Magnetic properties of single crystalline YbFe$_2$O$_4$

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Abstract. We have investigated the magnetic properties of a single crystal of multiferroic YbFe$_2$O$_4$. Ferrimagnetic ordering of Fe spins is observed at ~250 K. The magnetization measured during field cooling becomes negative below ~10 K owing to the antiparallel coupling between the Fe and Yb sublattices. The magnetization below ~10 K is flipped by changing the applied magnetic field in a positive direction, a property which may be used to the development of magnetic devices. Magnetocaloric measurements show a broad peak of the entropy change, likely owing to a multiple magnetic transition.

1. Introduction

YbFe$_2$O$_4$ belongs to a class of isostructural materials RFe$_2$O$_4$ with R=Y, Ho-Lu and In [1]. Previously we have reported that this system with R=Y, Ho-Lu becomes ferroelectric below ~330 K owing to the real-space charge ordering of Fe$^{2+}$ and Fe$^{3+}$ on triangular lattices [2]. This origin of ferroelectricity differs from the ordinary ion-displacement mechanism. In addition, RFe$_2$O$_4$ shows ferrimagnetic ordering of Fe spins at the Néel temperature ($T_N$) of 230-250 K [3-5]. Hence, the system is multiferroic below $T_N$. Many studies of RFe$_2$O$_4$ have revealed their intriguing magnetic properties, such as huge coercivity at low temperatures [6], a competition between ferro- and antiferromagnetic states [7], spin-glass behaviour [8], and exchange bias [9]. However, full details of the magnetic properties have not been elucidated yet.

In this study, the magnetic properties of a single-crystalline sample of YbFe$_2$O$_4$ are investigated, as polycrystalline YbFe$_2$O$_4$ showed the highest $T_N$ of 256 K among the RFe$_2$O$_4$ series [3]. Studies of RFe$_2$O$_4$ have been mainly confined to LuFe$_2$O$_4$, in which the R-site ion (Lu$^{3+}$) is nonmagnetic (4f$^{14}$) [3,6,7,8]. In contrast, reports on the properties of RFe$_2$O$_4$ with magnetic R$^{3+}$ ions are somewhat rare [3]. Although a magnetic study of single-crystalline YbFe$_2$O$_4$ (Yb$^{3+}$; 4f$^{15}$; 4.6 $\mu_B$) was reported about 30 years ago [10], this work reports some new properties of this system, such as the magnetization reversal and the magnetocaloric effect, in which the magnetic moment of Yb$^{3+}$ may be important.

2. Experimental

A single crystal of YbFe$_2$O$_4$ was grown by the floating zone method. X-ray diffraction measurements at room temperature showed that the crystal consisted of single-phase YbFe$_2$O$_4$ only. The magnetic measurements were carried out between 5 K and 300 K using a superconducting quantum interference
device (SQUID) magnetometer (Quantum Design MPMS). The applied magnetic field was changed within ±50 kOe. The other details have been noted elsewhere [3,5].

3. Results and discussion

Figure 1a shows the magnetization-temperature (MT) curves measured with the applied field (H) of 1 kOe. The direction of H was along the c-axis. The deviation between field-cooled (FC) and zero-field-cooled (ZFC) curves is rooted in the ferrimagnetic ordering. The inflection of the thermoremanent magnetization (TRM) shows the Néel temperature (T_N) of ~250 K, a temperature being close to those in previous studies [3,10]. The broad peak at ~130 K suggests a complicated change of magnetic structure, as reported for LuFe_2O_4 [11].

Figure 1b shows the MT curves measured in the FC mode with H parallel to the ab-plane. The magnetization was much smaller (typically, ~1/10) than that in Fig. 1a. This is because of the Ising properties of RFe_2O_4, arising from the low-dimensional crystal structure [6] and the single-ion anisotropy of Fe^{3+} and Fe^{2+} [12].

We can see the interesting behaviour in Fig. 1b. That is, the magnetization is decreased below ~110 K and has a negative polarity below ~10 K for H lower than ~700 Oe. The same tendency is observed in the c//H condition below ~60 K (Fig. 1) [3,10], although the FC magnetization remain positive down to 5 K. The negative magnetization is plausibly brought about by the antiparallel magnetic coupling between Yb and Fe sublattices [3]; this is a similar situation to that of perovskite chromites GdCrO_3 and La_{1-x}Pr_xCrO_3 [13].

Figure 2 shows that the data could be fitted by the Curie-Weiss behaviour of Yb^{3+} moments, which have an antiparallel coupling with the Fe sublattice [13]:

\[ M = M_{Fe} - \frac{C(H_I - H)}{T - \Theta} \]  

(1)

Here, M_{Fe} represents the magnetization of the Fe sublattice. C, H_I and H stand for the Curie constant, the internal magnetic field at Yb^{3+}, and the applied magnetic field, respectively. T and \Theta mean the temperature and the Weiss temperature, respectively. M_{Fe} was assumed to be independent of temperature (~94 emu/mol). The H_I and \Theta values were ~1100 Oe and ~7 K, respectively. As the negative magnetization is not observed for the H values greater than ~700 Oe (Fig. 1b), the obtained H_I seems to be roughly reasonable. The small absolute value of the Weiss temperature (~7 K) is
consistent with the previous result [10]. The magnetization reversal has not been observed for \( H \) parallel to the \( c \)-axis (i.e., \( c//H \)), even if \( H \) was lowered down to \( \sim 10 \) Oe (data not shown). This difference may originate from the larger \( M_{Fe} \) value (equation (1)) in the \( c//H \) condition than in \( ab//H \), owing to the Ising nature of \( RFe_{2}O_{4} \).

The negative magnetization offers an interesting method of magnetization switching [14]. This is shown in Fig. 3. The sample was cooled with \( H=500 \) Oe down to 5 K. As seen in Fig. 1b, the polarity of the magnetization is negative. The magnetization measured for \( \sim 600 \) s was almost unchanged. Then, the applied field was increased to 1220 Oe; the magnetization switched. This switching is repeatable by changing \( H \) between 500 and 1220 Oe. Note also that the switching is attained under \( H \) in a positive direction. This is different from the ordinary method, in which the magnetization is flipped by changing the direction of \( H \). Hence, the present method can avoid the sample heating caused by hysteretic losses, when the magnetic field crosses zero [14].

Figure 4a shows the magnetocaloric effect (MCE) of \( \text{YbFe}_{2}O_{4} \). The negative values of the change of magnetic entropy (-\( \Delta S \)) are plotted against the temperature. \( \Delta S \) is given by: [15]

\[
\Delta S = \int_{0}^{H} \left( \frac{\partial M}{\partial T} \right)_{H} dH
\]  

(2)

As usual, this value was calculated from magnetization-magnetic field (\( MH \)) curves [16]. The increment of the measurement temperature was 5 K. The applied field was parallel to the \( c \)-axis. The magnetic field (\( H \)) was increased from zero to 10, 20, 30, 40 and 50 kOe. Although the MCE is usually studied from the viewpoint of refrigerant applications, the sign of \( \Delta S \) gives the information on the type of magnetic ordering. In ferromagnetic ordering, \( \Delta S \) is negative at around the magnetic
transition temperature, whereas, the value is positive for antiferromagnetism [11]. As $\Delta S$ was positive at around $T_N$ due to the ferrimagnetic ordering, $-\Delta S$ is plotted in Fig. 4.

A peak of $-\Delta S$ appears near $T_N$ as reported for many systems thus far [15]. The peak value is $\sim 1 \text{ J kg}^{-1} \text{ K}^{-1}$ for $H=50 \text{ kOe}$, and is reasonably close to that of LuFe$_2$O$_4$ [11]. This value is smaller than those of the large or giant MCE materials ($-\Delta S \sim 10 \text{ J kg}^{-1} \text{ K}^{-1}$) [15]. Note that $-\Delta S$ exhibits a significantly broad peak, as found for LuFe$_2$O$_4$ [11]. Calculating the peak width, we have obtained the refrigerant capacity (RC) [15]. The temperatures of the hot and cold reservoirs in the refrigeration cycle are defined as the temperatures of the full width at half maximum of $-\Delta S$. The former and latter temperatures for $H=50 \text{ kOe}$ were $T_1 \sim 153 \text{ K}$ and $T_2 \sim 258 \text{ K}$, respectively. The RC values were calculated by the integration of $-\Delta S$ between $T_1$ and $T_2$. The RC was $\sim 80 \text{ J kg}^{-1}$, which is $\sim 25$-$50\%$ of those of the large or giant MCE materials [15]. However, the large difference between $T_1$ and $T_2$ ($\sim 105 \text{ K}$) is favourable for the so-called Ericsson cycle [17]. This property is possibly owing to either a multiple magnetic transition below $T_N$ or magnetic inhomogeneity [11], originating from a magnetic frustration on a triangular lattice. The discontinuous of $-\Delta S$ at $\sim 190 \text{ K}$ may be associated with a structural distortion [6], as a sharp change of $-\Delta S$ can be observed at a first-order transition [15].

The sign of $-\Delta S$ becomes negative below $\sim 130 \text{ K}$. This is a different result from that of LuFe$_2$O$_4$, in which $-\Delta S$ is positive at all temperatures [11]. The present behaviour is rooted in a decrease in the integral term (equation (2)), because of the shrinkage of the $MH$ curves (Fig. 4b) [9]. This shrinkage arises from the enhancement of coercivity [6,9]; we should measure the $MH$ curves at $H$ values greater than the highest field of the present apparatus (50 kOe). The zero value of $-\Delta S$ at $\sim 130 \text{ K}$ indicates a possible application to fabricate a constant temperature bath [14].

The $-\Delta S$ value increases again below $\sim 70 \text{ K}$ as seen in Fig. 4a. The true origin of this behaviour is unclear. However, paramagnetic Yb$^{3+}$ moments may play some roles, considering that the magnetic entropy is decreased since Yb$^{3+}$ spins are forced to be parallel to $H$ by the application of large fields. A role of Yb$^{3+}$ is also implied by the fit of the $MT$ data (Fig. 2), in which the Curie-Weiss term (equation (1)) of Yb$^{3+}$ is important below $\sim 60 \text{ K}$. Further studies are currently in progress, and will be published in the near future.

**Figure 4.** (a) Change of magnetic entropy ($-\Delta S$) plotted against the temperature. The $H$ values are defined in equation (2). (b) Magnetization-magnetic field curves at several temperatures below 110 K.
4. Summary

We have investigated the magnetic properties of a single crystal of multiferroic YbFe$_2$O$_4$. Ferrimagnetic ordering of Fe spins is observed at ~250 K. The magnetization measured during field cooling becomes negative below ~10 K owing to the antiparallel coupling between the Fe and Yb sublattices. The magnetization below ~10 K is flipped by changing the applied magnetic field in a positive direction, a property which may be used to the development of magnetic devices. Magnetocaloric measurements show a broad peak of the entropy change, likely owing to a multiple magnetic transition.

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