Diffuse Scattering in Bilayer Iron Oxides $Sr_3Fe_2O_{7-\delta}$

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Time-of-flight small-angle neutron scattering experiments have been carried out on the charge disproportionation compounds $Sr_3Fe_2O_{7-\delta}$. A large diffuse scattering was found at low-Q region in a wide temperature region around Néel temperature ($T_N \approx 100$ K). From the temperature dependence of the diffuse scattering, we propose that it consists of two components; one is a normal paramagnetic diffuse scattering, and the other is a diffusive magnetic reflection with antiferromagnetic Fe-spin arrangement. It is speculated that two different types of magnetic clusters are formed during charge disproportionation process.

KEYWORDS: Sr₃Fe₂O_{7- δ}, diffuse scattering, small-angle neutron scattering, charge disproportionation

§1. Introduction

Recently, iron oxides with an average oxidation state of +4 have attracted much interest, because some of them show the following charge disproportionation,

$$2Fe^{4+} \to Fe^{3+} + Fe^{5+},$$
 (1.1)

while others do not. For example, $SrFeO_3$ and $CaFeO_3$ have been studied comparatively to understand such charge disproportionation phenomenon.

SrFeO₃ has a cubic perovskite-type structure with a three-dimensional network of cornersharing [FeO₆] octahedra. It possesses an extremely large electrical conductivity. It is an antiferromagnet with a helical spin structure below $T_{\rm N} ~(\approx 134 {\rm ~K}).^{1)}$ Mössbauer spectra show a single line above $T_{\rm N}$ and a single magnetic hyperfine sextet below $T_{\rm N}$. Namely, the oxidation state of the iron is +4 at all temperatures.

In contrast, CaFeO₃ has an orthrombic perovskitetype structure. The electronic and magnetic behaviors are semiconducting and antiferromagnetic ($T_{\rm N} \approx$ 120 K), respectively. Takano *et al.* has studied it using Mössbauer spectroscopy,^{2,3)} and observed that below $T_{\rm N}$ Mössbauer absorption spectra consist of two sextets with equal aria. A pair of peaks were observed in the paramagnetic region, and those peaks overlapped around 290 K. They concluded that CaFeO₃ was a tetravalent iron oxide above 290 K, and charge disproportionation proceeded below it.

Compounds of the homologous series $\mathrm{Sr}_{n+1}\mathrm{Fe}_n\mathrm{O}_{3n+1}$ with two-dimensional network of the [FeO₆] octahedra also attract much attention, because charge disproportionation occurs in $\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$ (n = 2), while in the case of SrFeO_3 (n = ∞) and $\mathrm{Sr}_2\mathrm{FeO}_4$ (n = 1), such phenomenon is not observed. SrFeO_3 is metallic-like as mention above, $\mathrm{Sr}_2\mathrm{FeO}_4$ is semiconducting, and $\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$ is intermediate between them. The magnetic behavior of $\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_7$ is antiferromagnetic with $T_{\mathrm{N}} \approx 100$ K, which is also intermediate between SrFeO₃ ($T_{\rm N} \approx 134$ K) and Sr₂FeO₄ ($T_{\rm N} \approx 60$ K).

In spite of extensive studies have been carried out for these compounds by various authors,^{4–6)} charge disproportionation phenomenon is still poorly understood. For example, charge disproportionation is confirmed in $Sr_3Fe_2O_7$ at 4 K by Mössbauer measurements, but neutron powder diffraction experiments show no sign of structure distortion resulting from the charge disproportionation.^{4,8)}

Recently, Adler concluded from Mössbauer absorption spectra that charge disproportionation occured in $Sr_3Fe_2O_7$ even at room temperature (RT).⁶⁾ He also carried out magnetic susceptibility measurements and observed that χ curves of field-cooled (FC) and zero-fieldcooled (ZFC) started to separate each other below 40 K. He speculated that there were a competition between ferromagnetic and antiferromagnetic exchange interactions in $Sr_3Fe_2O_7$. In the case of Sr_2FeO_4 , however, FC and ZFC curves overlapped at all temperatures.⁷⁾ Above $T_{\rm N}$ the χ curve of Sr₃Fe₂O₇ deviated from straight line which would be expected from the Curie-Weiss law $\chi(T)$ C / $(T - \theta)$. The slope of the χ curve decreased with decreasing temperature, which corresponds to an increase in an effective magnetic moment μ_{eff} . In fact, the μ_{eff} was estimated from a linear regression of data between 220 K and 300 K, and its value was considerably lager than 4.9 μ_B expected in a d⁴ high spin configuration. In addition, the θ value was positive. From these results, he suggested that magnetic clusters were formed above $T_{\rm N}$, which were dominated by ferromagnetic exchange interactions, and the magnetic clusters grow in size with decreasing temperature which gives rise to the decrease of slope in the χ curve.

Such complicated magnetic behaviors are seen in $Sr_3Fe_2O_7$ during charge disproportionation process. In order to clarify the relationship between such magnetic behaviors and structure of $Sr_3Fe_2O_7$, we carried

out time-of-flight (TOF) small-angle neutron scattering (SANS) experiments.

§2. Experimental

 $m Sr_3Fe_2O_{7-\delta}$ was synthesized by the conventional solidstate reaction method from $m Fe_2O_3$ (99.999 %) and $m SrCO_3$ (99.999 %). The mixture was fired at 1100 °C for 36 h in air, pressed into disks, and heated at 1200°C for 30 h. Finally, the product was annealed at 450 °C for 96 h under 2000 atm of O₂ and Ar mixed gas in a molar ratio of 1 : 4. TOF-SANS data were collected on the small and wide-angle neutron diffractometer (SWAN) at KENS ⁹ between 4.2 K and RT.

§3. Results and Discussion

Figure 1 shows S(Q) of $\mathrm{Sr}_3\mathrm{Fe}_2\mathrm{O}_{7-\delta}$ between 4.2 K and RT, where a large diffuse scattering is clearly seen. It seems to consist of two components: one around $Q \approx 0.15$ Å⁻¹ (diffuse-A, hereafter), the other around $Q \approx 0.35$ Å⁻¹ (diffuse-B).



Fig.1. S(Q) of Sr₃Fe₂O_{7- δ} between 4.2 K and RT.

The diffuse-B gradually grows with increasing temperature and reaches the maximum around $T_{\rm N}$. Above $T_{\rm N}$, it slowly decreases up to RT. We could safely conclude that the diffuse-B is associated with magnetic scattering with short coherence lengths. On the other hand, the diffuse-A also gradually grows around $T_{\rm N}$, but it does not decrease above $T_{\rm N}$ and remains constant even at RT. Similar phenomena are seen in many of magnetic materials above $T_{\rm C}$ as paramagnetic scattering (*ex.* bcc-Fe).

We therefore assume that the intensity of the diffuse scattering S_{diff} is represented by the following equation,

$$S_{\rm diff}(Q) = D_{\rm A} \frac{(\sigma_{\rm A}/2)^2}{Q^2 + (\sigma_{\rm A}/2)^2} + D_{\rm B} \exp\left\{-\frac{(Q-Q_{\rm B})^2}{(\sigma_{\rm B}/2)^2}\right\},$$
(3.1)

where the first term corresponds to the paramagnetic scattering and the second one a diffusive magnetic reflection at $Q_{\rm B}$.

All the SANS data of $Sr_3Fe_2O_{7-\delta}$ were fitted by the following equation,

$$S(Q) = C_1 Q^{-4} + C_2 \frac{1}{\left(1 + \xi^2 Q^2\right)^2}$$

$$+S_{N}(Q) + S_{M}(Q) + S_{diff}(Q) + S_{b.g.}, \qquad (3.2)$$

where $S_{\text{b.g.}}$ indicates a constant background, $S_{\text{N}}(Q)$ and $S_{\text{M}}(Q)$ correspond to nuclear and magnetic Bragg scattering, respectively. Profile shapes of both $S_{\text{N}}(Q)$ and $S_{\text{M}}(Q)$ were assumed to be a Gauss function. We assumed that S(Q) includes the first term which indicates the Porod law $(S(Q) \propto Q^{-4})$ and the second one which represents scattering from voids, because the present sample is polycrystalline and porous. The second term, which is described by the Debye-Bueche formula, ¹⁰ represents scattering from voids with ξ , the correlation length.

Analysis of SANS data was performed on the basis of Eq. (3.2) by the following process: firstly, all parameters except those in $S_{\rm M}(Q)$ and $S_{\rm diff}(Q)$ were obtained from fitting of S(Q) at 4 K, because those should remain constant at all temperatures. Secondly, $\sigma_{\rm A}$, $\sigma_{\rm B}$ and $Q_{\rm B}$ were derived from the fitting of S(Q) at 95 K, and fixed for S(Q) at other temperatures. Finally, only $D_{\rm A}$ and $D_{\rm B}$ were refined for the rest of S(Q). Obtained parameters by the fit are listed in Table 1. As shown in Fig. 2, an excellent fit between observed and calculated patterns was obtained.

Figure 3 shows the integrated intensities of the diffuse-A and B vs. temperature T. As expected, the diffuse-A gradually grows with increasing temperature, whereas the diffuse-B reaches the maximum around $T_{\rm N}$, then it slowly decreases up to RT.

As mention above, the diffuse-B was associated with a diffusive magnetic reflection. Since $2\pi/Q_{\rm B} \approx 20$ Å, it corresponds to the (001) Bragg reflection. Fe-spin arrangement is probably antifferomagnetic, because if Sr₃Fe₂O_{7- δ} has a ferromagnetic structure, the (001) reflection dose not appear.

The emergence of the reflection indicates the change of the Fe-spin arrangement, because the (001) reflection is not observed at 4 K. The Fe-spin arrangement is not long-range, as is seen from the diffusive nature of this magnetic Bragg peak. It indicates that small domains of magnetic clusters formed on $Sr_3Fe_2O_{7-\delta}$. The size of the magnetic clusters estimated from $\sigma_{\rm B}$ was found to be several tens of Angstrom.

Such change of the Fe-spin arrangement would be caused by the reduction of the exchange interactions between layers. In our previous paper,⁸⁾ we showed that Fe-O(3) bond, where O(3) atoms interconnect double [FeO₂] planes, drastically expanded with increasing temperature up to 160 K and did not change much above 160 K. In contrast, Fe-O(1) bond, where O(1) is on [FeO₂] planes, gradually increased with increasing temperature. The

| Table I. | Main fixed parameters. | |
|------------------|------------------------|----------|
| Sb.g. | 0.027 | |
| C_1 | 3.05×10^{-5} | |
| C_2 | 0.082 | |
| ξ | 4.971 | Å |
| $\sigma_{\rm A}$ | 0.178 | $Å^{-1}$ |
| $\sigma_{\rm B}$ | 0.499 | $Å^{-1}$ |
| $Q_{\rm B}$ | 0.314 | Å-1 |



Fig.2. Fitted S(Q) of $Sr_3Fe_2O_{7-\delta}$. N and M indicate nuclear and magnetic Bragg scattering, respectively.

expansion of Fe-O(3) bond with increasing temperature is likely to result in the change of Fe-spin arrangement.

On the other hand, the diffuse-A was observed even at RT. Similar magnetic diffuse scattering is seen in many



Fig.3. The integrated intensities of the diffuse-A and B vs. temperature *T*. Solid lines are the guides to the eye.

of magnetic materials above $T_{\rm c}.$ Adler suggested from their magnetic susceptibility measurements that magnetic clusters dominated by ferromagnetic exchange interactions were formed above $T_{\rm N}.$ The exchange interactions probably remain on [FeO_2] planes, since the FeO(1) distance was about 0.04 Å shorter than Fe-O(3) one. Therefore, diffuse-A is most likely to result from the ferromagnetic clusters above $T_{\rm N}.$

We propose two different types of magnetic clusters are formed during charge disproportionation process. Such Fe-spin arrangements within each magnetic clusters are related with the competitions between the exchange interactions on planes and those between layers.

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