High field magnetization and multi-frequency ESR in the spin-ladder compound Na$_2$Fe$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$

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Abstract. We have performed high field magnetization and multi-frequency electron spin resonance (ESR) measurements on single crystal and powder samples of Na$_2$Fe$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$, abbreviated as SIO. The Fe$^{2+}$ ions in SIO are bridged by oxalate groups to make two-leg ladders. The temperature dependence of magnetic susceptibilities parallel and perpendicular to the leg direction show very different and anisotropic behavior. Experimental results of the isomorphous compound Na$_2$Co$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ (SCO) are well explained by isolated magnetic dimers with an Ising-type anisotropy. Therefore, we analyze the frequency dependence of the ESR resonance fields by the same model with a fictitious spin 1 as in SCO. The agreement between experiment and calculation is satisfactorily good. Magnetic susceptibility and magnetization curves calculated with the same parameters obtained in the ESR analyses, however, do not agree well with the experimental ones. This indicates the presence of the exchange interaction between the dimers, namely the interaction along the leg.

1. Introduction
Spin-ladder magnets which are considered as intermediates between one-dimensional and two-dimensional magnets have been investigated intensively in recent years. The spin-ladder magnets with a small spin value have various interesting characteristics caused by quantum effects. It was expected theoretically and confirmed by experiment that the spin-ladder has an energy gap between the singlet ground state and the excited ones when the number of ladders is even and it becomes gapless when the number of them is odd [1].

Many of spin-ladder materials reported so far are two-leg ladders with Cu$^{2+}$ ions which are regarded as the spin (S) 1/2 Heisenberg ladder. Recently, new two-leg ladder materials with Co$^{2+}$ or Fe$^{2+}$ ions, Na$_2$M$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ (M=Co, Fe), were synthesized. Na$_2$Co$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ (abbreviated to SCO) was studied by magnetic susceptibility and specific heat measurements, and the results were discussed in the context of a quantum phase transition [2]. We have performed electron spin resonance (ESR) and high field magnetization experiments on SCO and the results are interpreted as an isolated antiferromagnetic dimer with an Ising-type anisotropy [3], which is consistent with the results of neutron scattering experiments on SCO [4]. From the ESR study, the a axis is found to be tilted from the quantized z axis by about 30 degrees.
Na$_2$Fe$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ (abbreviated as SIO) has the same crystal structure as SCO and has been investigated by magnetic susceptibility, magnetization and specific heat measurements [5]. It has been reported that the magnetic susceptibilities show a broad maximum and decrease steeply with decreasing temperature for the directions parallel and perpendicular to the leg direction and the magnetic field versus temperature phase diagram is constructed from these experimental results.

In this paper, we performed ESR, high field magnetization, and magnetic susceptibility measurements on single crystal and powder samples of SIO to study the magnetic properties in more details.

2. Material and Methods
Single crystal and powder samples of SIO were synthesized according to the procedure described in Ref. [6]. The SIO has a monoclinic structure (space group $P2_1/c$) and the ladder runs along the $a$ axis as shown in Fig. 1. The principal $z$ axis is expected to be tilted from $a$ axis by about 30 degrees because of the same structure as SCO. The typical size of the single crystal is 1.0 0.7 0.7 mm$^3$. The details of the experimental set up for ESR, high field magnetization and magnetic susceptibility will be published somewhere [3].

Figure 1. Ladder structure of Na$_2$Fe$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$. Hydrogen atoms are omitted for clarity. Fe$^{2+}$ ions denoted by large solid circles are connected by oxalate groups. The leg direction of the ladder is the $a$ axis. In the right figure, a schematic view of the ladder is depicted.

3. Experimental results
The temperature dependence of magnetic susceptibilities parallel and perpendicular to the $a$ axis is shown in Fig. 2. The susceptibilities parallel (\(\chi_{||}\)) and perpendicular (\(\chi_{\perp}\)) to the $a$ axis show a broad maximum at a temperature of about 25 K and 20 K, respectively. The maximum values of them are about twice different and the SIO is largely anisotropic compared to the SCO. Both \(\chi_{||}\) and \(\chi_{\perp}\) decrease steeply with decreasing temperature down to 5 K, at which \(\chi_{||}\) shows an upturn as reported [5].

As shown in Fig. 3, magnetization parallel to the $a$ axis at 1.3 K increases gradually to 5 T, then shows a steep increase up to about 10 T and finally is nearly saturated with a gradual increase, while that perpendicular to the $a$ axis shows a gradual increase up to the saturation magnetization. The magnetization is largely anisotropic as well as the susceptibility. Figure 4(a) shows ESR spectra at 1.3 K of a powder sample of SIO. The resonance fields indicated by the arrows are plotted in the frequency-field plane (Fig. 4(b)).

4. Analyses and Discussion
In our analysis of the ESR results, we assume that the SIO is regarded as an isolated antiferromagnetic dimer as expected from the same structure as SCO. The orbital ground state
$H = 100\,\text{Oe}$

$T = 1.3\,\text{K}$

Figure 2. Temperature dependence of magnetic susceptibilities of SIO for $H\parallel a$ and $H\perp a$. The solid and broken lines are calculated susceptibilities for $H\parallel a$ and $H\perp a$ using the parameters determined from ESR analyses, respectively.

Figure 3. Magnetization curves of a single crystal of SIO at 1.3 K for $H\parallel a$ and $H\perp a$. The solid and broken lines indicate the experimental and calculated data, respectively.

Figure 4. (a) ESR spectra of a powder sample of Na$_2$Fe$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ at 1.3 K for designated frequencies. The arrows indicate the resonance fields. (b) The resonance fields plotted on the frequency-field plane. The broken, dotted, and solid lines are calculated resonance branches for the principal $x$, $y$, and $z$ axes, respectively. The inset shows the extended figure of the low frequencies and magnetic fields part.

of Fe$^{2+}$ ion in a octahedral crystal field is the triplet. Then, the lowest effective spin triplet state is well separated from the other excited ones due to the spin-orbit coupling. Therefore, the SIO can be described as the fictitious spin 1 system with an Ising-type anisotropy at low temperatures. The spin Hamiltonian of this magnet is written as,

$$\mathcal{H} = J(S_1zS_2z + \epsilon_xS_1xS_2x + \epsilon_yS_1yS_2y) + \mu_B(S_1 + S_2)\tilde{g}H$$

(1)
where $J$ is the intra-dimer exchange constant ($J > 0$, antiferromagnetic), $S_1$ and $S_2$ spin operators of the fictitious spin 1, $\epsilon_x, \epsilon_y < 1$, $\mu_B$ the Bohr magneton, $\tilde{g}$ the $g$-tensor, and $H$ the external magnetic field. The diagonal components for the principal axes of the $g$-tensor are $g_x, g_y,$ and $g_z$ and the other components are zero.

We calculate the energy branches from this Hamiltonian and then the resonance fields for the principal axes. We have found that the system has a singlet ground state, and a triplet and a highest quintet excited ones which are split by the anisotropy in the system. Figure 4 shows (a) ESR spectra of a powder sample measured at 1.3 K with the pulse magnet, and (b) plot of the resonance fields including those measured at 1.5 K with the superconducting magnet in the frequency-field plane. The calculated resonance branches for $H \parallel x$, $H \parallel y$, and $H \parallel z$ are drawn by the broken, dotted, and solid lines, respectively. The agreement between experiment and calculation is satisfactorily good using the following parameter values: $g_x=3.4$, $g_y=4.3$, $g_z=5.9$, $J/k_B=28$ K, $\epsilon_x=0.29$, $\epsilon_y=0.32$.

Since we determine the parameter values, we calculate the magnetic susceptibilities and magnetization curves for $H \parallel a$ and $H \perp a$ from the Hamiltonian (1) under the condition that the $z$ axis is tilted from the $a$ axis by 33.3° [3], and compare them with experimental results. In Fig.2, the calculated magnetic susceptibilities are larger than the experimental ones for both directions, and the temperatures at a broad maximum of the calculated susceptibilities are slightly lower than those of the experimental ones. The calculated magnetization processes also show a large difference from the experimental ones. The calculated magnetization curves for both directions exhibit a step-like increase before the saturation, while the experimental ones show a monotonical increase. In addition, the observed saturation magnetization is smaller than that of the calculated one for both directions. These small values of the susceptibilities and the saturation magnetization indicate the existence of inter-dimer antiferromagnetic interactions, probably the interactions along the leg.

5. Conclusions

We have performed magnetic susceptibility, high field magnetization and ESR measurements on single crystal and powder samples of SIO, which consists of two-leg ladders of Fe$^{2+}$ ions. We analyzed ESR experimental results with an isolated antiferromagnetic dimer Ising model with a fictitious spin 1, and the agreement between the calculation and the experiment is considerably good. But the observed magnetic susceptibilities and magnetization curves are largely different from the calculated ones with the parameters determined by the ESR analyses. These results suggest that we have to take into account inter-dimer antiferromagnetic interactions to explain the magnetic properties of SIO.

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