

## Mössbauer study of giant hard magnetic $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$

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**Abstract**  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  was prepared by hydrothermal synthesis. The crystal structure is the isomorphous phase of  $\text{K}_2\text{Co}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$ . Mössbauer spectra of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  were measured at low temperatures between room temperature and 14 K, and the hyperfine interactions were analyzed. The Neel temperature is 39 K. Two paramagnetic  $\text{Fe}^{2+}$  species were observed in the Mössbauer spectrum at room temperature, and Mössbauer spectra measured below 38 K were decomposed into four magnetic subspectra. From the temperature dependence, it is found that the local electron density at each site is largely deviating at low temperatures, which may induce the giant coercivity.

**Keywords** Magnetic material · Hard magnet · Potassium iron compound · Mössbauer spectra

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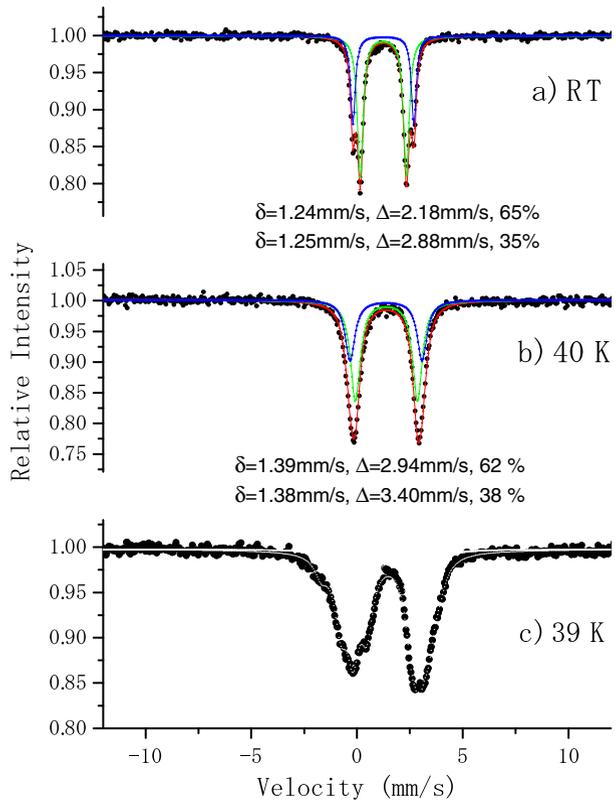
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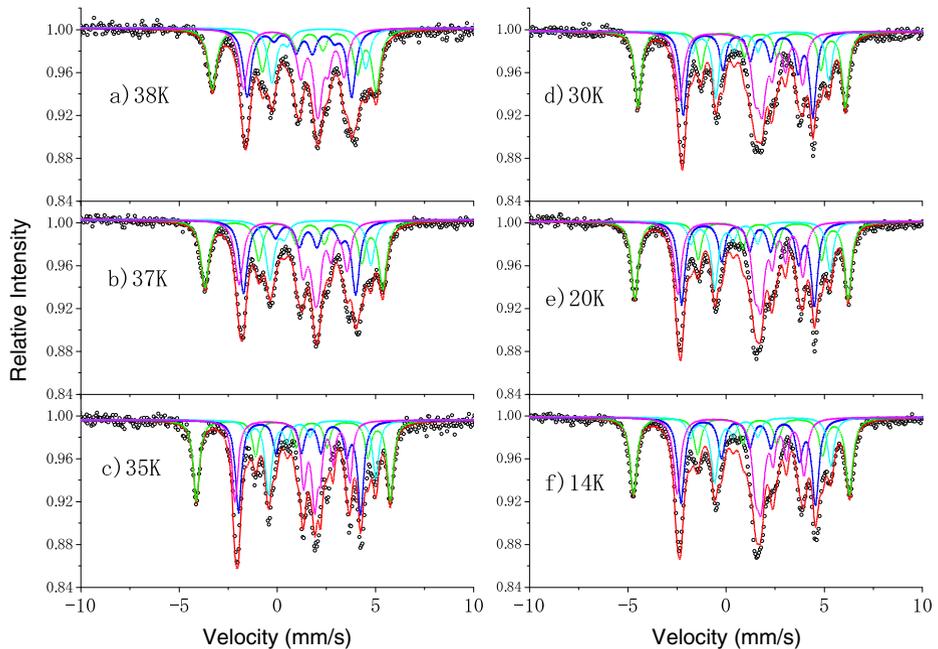
**Table 1** Lattice constant of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$ , compared with  $\text{K}_2\text{Co}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$ 

Space group: $\text{Cmc}2_1$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
Fe compound	17.9118(5)	7.6591(2)	9.8570(3)	1352.26(6)
Co compound	17.9496(9)	7.5576(4)	9.7594(6)	1323.93(12)

**Fig. 1** Mössbauer spectra of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  at room temperature, 40 K and 39 K

## 1 Introduction

A method for controlling coercivity in synthesizing magnetic materials is not well known though it is said that the anisotropy energy of the crystal increases magnetic coercivity. The anisotropic magnetic moments of transition metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Mn}^{3+}$  are large enough, but it is difficult to control the magnetic moments in crystals. It was reported that monocrystalline  $\text{K}_2\text{Co}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  is a ferrimagnetic material with large coercive fields ( $H//a$ ; 50 kOe,  $H//b$ ; 25 kOe at 1.8 K). Its Neel temperature is 30 K [1]. As oxides with high coercivity, it is known that  $\epsilon\text{-Fe}_2\text{O}_3$  [2] shows a high coercive field of 22 kOe at room temperature [3]. The coercive field of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  is 40 kOe at 4 K, and the Neel temperature is about 39 K. In order to clarify the local magnetic properties of this compound, we have studied the temperature dependence of the Mössbauer spectra, and determined the magnetic hyperfine fields at the iron atoms occupying each site.



**Fig. 2** Mössbauer spectra of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$ , measured at **a)** 38 K, **b)** 37 K, **c)** 35 K, **d)** 30 K, **e)** 20 K, and **f)** 14 K

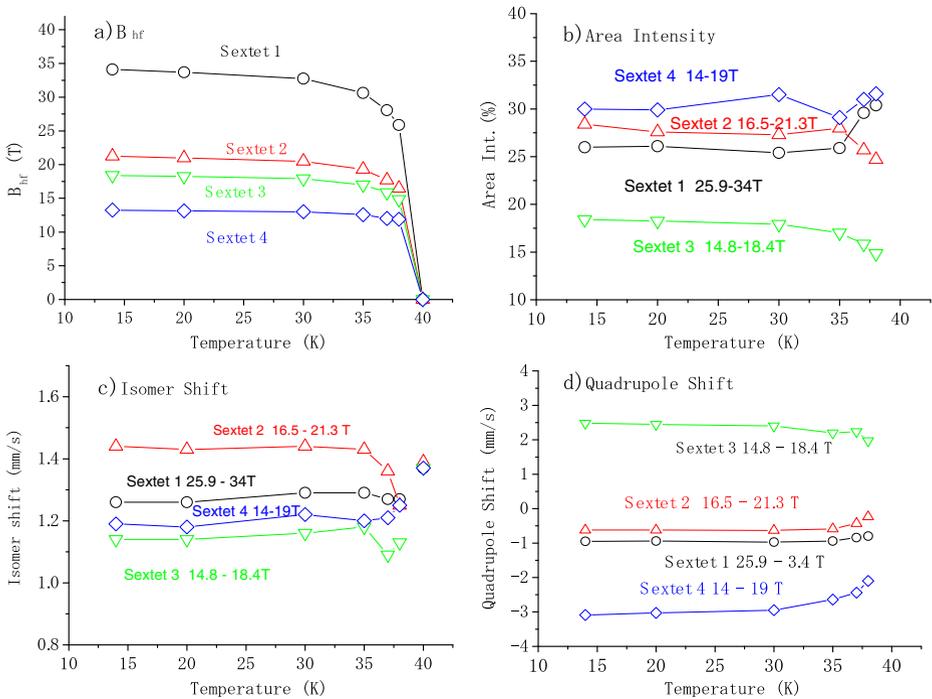
## 2 Experimental

A powder sample was synthesized in an autoclave for 48 h at the temperature of 200°C by mixing iron sulphate, potassium sulphate, and potassium hydroxide with the molar ratio at 2:1:1. The crystal structure of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  was determined being isomorphous with that of the Co system by X-ray diffraction [1] as shown in Table 1.

Mössbauer spectra were measured by using  $^{57}\text{Co}(\text{Cr})$  and a constant acceleration mode, and the Doppler velocity was calibrated using the data of an  $\alpha\text{-Fe}$  foil at room temperature. Low temperature Mössbauer spectra were measured using a mini cryostat (Iwatani Co.). Mosswin software was used for the analysis of the Mössbauer spectra.

## 3 Results and discussion

Two doublets of paramagnetic  $\text{Fe}^{2+}$  (isomer shift,  $\delta = 1.24 \pm 0.01$  mm/s, quadrupole splitting,  $\Delta = 2.18 \pm 0.02$  mm/s, line width,  $\Gamma = 0.30 \pm 0.01$  mm/s, Area relative intensity =  $65 \pm 1\%$ ;  $\delta = 1.25 \pm 0.01$  mm/s,  $\Delta = 2.88 \pm 0.02$  mm/s,  $\Gamma = 0.30 \pm 0.01$  mm/s, Area int. =  $35 \pm 1\%$ ) were observed in the room temperature Mössbauer spectrum as shown in Fig. 1. At 40 K, the isomer shift and quadrupole splitting of both doublets increased a little, and the difference between the two doublets became small. The electronic density at the two iron sites is not different, but the



**Fig. 3** Temperature dependence on **a** internal magnetic fields, **b** area intensity, **c** isomer shifts, and **d** quadrupole shifts of  $K_2Fe_3(OH)_2(SO_4)_3(H_2O)_2$ . The errors were estimated as follows; **a**  $B_{hf} \leq 0.1$  T, **b** Area Intensity  $\leq 0.5\%$ , **c** Isomer shift  $\leq 0.01$  mm/s, **d** Quadrupole shift  $\leq 0.02$  mm/s

electric field gradient around  $Fe^{2+}$  is strongly affected at low temperatures. At 39 K, magnetic ordering began to occur, but it was hard to analyze the Mössbauer spectrum precisely. Mössbauer spectra measured below 38 K were clearly developed into four magnetic sextets as shown in Fig. 2. The analysed Mössbauer parameters are shown in Fig. 3. Four magnetic sextets show  $B_{hf} = 34.0$  T, 21.3 T, 19.0 T, and 18.4 T at 14 K (Fig. 3a). The magnetic sextets with high magnetic field order are named as sextet 1, 2, 3 and 4. The area intensity ratios are shown in Fig. 3b). Considering the sites occupied by  $Fe^{2+}$  in the crystalline structure, there are two sites with 1: 2 ratios, in which the directions of magnetic moments are anti-parallel with respect to each other [1]. The site occupation ratio is reflected in the Mössbauer spectra measured above 40 K. This shows ferrimagnetism at the lower temperatures, but four different Fe sites were observed at the lower temperatures. It might arise from the distorted crystallites because the large synthesized polycrystals were crushed in order to make uniform thickness of absorbers for the measurement of the Mössbauer spectra. The powder may contain amounts of small crystals with oriented planes. The area intensity ratio of the sextet lines was not always 3:2:1:1:2:3 as for a random orientation of magnetic moments. When analysing Mössbauer spectra, the area intensity of second and fifth peaks was not fixed.

The isomer shifts of the four magnetic sextets are between 1.15 mm/s and 1.45 mm/s below 35 K, which mean completely  $Fe^{2+}$  states. The deviating isomer

shifts and area intensities observed at 37 and 38 K may be due to fitting errors because of overlapping sub-spectra. The isomer shift values of the four sextets are very different from those of the two doublets (1.38 mm/s) at 40 K. This means that a charge disproportion of each site may occur at lower temperatures as shown in Fig. 3c. One quadrupole shift value of a sextet increased while the quadrupole shift values of the other three sextets decreased when lowering the measurement temperature (Fig. 3d). Moreover, the quadrupole shifts of the magnetic components were somewhat enhanced when lowering the temperature, which may suggest a crystalline distortion. These Mössbauer results may support that the compounds have large coercive fields.

#### 4 Conclusion

$\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  was prepared by hydrothermal synthesis as an isomorphous phase of  $\text{K}_2\text{Co}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$ . Mössbauer spectra of  $\text{K}_2\text{Fe}_3(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_2$  were measured at low temperatures between room temperature and 14 K. Two paramagnetic  $\text{Fe}^{2+}$  species were observed in the Mössbauer spectra above 40 K, and Mössbauer spectra measured below 38 K were decomposed into four magnetic subspectra. From the temperature dependence of isomer shifts, quadrupole shifts and magnetic fields, it is found that the local electron density at each site is largely deviating at low temperatures, which may induce the giant coercivity.

#### References

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