Unexpected observation of splitting of skyrmion phase in Zn doped Cu$_2$OSeO$_3$

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Polycrystalline ($\text{Cu}_{1-x}\text{Zn}_x$)$_2$OSeO$_3$ ($0 \leq x \leq 0.2$) samples were synthesized using solid-state reaction and characterized by X-ray diffraction (XRD). The effect of Zn doping upon saturation magnetization ($M_S$) indicates that the Zn favors to occupying Cu(II) square pyramidal crystallographic site. The AC susceptibility ($\chi'_{ac}$) was measured at various temperatures ($\chi'_{ac}$–$T$) and magnetic field strengths ($\chi'_{ac}$–$H$). The Zn doping concentration is found to affect greatly the $M$–$T$ and $\chi'_{ac}$–$T$. The skyrmion phase has been inferred from the $\chi'_{ac}$–$H$ data, and then indicated within the $H$–$T$ phase diagrams for various Zn doping concentrations. The striking and unexpected observation is that the skyrmion phase region becomes split upon Zn doping concentration. Interestingly, second conical boundary accompanied by second skyrmion phase was also observed from $d\chi'_{ac}/dH$ vs. $H$ curves. Atomic site disorder created by the chemical doping modulates the delicate magnetic interactions via change in the Dzyaloshinskii-Moriya (DM) vector of distorted Cu(II) square pyramidal, thereby splitting of skyrmion phase might occur. These findings illustrate the potential of using chemical and atomic modification for tuning the temperature and field dependence of skyrmion phase of Cu$_2$OSeO$_3$.

Ever since the discovery of high-$T_c$ superconductivity$^1$, copper oxide materials have garnered significant attention due to exotic physical properties such as charge order stripes$^2$, electronic phase separation$^3$, giant magnetoresistance$^4$ and multiferroics$^5$. This family of materials produce complex and rich phase diagrams because of the strong interplay between their crystal lattices and the spin and orbital degrees of freedoms$^4$. The prime research focus is to address the underlying mechanism behind the physical insight and to establish the technological relevance of these materials.

Recently, a peculiar magnetic state called as “skyrmion or A-phase” has been stabilized in noncentrosymmetric B20 chiral magnetic systems, such as MnSi, FeSi and FeGe$^6$–$^8$. Magnetic skyrmion is a topologically stable particle-like spin configuration where spins mold into a vortex-like ordering. More recently, the recognition of skyrmion in insulating spin-1/2 Cu$_2$OSeO$_3$ was reported. It has further triggered the intensive research activity because skyrmion motion can be controlled by external electric fields instead of Joule heating currents, thus making it a good candidate for ultra-low power spintronic devices$^9$–$^{10}$. The skyrmion lattice can be probed with several experimental methods, such as Lorentz transmission electron microscopy$^{11}$, magnetic force microscopy$^{12}$, spin-polarized scanning tunneling microscopy$^{13}$ and small angle neutron scattering$^{14}$. The signature of skyrmion lattice can also be detected by relatively simple methods such as magnetic $\chi'_{ac}$, heat capacity$^{16}$, topological Hall effect$^{17}$ and electrical polarization$^{18}$–$^{20}$.

From the crystallographic view, the common point to both high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ and skyrmion Cu$_2$OSeO$_3$ systems is the presence of two different Cu sites. It indicates the microscopic picture of these novel phenomena are hidden in the local structures of two Cu ions and its complex magnetic interactions between Cu(I)/Cu(II) ions. In YBa$_2$Cu$_3$O$_7$, Cu ions are located on two different sites i.e. Cu(I)O chains and Cu(II)O$_2$ planes. The superconductivity mainly originates from the electron transport...
across the Cu(II)O$_2$ planes$^{21}$. In Cu$_2$OSeO$_3$, the two Cu$^{2+}$ ions occupy trigonal bipyramidal (Cu(I)) and square pyramidal (Cu(II)) of oxygen ligands, with the ratio of 1:3$^{22}$. Neutron scattering, μSR, and NMR experiments have established the ferrimagnetism of Cu spin with three up (Cu(II)) and one down (Cu(I)) spin alignment$^{22-24}$. However, a close inspection of the magnetic interactions and the crystal lattice of Cu$^{2+}$ spins reveal the presence of more complex superexchange interactions between the Cu-O-Cu bridges$^{25,26}$. Interestingly, unexpected two distinct coupled skyrmion sublattices, which arise from the two different magnetic active orbitals i.e. Cu(I) and Cu(II), have been identified in Cu$_2$OSeO$_3$ system using the orbital sensitive resonant X-ray scattering$^{27}$. It indicates that the site-specific chemical (Cu(I)/Cu(II)) doping might help to gain further insights of this novel skyrmion phase. Following the similar study in high- $T_c$ YBa$_2$Cu$_3$O$_7$ $^{21}$, we explore the chemical doping to shed the light on the microscopic origin of these two skyrmion sublattices. The primary goals of this work are to find out what is the role of Cu(I) and Cu(II) sites in the formation of skyrmion phase? What are the effects of nonmagnetic Zn doping on the skyrmion lattice? Consequently, what are the electronic and magnetic nature of skyrmion phase in Cu$_2$OSeO$_3$?

**Results and Discussion**

Figure 1(a) shows the X-ray diffraction pattern of Cu$_2$OSeO$_3$ sample. The pattern showed the cubic crystal structure and refined with P2$_1$3 space group using GSAS Rietveld program. The obtained lattice parameter (a = 8.9219(1) Å) consistent with the previous report indicates the good quality of the sample$^{22}$. The local structures trigonal bipyramidal and square pyramidal (represented in Fig. 1(b)) derived from Rietveld analysis. Fourier transforms moduli radial distribution functions of EXAFS spectra (c) Cu K-edge for Cu$_2$OSeO$_3$. (d) Cu and Zn K-edge for (Cu$_{0.94}$Zn$_{0.06}$)$_2$OSeO$_3$ respectively. Arrows near small hump in Fig. 1 (c,d) indicate Cu(II)-O$_4$ and Zn-O$_4$ bond lengths respectively.

Figure 1.

(a) Rietveld refinement of X-ray pattern of Cu$_2$OSeO$_3$ sample. (b) Trigonal bipyramidal and square pyramidal sites of Cu$_2$OSeO$_3$ derived from Rietveld analysis. Fourier transforms moduli radial distribution functions of EXAFS spectra (c) Cu K-edge for Cu$_2$OSeO$_3$. (d) Cu and Zn K-edge for (Cu$_{0.94}$Zn$_{0.06}$)$_2$OSeO$_3$ respectively. Arrows near small hump in Fig. 1 (c,d) indicate Cu(II)-O$_4$ and Zn-O$_4$ bond lengths respectively.
1.85 Å followed by the small hump at 2.35 Å. To understand the EXAFS spectrum we have compared the EXAFS spectrum with Fig. 1(b). The primary difference between these two structures of Fig. 1(b) is the axial bond length that is longer for the square pyramidal structure. By comparing EXAFS spectrum with bond lengths of Fig. 1(b), the small hump can be assigned to the axial bond length of Cu(II)-O 4. From the EXAFS spectrum with Fig. 1(b), the primary difference between these two structures of Fig. 1(b) is 1.85 Å followed by the small hump at 2.35 Å. To understand the EXAFS spectrum we have compared the EXAFS spectrum with Fig. 1(b). The primary difference between these two structures of Fig. 1(b) is 1.85 Å followed by the small hump at 2.35 Å.

Figure 2. (a) M vs. H curves of (Cu1-xZnx)2OSeO3 (0 ≤ x ≤ 0.2) series at T = 5 K; Inset shows the M vs. Zn doping concentration. Dashed lines indicate the theoretically predicted occupation probabilities of Zn at (Cu(I) or Cu(II)) crystallographic positions respectively. The experimental data matches the Cu(II) site occupation. (b) The graphical representation of resultant magnetic moment for (I) Cu2OSeO3 (II) Zn at Cu(I) site and (III) Zn at Cu(II) site respectively.

Figure 3 shows the M′ac–ac curves at (Cu1-xZnx)2OSeO3 (0 ≤ x ≤ 0.2). For x = 0, the M′ac–ac curves are in good agreement with those of measured in single crystal Cu2OSeO3. Moreover, both M′ac–ac curves are changed correspondingly and systematically with Zn doping concentration x. Just below ferrimagnetic transition TC ~ 58 K, a clear peak appeared at 56 K shown in M′ac–ac for x = 0, which is the hallmark signature of skyrmion phase. It is noted that the peak is lowered in temperature and becomes fainter with increasing x. On the other hand, a second smaller but notable peak is developed as x increases. These results clearly hint the possible formation of second skyrmion phase when x ≥ 0.02.

AC susceptibility is known to be a sensitive technique for revealing coexisting phases in complex magnetic materials, including skyrmion system. The H dependent χ′ac curves at 50–58 K are shown in Fig. 4(a) for Cu2OSeO3. Below the vicinity of peak temperature ~ 56 K as shown Fig. 3b, the evolution of peak anomalies is noticed in the intermediate field region 100 ≤ H ≤ 400 Oe in χ′ac vs. H curves (Fig. 4(a)). It confirms the growth of skyrmion phase as T ≤ 56 K. For low temperatures, the peak anomalies suppress in the χ′ac vs. H curves which indicates the skyrmion phase is almost disappeared for T < 52 K. To demonstrate the typical way of extracting the skyrmion phase boundaries, the χ′ac vs. H curves at selected temperatures T1 = 57 K, T2 = 56 K, T3 = 55 K, T4 = 53 K and T5 = 51 K are shown in Fig. 4(b). The H-T phase diagram with skyrmion zone marked in red for Cu2OSeO3 is successfully
constructed and displayed in Fig. 4(c). The evolution of different magnetic phase zones, i.e. helical, conical and skyrmion boundaries are in good agreement with previously published results.

To investigate the influence of Zn doping on the skyrmion phase of Cu$_2$OSeO$_3$, the $\chi^\prime_{ac}$ vs. $H$ for (Cu$_{1-x}$Zn$_x$)$_2$OSeO$_3$ ($0 \leq x \leq 0.2$) are performed for a broad range of $T$. The characteristic features of the $\chi^\prime_{ac}$ vs. $H$ curves for $x = 0.1$ at $51 \text{ K} \leq T \leq 53 \text{ K}$ are comparable to that of Cu$_2$OSeO$_3$ at $52 \text{ K} \leq T \leq 56 \text{ K}$ (shown in Fig. 4(a)), that the signature of skyrmion phase is noticed with two peaks. With decreasing temperature to $48 \text{ K} < T < 51 \text{ K}$, the two peaks become smeared. However, as the temperature is lowered to $47 \text{ K} \leq T \leq 48 \text{ K}$, the signature of skyrmion peaks reappeared for $H$ between 80 and 210 Oe. This unexpected observation of second skyrmion phase is a quite novel phenomenon and never been reported in the Cu$_2$OSeO$_3$ system. Along with second skyrmion signature, $\chi^\prime_{ac}$ displays second inflection point in the $d\chi^\prime_{ac}/dH$ vs. $H$ (see supplementary material) curves. It might indicate the appearance of the second conical boundary in the phase diagram accompanied with the second skyrmion phase. However, further experimental verification needed to confirm these signatures. It is important to emphasize that, similar atomic doping effect in a metallic skyrmion systems such as Mn$_{1-x}$Fe$_x$Si and Mn$_{1-x}$Co$_x$Si lead to Quantum phase transitions with a suppressed of helical magnetic and skyrmion phases. Contradictory, the present study indicates the atomic disorder strongly influence the ground state magnetic properties of the Cu$_2$OSeO$_3$ system that lead to more complex magnetic behavior with the generation of additional novel phases in the H-T phase diagram. The multiple inflection points in $d\chi^\prime_{ac}/dH$ vs. $H$ curves are systematically changes with the Zn doping concentration in a selected temperature window, which are displayed in the supplementary material. Following the same plotting procedure as mentioned in Fig. 4(b,c), the Fig. 5(b) is successfully constructed from Fig. 5(a).

Applying the same method as described in Figs 4 and 5, the H-T phase diagrams derived from $\chi^\prime_{ac}$ vs. $H$ data at selected temperatures for each of 8 samples (Cu$_{1-x}$Zn$_x$)$_2$OSeO$_3$ ($0 \leq x \leq 0.2$) are established and shown in Fig. 6, where the boundaries of conical, helical and skyrmion phases are plotted (with various colors) approximately using limited and discrete data points. The surprising finding is that the single skyrmion phase at $x = 0$ is splitted into two well-defined small branches in two different temperature regions and about the same magnetic field as $x \geq 0.02$. Moreover, the second skyrmion phase is hosted by

![Figure 3. (a) $M$ vs. $T$, (b) $\chi^\prime_{ac}$ vs. $T$ curves for (Cu$_{1-x}$Zn$_x$)$_2$OSeO$_3$ ($0 \leq x \leq 0.2$).](image)
the second conical phase boundary. Both branches of skyrmion phase are systematically shifted towards low temperature side with x. The opening of temperature gap between two branches of skyrmion phase is larger for higher Zn doping concentration. The second skyrmion phase and its associated conical phase boundaries are firmly decoupled with that of the initial skyrmion phase; this can be clearly visible for the doping concentration $x \geq 0.1$. Meanwhile, the high-temperature branch becomes harder to extract from the data as $x > 0.15$. In fact, the trends of splitting, suppression, and decreasing in temperature of skyrmion phases found in Fig. 6 are consistent with those observed in Fig. 3(b).

The splitting of skyrmion phase for Zn doping Cu$_2$OSeO$_3$ is a novel and interesting phenomenon. Similar to high-$T_c$ superconducting materials, it might be associated with the two crystallographic sites of...
Cu ions and their complex magnetic interactions. From the magnetic point of view, Cu$_2$OSeO$_3$ exhibits a quite complex behavior with several magnetic interactions between Cu(I)/Cu(II) via oxygen bridging\(^{25}\). In the unit cell of Cu$_2$OSeO$_3$ structure, the 4 Cu(I) ions are placed in the undistorted trigonal bipyramidal, whereas 12 Cu(II) ions are distributed among the distorted square pyramidal sites. According to Goodenough-Kramer (G-K) rules, a negative superexchange interaction ($\langle J \rangle$) corresponds to the orbital overlap angle of Cu ions close to 90°, and it goes to positive ($\rangle J$) if it deviates from 90°\(^{32}\). A close examination of Cu$_2$OSeO$_3$ using an AC susceptibility technique exposed the antiferromagnetic (AFM) ordering at 59 K followed by ferromagnetic (FM) ordering at 58 K\(^{25}\). The complicated behaviour originates from the unequal strength of three nearest neighbors (NN) AFM interaction of Cu(I)-Cu(II) and three NN FM interaction of Cu(II)-Cu(II) ions\(^{25}\). The crystallography studies in Fig. 1 along with magnetization studies in Fig. 2 suggest that the Cu(II) is the preferable site for Zn doping. Replacing of nonmagnetic Zn$^{2+}$ for Cu$^{2+}$ site enhances the Coulombic repulsion of electronic orbital that leads to the decrease in $T_C$. Moreover, the presence of nonmagnetic dopant along with the weak perturbation for the overlaps of electronic orbital can show a significant impact on the complex magnetic exchange interactions between Cu(I)/Cu(II) ions. In general, the helical ground state originates from the competition between Heisenberg superexchange and DM interactions of Cu ions\(^8\). The strength of DM interaction depends on the relative change of g-factor from the free electron g-value, i.e. DM $\propto (\Delta g/g)J$, where J is the exchange interaction term\(^{33}\). Symmetry calculation analysis using Raman modes by Gnezdilov et al. indicates the change of DM strength is more significant for the distorted Cu(II) square pyramidal\(^{33}\). The disorder effect is further amplified by doping the nonmagnetic Zn that strongly modulates the DM interaction strength via the change of radial vector and the canting angle between the adjacent spin pairs. Consequently, it manipulates the complex magnetic interactions between Cu(I)/Cu(II) ions. Similar to resonant X-ray scattering studies on Cu$_2$OSeO$_3$, these two skyrmion phases can be possibly associated with the two Cu sublattices\(^{27}\). Chemical doping might alters the modulation vector of Moirelike skyrmion phase of pure Cu$_2$OSeO$_3$. These results reminiscent the recent observation of unexpected coupled skyrmion sublattices\(^{27}\) and theoretical prediction of novel half skyrmion state in Cu$_2$OSeO$_3$ system\(^{34}\). However, it needs more experimental verifications whether the second skyrmion

Figure 5. (a) $\chi'$ vs. H of at temperatures 44–55 K and (b) corresponding H vs. T phase diagram for (Cu$_{1-x}$Zn$_x$)$_2$OSeO$_3$ ($x = 0.1$). The two red circles in (a) corresponding to respective skyrmion zones in (b). Solid and dashed green lines denote the conical phase boundaries.
Figure 6. H-T phase diagrams of all (Cu_{1-x}Zn_x)_{2}OSeO_3 (0\leq x \leq 0.2) samples. Skyrmion zone is indicated by two red areas respectively. Solid and dashed green lines denote the two conical phase boundaries respectively.
and its accompanied conical phase are originated from decoupling of coupled Cu skyrmion sublattices or it is related to new kind of spin skyrmion structure. A detailed reciprocal space map using the neutron scattering and scanning tunneling microscope studies are particularly required to shed light on this complex skyrmion behavior. Our findings open up a new pathway for further experimental and theoretical research to elucidate the exotic quantum topological skyrmion phases using chemical doping.

In summary, we have successfully synthesized and well characterized the high quality polycrystalline \((\text{Cu}_{1-x}\text{Zn})_2\text{OSeO}_3\) \((0 \leq x \leq 0.2)\) samples. Zn doped skyrmion exhibits the complex and rich phase diagram. The significant findings are: (1) The dopant Zn is favored to occupy the Cu(II) square pyramid crystallographic site. (2) The M-T and \(\chi_T\) are changed dramatically with the increase of Zn doping concentration. (3) The skyrmion phase shown in H-T phase diagram of CuO2SeO3 is split with Zn doping as demonstrated in detailed H and T dependent \(\chi_T\) data. (4) Second conical boundary extracted from the \(\chi_T\) vs. H curves accompanied by the second skyrmion phase. All these results suggest a interesting novel scenario and this unexpected observed appearance of second skyrmion and its conical boundary might be related to the way that the Zn doping manipulates the DM vector of the distorted Cu(II)O3 square pyramid through the influence of delicate magnetic interactions. These results point to a new direction of tuning the skyrmion lattice in CuO2SeO3 by assorted chemical and atomic modification.

**Methods**

In this study, polycrystalline samples of \((\text{Cu}_{1-x}\text{Zn})_2\text{OSeO}_3\) \((0 \leq x \leq 0.2)\) were prepared by solid-state reaction method. Nominal mixtures of high purity CuO, ZnO, and SeO2 powders were pressed into pellets. The pellets were sealed in an evacuated quartz tube and heated to a temperature range of 520°C to 600°C for 72 h, then slowly cooled over several hours to room temperature. This process was repeated at least twice with intermediate grinding. X-ray diffraction patterns show good quality of samples, with only a minor impurity phases appearing when \(x \geq 0.06\). Homogeneity of Zn distribution was analyzed with energy dispersive X-ray analysis, which indicated a uniform distribution of Zn throughout the sample (the supplementary material). Temperature and field dependent DC magnetization and AC susceptibility measurements were performed by a SQUID magnetometer (MPMS-XL7, Quantum Design). EXAFS K-edge experiments were carried out in transmission mode for Cu and fluorescence mode for Zn respectively at the 17C beamline in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

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Author Contributions
H.D.Y. supervised the project. K.D.C. and H.C.W. have equal contribution to this work for the characterization and analysis of the experimental data. H.D.Y. and H.B. initiated the original idea. T.Y.W. and T.Y.C. involved in sample synthesis and characterization. K.D.C., H.D.Y. and H.C.W. wrote the manuscript.

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