nature portfolio

Peer Review File

Spectroscopic signatures and origin of hidden order in Ba_2MgReO_6

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors used resonant x-ray diffraction experiments at the Re L_3 edge combined with computations to study the presence of quadrupolar ordering in the double perovskite material BMRO. Energy-, azimuthal-, and temperature-dependent measurements support previous discussions (Ref. 3) that there exists antiferroic ordering of q_(x^2-y^2) quadrupoles and ferroic ordering of q_(z^2) quadrupoles. One novel result here is the direct detection of the quadrupolar order using resonant x-rays. The quadrupolar ordering occurs in conjunction with lattice distortions of the same kind (d_(x^2-y^2) and d_(z^2)). Using computations, it is determined that neither the electronic ordering nor lattice distortions alone drives the transition at T_q, and both must be considered to explain the experimental results.

X-ray scattering studies of quadrupolar order can be quite niche, but I found this manuscript compelling and framed well for a wider audience. While the same material (BMRO) was studied Ref. 3 (including a discussion of the quadrupolar order studied with non-resonant x-ray diffraction, as well as the magnetic order studied with resonant x-ray diffraction), the current manuscript presents results on quadrupolar order studied with resonant diffraction as well as extensive computational work. The experiment seems well done, and the conclusions are valid. Overall, I think this could be of interest to a broader audience given the relevance to understanding phase transitions in condensed matter.

I do have a few comments/question:

1. In Figure 1 a-c, I found it difficult to parse all the labels. In particular, the g_θ labels were confusing because I initially thought that the position of the wavy line representing the electron-lattice coupling was relevant. I think the line is meant to represent the coupling in general, but I thought that there was something special about the specific electron/lattice pair that was connected. I would suggest removing g_θ labels and connecting lines since they are not adding anything to the figure. It may be sufficient to label q_θ and d_θ and say that there is electron-lattice coupling without indicating it in the figure.

2. Are the indices used here for the cubic or tetragonal unit cell? In Ref. 3 it is noted that the (1, 1, 0) cubic reflection only appears below T_m, so I am assuming that the notation used in the current manuscript references the tetragonal unit cell.

3. On page 2, it is stated that the results represent “a clear experimental verification of several theoretical studies [16, 19-21]”. I am curious about the author’s comments on Refs. 16 and 20, which both state that only one e_g quadrupole (the x^2-y^2 and not the z^2) is present the ordered quadrupole phase.

4. Regarding Fig. 2d, how were the calculated azimuthal dependences determined?

5. Fig. 2i is a bit confusing. On page 3 when discussing Fig. 2i, it says that Fig. 2i shows splitting of the (10, 0, 0) structural peak. I think that what is being plotted is the peak splitting in degrees (labeled as gamma on the x-axis), but this should be stated clearly because it is easy to assume that it is plotting integrated intensity like Fig. 2e-h.

6. In Fig. 3a, is there also meant to be a red dot for the experimental d_(z^2)distortion?

7. I am curious about the predictions of a q_xy[000] order. Is it possible that this type of ordering occurs as well? How would you check experimentally? The possibility of of q_xy[001] order is dismissed by the scattering azimuthal dependence, but

what would the signature of q_xy[000] be?

8. The last paragraph refers to section ii, but the sections are not labeled in the text. Also, this seems to end fairly abruptly without much conclusion.

Reviewer #2

(Remarks to the Author)
The manuscript reported resonant elastic X-ray scattering (REXS) measurement on Ba2MgReO6, finding resonantly enhanced ATS scattering in this material which provides direct evidence for quadrupolar ordering below Tq=33K. The authors then carried out ab initio calculations and attributed to the observed quadrupolar order (of both z2 and x2-y2) symmetry to a combined effect of quadrupolar interaction and Jahn Teller effect. The data quality seems good (although with important questions that need to be addressed-see below). The manuscript is also well written.
I have no doubt that the results will be of interest to people studying multipolar physics in heavy transition metal systems. However, I think it belongs to a more specialized journal because compelling structural evidence for the two types of quadrupolar order in the same material has already been reported by Hirai et al (Phys Rev Research, 2:022063 (2020)) using non-resonant X-ray scattering. I acknowledge that the evidence in the present manuscript is in a sense 'more direct' as it uses REXS that directly probes electronic order. However, one always expects structural distortion to induce orbital order and vice versa. The observation of resonantly enhanced Bragg peak at the same superlattice position is therefore not surprising. I therefore consider the present work to be a continuation of Phys Rev Research, 2:022063 (2020) and consequently more appropriate for a specialized journal like PRB.
In addition to the above general comment, I also have the following specific questions that I would like to see addressed:
1. In Fig 2, the authors should also show the azimuthal dependence at Em to show unambiguously that Em and Eq probes different order.
2. I don't understand why there is such a large energy difference (almost 7eV) between Eq and Em. After all, the quadrupolar order and magnetic order are both associated with the Re t2g electrons. On the other hand, the 7eV difference is almost the charge transfer energy. So, the question is, what electronic order is the REXS actually probing? Please explain.
3. Why is Fig 2f (on res) and Fig 2g (off res) measured at different Bragg peak positions (550) and (530)? For proper comparison, the authors should show on-res and off-res at the same Q. (In case the sigma-pi intensity using E_non-res is too small, do the measurement in the sigma-sigma channel) In addition to a temperature dependence of the (550) Bragg peak intensity using E_non-res. An azimuthal dependence at (550) using E_non-res is also necessary to rule out any (extrinsic) azimuthal dependence due to, for example, varying beam footprint.
4. Fig 2g shows that (530) intensity levels off below Tm, whereas Phys Rev Research, 2:022063 (2020) shows that the intensity of this superlattice peak is suppressed below Tm. Please comment.
5. I have great issue with the interpretation of Fig 2h as evidence for quadrupolar order with a z2 symmetry. Given that there is always leakage of the strong charge scattering into the sigma-pi channel, it is important to rule this out as the reason for the observed intensity
a. The authors should show i) energy dependence in the sigma-pi and sigma-sigma channel and ii) azimuthal dependence using E_res and E_non-res in both the sigma-pi and sigma-sigma channel. If the observed intensity between Tm<T<Tq is associated with quadrupolar order, i) there should be a resonance enhancement at Eq in the sigma-pi channel but a dip in the sigma-sigma channel ii) the azimuthal dependence using E_res in the sigma-pi channel should reflect the z2 symmetry while the same azimuthal dependence using E_nonres or measured in the sigma-sigma channel should reflect the varying beam footprint.
b. Temperature dependence using E_nonres or measured in the sigma-sigma channel should show no anomaly at Tq or Tm
c. Presumably, the intensity in Fig 2h at T>Tq (when there is no quadrupolar order) is related to the leakage of the charge scattering and should be taken as a background. Interestingly, the intensity returns to this background level at T<Tm, indicating that the z2-quadrupolar order is suppressed below Tm. How is this consistent with an enhancement of the splitting (gamma) in Fig 2i which shows the exact opposite?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all my questions and comments, and I would recommend it for publication.

Reviewer #2

(Remarks to the Author)
The authors have competently addressed all my concerns by supplying very compelling additional data. If not already, I think the readers would appreciate that these additional data (Fig R1-R9) and the discussions (e.g. discussions on the resonance energy/ temperature dependence of the (10,0,0) peak etc) to be included as separate Supplemental Materials. Once the authors have done that, I am very happy to recommend the publication of the manuscript in nature communications.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

1. One novel result here is the direct detection of the quadrupolar order using resonant x-rays. ….. Using computations, it is determined that neither the electronic ordering nor lattice distortions alone drives the transition at T_q, and both must be considered to explain the experimental results.

We thank the reviewer for a nice summary of our results, highlighting the novelty of our study.

2. *I found this manuscript compelling and framed well for a wider audience. … the current manuscript presents results on quadrupolar order studied with resonant diffraction as well as extensive computational work. The experiment seems well done, and the conclusions are valid. Overall, I think this could be of interest to a broader audience given the relevance to understanding phase transitions in condensed matter.*

Again, we thank the reviewer for acknowledging the impact of our manuscript to a broad audience.

3. In Figure 1 a-c, …. I would suggest removing g_θ labels and connecting lines since they are not adding anything to the figure. It may be sufficient to label q_θ and d_θ and say that there is electron-lattice coupling without indicating it in the figure.

We thank the reviewer for a careful reading of our manuscript and this suggestion. Indeed, we were vacillating between including and excluding the g_θ labels, and the reviewer has tipped us towards removing it. We have made the change in the manuscript to reflect this.

4. Are the indices used here for the cubic or tetragonal unit cell? In Ref. 3 it is noted that the (1, 1, 0) cubic reflection only appears below T_m, so I am assuming that the notation used in the current manuscript references the tetragonal unit cell.

This is a great question. Throughout the paper we adopt the cubic unit cell to index the peaks for the sake of consistency. Indeed, for the Fm-3m space group the (1,1,0) reflection is forbidden. However below T_q, the (1,1,0) peak becomes allowed as it corresponds to the (1,0,0) in tetragonal indexation.

5. On page 2, it is stated that the results represent "a clear experimental verification of several theoretical studies [16, 19-21]". I am curious about the author's comments on Refs. 16 and 20, which

both state that only one e_g quadrupole (the x^2-y^2 and not the z^2) is present the ordered quadrupole phase.

In Ref. 20, Lovesey *et al.* mentions that both the antiferro x^2-y^2 and ferroic z^2 order should be present in BMRO. The former is described in great detail in Section III of the paper as E_g type quadrupoles with an antiferro $\boldsymbol{k}$= (0,0,1) order, which we verify in our work. The latter is described as such, "In fact, T_{2g} distortions are secondary and associated with $\boldsymbol{k}$ = (0, 0, 0), meaning some ferro ordering of the T_{2g} -type quadrupoles should be allowed.", which is the ferroic z^2 order that we also verify in our work. We believe that the reason why Lovesey *et al.* chose to stress on the former because the signal is expected to be cleaner.

In Ref. 16, Gang Chen *et al.* reports the mean field calculations of *4d* and *5d* double perovskites (DPs) which sparked of the growth in interest in the system. Although the authors did not consider BMRO in Ref 16 explicitly, the main author did consider BMRO in a subsequent paper in Ref. 3, where both the antiferro x^2-y^2 and ferro z^2 were predicted. Our manuscript verifies Ref. 3 not Ref. 16 so, we have changed the references.

6. Regarding Fig. 2d, how were the calculated azimuthal dependences determined?

We describe the electric quadrupoles on the Re ions in terms of rank-2 tensors. Depending on the relative arrangement and orientation of the quadrupoles on the two Re sites, we can work out the structure factor at each reciprocal space vector, **Q**. This formalism also takes in to account the experimental geometry and also the linear polarization of the incident and out going photons, which we describe as vectors. To include the azimuthal dependence, we apply a rotation matrix within the formalism. This is described explicitly in Phys. Rev. B **103**, 174409 (2021).

7. Fig. 2i is a bit confusing. On page 3 when discussing Fig. 2i, it says that Fig. 2i shows splitting of the (10, 0, 0) structural peak. I think that what is being plotted is the peak splitting in degrees (labeled as gamma on the x-axis), but this should be stated clearly because it is easy to assume that it is plotting integrated intensity like Fig. 2e-h.

The reviewer as raised a good point. We have made a change to the figure caption to reflect this.

8. In Fig. 3a, is there also meant to be a red dot for the experimental d_(z^2)distortion?

That is a very good question and the answer is fairly subtle. The two red dots describe the experimentally determined long-range ordering of the local octahedral distortion for a given structural domain. Within that domain, the structural order has two components, comprising a linear combination of (1) an antiferroic order of local octahedra distortion of about 0.05 Angstrom with $d_{x2\text{-}y2}$ symmetry and (2) a ferroic order of local

octahedra distortion of about 0.01 Angstrom with d_{z2} symmetry. The two points are located as such because we designated the tetragonal 2_1 axis of the $P4_2/mnm$ space group as z.

If we had defined instead the 2_1 axis of the tetragonal space group as x or y, then the two red points should appear at positions obtained by rotating the plot by +/- 120° about the origin. In fact, since the cubic crystal splits into three structural domains below T_q, one along x, another along y and the last along z, there should be 6 red points in total. However, we omitted the four other points arising from the other structural domains to reduce clutter.

Now, the white dots obtained from the calculations is not describing long-range ordering of local octahedron distortion, across the lattice. Instead, it actually describes the distortion of a single local octahedron that lives within the BMRO lattice. So, the white points are not indicating that the local octahedron comprises a linear combination of d_{x2}, d_{y2} and d_{z2} distortion. Rather it is saying that these three distortions are degenerate in energy (by symmetry).

9. I am curious about the predictions of a q_xy[000] order. Is it possible that this type of ordering occurs as well? How would you check experimentally? The possibility of of q_xy[001] order is dismissed by the scattering azimuthal dependence, but what would the signature of q_xy[000] be?

A $q_{xy}^{[000]}$ order will give rise to an azimuthal dependence with a π periodicity in the σ-π' channel for the (0,0,10) reflection. This is distinguished from the $q_{z2}^{[000}$ order, which should be independent of azimuth.

To check this experimentally, we will need to measure the (0,0,10) reflection in the σ-π' channel to reject any charge scattering from the σ-σ' channel. Since the (0,0,10) splits into three satellite peaks for the temperature range between T_m and T_q, we will need to isolate the signal from one of the three satellites and measure its angular dependence. Now, this is technically challenging because the peaks are not well resolved in reciprocal space for the temperature range between T_m and T_q. So, the azimuthal dependence will pick up contributions from the two other satellites. Moreover, even if we start with a specular scattering geometry for temperatures above T_q, the diffraction will not be specular when we go below T_q due to the peak splitting. As such there will a large, non-negligible contribution from the varying beam footprint on the sample surface. Unfortunately, both these extrinsic effects have the same π periodicity so it will be very difficult to distinguish the various contributions and make a decisive statement. On the contrary, the antiferroquadrupolar order for BMRO at (5,5,0) shown in our work is a very clean example where the peak is specular and does not split, which allows for an unambiguous determination of the $q_{x2\text{-}y2}^{[001]}$ symmetry.

10. The last paragraph refers to section ii, but the sections are not labeled in the text. Also, this seems to end fairly abruptly without much conclusion.

We thank the reviewer for highlighting this point. We have made some changes in the text to reflect this.

Response to reviewer #2:

> *1. I have no doubt that the results will be of interest to people studying multipolar physics in heavy transition metal systems.*

We thank the reviewer for recognising that our work will be of interest to the multipolar physics community.

> *2. However, I think it belongs to a more specialized journal because compelling structural evidence for the two types of quadrupolar order in the same material has already been reported by Hirai et al (Phys Rev Research, 2:022063 (2020)) using non-resonant X-ray scattering. I acknowledge that the evidence in the present manuscript is in a sense 'more direct' as it uses REXS that directly probes electronic order. However, one always expects structural distortion to induce orbital order and vice versa. The observation of resonantly enhanced Bragg peak at the same superlattice position is therefore not surprising. I therefore consider the present work to be a continuation of Phys Rev Research, 2:022063 (2020) and consequently more appropriate for a specialized journal like PRB.*

Multipolar order in *5d* double perovskite (DP) systems, was first predicted back in 2010. It is an interesting system as the fine balance of spin-orbit coupling and inter-site exchange coupling have been predicted to give rise to new exotic phases of matter. As such, since then, there have been many attempts to verify this multipolar order experimentally but the reports thus far are indirect at best, detecting only a structural transition or symmetry breaking [Nat. Comms. **8**, 14407 (2017)]. In particular, Phys Rev Research 2 022063 (2020) is just one of the many experimental papers on *5d* DPs which present structural transition data as an indirect evidence for quadrupolar order.

Indeed, this lack of direct evidence of quadrupolar order in *5d* DPs has prompted several subsequent theoretical studies [e.g. Phys. Rev. B 103, 235160 (2021); Phys. Rev. B 104, 024437 (2021); Phys. Rev. B 107, L220404 (2023)] to call for experimentalists to produce direct evidence of quadrupolar order. In other words, the indirect evidence of quadrupolar order [e.g. in Phys Rev Research **2** 022063 (2020)] was not compelling enough for the community.

Quite simply, our work presented here amounts to the first ***direct*** demonstration of quadrupolar order in *5d* DPs, which is a culmination of the experimental work that has gone before. Our experimental results establish the numerous theoretical and computational predictions put forth since 2010, that *5d* DPs do indeed manifest spontaneous quadrupolar order. We believe, therefore, that Nature Communications is the fitting platform to communicate our work, joining alongside the recent works on *5d* DPs in the same journal [e.g. Nat. Comms. **8**, 14407 (2017); Nat. Comms. **15**, 2429 (2024)] which do not probe the quadrupoles directly.

Moreover, given that BMRO is such a clean system, we are able to ascertain for the first time the symmetry of the antiferroquadrupolar order in *5d* DPs.

Furthermore, on the theoretical front, our work goes well beyond applying readily available *ab-initio* packages, as is the practice of most computational studies of *5d* DPs. Instead, we have developed new *ab-initio* methods to determine how different magnitudes and configurations of quadrupolar orders along with structural

distortion shape the energy landscape of *5d* DPs. Extensive calculations were performed to address the central question we pose in the paper, which is what ***ultimately drives*** the ordering in BMRO. As such, even on the theoretical front, our work goes well beyond the previous (dynamical) mean field or density functional calculations by providing a mechanism that drives the order in BMRO. This has not been attempted before and the *ab-initio* methods we developed (which we made available open source) is widely applicable to the wider family of other *5d* DPs and beyond. As such, we believe that Nature Communications will be a fitting platform to highlight our computational technique to the wider *5d* DP community, as well.

3. In Fig 2, the authors should also show the azimuthal dependence at Em to show unambiguously that Em and Eq probes different order.

To demonstrate that E_m and E_q probes different order, unambiguously, we plot the azimuthal dependence at E_m (top curve in blue, at 6 K) and E_q (bottom curve in red, at 20 K) in Fig. R1. The E_m dependence has a maximum at $\psi = 0^o$ and while E_q dependence has a maximum at $\psi = 90^o$.

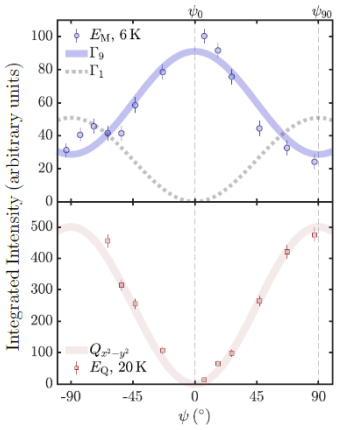

Figure R1. Azimuthal dependence of the (5,5,0) peak measured in the sigma-pi' channel at 6 K and Em (top) and 20 K and Eq (bottom) to probe the antiferro magnetic and quadrupolar order respectively.

4. I don't understand why there is such a large energy difference (almost 7eV) between Eq and Em. After all, the quadrupolar order and magnetic order are both associated with the Re t2g electrons. On the other hand, the 7eV difference is almost the charge transfer energy. So, the question is, what electronic order is the REXS actually probing? Please explain.

The reviewer has raised a good question. First, we agree that the quadrupolar and magnetic order are both associated with the Re t_{2g} electrons, so naively we would expect that the resonant energy E_q and E_m to be identical. However, quadrupoles are more sensitive to the local crystal electric field and hybridization with the ligands which tend to broaden the ATS resonances compared to magnetic dipoles.

To really understand what REXS is probing at E_m and E_q will require resonant inelastic x-ray scattering (RIXS) at the Re edge. Although this goes beyond the scope of the current manuscript, we have performed RIXS on BMRO at the Re L_3 edge. First, we confirm that E_m probes the Re t_{2g} electrons. In addition, we also found a sharp peak at an energy transfer of 5.5 eV arising from the t_{2g}-e_g splitting. On the other hand, we also find a broad charge transfer gap occurring at an energy transfer of 7.5 eV.

Figure R2 plots the representative energy scan associated with the magnetic dipoles (in black) and charge quadrupoles (in green). First, we note that the quadrupolar resonance contain a peak at E_m, so the ATS also couples to the Re t_{2g} states, directly. In addition, it also has a strong peak at E_q with a large tail that extends to 10.56 keV.

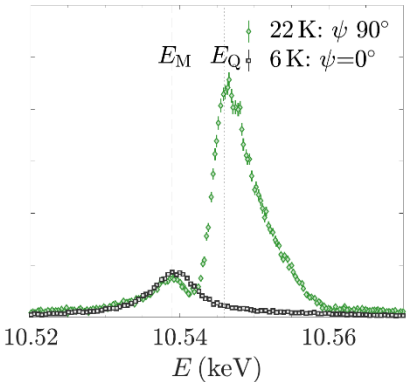

Figure R2. Energy dependence measured in the sigma-pi' channel at 22 K and psi = 90 (green curve) and 6 K and psi = 0 (black curve) for the charge quadrupolar and magnetic dipoles.

The question that needs to be address is actually two-fold: first, why is the ATS resonance so broad, and second, what is causing this dip between E_q and E_m?

One plausible explanation for the broadness of the resonance is that the E1-E1 resonant scattering process of charge quadrupoles excite the $2p_{3/2}$ core electrons not just into the Re t_{2g} states but also the Re e_g electronic states. Based on our calculations, there is a strong coupling between the Re t_{2g} and e_g states. Moreover, there is strong hybridization of the Re with the surrounding oxygen ligands. This tends to broaden the resonance associated with the charge quadrupoles.

This distinct ATS and magnetic resonances were also observed in various studies: GdB_4, [Phys. Rev. Lett **91** 257205 (2003)]; DyB_4 [Phys. Soc. Jpn., **74**, 9, 2434 (2005)]. In both cases, the difference between E_q and E_m arises from the hybridisation with the crystal electric field of the local crystal environment. Also, the ATS resonance in $Sm_2Ir_2O_7$ shows transition from core electrons into the Ir t_{2g} and e_g states [Phys. Rev. Lett. **117** 037201 (2016)]. Hence, this effect is not unique to BMRO.

Now, regarding the dip that has been observed in the spectrum. Two possible explanations can account for it. First, it could be due to quadrupolar-magnetic interference. This is because, within the complex plane, the rank-2 tensors describing charge quadrupoles are real, whereas those describing magnetic dipoles is purely imaginary. In Fig R3 we plot the envelope of the two peaks with (thin line) and without (thick line) accounting for quadrupolar-magnetic interference. It is clear that the interference between the two can account for the dip. Another plausible explanation is that the separation of the peaks come from absorption of the sample [See J. Phys.: Condens. Matter 15 L59 (2003)].

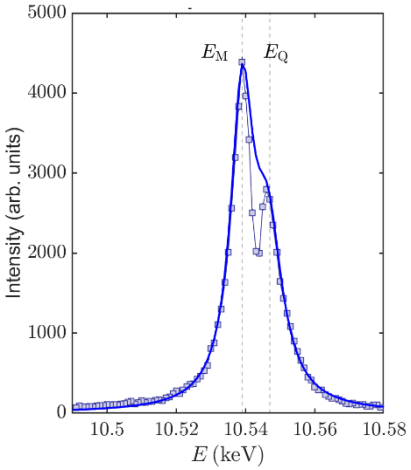

Figure R3. Fitting the double peak resonance of the (5,5,0) peak with (thin line) and without (thick line) quadrupolar-magnetic interference.

We are still in the midst of modelling the RIXS spectrum of BMRO, which is the subject of another manuscript and beyond the scope of this current work.

5. Why is Fig 2f (on res) and Fig 2g (off res) measured at different Bragg peak positions (550) and (530)? For proper comparison, the authors should show on-res and off-res at the same Q. (In case the sigma-pi intensity using E_non-res is too small, do the measurement in the sigma-sigma channel) In addition to a temperature dependence of the (550) Bragg peak intensity using E_non-res. An azimuthal dependence at (550) using E_non-res is also necessary to rule out any (extrinsic) azimuthal dependence due to, for example, varying beam footprint.

We chose the (5,5,0) peak in Fig. 2f to demonstrate the antiferro-order of charge quadrupoles because the peak occurs in the specular scattering geometry, so that the azimuthal dependence due to the varying beam footprint is kept to a minimum. On the other hand, the (5,3,0) peak off resonance was chosen because the scattering cross section of the antiferro structural order of d_{x2-y2} symmetry is stronger than that of the (5,5,0) reflection.

Nonetheless, to address the reviewers concern, we plot the following:

Azimuthal dependence at (550) using E_non-res. Figs. R4 shows the azimuthal dependence in the energy scans of the (5,5,0) peak at various azimuthal angles in the σ-π' channel. The low background at off-resonance energies (e.g. 10.5 keV) rules out any extrinsic azimuthal dependence due to varying beamfoot print.

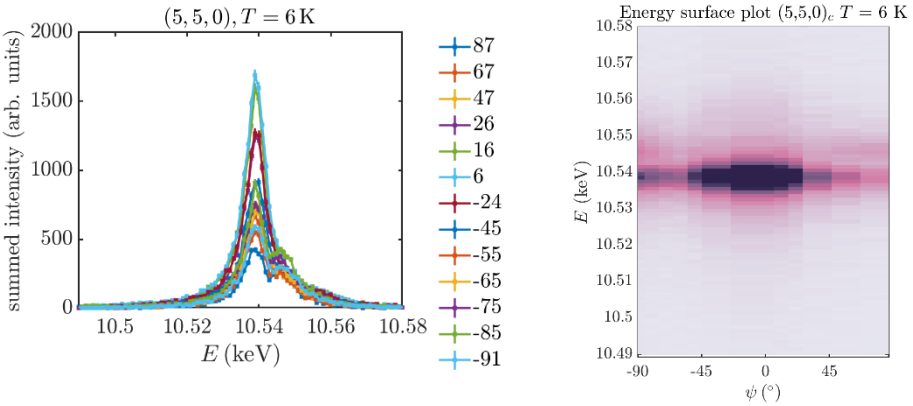

Figure R4. Energy dependence of the (5,5,0) reflection measured at various azimuthal angles at 6 K in the σ-π' channel. (left) line plot. (right) surface plot.

A temperature dependence of the (5,5,0) Bragg peak intensity using $E_{non-res}$. Figure R5 plots the temperature dependence of energy scan of the (5,5,0) reflection, in the σ-σ' channel. We see that away from the resonance, the intensity grows below T_q, just as it the case for (5,3,0) in Fig. 2g. But we chose (5,3,0) as it has a stronger structure factor.

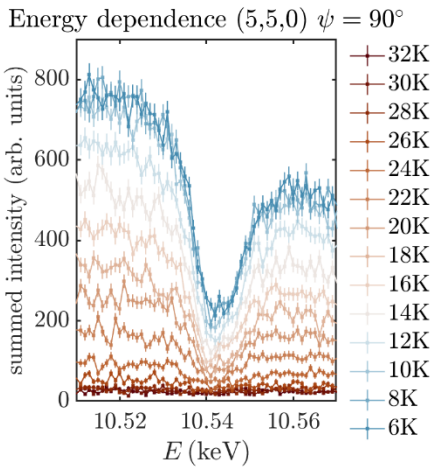

Figure R5. Energy dependence of the (5,5,0) reflection measured in the σ-σ' channel at various temperatures.

Energy dependence of the (5,3,0) Bragg peak intensity. We also show for completeness, the energy dependence of the (5,3,0) peak in the σ-σ' and σ-π' channel in Fig. R6, which is exactly the same as (5,5,0) but it is not in the specular scattering geometry.

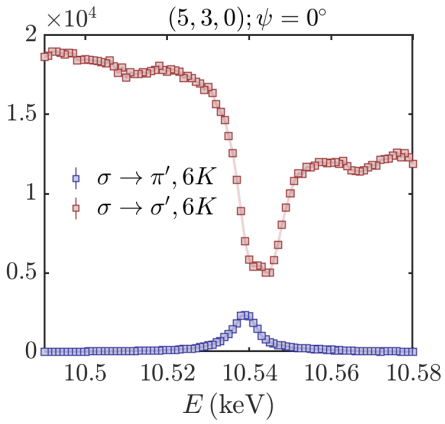

Figure R6. Energy dependence of the (5,3,0) reflection measured in the σ-π' (blue curve) and σ-σ' (red curve) channel at 6 K.

6. Fig 2g shows that (530) intensity levels off below Tm, whereas Phys Rev Research, 2:022063 (2020) shows that the intensity of this superlattice peak is suppressed below Tm. Please comment.

First, we would like to comment that the data presented in Fig. 2d in Phys. Rev. Research 2 022063 (2020) is very noisy, compared to our data, which shows a much cleaner signal. One possibility is that in our case, the scattering vector of the (5,3,0) reflection is very close to specular scattering geometry at (5,5,0). As such the peak intensity of the (5,3,0) does not suffer much from the miscut of the sample.

On the other hand, for the report in Phys. Rev. Research 2 022063 (2020), the scattering vector of the $(5,3,0)_c$ peak deviates greatly from the specular scattering geometry at (0,0,1). As such, there is a large angle between the scattering plane and the surface of the sample. One possibility is that the beam drifts a lot when tracking the temperature dependence of the $(5,3,0)_c$ peak, which perhaps is the reason why the signal in Phys. Rev. Research 2 022063 (2020) is rather noisy.

7. I have great issue with the interpretation of Fig 2h as evidence for quadrupolar order with a z2 symmetry. Given that there is always leakage of the strong charge scattering into the sigma-pi channel, it is important to rule this out as the reason for the observed intensity

To rule out the leakage of the σ-σ' to the σ-π' channel, we plot the energy dependence of the (5,3,0) peak collected at 6 K in Fig. R7. The σ-σ' channel (red curve) shows a dip whereas the σ-π' channel shows a peak. This is even more apparent in the log scale, which show that the suppression of the charge contribution by at least two-orders of magnitude off resonance. As such the leakage from the σ-σ' channel can be ruled out. This is because, fortuitously the scattering angle of the analyser crystal is very close to 90 degrees.

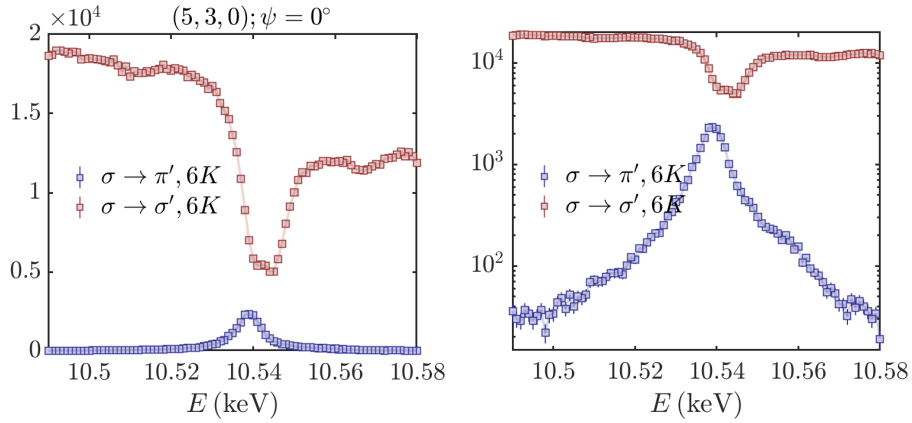

Figure R7. Energy scan of the (5,3,0) reflection measured in the σ-σ' and σ-π' channels at 6 K. (left) linear and (right) log y scale.

7a. The authors should show i) energy dependence in the sigma-pi and sigma-sigma channel and ii) azimuthal dependence using E_res and E_non-res in both the sigma-pi and sigma-sigma channel. If the observed intensity between Tm<T<Tq is associated with quadrupolar order, i) there should be a resonance enhancement at Eq in the sigma-pi channel but a dip in the sigma-sigma channel ii) the azimuthal dependence using E_res in the sigma-pi channel should reflect the z2 symmetry while the same azimuthal dependence using E_nonres or measured in the sigma-sigma channel should reflect the varying beam footprint.

Indeed, as shown above in Figs. R7, there is a dip in the energy dependence in the σ-σ' channel and a resonant enhancement in the σ-π' channel. We also plot the energy scan of the (10,0,0) peak in the σ-π' channel [Fig. R8], which shows a peak at E_{res} and also a rejection of the leakage from the underlying charge peak at the $E_{non\text{-}res}$ energies.

We agree with the reviewer that to directly demonstrate that the ferro order of the quadrupoles has z^2 symmetry, we will need to do an azimuthal dependence on the (10,0,0) reflection at E_{res} in the σ-π' channel (e.g. just as we have shown for the (5,5,0) reflection). Since the (10,0,0) peak splits into three satellite peaks below T_q, an azimuthal dependence has to be performed on one of three satellite peaks, to determine the symmetry of the ferroic order. (In fact, all of the peaks in BMRO which are sensitive to ferroic order will split. We chose the (10,0,0) because the charge scattering cross-section is very small, close to 0, to reduce leakage from the σ-σ' channel.)

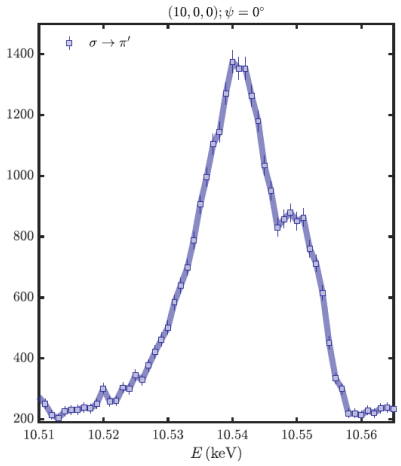

Figure R8. Energy scan of the (10,0,0) reflection in the σ-π' channel.

However, due to the very small splitting of the (10,0,0) peak, an azimuthal dependence of one of the satellites will contain the contribution from the other two satellite peaks. Moreover, even if we were to prepare a [100] face of the crystal for specular diffraction, the peak splitting, although small, also lead to a non-negligible varying beam footprint. Discerning the underlying symmetry of the ferro order will require disentangling of the real signal from these other contributions, which we are not convinced will yield a very clean and decisive result. As a comparison, the antiferroic quadrupolar order which we show from the (5,5,0) peak is a very clean example, since there is (1) no underlying structural peak, (2) where the [110] face is a natural facet of the crystal and (3) the peak does not split.

While we can say that the signal of the (10,0,0) peak in the σ-π' channel is due to a ferroic order that arise from the Re ions, we agree with the reviewer that we do not have direct evidence that it displays z^2 symmetry. As such, we have changed the wording of the text, to soften our interpretation of the signal in Fig 2h.

7b. Temperature dependence using E_nonres or measured in the sigma-sigma channel should show no anomaly at Tq or Tm

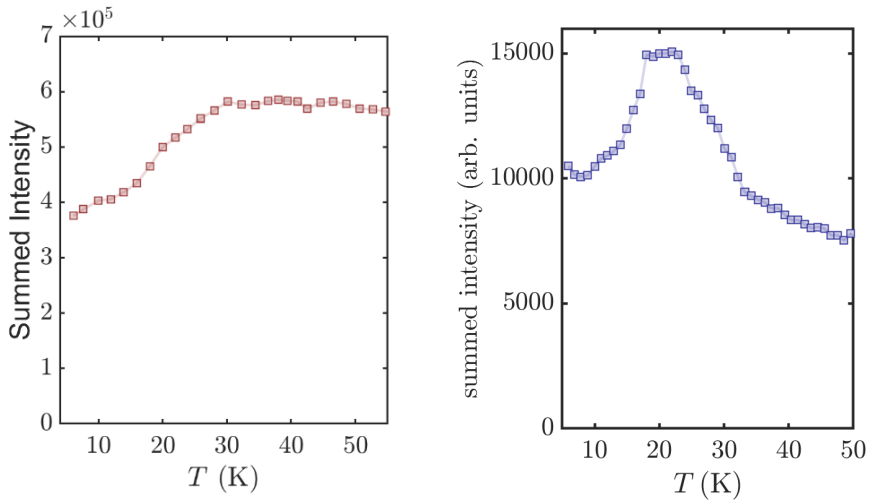

Figure R9. Temperature dependence of the (10,0,0) reflection measured in the (left) σ-π' and (right) σ-π' channels, respectively.

In Figure R9, we plot the temperature dependence of the (10,0,0) peak measured in the σ-σ' and the σ-π' channel, side by side. The data were collected at the same angles and energy (E_q). The red curve was collected in the σ' out-going polarization with an attenuation factor of 3 while the blue curve was measured in the π' out going polarization channel with an attenuation factor of 2. As such, the signal in the σ-σ' channel is 2 orders of magnitude stronger than that of the σ-π' channel.

First, we note that the signal in the σ-σ' channel (red data points) is flat above T_q but decreases below T_q due to the splitting of the peak. On the other hand, the signal in the σ-π' channel, ***increases*** by 50 %, just below T_q, ***contrary*** to the behavour of the σ-σ' signal. Therefore, we can safely rule out the increase in the σ-π' channel to leakage from the σ-σ' channel, which (1) is two orders of magnitude larger in intensity, and (2) has a different temperature dependence.

> *7c. Presumably, the intensity in Fig 2h at T>Tq (when there is no quadrupolar order) is related to the leakage of the charge scattering and should be taken as a background. Interestingly, the intensity returns to this background level at T<Tm, indicating that the z2-quadrupolar order is suppressed below Tm. How is this consistent with an enhancement of the splitting (gamma) in Fig 2i which shows the exact opposite?*

To understand Fig 2h rightly, we need to understand the two effects that are occurring simultaneously. First, the (10,0,0) peak is splitting into three satellites on cooling below T_q. Second, the signal intensity on each satellite in the σ-π' channel is also increasing below T_q (See previous point). Ideally, we should follow one satellite at all temperatures below T_q. However, just below T_q, the splitting is small so it is difficult to isolate the contributions from each satellite. On further cooling, the satellites become better distinguished.

So, the reason why the signal increases for temperatures just below T_q is because the increase in the signal due to the quadrupolar order outweighs the decrease in the signal due to the splitting of the peak, into three satellites. On further cooling, the decrease in the signal due to the peak splitting outweighs the increase in the due to the ferro quadrupolar order.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed all my questions and comments, and I would recommend it for publication.

We thank the reviewer for recommending our manuscript for publication.

Reviewer #2 (Remarks to the Author):

The authors have competently addressed all my concerns by supplying very compelling additional data. If not already, I think the readers would appreciate that these additional data (Fig R1-R9) and the discussions (e.g. discussions on the resonance energy/ temperature dependence of the (10,0,0) peak etc) to be included as separate Supplemental Materials. Once the authors have done that, I am very happy to recommend the publication of the manuscript in nature communications.

We thank the reviewer for recommending our manuscript for publication. We have uploaded a copy of the Supplemental material.