitting in the paramagnetic and magnetic regimes, respectively (± 0.02 mm/s), W is the half-line width (±0.06 mm/s), dH_{hf} is the hyperfine magnetic field spread modulating the line-width, A is the area of the corresponding component (the iron occupation factor) (± 0.03 a.u.).

T (K)		IS (mm/s)	H_{hf} (kOe)	QS, 2ε (mm/s)	W (mm/s)	dH (mm/s)	A (a.u.)
147	D1	0.49		1.91	0.34		0.10
	D2	0.46		1.14	0.37		0.51
	D3	0.48		0.92	0.26		0.25
	D4	0.48		0.66	0.27		0.14
120	D1	0.50		1.89	0.39		0.12
	D2	0.48		1.16	0.36		0.49
	D3	0.48		0.92	0.26		0.24
	D4	0.48		0.63	0.29		0.15
60	S1	0.52	493	1.60	0.44	0.08	0.17
	S2	0.48	495	0.20	0.53	0.13	0.26
	S3	0.47	446	0.67	0.52	0.68	0.25
	S4	0.49	402	-0.44	0.81	2.15	0.32
20	S1	0.53	517	1.86	0.28	0.15	0.20
	S2	0.53	527	0.27	0.40	0.00	0.27
	S3	0.48	513	0.54	0.41	0.00	0.36
	S4	0.51	462	-1.16	1.17	0.00	0.18

Table S2. Lattice parameters and unit-cell volume for Co_2FeBO_5 calculated from the DFT-optimized structure for the "Fe4(HS)", "Fe4(HS,LS)", and "Fe4-Fe2-Fe4" models at T=0 K and obtained from single crystal X-ray diffraction experiment at T=296 K [17].

	"Fe4(HS)"	"Fe4(HS,LS)"	"Fe4-Fe2-Fe4"	Experiment [16]
Space group	*Pbam*(55)	*Pbam*(55)	*Pbam*(55)	*Pbam*(55)
a (Å)	9.3224	9.2547	9.1956	9.3818
b (Å)	12.259	12.2266	12.1626	12.3445
c (Å)	3.0095	2.9721	3.0106	3.0578
V (Å^3)	343.94	336.31	336.72	354.13

Table S3. The occupation numbers and anisotropy Δn_d of the spin-up and spin-down Fe3d-shell of Fe ions occupying metal sites in Co_2FeBO_5 according to three cation distribution.

Model	Fe site		n_{xz}	n_{yz}	n_{xy}	n_{x2-y2}	n_{z2}	Δn_d
"Fe4(HS)"	Fe4(HS)	spin-up	0.27	0.21	0.21	0.27	0.19	0.050
		spin-down	0.95	0.93	0.95	0.95	0.95	0.010
"Fe4(HS,LS)"	Fe4(HS)	spin-up	0.27	0.21	0.21	0.26	0.21	0.020
		spin-down	0.94	0.95	0.93	0.95	0.95	-0.015
	Fe4(LS)	spin-up	0.43	0.66	0.54	0.60	0.48	0.115
		spin-down	0.47	0.84	0.72	0.67	0.71	0.025
"Fe4-Fe2-Fe4"	Fe4(HS)	spin-up	0.27	0.21	0.21	0.26	0.20	0.030
		spin-down	0.94	0.93	0.95	0.95	0.95	0.015
	Fe2(LS)	spin-up	0.43	0.87	0.54	0.79	0.84	-0.160
		spin-down	0.66	0.52	0.41	0.94	0.45	0.310