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Neutron Diffraction Study on the Magnetic Structure of $^{153}EuMnO_{3-\delta}$: One Way to Assess the Magnetic Structure of $EuMnO_{3-\delta}$

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Abstract:
Owing to the strong neutron absorption of ^{151}Eu, ^{151}Eu free $^{153}EuMnO_{3-\delta}$ has been synthesized to collect the neutron diffraction data for analyzing the magnetic structure of $EuMnO_{3-\delta}$. The obtained neutron diffraction data of $^{153}EuMnO_{3-\delta}$ indicates that the magnetic diffraction peaks corresponding to cAAFM (canted A-type antiferromagnetic) phase can be observed, but the magnetic diffraction peaks corresponding to expected ICAFM (incommensurate antiferromagnetic) phase may be too weak to be observed.

Keywords: *Magnetic structure; Neutron diffraction; $^{153}EuMnO_3$; Perovskite*

1 Introduction

The multiferroicity in $LnMnO_{3-\delta}$ (Ln=Y, Tb, Ho)[1-3] and the colossal magnetoresistance or charge-ordering in $La_{1-x}A_xMnO_3$ (A= alkaline earth)[4,5], have induced a lots of studies on the series $LnMnO_{3-\delta}$ (Ln=Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). During a systematical study of the magnetic and orbital structures in the series of $LnMnO_{3-\delta}$ as a function of Mn-O-Mn bond angle φ, T. Kimura et al.[6] established a magnetic phase diagram for orthorhombic $LnMnO_{3-\delta}$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) using the neutron diffraction data of $LnMnO_{3-\delta}$ (Ln=La, Pr, Nd, Tb, Dy, Ho)[7-11] and X-ray diffraction data of $LnMnO_{3-\delta}$ (Ln= Sm, Eu, Gd, the corresponding neutron diffraction data contain less information given the high neutron absorption cross section of the corresponding rare earths) to obtain the value of Mn-O-Mn bond angle φ for each compound by Reitveld refinement.[12] This magnetic phase diagram[6] indicates that $EuMnO_{3-\delta}$ is paramagnetic (PM) above 51K, incommensurate antiferromagnetic (ICAFM) between 51K and 46K, and canted A-type antiferromagnetic (cAAFM) below 46K. The phase transition temperatures are different from the values of 47K and 35K reported by Y. M. Mukovskii et al.[13] This difference may be due to the composition of the so-called $EuMnO_{3-\delta}$ sample obtained in different research group is different as indicated by I.O. Troyanchuk et al. [14] and J. M. Deng et al.[15]. Similar phenomena can also be found in other $LnMnO_{3-\delta}$ system.[16-23] As well known, magnetic phase transitions usually relate to the changes of magnetic structure, which may induce the change of magnetic reflections in the neutron diffraction data collected around the phase transition temperature.[21,22] However, the neutron diffraction data of $EuMnO_{3-\delta}$ is not easy to be analyzed because ^{151}Eu (50% of natural Eu is ^{151}Eu, the other ~50% is ^{153}Eu) can strongly absorb neutrons to let the obtained data showing very weak useful information. This is why there is no data found in literature. Until 2005, B. Dabrowski et al. presented the room temperature neutron diffraction data of $^{153}EuMnO_{3-\delta}$ in their published work [24] to obtain a precise value of Mn-O-Mn bond angle by Rietveld refinement. Soon after, the neutron diffraction data of $^{153}EuMnO_{3-\delta}$ at 3 K have been obtained,[15] which shows the magnetic reflections related to the cAAFM phase of $EuMnO_{3-\delta}$. The corresponding magnetic space group for the cAAFM phase of $EuMnO_{3-\delta}$ is *Pnma*1, with a = 5.8183(2), b = 7.2082(3), c = 5.3269(2) Å at 3 K. However, the expected ICAFM phase of $EuMnO_{3-\delta}$ around 50 K is still waiting for confirmation. Therefore, it is very important to obtain the neutron diffraction data of $^{153}EuMnO_{3-\delta}$ around

50 K. The corresponding neutron diffraction data obtained by us could not confirm the existence of the expected ICAFM phase of $EuMnO_{3-\delta}$.

2 Experimental

$^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ are synthesized using a traditional solid-state reaction from stoichiometric $^{153}Eu_2O_3$ (99.995%), Eu_2O_3 (99.995%) and $MnCO_3$ (A.R.) for the comparing studies. The oven-dried reagents were homogenized for about 30 min of grinding with an agate mortar and a pestle. The mixture was subjected to 6 h of calcination at 800 ℃. They were then pressed into pellets to undergo four 12 h heat treatments at 1200 ℃, followed by a furnace cooling every time with intermediate grinding. All the treatments were carried out under air. The weights of the samples were monitored before and after heat treatment. The maximum difference was about 4 mg for the 6 g samples. Therefore, the final compositions of the samples were considered the same as the initial ones. Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert3 Powder diffractometer with Cu K_α (λ1=1.5405 Å and λ2=1.5443 Å) radiation (2θ range: 5–120° ; step size: 0.0131; scan speed: 1°/min) at 40 kV and 40 mA at room temperature. Neutron powder diffraction (NPD) data for $^{153}EuMnO_{3-\delta}$ were collected on the instrument Echidna at the OPAL reactor (Lucas Heights, Australia) at the Australian Nuclear Science and Technology Organization (ANSTO) at λ= 2.43950 Å. The X-ray diffraction data and the neutron diffraction data were analyzed using GSAS software.[12, 25] The magnetic properties were investigated using a Cryogenic physical property measurement system (PPMS, supplied by East Changing, China) from 2 to 300 K.

3 Results and discussions

Usually, one may believe that the structure and magnetic properties of $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ are almost the same. However, it is still better to have a careful check if one keeps in mind the isotope effect in superconductor.[26-28] Therefore, $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ have been synthesized under the same condition as described above. Their X-ray diffraction data and magnetic properties have been compared carefully. No significant differences are found between $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$. Therefore, the magnetic structure obtained from the neutron diffraction data of $^{153}EuMnO_{3-\delta}$ should be applicable to $EnMnO_3$. The details are presented below.

3.1 X-ray diffraction data

The X-ray diffraction data of the synthesized $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ can be refined well using the same crystallographic parameters. The corresponding Reitveld plots are shown in figure 1. The space group *Pnma* is used in the refinement with ^{153}Eu or Eu at (0.0781(3), 0.2500, 0.9831(2)), Mn at (0.0000, 0.0000, 0.5000), and O1 at (0.4800(2), 0.2500, 0.1009(3)), O2 at (0.3126(3), 0.0441(2), 0.7131(3)). The obtained lattice parameters are a=5.8401(3), b=7.4601(3), and c=5.3347(3) Å. These data agree well with the reported ones,[13-15] which indicates the samples studied in this work are similar to that reported by other researchers and the replacement of Eu (a natural mixture of 50% ^{153}Eu and 50% ^{151}Eu) by pure ^{153}Eu isotope does not change the structure significantly.

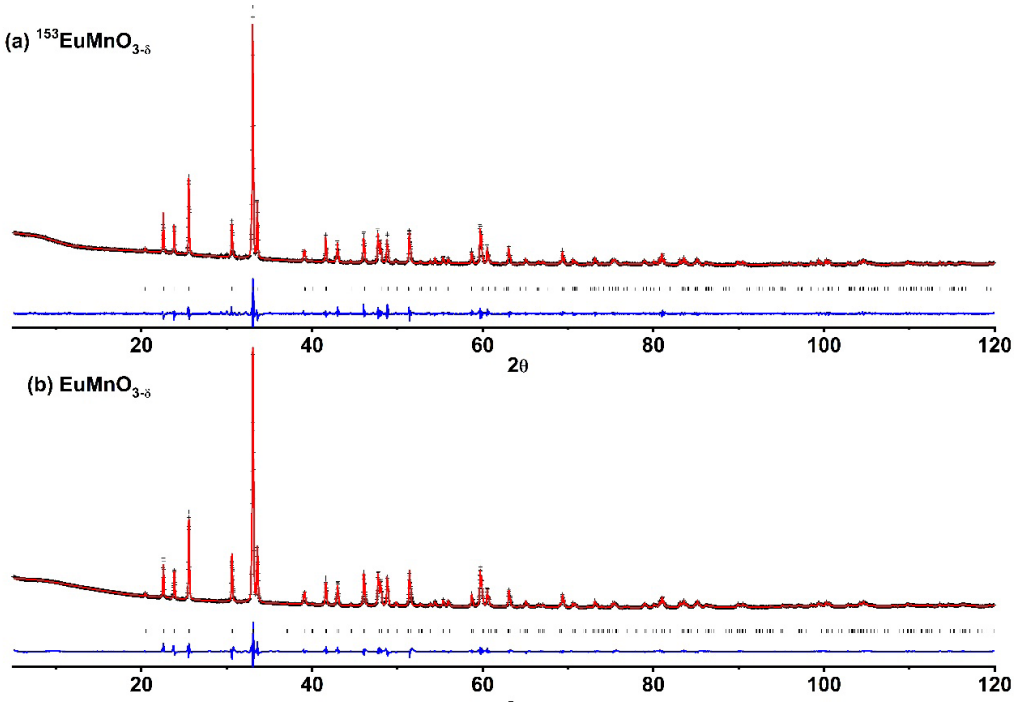

Figure 1 Rietveld plot of X-ray diffraction data of $^{153}EuMnO_{3-\delta}$ (a) and $EuMnO_{3-\delta}$ (b).

3.2 Magnetic properties

The temperature dependence of magnetization of the sample $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ in ZFC (Zero Field Cooling) and FC (Field Cooling) modes is shown in figure 2. As mentioned in the previous studies, [29-32] it is not easy to perform a zero-field cooling. The so called zero-field is usually a very small field, which is randomly positive or negative. Therefore, the "ZFC" is used instead of simple ZFC in figure 2. The "ZFC" curves for $EuMnO_{3-\delta}$ and $^{153}EuMnO_{3-\delta}$ are similar. They seem to be obtained by first cooling the sample under a very small negative field because a negative magnetization is found at low temperature. This can be understood from the field dependent magnetization (M-H) curves obtained at selected temperature shown in figure3 for $EuMnO_{3-\delta}$ and figure 4 for $^{153}EuMnO_{3-\delta}$. The details are described below.

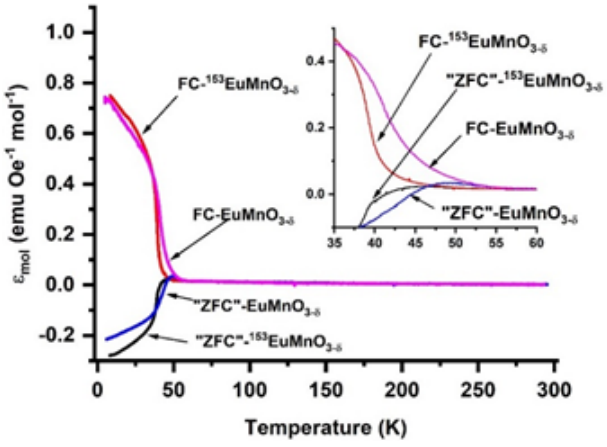

Figure 2 Temperature dependent magnetization of $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ measured at 500 Oe.

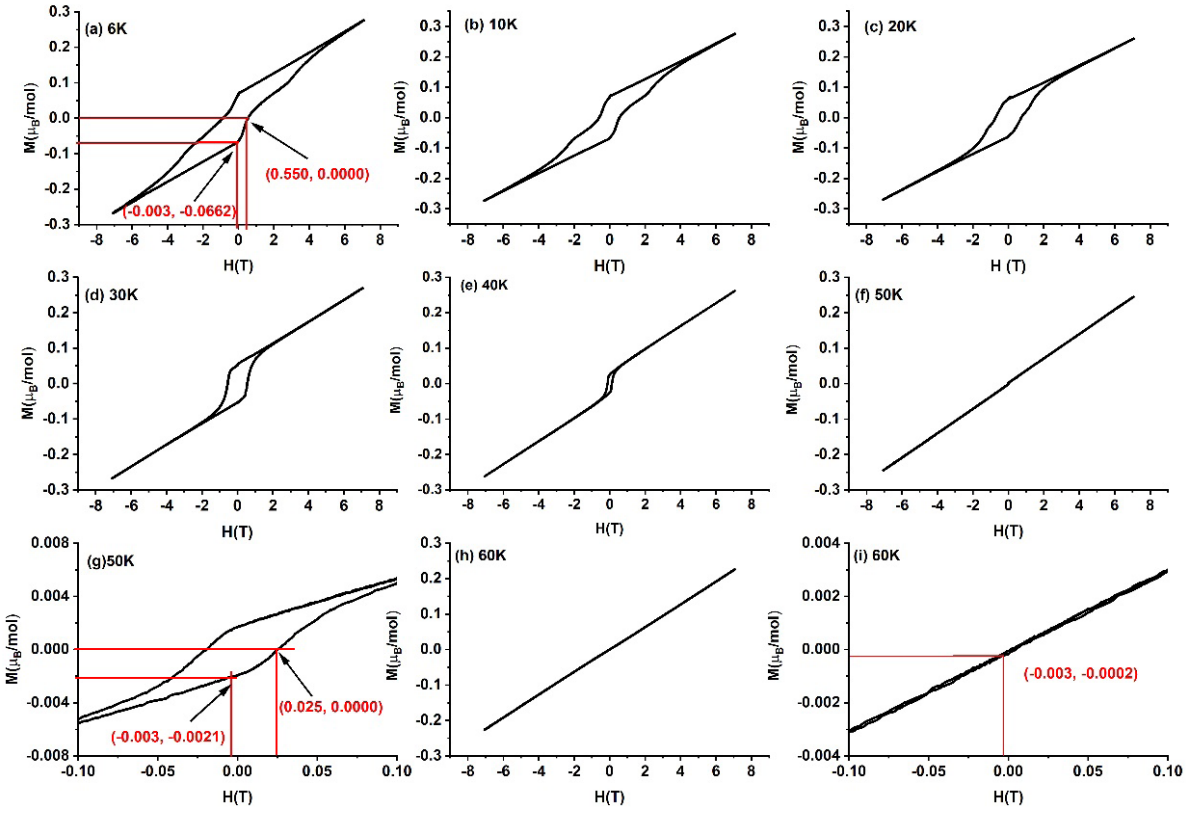

Figure 3 Field dependent magnetization of $EuMnO_3$ at 6 K(a), 10 K(b), 20 K(c), 30 K(d), 40 K(e), 50 K(f), and 60 K (h), enlargement of the data at 50 K (g) and 60 K(i).

Above 60 K, the M-H curve is a straight line for $EuMnO_{3-\delta}$ with a positive slope. The magnetization is positive when the field is positive, or is negative when the field is negative. This is a typical case for a paramagnetic compound. For simplicity, only the data at 60 K is shown in figure 3h and figure 3i. The data shown in figure 3i is the enlarged part of the data shown in figure 3h at the weak magnetic field between -0.10 and 0.10 T to show a clear linear relationship. Let's set the random "zero field" to be a small negative field about -0.003 T, the magnetization for the present sample $EuMnO_{3-\delta}$ at 60 K may be -0.0002 μ_B/*mol* as indicated in figure 3i. If a positive magnetic field is applied at this temperature, positive magnetization should be obtained immediately. When the temperature decreases to about 50 K, the relationship between magnetization and magnetic field becomes complex. A loop is found when the magnetic field is between -0.10 and 0.10 T as shown in figure 3g. This means a magnetic phase transition occurs above 50K. As shown in figure 3g, if the magnetic field is still about -0.003 T, the corresponding magnetization at 50

K may be -0.0021 μ_B/mol. At this case, if a positive magnetic field less than 0.025 T is applied, a negative magnetization can be obtained as shown also in figure 3g. The magnetic loop became larger and larger when the temperature decreases. As indicated at figure 3a, the observed magnetization of $EuMnO_{3-\delta}$ at 6 K may be -0.0662 μ_B/mol for the small negative field of -0.003 T. If a positive field about 0.05 T is applied at 6 K for measurement, the observed magnetization should be negative. This is an explanation for the observation of "ZFC" curve of $EuMnO_{3-\delta}$ shown in figure 2. If one wants to obtain a positive magnetization, the applied field should be larger than 0.55 T as indicated in figure 3a. This agrees well with the previous studies.[29]

The "ZFC" curve for $^{153}EuMnO_{3-\delta}$ presented in figure 2 also shows negative magnetization, which indicates the data is obtained by first cooling the sample under a very small negative field. The understanding of this observation for $^{153}EuMnO_{3-\delta}$ is similar to that for the sample $EuMnO_{3-\delta}$, which is shown in figure 4.

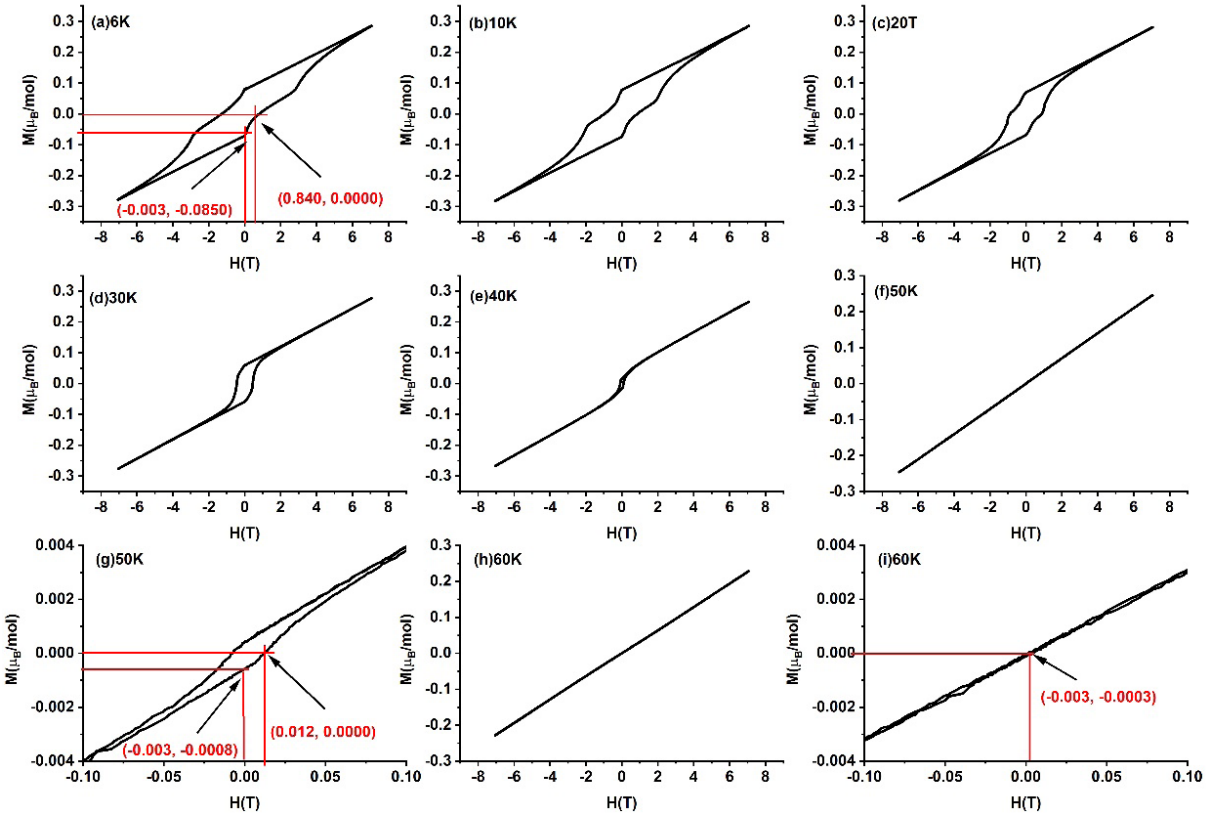

Figure 4 Field dependent magnetization of $^{153}EuMnO_3$ at 6 K(a), 10 K(b), 20 K(c), 30 K(d), 40 K(e), 50 K(f), and 60 K (h), enlargement of the data at 50 K (g) and 60 K(i).

The FC curves of $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ are very similar but not the same (see figure 2). This may mean that the difference between the value of δ of $^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ is very small because I. O. Troyanchuk et al. [4] reported that the magnetic properties of $EuMnO_{3-\delta}$ may be different when the value of δ is different. The second possibility may be that the obtained sample is $^{153}Eu_{1-x1}Mn_{1+x1}O_{3-\delta}$ or $Eu_{1-x2}Mn_{1+x2}O_{3-\delta}$ with x1～x2 because the magnetic properties of $Eu_{1-x}Mn_{1+x}O_{3-\delta}$ are different when x is different. [15, 23]

The departure of the FC and "ZFC" curves of $EuMnO_{3-\delta}$ is around 52 K, which can be clearly found from the inset of figure 2. This value agrees well with the reported data. [6, 33] The departure of the FC curve and "ZFC" curve of $^{153}EuMnO_{3-\delta}$ seems to be around 51 K. An M-H loop can be observed at 50 K for $^{153}EuMnO_{3-\delta}$ as shown in figure 4. The M-H curves for $EuMnO_{3-\delta}$ (figure 3) and $^{153}EuMnO_{3-\delta}$ (figure 4) are very similar, which also agree well with the data for $EuMnO_3$ reported previously. [29] Therefore, the present data indicates that the replace of Eu by ^{153}Eu does not change the magnetic properties significantly.

3.3 Neutron diffraction data for $^{153}EuMnO_{3-\delta}$

As mentioned in section 3.2, negative magnetization can be observed for $EuMnO_3$ if it cooled down to low temperature under a negative field. In order to know what happens in this negative magnetization, neutron diffraction data of $^{153}EuMnO_{3-\delta}$ between 10 K and 60 K at a magnetic field of 1 T after field cooling under a magnetic field of -0.05 T are obtained. For comparison, neutron diffraction data of $^{153}EuMnO_{3-\delta}$ between 10 K and 60 K at a magnetic field of 1 T after zero field cooling, and between 42 and 48 K at a zero field, are also obtained. The corresponding data are shown in figure5.

The neutron diffraction data after negative field cooling and zero field cooling are very similar to each other, which

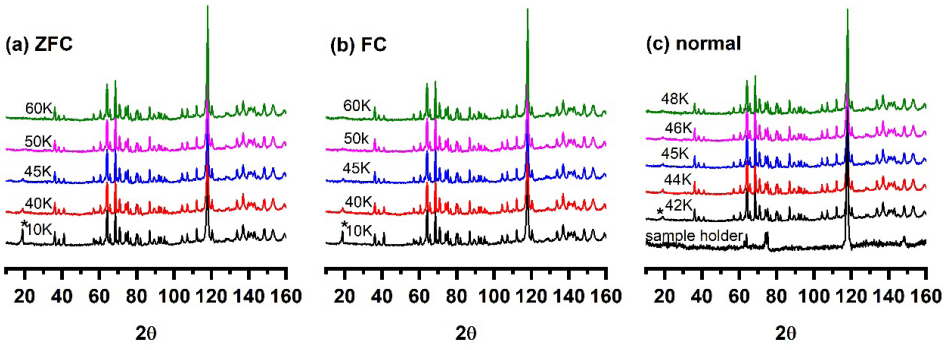

Figure 5 Neutron diffraction data of $^{153}EuMnO_{3-\delta}$ at selected temperature under a magnetic field of 1 T after zero field cooling (a), field cooling (the magnetic field is about -0.05 T) (b), and under a zero magnetic field (c).

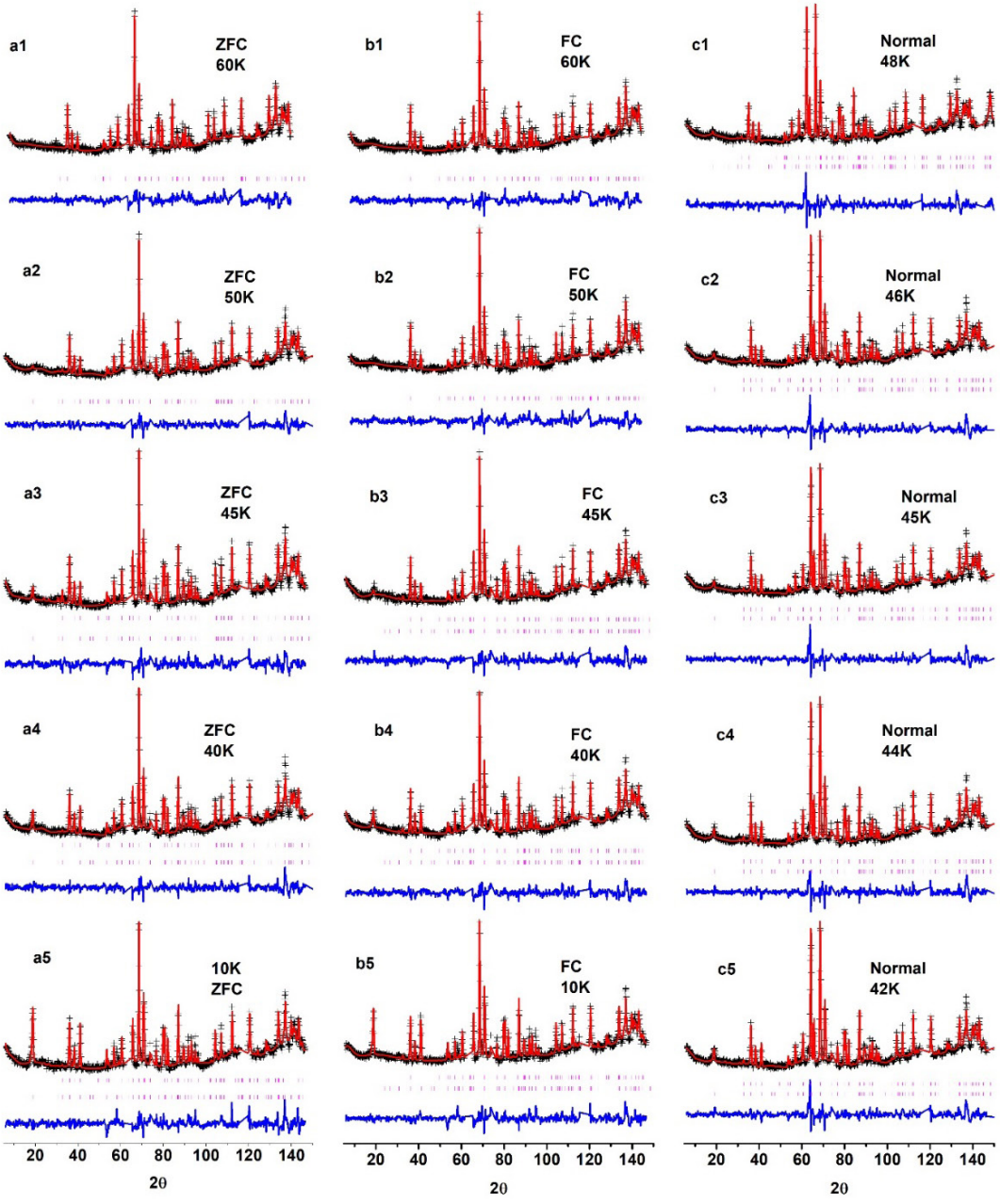

Figure 6 Rietveld plots of the neutron diffraction data of $^{153}EuMnO_3$ at selected temperature under a magnetic field of 1 T after zero field cooling (a), field cooling (the magnetic field is about -0.05 T) (b), and under a zero magnetic field (c).

means that the structure of $^{153}EuMnO_{3-\delta}$ (both nuclear structure and magnetic structure) are almost the same at two different situations. The diffraction peak marked by star in figure5 is a magnetic diffraction peak from the cAAFM phase of $EuMnO_{3-\delta}$, which had been described in a previous paper.[15] This magnetic diffraction peak can be observed at the temperature of 50K or lower and disappear at the temperature of 60K.

The temperature dependent magnetization of $^{153}EuMnO_{3-\delta}$ (see figure 2) indicates a magnetic phase transition around 51K. Therefore, it is easy to accept that the magnetic diffraction peak can be observed in the neutron diffraction data at 50K and disappears in the neutron diffraction data at 60K. The field dependent magnetization of $^{153}EuMnO_3$ (see figure 4) also indicates that a loop can be observed around 50K and no loop is found at 60K. It is very surprising that only one set of magnetic peaks for the cAAFM phase of $EuMnO_{3-\delta}$ are found in the obtained data (see figure 5a and 5b). This may mean the ICAFM phase of $EuMnO_{3-\delta}$ does not exist. One may argue that the ICAFM phase of $EuMnO_3$ is restrained by a magnetic field of 1T. Therefore, the neutron diffraction data of $^{153}EuMnO_{3-\delta}$ was obtained between 42K and 48K without an applied magnetic field (called as the normal state). The corresponding data are shown in figure 5c. It is found that the diffraction data are similar to that shown in figure 5a and 5b. The magnetic diffraction peaks shown in the data belong to the cAAFM phase of $EuMnO_{3-\delta}$. The ICAFM phase of $EuMnO_{3-\delta}$ expected around this temperature was not be observed. Really some diffraction peaks are not belonging to the nuclear phase of $EuMnO_{3-\delta}$ and the ICAFM phase of $EuMnO_{3-\delta}$. These diffraction peaks come from the sample holder as shown in figure 5c.

The data at 60 K are refined with only the nuclear phase in the space group *Pnma*. The data at 10 to 50K are refined with both the nuclear phase in the space group *Pnma* and the magnetic phase in magnetic space group *Pnma*1'. The corresponding Rietveld plots of the obtained neutron diffraction data are shown in figure 6. All the data can be refined well. The obtained lattice parameters are shown in figure 7. Lattice parameters *a*, *b*, and volume of unit cell of $^{153}EuMnO_3$ increases with the increase of temperature, while lattice parameters *c* decreases with the increase of temperature.

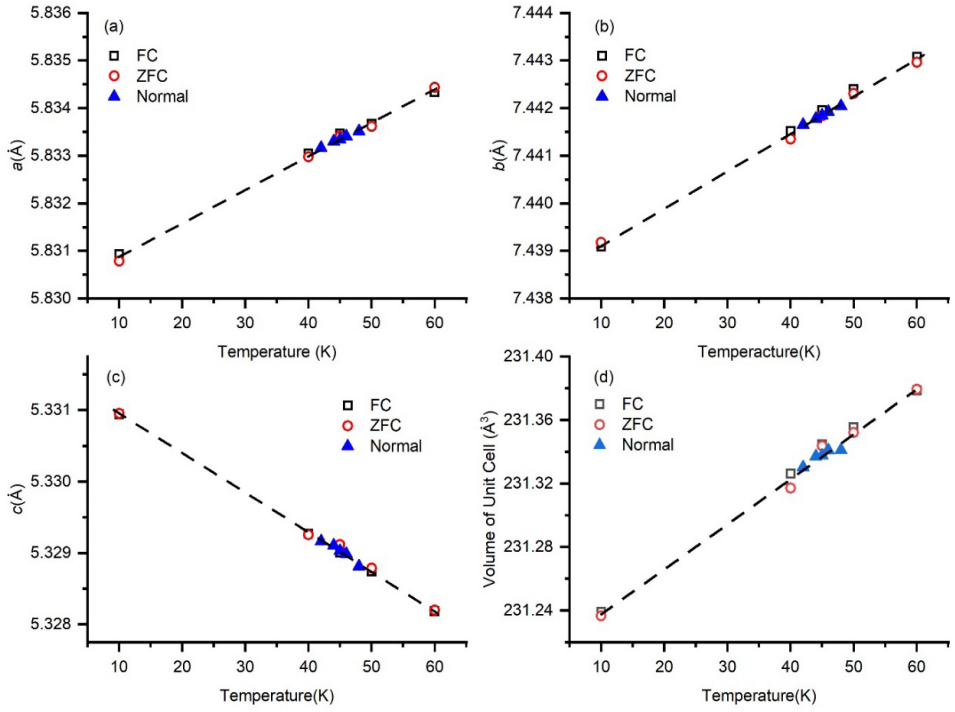

Figure 7 Lattice parameters *a* (a), *b* (b), *c* (c) and volume of unit cell (d) of $^{153}EuMnO_3$ at selected temperature under a magnetic field of 1 T after zero field cooling (ZFC), field cooling (the magnetic field is about -0.05 T) (FC), and under a zero magnetic field (Normal). The dash line in the figure is for the guide of eye.

4 Conclusion

$^{153}EuMnO_{3-\delta}$ and $EuMnO_{3-\delta}$ have similar structural and magnetic properties. Neutron diffraction data of $^{153}EuMnO_{3-\delta}$ between 10 K and 60 K has been analyzed carefully. The magnetic diffraction peak can be observed at the temperature of 50K or lower and disappear at the temperature of 60K. It is very surprising that only one set of magnetic peaks for the cAAFM phase of $^{153}EuMnO_{3-\delta}$ are found in the obtained data. No other magnetic peaks are found even after applying ZFC, FC (the magnetic field is about -0.05 T) and under normal condition (a zero magnetic field). The present results indicate that the ICAFM phase of $EuMnO_3$ could not be confirmed by neutron diffraction data.

Conflict of Interest: No conflict of interest was reported

by the authors.

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