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The magnetic excitations of an infinite-layer antiferromagnetic insulator SrFeO\textsubscript{2} were examined by powder inelastic neutron scattering to find dispersive magnetic excitations from \textasciitilde15 up to 63 meV. The scattering intensity distribution is well described by a spin wave model, confirming that the out-of-plane direct Fe--Fe exchange is comparable in strength to the in-plane Fe--O--Fe superexchange. SrFeO\textsubscript{2} shows an additional magnetic excitation mode around 30 meV, which is suggestive of an orbital magnon arising from small orbital moment on Fe\textsuperscript{2+} brought about by spin–orbit coupling.

KEYWORDS: spin wave, orbital wave, orbital angular momentum, Mott insulator
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1. Introduction

Recently, a new iron-based antiferromagnetic insulator SrFeO\textsubscript{2} (Fe\textsuperscript{2+}: \(\delta^6, S = 2\)) constructed from square-planar FeO\textsubscript{4} units was obtained.\textsuperscript{1)} This material has the crystal structure in which FeO\textsubscript{4} square planes of corner-sharing FeO\textsubscript{4} square-planes alternate with layers of Sr as shown in Fig. 1(a), and is isostructural with the infinite layer compound (Sr\textsubscript{1−x}Ca\textsubscript{x})CuO\textsubscript{2}.\textsuperscript{2,3)} SrFeO\textsubscript{2} exhibits several unexpected structural and physical properties. Its antiferromagnetic transition temperature \(T_N \approx 473\) K is unusually high despite its two-dimensional layered structure,\textsuperscript{11)} and its infinite layer structure with P4/mmm space group is robust against cation substitution (Sr\textsuperscript{2+}/Ca\textsuperscript{2+}) as well as against temperature.\textsuperscript{4)} Furthermore, it undergoes a pressure-induced spin transition into an intermediate spin state with \(S = 1\), which is accompanied by insulator-to-metal and antiferromagnet-to-ferromagnet transitions.\textsuperscript{5)} Density functional calculations for SrFeO\textsubscript{2}\textsuperscript{6,7)} showed that the down-spin of the high-spin Fe\textsuperscript{2+} occupies the nondegenerate \(d_{z^2}\), which shows \(L = 0\) for the Fe\textsuperscript{2+} ions and explains why Jahn–Teller instability is absent in SrFeO\textsubscript{2}, and that the direct Fe–Fe spin exchange between adjacent FeO\textsubscript{4} layers is strong, hence accounting for the high \(T_N\)\textsuperscript{1)} and the unprecedented spin transition for a square-planar coordinate system.\textsuperscript{5,8)} However, there has been no experimental verification of the three-dimensional magnetic character on the basis of magnetic excitation energy measurements. The magnetic susceptibility of SrFeO\textsubscript{2} has not been reported because it is unstable at temperatures above \(\sim450\) K and because as-prepared samples possess ferromagnetic impurities difficult to remove.\textsuperscript{3)} In this paper, we show on the basis of powder inelastic neutron scattering measurements that the out-of-plane direct Fe–Fe exchange is comparable in strength to the in-plane Fe–O–Fe superexchange, and SrFeO\textsubscript{2} exhibits an additional magnetic excitation mode similar in nature to an orbital magnon proposed for a Mott insulator with unquenched orbital angular momentum.\textsuperscript{9)}

2. Experiments and Computational Details

Neutron scattering experiments were performed using direct geometry chopper spectrometers Mari at ISIS (UK) and Pharos at LANSCE (USA) installed at their respective spallation neutron sources. The incident energies (\(E_i\)) were fixed at 120 and 240 meV in the Mari and Pharos experiments, respectively. The data shown in the inset in Fig. 1(d) were obtained using Pharos, while all other data were obtained using Mari. The energy resolution at elastic condition was approximately 3% for \(E_i\) in both experiments. Powder samples of SrFeO\textsubscript{2} were synthesized in the manner described in ref. 1. The 33 g and 36 g samples of SrFeO\textsubscript{2} were used for the Mari and Pharos experiments, respectively. Each sample was wrapped in a thin aluminum foil, which was then enclosed with \(^4\)He exchange gas in an aluminum container, and set under the cold head of a closed-cycle \(^4\)He refrigerator.

To determine the preferred spin orientation in the antiferromagnetic ground state of SrFeO\textsubscript{2}, we carried out density-functional calculations for the crystal structure at 10 K\textsuperscript{1)} using the full-potential linearized augmented plane wave method encoded in the WIEN2k program package\textsuperscript{10)} with the generalized gradient approximation (GGA)\textsuperscript{11)} for the exchange–correlation functional, the on-site repulsion \(U\)\textsuperscript{12)} on Fe to describe the strong electron correlation associated with the Fe 3d states, and the spin–orbit coupling (SOC) on the Fe atom. Further details of our GGA+U+SOC calculations (with several \(U\) values between 0.0 and 4.6 eV) are summarized in ref. 13.

3. Results

Figure 1(b) shows neutron scattering intensity distribution in the \((Q,E)\) space, \(S(Q,E)\), measured at \(T = 5\) K, where \(Q\) is the magnitude of momentum transfer and \(E\) is the energy transfer. The magnetic excitations, whose intensity becomes...
stronger in a lower $Q$ range, are observed, and the phonon density of states (nondispersive excitations), whose intensity becomes stronger in a higher $Q$ range, is distributed over the entire $Q$ region. Figure 1(c) magnifies the low $Q$ region in Fig. 1(b). Clear dispersive magnetic excitations are observed on the trail of the phonon density of states around 20 meV, which open up from energy minima located at $Q_c = 1.4$ and 2.7 Å$^{-1}$ to energy maximum ($E_i = 63$ meV) widely distributed in the $Q$ range. The positions of $Q_c$ correspond approximately to the magnetic Bragg points (1/2, 1/2, 1/2) and (3/2, 1/2, 1/2), consistent with the observed magnetic structure. In general, $S(Q, E)$ for a low-dimensional system is smeared along the $Q$ direction (e.g., see refs. 14 and 15). Thus the observed clear pattern qualitatively suggests a three-dimensional nature of the spin exchange interactions in SrFeO$_2$. The $Q$ dependence of the energy-integrated scattering intensity around $E_i$ [Fig. 2(a)] exhibits monotonic decrease up to $\sim 5$ Å$^{-1}$.

To estimate the energy minimum at $Q_c$, we roughly extracted the magnetic components:

$$S_{\text{mag}}(E) = \int_{Q_c - 0.4}^{Q_c + 0.4} S(Q, E) \, dQ - 2 \left( \int_{Q_c - 0.6}^{Q_c - 0.4} S(Q, E) \, dQ + \int_{Q_0 + 0.4}^{Q_0 + 0.6} S(Q, E) \, dQ \right).$$  

As seen in Fig. 1(b), the energy region below $\sim 40$ meV involves considerable phonon contributions. The $Q$ integrated range of the first term consists of both the magnetic excitations and phonons, while that of the second term can be regarded as the phonon background, as seen in Fig. 1(c). The first and second terms (S1 and S2) and their difference (S1 − S2) for $Q_c = 1.4$ Å$^{-1}$ are shown in Fig. 2(b). We confirmed that the $E$ dependence of S2 is almost the same as the phonon density of states obtained in the high $Q$ range in Fig. 1(b). In the S1 − S2, the peak structure of phonons disappears, indicating that no significant phonon contributions remain, and the energy minimum at $Q_c$ is estimated as $15 \pm 5$ meV, which corresponds to the gap energy ($E_g$).

Figures 1(d) and 1(e) show $S(Q, E)$ measured at $T = 300$ and 353 K, respectively. With increasing $T$, the intensity of the magnetic excitations in the energy range higher than $T$ (such as around $E_i$) decreases, while the opposite happens in the energy range lower than $T$ because of the Bose population factor.

4. Discussion

The magnetic excitation energies of SrFeO$_2$ can be described by the Heisenberg spin Hamiltonian,

$$H = \sum_{m \neq n} J_{mn} S_m \cdot S_n + D \sum_m (S_m)_{z}^2,$$

where $m$ and $n$ are Fe$^{2+}$ sites, the spin exchange parameters $J_{mn}$ are defined in Fig. 1(a), and $D$ is the spin anisotropy constant. The LDA (local density functional) + U calculations gave the estimates $(J_{11}, J_{1'}, J_{1''}, J_{1'}) = (1.09, 3.52, -0.12, 0.3)$. 

![Fig. 1](image1.png)

**Fig. 1.** (Color online) (a) Crystal and magnetic structures of SrFeO$_2$, where the solid arrows on the Fe$^{2+}$ ions indicate magnetic moments, which lie on the $ab$ plane. The magnetic structure is represented by a propagation vector (1/2, 1/2, 1/2). The dotted arrows define exchange interactions $J_L$, $J_J$, $J_{1'}$, and $J_{1''}$; (b–e) Experimental $S(Q, E)$ maps measured with $E_i = 120$ meV. The intensity tone is shown in the inset of (e). The inset of (c) shows the $Q$ dependence integrated from $E = 42$ to 48 meV, demonstrating the dispersion relation of the magnetic excitations. The inset of (d) shows the energy spectrum integrated from $Q = 0$ to 6 Å$^{-1}$ measured with $E_i = 240$ meV. (f,g) Calculated $S(Q, E)$ maps with $E_i = 120$ meV based on a spin wave model. (f) shows the best fit and (g) shows the map for a two more dimensional case ($E_i/E_i = 0.1$). The intensity tone is shown in the inset of (g).
The obtained ratio \( J_{1}/J_{2} = 0.57 \pm 0.14 \) demonstrates that the magnetism in SrFeO\(_3\) is three dimensional. The theoretically obtained \( J \) values\(^{6,7}\) also exhibit the \( S(Q,E) \) pattern similar to that shown in Fig. 1(f); the experimental \( E_{1}/E_{2} \) ratio agrees well with the theoretical one (0.23 and 0.21). The three dimensional magnetic character of SrFeO\(_3\) reflects that the direct Fe···Fe exchange associated with the out-of-plane magnetic orbitals (i.e., the \( d_{xy} \) and \( d_{yz} \) orbitals) is substantial. In contrast, the isostructural compound (Sr\(_{1-x}\)Ca\(_x\))CuO\(_2\) (Cu\(_{2}^{+}\); \( 3d^{9}, S = 1/2, k_{B}T_{N}/E_{g} \sim 0.1 \))\(^{20}\) has no three-dimensional character because its magnetic orbital Cu \( 3d_{xy} \) possesses no out-of-plane character. The experimental value of \( D \) (i.e., \(-0.5 \pm 0.3 \text{ meV}\)) is in good agreement with the theoretical value estimated from the present GGA+U+SOC calculations for the antiferromagnetic state (i.e., \(-0.39 \text{ meV}\)).

The obtained ratio \( J_{1}/J_{2} = 0.57 \pm 0.14 \) (\( E_{1}/E_{2} = 0.28 \pm 0.07 \)) demonstrates that the magnetism in SrFeO\(_3\) is three dimensional. The theoretically obtained \( J \) values\(^{6,7}\) also exhibit the \( S(Q,E) \) pattern similar to that shown in Fig. 1(f); the experimental \( E_{1}/E_{2} \) ratio agrees well with the theoretical one (0.23 and 0.21). The three dimensional magnetic character of SrFeO\(_3\) reflects that the direct Fe···Fe exchange associated with the out-of-plane magnetic orbitals (i.e., the \( d_{xy} \) and \( d_{yz} \) orbitals) is substantial. In contrast, the isostructural compound (Sr\(_{1-x}\)Ca\(_x\))CuO\(_2\) (Cu\(_{2}^{+}\); \( 3d^{9}, S = 1/2, k_{B}T_{N}/E_{g} \sim 0.1 \))\(^{20}\) has no three-dimensional character because its magnetic orbital Cu \( 3d_{xy} \) possesses no out-of-plane character. The experimental value of \( D \) (i.e., \(-0.5 \pm 0.3 \text{ meV}\)) is in good agreement with the theoretical value estimated from the present GGA+U+SOC calculations for the antiferromagnetic state (i.e., \(-0.39 \text{ meV}\)).

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Figure 2(c) shows the experimental energy spectrum of magnetic excitations (symbols) and the spin-wave density of states calculated by integrating the spin-wave scattering intensity over the whole Brillouin zone with resolution

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Fig. 2. (Color online) \( Q \) dependence of the scattering intensity integrated from \( E = 60 \) to \( 66 \text{ meV} \) (a), \( Q \)-integrated energy spectra around \( Q_{c} = 1.4 \text{ Å}^{-1} \) (b), and the comparison between with experimental magnetic energy spectrum and calculated spin-wave spectrum (c). The experimental (symbols) and calculated (solid lines) data are obtained from the data shown in Figs. 1(c) and 1(f), respectively. The dotted lines are guide for eyes. In (a), the experimental errors are smaller than the size of symbol. In (b) and (c), the solid and open circles correspond to \( S_{1} \) and \( S_{2} \), respectively, and the solid triangles indicate the raw spectrum integrated from \( Q_{c} = 0 \) to \( 4 \text{ Å}^{-1} \). The intensity scales of these three data sets, which are different because of a magnetic form factor, are adjusted to smoothly connect the data points. The gray shaded area suggests the existence of another magnetic mode.
correction (solid curve). In this calculation, the scale factor was adjusted such that the intensity around $E_t$ coincides with the experimental data. As expected, the calculated spin-wave density of states is convex downward. However, the experimental data exhibits a broad convex-upward feature in the $E_{2nd}$ ~ 30 meV region, which shows the presence of an additional magnetic excitation mode superposed on the spin wave in the $E_{2nd}$ region. This additional excitation mode cannot be related to the excitations between the crystal-field-split $d$-states, because the smallest excitation gap (from the down-spin $d_z$ to the down-spin $d_{xz}$ and $d_{yz}$ levels) is much greater than 0.1 eV from the density functional calculations.  

It is of interest to consider a probable cause for the additional magnetic excitation in the ~30 meV region. The single-crystal inelastic neutron scattering study of the Mott-type antiferromagnetic insulator CoO with high-spin Co$^{2+}$ (effective $L = 1$, $S = 3/2$) ions showed that, in addition to the spin wave excitations with $E_g$ ~ 20 meV and $E_t$ ~ 70 meV, it exhibits excitations centered around $E_{2nd}$ ~ 40 meV. The latter have been suggested to arise from an orbital magnon, i.e., a collective excitation in which the tilting of $L$ is propagated like a spin wave. The magnetic excitations of SrFeO$_2$ exhibit similar features. Namely, in addition to the spin wave excitations with $E_g$ ~ 15 meV and $E_t$ ~ 63 meV, it exhibits excitations centered around $E_{2nd}$ ~ 30 meV. This similarity leads us to suggest that the additional excitations of SrFeO$_2$ centered around ~30 meV are due to an orbital magnon, although some phonon contributions to the ~30 meV excitations cannot be ruled out completely because unpolarized neutrons were used in our scattering experiments. Given that an orbital magnon mode can occur in SrFeO$_2$ with small orbital moment on Fe$^{2+}$ as well as in CoO with large unquenched orbital moment on Co$^{2+}$, it appears that orbital magnon is a universal phenomenon in magnetic insulators of 3$d$ magnetic ions with nonzero orbital moment.

### 5. Conclusions

In summary, our powder inelastic neutron scattering study confirms that SrFeO$_2$ has a three-dimensional magnetic character, and shows a magnetic excitation mode superposed on the spin wave in the ~30 meV region. The latter is suggestive of an orbital magnon, which arises from small orbital moment on Fe$^{2+}$ induced by SOC.

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13. Our GGA+U+SOC calculation employed the 64 $k$-points for the irreducible Brillouin zone, the threshold of $10^{-4}$ Ry for the energy convergence, $R_{\text{E}} = 7.0$ and $R_{\text{max}} = 12.0$, and the energy threshold of $6.0$ Ry for the separation of the core and valence states.