

Experimental Evidence for Jahn–Teller Transition in a Fe(II)Fe(III) Bimetallic Oxalate

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Bimetallic oxalate $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ has been investigated by the Mössbauer spectroscopy. The Mössbauer studies confirm that high-spin Fe(III) ($S = 5/2$) and Fe(II) ($S = 2$) ions are present in the compound. These spectra above 60 K consist of three quadrupole doublets, indicating that there are three different Fe sites in the material. The Mössbauer results reveal that spontaneous magnetization of Fe(II) sublattices increases more steeply than that of Fe(III) sublattices as the temperature decreases from T_C . Great increase of quadrupole splitting at 50 K provides compelling evidence for the predicted Jahn–Teller transition.

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1. Introduction

An important class of molecule-based magnets, the bimetallic oxalate with the chemical formula $A[M(II)M'(III)(ox)_3]$ has been extensively studied due to their novel magnetic properties [1–11]. Bimetallic oxalate $A[M(II)M'(III)(ox)_3]$ has basic layer structure in which a two-dimensional bimetallic honeycomb lattice consisting of coordinated oxalato-anions is interleaved with organic cation A^+ [1, 12, 13]. Depending on the organic cation, bimetallic oxalates can be optically activated, metallic, or disordered. Some of highest magnetic transition temperature T_C among the bimetallic oxalates are found in the ferrimagnetic Fe(II)Fe(III) bimetallic oxalates [1, 12]. The magnetic pole reversal and magnetic compensation have been intensively documented in the Fe(II)Fe(III) bimetallic oxalates [8–11]. The multiple magnetic pole reversals and two magnetic compensation temperatures were observed by us in an Fe(II)Fe(III) bimetallic oxalate $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ [7].

Recently, Fishman et al. predicted fascinating Jahn–Teller (JT) transition in Fe(II)Fe(III) bimetallic oxalates based on first-principles calculation [14]. However, the experimental evidence for it has not been reported in these materials up to now. A JT transition removes the degeneracy of a single-occupied orbital by a crystal distortion. The Mössbauer hyperfine parameters had strong correlation with structural symmetry. As a particularly useful probe, the Mössbauer spectroscopy may provide strong evidence for JT transition. The significant discovery inspires us to verify their prediction by performing the Mössbauer measurements on Fe(II)Fe(III) bimetallic oxalates.

Here, we investigate Fe(II)Fe(III) bimetallic oxalate $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ by ^{57}Fe Möss-

bauer spectroscopy. Great increase of quadrupole splitting (QS) at 50 K provides compelling evidence for the predicted JT transition in the material. Meanwhile, the Mössbauer results reveal that the spontaneous magnetization of Fe(II) sublattices increases more steeply than that of Fe(III) sublattices as the temperature decreases from T_C .

2. Experimental section

Preparation of $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ used in this investigation was described previously [7]. Analytically calculated for $C_{22}H_{36}NO_{12}Fe_2$: C, 42.60; H, 5.86; N, 2.26. Found: C, 42.29; H, 5.85; N, 2.20. The phase purifying of the sample was examined by X-ray diffraction (XRD) with Cu K_α radiation. XRD confirms that a single phase compound is obtained. Magnetic measurements were performed with a superconducting quantum interference device measurement system.

The radioactive source used for the Mössbauer measurements was ^{57}Co (Pd). We recorded the absorption Mössbauer spectra with a conventional constant acceleration spectrometer and a helium bath cryostat. All spectral patterns were fitted with the MössWin3.0 software and the hyperfine parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shifts are relative to α -Fe at room temperature.

3. Results and discussions

The Mössbauer spectra at different temperatures are present in Figs. 1 and 2. The values of isomer shift (IS), quadrupole splitting (QS) and hyperfine magnetic field (H_{hf}) are listed in Table. The spectra above 60 K consist of three quadrupole doublets. The doublet one is typical for the high-spin Fe(III) ($S = 5/2$) complex $[Fe(III)(ox)_3]^{3-}$. The doublet two has the characteristic of the high-spin Fe(II) (I) ($S = 2$) which is involved in the oxalate bridge to the adjacent Fe(III) ion. It is

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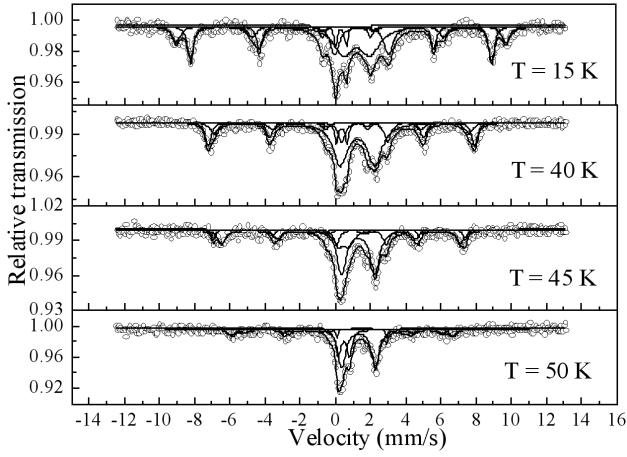


Fig. 1. Mössbauer spectra of $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ at 15, 40, 45 and 50 K.

worthy to note that weak high-spin Fe(II)(II) ($S = 2$) resonances (which represent $\approx 3.9\%$ of the spectrum at 50 K) are present, which can be attributed to the existence of $[Fe(II)(ox)_3]^{4-}$ complex. A small fraction of these Fe(II)(II) ions has obviously been incorporated into

the nearest $[Fe(III)(ox)_3]^{3-}$ network during the preparation procedures [15]. Our results are consistent with previous report that an impurity of a few percent of $Fe(C_2O_4) \cdot 2H_2O$ is evidenced [16].

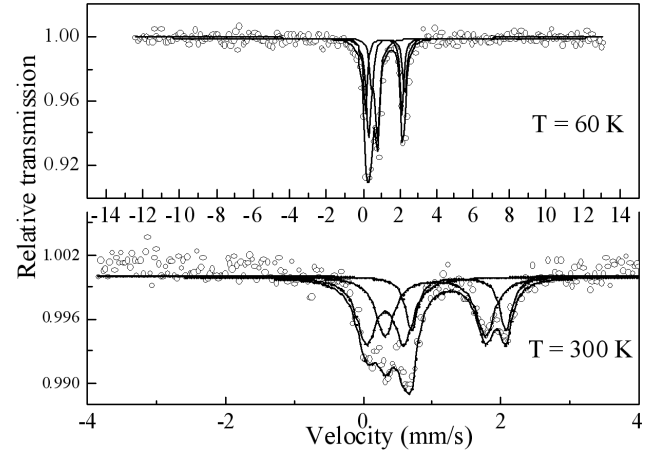


Fig. 2. Mössbauer spectra of $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ at 60 K and 300 K.

Mössbauer parameters of $\{[N-(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ at various temperatures.

TABLE

T [K]	Fe(II)(I) doublet			Fe(II)(II) doublet			Fe(III) doublet			Fe(III) sextet			
	IS [mm/s]	QS [mm/s]	Area [%]	IS [mm/s]	QS [mm/s]	Area [%]	IS [mm/s]	QS [mm/s]	Area [%]	IS [mm/s]	QS [mm/s]	H_{hf} [T]	Area [%]
300 K	1.04	1.46	37.1	1.39	1.37	22.1	0.32	0.54	40.8				
60 K	1.12	2.03	29.3	1.39	1.82	25	0.44	0.52	45.7				
50 K	1.32	1.90	46.4	1.48	2.82	3.9	0.49	0.63	21.9	0.55	−0.33	39	15.7
45 K	1.3	1.90	42.6	1.48	2.83	9.8	0.47	0.60	15.6	0.48	−0.28	42.1	23.8
40 K	1.26	1.97	47.8	1.67	2.61	10.2	0.36	0.60	6.1	0.50	−0.29	47	21.2
15 K	1.23	1.53	33.8	1.60	3.07	17.4	0.40	0.61	3.9	0.50	−0.31	53.2	25.8
T [K]		Fe(II)(I) sextet											
		IS [mm/s]		QS [mm/s]		H_{hf} [T]		Area [%]					
50 K		0.54		−0.15		34.8		12.2					
45 K		0.42		−0.38		44.4		8.1					
40 K		0.50		−0.28		44.9		14.9					
15 K		0.54		−0.38		58.2		19.1					

The isomer shift (IS) values relative to α -Fe at room temperature (with error of ± 0.02 mm/s). QS, quadrupole splitting; T , temperature.

In Table, QS of both Fe(II)(II) and Fe(III) increases markedly when the temperature reduces from 60 K to 50 K. Both lattice distortion and asymmetric charge distribution contribute to QS. It is deduced that the lattice distortion causes QS increase significantly. We ascribe the lattice deformation to the Jahn–Teller distortion. Because Fe(II)(II) and Fe(III) ions are coordinated by oxalate molecule C_2O_4 , the Jahn–Teller transition plays an important role in breaking octahedral symmetry ($Fe(ox)_3$). Fishman et al. firstly predicted JT transitions in bimetallic oxalates based on the first-principles calcu-

lations [14]. Our Mössbauer experiments provide compelling evidence for the predicted JT transition. Indeed, recent X-ray measurements on the compound confirm that the hexagonal symmetry present at room temperature is absent in the monoclinic lattice below 60 K [17].

These spectra below 50 K show three quadrupole doublets and two sextets. One magnetic splitting spectrum is designated as Fe(III) sextet and another as Fe(II)(I) sextet. The appearance of nuclear Zeeman splitting suggests that the long range magnetic ordering takes place below 50 K. The ferrimagnetic transition [1] is responsi-

ble for the spectral changing from a doublet to a sextet. From Table, we find that the hyperfine magnetic field is proportional to the spontaneous magnetization and increases as the temperature decreases. It is found that the spontaneous magnetizations for Fe(II)(I) and Fe(III) sublattices have different temperature dependences. As a result, the spectrum recorded at 15 K exhibits one Fe(III) sextet corresponding to an internal field of 53.2 T and another Fe(II)(I) sextet estimated to an internal field of 58.2 T. The Mössbauer results reveal that the spontaneous magnetization of Fe(II)(I) sublattices increases more steeply than that of Fe(III) sublattices as temperature decreases from T_C , in agreement with the results reported in Refs. [16, 18], and [19]. This may result in observed multiple magnetic-pole reversals [7].

Then, we address the problem of the coexistence of doublet and sextet at low temperatures. We think that the existence of a small fraction of metal vacancies because of Fe(II) becoming oxidized [16] Fe(III) reduces the magnetic exchange interaction between neighboring Fe(II)(I) and Fe(III) ions. Metal vacancies have also much effect on the intraplanar cation–cation separation, the “bite” angle subtended by the bidentate $C_2O_4^{2-}$ bridging group and the degree of trigonal distortion around the cation sites in the compound. The magnetic exchange interaction between neighboring Fe(II)(I) and Fe(III) ions is diminished via these effects.

4. Conclusion

This paper has investigated bimetallic oxalate with JT transition by the Mössbauer measurements. High-spin Fe(III) ($S = 5/2$) and Fe(II) ($S = 2$) electronic states are determined in the compound. The Mössbauer analysis indicates that there are three different Fe sites in the material. It reveals that the spontaneous magnetization of Fe(II) sublattices increases more steeply than that of Fe(III) sublattices as the temperature decreases from T_C . Great increase of QS at 50 K testifies the predicted JT transition in the material. The appearance of nuclear Zeeman splittings suggests the occurrence of long range magnetic ordering below 50 K.

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