Magnetic and orbital correlations in multiferroic CaMn$_7$O$_{12}$ probed by X-ray resonant scattering

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Novel magnetic and orbital reflections are unveiled in the manganese quadruple perovskite CaMn$_7$O$_{12}$ by the application of X-ray resonant scattering (XRS) approach which combines the use of micron-sized polarized X-rays with analysis of the polarization of the diffracted beam. A complete description of the magnetic and orbital correlations is presented. The multi-$k$ orbital structure below $T_{N1}$ ($\sim 90$ K) is observed due to quadratic magneto-elastic interaction between spin and lattice modulations. A de-locked phase between orbital and spin modulation appeared with broad orbital mediated first-order phase transition between $T_{N2}$ ($\sim 45$ K) and $\sim 30$ K, below this temperature magnetic and orbital modulation locks again, with the unique relation $k_0 = 3 - 2\delta$. For the first time, coexisting two distinct types of the orbital order, one driven by a purely electronic mechanism, and one originating due to the Jahn-Teller distortion are also identified.

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The complexity of coexisting and correlated magnetic and the charge ordering instabilities in multiferroics harbors opportunities for the discovery of novel emergent phases. The ordered phases in such materials couple strongly to external fields and has potential for technological applications, i.e., in magneto-electric random access memory and multiferroic tunnel junctions [1,2]. Among type-II multiferroic materials [1], CaMn$_7$O$_{12}$ features the largest known electrical polarization induced by magnetic order, at a particularly high temperature, $\sim 90$K. In this compound incommensurate orbital order (OO) with propagation vector $q_{oo}$ develops at $T_{ oo} \sim 250$ K, followed by magnetic order at $T_{N1} \sim 90$ K. The fact that the periodicity of the incommensurate magnetic order in this first magnetic phase ($T_{N1} < T < T_{N2} \sim 48$ K) is exactly twice that of the orbital modulation ($q_{m1} = q_{oo}/2$) points to the intimate coupling between the orbital and spin instabilities in CaMn$_7$O$_{12}$ [3,4]. The orbital ordering phenomenon in CaMn$_7$O$_{12}$ is unusually complex due to presence of the Jahn-Teller active Mn$^{+3}$ ($d^4$) ion on two different Wyckoff sites. Each of these sublattices develop a distinct type of distortion: (i) the $A$-type Mn$^{+3}$ ions (Wyckoff site 9e) are situated at the center of a rhombic prism resembling an elongated octahedron, whereas (ii) the $B$-type Mn$^{+3}$ ions (Wyckoff site 9d) are contained in an apically contracted octahedral environment, a rare case among Jahn-Teller distortions [3].

Two mechanisms are known that may give rise to OO in CaMn$_7$O$_{12}$ like other manganites [3]: (i) the Jahn-Teller distortion, in which a spontaneous symmetry breaking energetically lowers the occupied crystal-field-split $d$-electronic states, and (ii) an exchange mechanism, in which the crystal relaxes to accommodate complex couplings between magnetic spin and orbital pseudo-spin degrees of freedom (the pseudo-spin $\tau = \pm 1/2$ corresponding to the choice between occupying $d_{x^2-y^2}$ or $d_{z^2}$ orbitals). Using traditional techniques, it is often not straightforward to distinguish between these mechanisms [3,11]. However, through its capability of disentangling magnetic, orbital and charge order, resonant X-ray scattering has proven particularly helpful in identifying which is the dominant effect [10,11].

The structural complexities lies at the heart of its correlations between charge, spin, orbital and lattice degrees of freedom. How these order parameters are coupled to each other near the magnetic and ferroelectric transitions is not clear. Earlier experimental studies of CaMn$_7$O$_{12}$ have addressed spin and orbital correlations by X-ray (XPD) and neutron powder diffraction (NPD), respectively. Although these techniques are each sensitive to only two of the four (charge, orbital, structural and magnetic) ordering channels, the synthesis of these complementary results provides a useful picture of ordering phenomena in CaMn$_7$O$_{12}$. Complete description of propagation vectors in CaMn$_7$O$_{12}$ from earlier NPD and XRD measurements is provided in supplementary file.

In XRS, the photon energy is tuned to the proximity of atomic absorption edges to enhance magnetic and multipolar scattering cross sections. The technique thus provides a powerful means to determine both complex magnetic structures and orbital order. Due to the
selectivity of the resonant process and its polarization dependence, XRS is particularly suited to disentangle the interplay between charge, orbital and spin degrees of freedom in such complicated systems [12, 13].

Our XRS results on CaMn$_2$O$_{12}$ allows us to make important observations to the magnetic and orbital relations proposed on the basis of neutron and X-ray powder diffraction and unveil the direct correlations between magnetic and orbital orders. Moreover, we are also able to disentangle two different types of orbital orderings.

![Image](image_url)

**FIG. 1.** (a) X-ray fluorescence across the Mn-K absorption edge in CaMn$_2$O$_{12}$, and a corresponding energy scan of the magnetic $q_m = (0,0,1.035)$ reflection at 65 K in the $\sigma\pi'$ polarization channel. (b) $L$-scans across this reflection in the $\sigma\pi'$ and $\sigma\pi$ channels at 65 K and 6550 eV, confirming its magnetic origin.

XRS measurements were performed on high-quality CaMn$_2$O$_{12}$ single crystals grown by the self-flux method, as reported in our earlier study [14]. Informations related to crystal structure, orientation and alignment is described in supplementary file. The CaMn$_2$O$_{12}$ platelet was mounted on the cold finger of a CCR cryostat and probed in the vertical scattering geometry, using the 6-circle diffractometer at instrument P09, PETRA III (DESY) [15]. The X-ray energy was tuned to the Mn-K edge ($\sim 6.5$ keV) and a Cu(110) crystal was used as analyzer. Compound refractive lenses focused the beam to $\sim 20 \mu m$.

In the following, $\sigma$ ($\sigma'$) and $\pi$ ($\pi'$) denote incident (scattered) X-ray polarization perpendicular and parallel to the scattering plane, respectively [see inset to Fig. (Ia)]. Magnetization measurements as a function of temperature and magnetic field were performed in a commercial 7 T SQUID vibrating sample magnetometer (Quantum Design).

In the rhombohedral ($R\bar{3}$) phase of CaMn$_2$O$_{12}$, the reflection condition for $(0,0,L)$ peaks is $L = 3n$ (integer $n$). Below $T_{N1}$, $\theta$-2$\theta$ scans along the specular $(0,0,L)$ direction reveal a magnetic superstructure peak at $q_{m1} = (0,0,1.035)$, in agreement with earlier reports [4, 16]. Fig. (I) demonstrates an energy and polarization analysis that confirms the magnetic origin of this peak (all measurements at 65 K). Panel (a) shows the energy dependence of the integrated magnetic ($\sigma\pi'$) intensity across the Mn-K edge, along with the X-ray fluorescence signal. Three resonances are observed, corresponding to a pre-edge (6539 eV) $1s \rightarrow 3d$ quadrupole transition (indicative of breaking of local inversion symmetry), and two $1s \rightarrow 4p$ dipole transitions (at 6550 and 6559 eV, corresponding to the two distinct Mn sites). Although it couples directly to the $3d$ valence shell, the quadrupole resonant enhancement is only around one fifth of that at the dipole transitions. Fig. (Ib) illustrates that the $q_m = (0,0,1.035)$ reflection intensity at 6550 eV is observed entirely in the crossed polarization channel, which confirms the magnetic origin of this reflection. In agreement with the neutron diffraction study by Johnson et al., the character of this reflection showed no thermal variation between $T_{N1}$ and $T_{N2}$ [4].

Apart from the magnetic $q_{m1} = (0,0,1.035)$ reflection, we also characterized the $q_s = (0,0,L \pm \delta)$ superstructure reflections ($\delta \sim 0.93$), as reported in earlier X-ray and neutron studies [4, 5, 16]. In contrast to $q_{m1}$-type peaks, $q_s$ reflections are observed both in the $\sigma\sigma'$ and $\sigma\pi'$ channels. This indicates that they are not due to magnetic order, but to a periodic anisotropy in the occupation of the Mn 3d $e_g$ ground state manifold. The intensity map in Fig. (IIa) illustrates the thermal variation of $L$ scans around $(0,0,0.93)$ in $\sigma\sigma'$. The associated order exists at temperatures above the onset of magnetic order ($T_{N1} = 90$ K), and its modulation length is not affected down to $T_{N2} = 48$ K. However, at $T_{N2}$, $q_s$ splits into a pair of propagation vectors separated by only $\sim 0.01$ r.l.u., which had not been resolved in earlier studies [4].

We label these branches by their values at low temperatures, $\delta_1 = 0.93$ and $\delta_2 = 0.94$. The disparate temperature dependence of $\delta_1$ and $\delta_2$ suggests that they may be associated to different underlying order parameters. While $\delta_1 \sim 0.93$ does not deviate from the higher-temperature value of $\delta$, $\delta_2$ below $T_{N2}$ increases with a constant slope and, below 20 K, settles rather abruptly on the new constant value of $\sim 0.94$. The two instabilities also display distinct behavior in their integrated peak intensity and correlation lengths, as illustrated in Fig. (IIb). Below $T_{N2}$, $\sigma\sigma'$ spectral weight is continuously transferred from $\delta_2$ to $\delta_1$. As it is de-locked from the constant $\delta_1$, the $\delta_2$ modulation retains a constant correlation length, while that of $\delta_1$ increases significantly (see inset). As a check for consistency, we also investigated the above phenomenon at the higher order reflection $(0,0,2.07) = (0,0,3) - \delta$ and found the same behavior. In Fig. (IIc), we show $\sigma\sigma'$ $L$ scans across $(0,0,2.07)$, at 10 K and 60 K. As at $(0,0,0.93)$, the reflection splits into $\delta_1$ and $\delta_2$ components at low temperatures (here corresponding to $L = 2.07$ and $L = 2.06$, respectively). In analogy to the previously known higher-temperature phase, in which orbital and magnetic order locks in with the relation $q_{m1} = q_{oo}/2$ ($T_{N1} < T < T_{N2}$, liii) [4], below $\sim 30$ K we denote this newly identified phase as lock-in phase II (liii).
modulations lie at $E_{\text{res}}^{\sigma_1,\delta_2} \sim 6530\text{ eV} \sim 6534\text{ eV}$, well below the magnetic resonance $E_{\text{res}}^{\sigma_\prime} \sim 6550\text{ eV}$. This is an indication that this OO superstructure is affected by the Jahn-Teller distortion \cite{17}. Figs. 2(g,h) show that within the liII phase (in $\sigma\pi'$), the resonant enhancement for $\delta_2$ is more pronounced than that of $\delta_1$, while there is an opposite trend for $\sigma\sigma'$.

The resonant behavior discussed above reveals that combined effects of charge (Thompson) and resonant orbital scattering are observed at both $\delta_1$ and $\delta_2$. This supports the previous hypothesis that the stabilization of the $d_{z^2}-y^2$ orbital order on the Mn$^{3+}$ (9d) site (coupled to the oxygen displacements modes of the Jahn-Teller distortion) is driven by charge order on both Mn$^{3+}$ (9d) and Mn$^{4+}$ (3b) sites \cite{2,18}. Furthermore, a monotonous increase in intensity of the $\delta_1$ peak, while cooling down to $\sim 90\text{ K}$ [see Fig. 2(a,b)], indicates that the Jahn-Teller distortion reaches a maximum at $T_{N1}$, and is then constant down to $T_{N2}$. This is followed by the bifurcation at $T_{N2}$, which points to the establishment of a new OO on the basis of the pre-existing orbital and magnetic order.

In a recent single crystal neutron diffraction study, Johnson et al. \cite{4} observed a reflection at $(0, 0, k_0) = (0, 0, 1.12)$ (at 2 K), and interpreted this as the fundamental magnetic wave vector in the ground state of CaMn$_2$O$_{12}$. The presence of this peak (at base temperature, $\sim 4.5\text{ K}$) was also confirmed in the present RXS study. However, its polarization analysis shows significant intensity not only in $\sigma\pi'$, but also in $\sigma\sigma'$, which is at odds with purely magnetic order. A detailed temperature dependence reveals that $k_0$ actually originates from the $(0, 0, 1.14)$ peak. It can be indexed as a second order orbital reflection, $(0, 0, 3)-2\delta$ and first arises below $T_{N1}$ (i.e. in the liI phase). Such higher harmonic reflections have previously been observed when an incommensurate magnetic structure is accompanied by structural distortions, allowing quadratic magnetoelastic coupling \cite{19}. As shown in Fig. 3(a), below $T_{N2}$, the $(0, 0, 1.14)$ peak splits into $(0, 0, 3 - 2\delta_1) = (0, 0, 1.14)$ and $(0, 0, 3 - 2\delta_2) = (0, 0, 1.12)$, in a similar fashion as at the first harmonic [cf. Fig. 2(a)].

Figs. 3(a) and (b) illustrate that below $T_{N2}$, the new $2\delta_2$ branch gains continuously in $\sigma\sigma'$ spectral weight, while the $2\delta_1$ instability maintains the constant modulus and intensity of the $\delta$ modulation vector. The inset to Fig. 3(a) shows that the correlations lengths of $2\delta_1$ and $2\delta_2$ behave similarly as their parent reflections [cf. Fig. 2(b)]. Energy scans of $2\delta_2$, in both polarization channels, are shown in Fig. 3(c) and (d), for 4.5 K and 20 K, respectively. Notably, the resonant behavior of these second order reflections differs from the $\delta_1$ and $\delta_2$ in that the $\sigma\sigma'$ and $\sigma\pi'$ signals are perfectly proportional to each other. As a common feature of these energy scans, the signal is suppressed at the absorption edge, which can be explained in terms of the structural modulation caused by a displacement of the Mn$^{3+}$ ions (due to the

The liII regime features a reduction in $\sigma\pi'$ intensity at $\delta_2$, as well as a significant change in the relative intensities between the two peaks ($\delta_1/\delta_2$), in both $\sigma\sigma'$ and $\sigma\pi'$. As shown in Fig. 2(d), at 4.5 K, the relative intensity is three times higher in the $\sigma\pi'$ compared to $\sigma\sigma'$. In Fig. 2(e,f) energy scans of the $\delta_1$ and $\delta_2$ peaks, in both polarization channels, are shown for the liII phase. A resonance appears in $\sigma\pi'$, indicating enhanced scattering from the orbital order, while the $\sigma\sigma'$ channel shows only characteristics of charge scattering. Similar behavior is observed in the energy scans of the $\delta_2$ in other phases (at $T > T_{N1}$, and $T_{N1} < T < T_{N2}$) (see supplementary information). Notably, the resonance energies of the two
Jahn-Teller crystal distortion). This was also observed in other manganites [20].

It is interesting to consider the different types of orbital order that give rise to the first and second order Fourier components measured in this experiment. The first-order OO ($\delta_1, \delta_2$) is driven exclusively by the Jahn Teller distortion, as is revealed by its onset at 250 K ($\gg T_{N1}$) and significant shifts in resonance energy. On the other hand, the second-order OO ($2\delta_1, 2\delta_2$) is induced by magneto-orbital coupling below $T_{N1}$. This scenario is also consistent with anomalies in the magnetic entropy that were recently reported by Parul et al. [21] for the temperature regime in which the $2\delta$ reflection begins to appear ($\sim 65$ K). In the following, we will discuss the entanglement of order parameters below $T_{N2}$. Slawinski et al. [22], using NPD, showed weak inflection for the magnetic propagation vector near 37 K, and were not able to achieve a reliable refinement of the modulus of the ordered magnetic moment between 30 K and 48 K. As seen in the magnetization curves shown in Fig. 3(a), we observe a hysteresis between cooling and warming ramps in a similar temperature regime (20 K – 48 K), which we interpret as a first order magnetic order-order transition. Fig. 3(b) illustrates that the same hysteresis is also manifested in the modulation length $k_z$ of the (0,0,2.07) reflection, which indicates that this first order phase transition is mediated by the orbitals.

In a theoretical study of this low temperature regime, Dai et al. [23] concluded that the structural symmetry in the ground state of CaMn$_2$O$_{12}$ should be described by the space group $P\bar{3}$, rather than $R\bar{3}$. The predicted lattice distortion of $10^{-4}$ A for a $P\bar{3}$ structure is however below the resolution of the present study. Filip et al. [24], observed a dielectric anomaly near 20 K and changes in the far IR transmittance below $T_{N2}$. Based on the Landau theory of phase transition, Johnson et al. [3] also associated the dielectric anomalies below $T_{N2}$ with a first order transition.

Taken together, the present results allow us to establish a relation between the orbital and the magnetic modulations at low temperatures. The phase diagram shown in Fig. 3(c) provides an overview of the Fourier components that have so far been observed in CaMn$_2$O$_{12}$. The propagation vectors determined in the present XRS study are shown along the neutron scattering results by Johnson et al., reproduced from Ref. [3]. As discussed above, we identify two locked-in phases (lii and liii) that are separated by a de-locked regime. In the lii phase ($T_{N2} < T < T_{N1}$), spin and orbital modulations are constant and locked to each other by the relation $q_{OO} = q_{m1} = (3 - \delta)/2$ with $\delta \sim 0.93$, which is confirmed by the perfect consistency of the neutron and X-ray results. No such relation seems to exist in the de-locked phase (30 K < $T < T_{N2}$), where $q_{m1}$ splits into $q_0(0,0,0.96)$ and $q_{1-}(0,0,1.12)$ [2]. A fixed relation between the magnetic an orbital modulation is then re-established in the liii phase, where $q_{1-}$ locks into (3–2$\delta$). This indicates a re-entrant direct coupling between the spin and orbital order.

In summary, we have used resonant X-ray scattering to investigate the correlation of magnetic and orbital modulations in multiferroic CaMn$_2$O$_{12}$. Our observations show that the orbital degrees of freedom play a leading role in emergence of the magnetic ordering and the large spontaneous electrical polarization below $T_{N1}$. We found that the orbital and magnetic modulations are coupled in between $T_{N1}$ and $T_{N2}$ through the relation $q_{m1} = (3 - \delta)/2$, where $\delta = 0.93$. Between $T_{N2}$ and $\sim 30$ K, these modulations de-locks, a broad orbital-mediated first order phase transition occurs. Below 30 K, magnetic and orbital modulations couple again, with the previously unknown relation $k_0 = 3 - 2\delta$. This direct observation of an orbital-mediated first order phase transition also provides an explanation for a number of anomalies that had been observed in bulk measurements [22–24]. Our measurements of the photon energy dependence of the resonant X-ray scattering intensity allows to disentangle two different driving mechanisms of the orbital orderings (purely electronic vs. Jahn-Teller distortion driven). Orbital ordering at the wave vector
\( \delta \) is induced by the Jahn-Teller distortion, while the previously unknown higher harmonic 2\( \delta \) arises purely due to the exchange interactions. The observation of 2\( \delta \)-type superstructure reflections also confirms the existence of quadratic magnetoelastic coupling below \( T_{N1} \) in CaMn\(_7\)O\(_{12}\).

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Magnetic and orbital correlations in multiferroic CaMn$_7$O$_{12}$ probed by X-ray resonant scattering

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CRYSTAL STRUCTURE, ORIENTATION AND ALIGNMENT

The compound CaMn$_7$O$_{12}$ forms a quadruple perovskite structure $A_3A'_3B_3B'_3O_{12}$, in which the $A$ and $B$ sites are occupied by Mn$^{+3}$, $A'$ by Ca$^{+2}$, and $B'$ by Mn$^{+4}$. At $T_s \sim 440$ K, the material undergoes a lattice distortion from cubic ($Im$/$\bar{3}$, $a = 7.39 \text{ Å}$ for $T > T_s$) to rhombohedral symmetry ($R$/$\bar{3}$, $a = 10.4414 \text{ Å}$, $c = 6.3433 \text{ Å}$ for $T < T_s$). The CaMn$_7$O$_{12}$ crystals were obtained resembling perfect cubes with dimensions of $\sim 100 \mu$m (the size being limited by thermodynamical constraints [1]). To allow specular scattering from $(0,0,L)$ reflections of the hexagonal cell, a cubic crystal was polished into a platelet orthogonal to one of its vertices (i.e., parallel to a pseudo-cubic-[1,1,1] plane). Due to twinning, the pseudo-cubic $(2,2,2)$ Bragg-reflection is split into the $(4,0,1)$ and $(0,0,3)$ reflections of the hexagonal cell, which can be distinguished by their intensity ratio of ca. 1:120.

DESCRIPTION OF PROPAGATION VECTORS IN CaMn$_7$O$_{12}$ FROM EARLIER XRD AND NPD EXPERIMENTS

Based on XPD data, Slawinski et al. indexed the superstructure below $T_{oo}$ with the propagation vector $q_{oo} = (0, 0, k_{oo}^z) = (0, 0, 0.079)$, concluding that this phase transition is due to charge ordering [2]. The same authors later performed a NPD study and revised the notation of the charge superstructure to $k_{oo}^z = 2.07$, in line with the observed magnetic propagation vector $q_{m1} = (0, 0, k_{m1}^z/2) = (0, 0, 1.035)$ (for the magnetic phase, at $T_{N2} < T < T_{N1}$) [3]. Slawinski et al. also inferred from these studies that below $T_{N2} \sim 48$ K the relation $k_{m1}^z = k_{oo}^z/2$ is no longer valid, and, instead, a knotty magnetic phase described by two modulations $q_{m2} = (0, 0, 0.96)$ and $q_{m3} = (0, 0, 1.12)$ appears [4]. This second magnetic phase ($T < T_{N2} \sim 48$ K) is particularly intriguing, because the changes in the coupling between orbital and spin order at $T_{N2}$ are not well understood. Recently, Johnson et al. revealed the presence of a multi-$q$ magnetic structure in this phase [5]. Moreover, a number of additional unusual properties were reported for the low temperature regime, including an anomaly in dielectric and the pyroelectric measurements [6] and fluctuations of the magnetic moment coefficient in NPD (for $30$ K $< T < 50$ K) [5].

FIG. 1. (a,b and c) Laue diffraction images of CaMn$_7$O$_{12}$ crystal in three different axis, and (d) scaled photograph of the crystal and an optical image of the crystal (prepared for Laue diffraction experiment).
FIG. 2. (a) $L$-scans across $q_{m1} = (0, 0, 1.035)$ reflection at temperatures between $T_{N1}$ to $T_{N2}$ at 6550 eV in the $\sigma \pi'$ channels.

FIG. 3. (a, b) Energy scans of the (0,0,2.07) intensity, at 150 K ($> T_{N1}$), and at 65 K (between $T_{N1}$ and $T_{N2}$ ), measured in $\sigma \sigma'$ and $\sigma \pi'$.

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