Resonant Elastic X-ray Scattering from the Skyrmion Lattice in Cu$_2$OSeO$_3$

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We report the study of the skyrmion state near the surface of Cu$_2$OSeO$_3$ using soft resonant elastic x-ray scattering (REXS) at the Cu $L_3$ edge. Within the lateral sampling area of 200 × 200 µm$^2$, we found a long-range-ordered skyrmion lattice phase as well as the formation of skyrmion domains via the multiple splitting of the diffraction spots. In a recent REXS study of the skyrmion phase of Cu$_2$OSeO$_3$ [Phys. Rev. Lett. 112, 167202 (2014)], Langner et al. reported the observation of the unexpected existence of two distinct skyrmion sublattices that arise from inequivalent Cu sites, and that the rotation and superposition of the two periodic structures leads to a moiré pattern. However, we find no energy splitting of the Cu peak in x-ray absorption measurements and, instead, discuss alternative origins of the peak splitting. In particular, we find that for magnetic field directions deviating from the major cubic axes, a multidomain skyrmion lattice state is obtained, which consistently explains the splitting of the magnetic spots into two—and more—peaks.

I. INTRODUCTION

Magnetic skyrmions are swirls in a magnetic spin system, analogous to the skyrmion particle originally described in the context of pion fields$^4,5$. Due to their unique topological properties, they are proposed as a promising candidate for the advanced spintronics applications$^6$. The most famous skyrmion-carrying materials system are the helimagnets with the crystalline space group $P2_13$, such as MnSi, FeGe, and Cu$_2$OSeO$_3$ $^7,8,9,10,11$. The magnetic phases and formation of the skyrmion lattice phase is well-described by the Ginzburg-Landau equation that takes into account thermal fluctuations$^6,12$. The field dependence measurements at 5 K give a saturation value of 0.5 µ$_B$/Cu, i.e., half the value expected for Cu$^{2+}$, where only the spin moment plays a role. Such a reduced moment is commonly found in metal oxides. The field dependence measurements at 5 K give a saturation value of 0.5 µ$_B$/Cu, i.e., half the value expected for a $S = 1/2$ spin system, indicative of a collinear ferromagnetic alignment. The anti-aligned spins are situated in the two chemically distinct copper sites in a ratio of 3:1. The Cu sites have a strong Dzyaloshinskii-Moriya interaction, which is at the origin of the ferroelectricity of this material$^13$.

Cu$_2$OSeO$_3$ has an energy hierarchy similar to other metallic helimagnets$^8$. For the skyrmion phase, the helix propagation orientation is weakly pinned by the cubic anisotropy, and can be easily unpinned by introducing fluctuations, such as an electrical field$^14$ or a thermal gradient$^15$. Density-functional-theory calculations show that the propagation wave vectors along all orientations are degenerate for the skyrmion phase$^15$. Therefore, it is expected that under weak perturbation condition, multiple skyrmion domains can exist. The domains have identical absolute values of the propagation vectors, but differ in orientation. This has been observed in both MnSi and Cu$_2$OSeO$_3$ systems by real-time LTEM, and in Fe$_{1-x}$Co$_x$Si by SANS$^12,13$. One can observe the rotating skyrmion domains, confirmed by the two sets of six-fold symmetric spots of the Fourier transform images$^14$.

In a recent study, Langner et al.$^{16}$ reported resonant soft x-ray scattering (REXS) of Cu$_2$OSeO$_3$. In their experiment the wavelength of the polarized x-rays
was tuned to the Cu $L_3$ edge, and the magnetic diffraction spots were captured on the CCD camera plane in the (001) Bragg condition. In the camera image, the shape of the magnetic satellites is field- and photon energy-dependent, and develops a fine structure, ultimately splitting into more than one spot. The authors interpret this spot splitting as arising from the moiré pattern of two superposed skyrmion sublattices, which originate from two inequivalent Cu sites, as evidenced by a 2 eV split in their x-ray absorption spectra.

We performed resonant soft x-ray diffraction experiments on a well-characterized Cu$_2$OSeO$_3$ single crystal and obtained a reciprocal space maps in the $hk$-plane of the skyrmion phase. In the following we give a detailed description of these measurements and present a critical discussion of Langner et al.’s results together with an alternative explanation for the peak splitting of the magnetic diffraction peaks observed in Cu$_2$OSeO$_3$ based on the formation of a multidomain state.

II. RESONANT SCATTERING

For resonant scattering at the $L_{2,3}$ edge of 3$d$ transition metals it is sufficient to take only electric-dipole transitions into account. Further, there are two main characteristics of 3$d$ materials worth noting. First, the photon energy falls into the range of 0.4-1 keV, leading to relatively long wavelengths, which limits the number of accessible materials for experiments in reflection geometry. At the Cu $L_3$ edge, the x-ray wavelength $\lambda$ is 13.3 Å. For B20 helimagnetic metals, such as MnSi, Fe$_x$Co$_{1-x}$Si, or FeGe, the (structural) lattice constant $d$ is around 4.5-4.7 Å. Since $\lambda = 2d \sin \theta$, where $\theta$ is the Bragg angle, no structural Bragg reflection is accessible. Cu$_2$OSeO$_3$, on the other hand, has a relatively large lattice constant ($d = 8.925$ Å) so that the (forbidden) (001) peak is accessible. This provides an ideal condition for performing resonant elastic x-ray scattering (REXS) on Cu$_2$OSeO$_3$ based on the formation of a multidomain state.

\[ m_1^{\text{sky}}(\rho, \phi) = M_S \sin[\theta(\rho)] \cos[\kappa(\phi + \phi_0)], \]
\[ m_2^{\text{sky}}(\rho, \phi) = M_S \sin[\theta(\rho)] \sin[\kappa(\phi + \phi_0)], \]
\[ m_3^{\text{sky}}(\rho, \phi) = M_S \lambda \cos[\theta(\rho)] \]

Using polar coordinates with $\rho = \sqrt{x^2 + y^2}$ and $\phi = \arctan(y/x)$. $\theta(\rho)$ satisfies the Euler equation and $\kappa$ is the winding number.

Thus, the form factor for an individual skyrmion can be written in the form of

\[ f_{\text{sky}} = \mathbf{V} \int f_{\text{sky}}(\mathbf{r}) (m_1^{\text{sky}}n_1 + m_2^{\text{sky}}n_2 + m_3^{\text{sky}}n_3)e^{i\mathbf{q}\cdot\mathbf{r}} \, d\mathbf{r}. \]
The elemental units give rise to the form factors for resonant scattering, as well as the magnetic unit cell. The magnetic elemental unit for the skyrmion phase is indicated in (c) along with the basis vectors of the magnetic unit cell. The elemental units give rise to the form factors for resonant diffraction and the magnetic unit cells to the structure factors of resonant scattering, as well as the magnetic reciprocal space maps.

The integral is taken over the circular area of a skyrmion vortex. In contrast to the helical and conical states, the skyrmion state is a two-dimensional solution. The ‘crystal’ structure is essentially a hexagonal-type two-dimensional lattice. Therefore, the two-dimensional unit cell can be chosen as shown in Fig. 1(c). The structure factor then becomes

\[
F_{\text{sky}} = F_{\text{sky}}(1 + e^{i\mathbf{q}\cdot\mathbf{a}_1} + e^{i\mathbf{q}\cdot\mathbf{a}_2} + e^{i\mathbf{q}\cdot\mathbf{a}_3})
\]

where \(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\) are the real-space basis vectors, which are rotated by 60° with respect to each other. The core-to-core distance is \(a_1 = a_2 = a_3\), which can be regarded as the ‘lattice constant’ of the skyrmion crystal.

Using the form factors of the helical \((f_h)\), conical \((f_c)\), and skyrmion \((f_{\text{sky}})\) motifs, as well as their structure factors \(F_h, F_c, \) and \(F_{\text{sky}}\) of the unit cells, one can easily obtain the reciprocal space maps. In the helical state, the ‘lattice constant’ is equal to the helical pitch. Therefore, the first-order diffraction peaks appear at \(\pm \mathbf{q}_h\), and the reciprocal lattice is purely one-dimensional. In Cu$_2$OSeO$_3$, the direction of \(\mathbf{q}_h\) is not entirely degenerate, but additionally governed by the sixth order magnetic anisotropy, giving rise to the three-fold degenerate preferred orientation along the three equivalent \((001)\) directions. Consequently, three spatially separated helical domains are expected. Moreover, the helical magnetic reciprocal space lattice has to be imposed on the crystalline reciprocal space lattice in order to obtain the diffraction condition. The reciprocal space of the helical crystal is plotted in Fig. 2(a), and summarized in Table I. In the conical state, the reciprocal space is similar to the one of the helical phase in that the first-order diffraction peaks (modulation vector) appear at \(\pm \mathbf{q}_h\). On the other hand, the direction of \(\pm \mathbf{q}_h\) is entirely governed by the magnetic field direction, and in fact parallel to it. Therefore, there is only a ‘single domain’ state observed, as summarized in Table I. In the skyrmion state, the reciprocal space [cf., Fig. 2(b)] has three reciprocal-space basis vectors \(\tau_1, \tau_2, \) and \(\tau_3\). They are separated by 60° and are related to the three lattice constants by \(a_i = 2\pi/\langle 3\tau_i \rangle\). Therefore, the diffraction peaks appear at \(\pm \tau_i\) around the \((001)\) diffraction, as shown in Fig. 2(b) and Table I.

### III. EXPERIMENTAL REXS RESULTS

We performed REXS experiments on a well-characterized Cu$_2$OSeO$_3$ single crystal. Instead of taking single CCD images at the crystalline \((001)\) Bragg condition, we carried out reciprocal space maps (RSMs) by rocking the sample ±2.5° around the \((001)\) peak such that the entire helix propagation-related reciprocal space is covered. Figure 3(a) shows the RSM of the \(hk\) plane \((l = 1)\) at 56.6 K in an applied field of 30 mT along the \((001)\) direction. The incident x-rays are linearly polarized with a photon energy of 931.25 eV. Six sharp satellite...
peaks can be observed, corresponding to the skyrmion phase. Moreover, when scanning both temperature and field across the skyrmion phase region, no peak splitting is observed. This suggests a six-fold symmetric equilibrium ordering in the entire skyrmion phase pocket.

We performed RSMs for each energy point, and plot the spectroscopic profile using the integrated satellite intensity in Fig. 3(b), bottom panel. Figures 3(c-e) show single-shot CCD images in the (001) Bragg condition with the field orientation rotated 15° away from the (001) direction (in the scattering plane) and from the direction of the incoming x-rays. Now, the well-defined six spots split into two, and finally three sets. This confirms the existence of a multidomain skyrmion state, where each domain has a different helix propagation orientation, which can be intentionally created by introducing a magnetic field gradient. This observation of a multidomain state is consistent with earlier LTEM work by Tokura et al. [10], where split peaks (in the Fourier transforms of the LTEM domain patterns) were observed as part of a dynamic domain rotation process (see Supplementary Movie S2 in Ref. [10]). It has to be noted that x-ray based techniques are sampling a much larger area than electron microscopy based techniques, meaning that a multidomain state observable by LTEM will be picked up by REXS as well.

IV. DISCUSSION

Resonant soft x-ray diffraction experiments on Cu$_2$OSeO$_3$ single crystals has been previously carried out by Langner et al. [16], where the observation of two sets of six-fold symmetric spots has been reported. The authors state that the peak splitting arises from the two inequivalent Cu sites. They support this statement by an observed 2-eV difference in energy profiles for the so-called ‘left’ and ‘right’ spot spectra (shown in Fig. 2 of Ref. [16]). They further argue that the two-fold splitting is linked to an in-plane rotation of two skyrmion sublattices, leading to a moiré pattern (Fig. 4 in Ref. [16]).

Bond valence sum calculations show that the two inequivalent Cu$^+$ and Cu$^{11}$ sites in Cu$_2$OSeO$_3$ (where the superscripts I and II refer to the different lattice sites, not to different oxidation states) have practically the same valence charge [18], and density functional theory calculations show that their unoccupied states have very similar energies [19]. We note that the Cu $L_{2,3}$ transition for Cu$^{2+}$ is $3d^9 \rightarrow 2p^3 3d^{10}$. In the final state the $3d$ shell is full, which reduces the transition to a one-electron process without 2p-3d core-hole interaction. This gives a single absorption peak at 931 eV without multiplet splitting [22]. There are no known Cu $d^9$ compounds with such a large splitting energy, and in fact, the energy splitting that could be expected would be well below $\sim 1$ eV. As reported by Bos et al. [18], and earlier by other others, Cu$^+$ and Cu$^{11}$ have practically the same valence charge, which can only result in a minute energy shift in the Cu
Bragg condition, which is not the correct diffraction condition for either of the magnetic satellites. As a result of this, the satellites still have intensity, analogously to sitting at the edge of a rocking-curve peak. A single-shot CCD image corresponds to a curved plane in reciprocal space, which is not equal to the skyrmion plane in reciprocal space. As a result of this, the skyrmion diffraction spots will not end up on a circle, but on an oval, as can be seen in Fig. 2(a) in Ref. [16]. These satellite spots on the camera do not correspond to the peak position of (001)+τ, but a poorly-defined reciprocal space point that could largely deviate from (001)+τ. Also, the magnetic peaks of (001)+τ will not necessarily appear on the same oval for a single goniometer angle as they do not reach the diffraction conditions at this angle.

Instead, a much more simple explanation of a peak splitting in this context is the occurrence of two non-superimposed skyrmion lattice domains that are simultaneously sampled by the wide x-ray beam.

V. SUMMARY AND CONCLUSIONS

In conclusion, we used REXS on the chiral magnet Cu2OSeO3. We presented a detailed discussion of the magnetic contrast stemming from the magnetic phases. We showed experimental results of the six-fold symmetric magnetic diffraction pattern, in which the peaks were unsplit, double-split, as well as triple-split, depending on the magnetic history of the sample. This clearly contradicts the interpretation given in Ref. [16] where the double-split peaks have been associated with the two chemically distinct Cu sites. Instead, by carefully performing XAS measurements, we find no evidence of a peak splitting. Oppositely, a more simple explanation is the occurrence of a multidomain skyrmion state, sampled by the relatively wide x-ray beam.

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