

Dynamic Jahn-Teller effect in the strong spin-orbit coupling regime



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In this work, Živković *et al.* investigated the nature of the multipolar phases of a $5d$ transition metal system, $\text{Ba}_2\text{MgReO}_6$, by using resonant inelastic x-ray scattering (RIXS) technique, magnetic and thermodynamic measurements, and quantum chemical calculations. In this material, the ground spin-orbit states of Re site are four-fold degenerate $j = 3/2$ states, which can be subject to the Jahn-Teller effect. The authors investigated the impact of the Jahn-Teller effect on the RIXS spectra. The authors found the spin-orbit and ligand-field splittings from the Re L_3 edge RIXS spectra. The O K edge RIXS spectra show a strong low-energy peak. The authors interpreted that the peak indicates the Jahn-Teller splitting of the $j = 3/2$ states. Due to the split $j = 3/2$ states, the electronic entropy reaches only $\ln 2$ above the quadrupole transition temperature. The multipolar physics of the $5d^1$ compounds is growing, and this work provides interesting insight into the Jahn-Teller effect in these materials. I recommend publishing this work in Nature Communications after the authors give convincing replies to my comments below.

Could the authors discuss the relations between the present interpretations and the conclusions of the recent similar works? Recently, several x-ray scattering data on the $5d^1$ compounds appeared on a preprint server [(1) Frontini *et al.* arXiv:2311.01621 and (2) Agrestini *et al.* arXiv:2401.12035]. These authors also reached similar conclusions as this work with the RIXS measurements. The discussion on the differences and similarities between the present and these works is helpful for the readers.

Besides, the authors also published a related work on the same compound with resonant elastic x-ray scattering measurement (Soh *et al.* arXiv:2312.01767). Above the quadrupolar transition temperature in the work, the deformations disappear. Can the authors discuss the relations between the present work and the former REXS work?

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

The authors presented Re-L and O-K edge RIXS measurement of the rhenium electronic excitations in Ba₂MgReO₆. The most important discovery of the present work is a small splitting of the Re⁶⁺ $j_{\text{eff}}=3/2$ level resolved by the high resolution oxygen K edge measurement, that suggests the existence of non-cubic local distortion in Ba₂MgReO₆ well above the magnetic/quadrupolar ordering temperatures. This is explained by a dynamical JT effect. The present work seems to provide an explanation for the missing electronic entropy seen in Ba₂MgReO₆ and other double perovskite material. I think this is an interesting work that potentially has wide implication in the study of 5d double perovskite, and hence suitable for nature communications. However, I cannot recommend its publication in the current form as there are some important questions that were not properly addressed as I explain below. However, once the authors address them, I am willing to consider recommending it for publication.

1) My most important comment is the following: RIXS measurement of the Re⁶⁺ electronic excitation only provides part of the evidence for a dynamical JT scenario, the current work lacks a direct structural evidence for it.

According to the calculations, the observed splitting is consistent with a structural distortion about 1-2% that does not change up to ~200K. This should be quite observable by PDF measurement. Including such a measurement will greatly strengthen the current manuscript.

Moreover, based on the current measurement (even combined with the PDF measurement), it is difficult to distinguish between a dynamical JT scenario versus a scenario where the local distortions are random but static. Since the time-scale for lattice fluctuation is much slower than the electronic time scale, both will give the same electronic excitations. Complementary phonon measurements showing softening at appropriate Q's are necessary for this purpose.

2) Can the authors provide an explanation for the long tail of the inelastic features observed in the K-edge spectrum. The tail is clearly longer than the instrumental resolution as seen from Fig S5-S6 and hence represent a real broadening of the inelastic features. Is it consistent with a distribution of Δ_{JT} shown in Fig3g?

3) In TABLE 1, the agreement between the calculated/observed values for Δ_{JT} seems pretty good (~10% discrepancy). On the other hand, there is a large discrepancy between theory and experiment for the splitting of Δ_O (eg-eg excitation): the observed splitting is about 250meV whereas the calculated one is about 385meV (~50% larger). Do the authors have an explanation for this?

It is useful to include a temperature dependence of Δ_O alongside Δ_{SO}/Δ_{JT} in Fig 2d/2e to show that they have the same temperature dependence.

4) The existence of electronic symmetry breaking due to dynamical JT effect provides an interesting explanation for the missing entropy in the specific heat data in Fig 4. However, if the additional entropy (other than that guaranteed by the time reversal symmetry (TRS)) is already removed well above TQ (according to Fig 2e, there is no change in Δ_{JT} below 200K), what is the driving force for the quadrupolar ordering?

5) Since I am an experimentalist, this question is perhaps intended more for clarifications. The authors calculation in Fig 3e appears to be for a single octahedra sitting in a background of fixed ions (please correct me if I am wrong). On the other hand, the distortion of the octahedra should take the form of a collective lattice distortion. How is the latter accounted for in the calculation?

Reviewer #3 (Remarks to the Author):

The authors propose a demonstration of dynamic Jahn-Teller effect in $\text{Ba}_2\text{MgReO}_6$ by combining RIXS, transport measurements (susceptibility and specific heat) and embedding multi-reference quantum chemistry calculations where SOC is taken into account.

While the manuscript is well structured, the main idea is very appealing and the interest of the topic is well contextualized and presented in the introduction, the analysis of the RIXS data show some important deficiencies that questions the main conclusion and therefore the paper itself.

On the one hand, the manuscript considers central to the analysis the RIXS data measured at the Re L3 RIXS edge since they are the ones for which a deconvolution and a temperature dependence is presented in the manuscript. This is done after confirming that the energy resolution of 140 meV is much larger than the expected Jahn-Teller gap, 88 meV, which is the essential to understand the main claim of the manuscript.

In contrast, the O K-edge data, which have sufficient energy resolution to study the energetics of the system is reduced to figure 2.b without any fit and to figure 6 in the supplement material. In this figure the temperature dependence is presented, again without a detailed analysis. This is very puzzling since the visual inspection of figure 6 indicates that the spectra have a double peak structure between 0.05 and 0.25 eV and between 0.45 and 0.65 eV at low temperatures. Furthermore, there is a clear temperature dependence in the evolution of the lineshape and the energy levels that is not discussed in the text. Moreover, there is also a dependence of the level upon changing the incoming photon energy that it is not also not analyzed.

Based on the above, I cannot recommend the publication of the paper in its current form. Instead, a detailed analysis of the O K-edge data is required in order to ambiguously proof the main conclusion of the manuscript. Since these data seem to be more critical to understand the system, I think they shall be central in the manuscript.

One further suggestion: the symbols used in the transport measurements makes it very difficult to compare the evolution of the different curves. This is especially inconvenient in figure 4a.

Dear Editor,

We thank the reviewers for their critical reading of the manuscript and comments. Below, we provide a point-by-point response to their concerns/questions and recommendations.

REPLY TO REFEREES

The text written by Referees is coloured blue. The pdf titled 'mainDIFF' highlights all the changes made to the manuscript. The supplement has been expanded with detailed analysis of RIXS spectra.

Reviewer 1

In this work, Zivkovic et al. investigated the nature of the multipolar phases of a 5d transition metal system, Ba₂MgReO₆, by using resonant inelastic x-ray scattering (RIXS) technique, magnetic and thermodynamic measurements, and quantum chemical calculations. In this material, the ground spin-orbit states of Re site are four-fold degenerate $j = 3/2$ states, which can be subject to the Jahn-Teller effect. The authors investigated the impact of the Jahn-Teller effect on the RIXS spectra. The authors found the spin-orbit and ligand-field splittings from the Re L3 edge RIXS spectra. The O K edge RIXS spectra show a strong low-energy peak. The authors interpreted that the peak indicates the Jahn-Teller splitting of the $j = 3/2$ states. Due to the split $j = 3/2$ states, the electronic entropy reaches only $\ln 2$ above the quadrupole transition temperature. The multipolar physics of the 5d1 compounds is growing, and this work provides interesting insight into the Jahn-Teller effect in these materials. I recommend publishing this work in Nature Communications after the authors give convincing replies to my comments below.

We thank Referee 1 for reading carefully the manuscript, we agree with the short summary of the findings presented in it, and we hope to convincingly answer her/his comments.

Could the authors discuss the relations between the present interpretations and the conclusions of the recent similar works? Recently, several x-ray scattering data on the 5d1 compounds appeared on a preprint server [(1) Frontini et al. arXiv:2311.01621 and (2) Agrestini et al. arXiv:2401.12035]. These authors also reached similar conclusions as this work with the RIXS measurements. The discussion on the differences and similarities between the present and these works is helpful for the readers.

We agree that those works are also relevant in the context of 5d1 materials. In the new version of the manuscript we have included throughout the text few sentences where we address how they relate to our findings. Here we elaborate in more detail how are those articles compared to our contribution.

Frontini's article is focused on the study of the Re line-shape seen in RIXS data on Ba-, Sr- and Ca-based double perovskites containing 5d1 on Re ions. They are focusing solely on the excitation characterizing $j_{3/2} - j_{1/2}$ splitting, which in our manuscript is designated with Δ_{SO} . They introduce a model which includes spin-orbit-vibronic coupling in order to explain the asymmetric line-shape and obtain some additional modes at $E > \Delta_{SO}$. From their Fig3 it seems that those additional modes are aligned with weak features seen in the RIXS spectra of Ca₂MgReO₆ but for Ba₂MgReO₆ the line-shape does not reveal any additional features. Even for this level of qualitative agreement they state:

"The peak shift and broadening can be matched by arbitrarily increasing g at high temperature, however, the physical mechanism for such an increase is not understood and as such is not done."

In our case, we do not observe any significant asymmetry in our Re RIXS line-shape, simple Gaussians are enough to reliably extract the positions of excitations. On the other hand, here we would like to emphasize that the study of RIXS line-shapes is notoriously difficult, and that our use of Gaussians does not imply a certain underlying physical mechanism, or the lack of. The difference between the two sets of data in terms of the exact line-shape could well originate from different beamlines used, or the exact experimental conditions. In any case, the agreement between the two results where the excitations appear is very good.

For Agrestini’s article, the main difference is a different compound studied. In that context, their contribution is complementary to ours since it confirms that two different compounds, which so far have been linked through their similar thermodynamic properties, are also similar in terms of excitations. In addition to RIXS, they also use XMCD with supporting calculations to extract the doublet-doublet splitting in their compound. As their title states, they are focused on answering the question why is there magnetism in this compound since theoretically the spin and orbital contributions should cancel exactly. Undoubtedly, they speculate that Jahn-Teller is at the origin but they do not go any further. We believe that our contribution does go significantly further, with local cluster calculations leading to the ground state energy above the energy barriers, implying a dynamic Jahn-Teller effect. On top of that, we do link the spectroscopic evidence with thermodynamic data and resolve the ‘missing entropy’ problem. Note that the previous specific heat report by Hirai et al. (JPSJ2019) indicated $R\ln 4$ entropy release for $\text{Ba}_2\text{MgReO}_6$.

Besides, the authors also published a related work on the same compound with resonant elastic x-ray scattering measurement (Soh et al. [arXiv:2312.01767](https://arxiv.org/abs/2312.01767)). Above the quadrupolar transition temperature in the work, the deformations disappear. Can the authors discuss the relations between the present work and the former REXS work?

We have expanded the discussion about the consequences of both the present and previously published REXS data related to the appearance of distortions at T_Q .

Fundamentally, the RIXS data presented in our current submission are collected as an incoherent scattering, i.e. originating from individual inelastic processes on ions. REXS data, on the other hand, are obtained through coherent scattering from correlated regions. REXS data reported in Soh et al. contain both resonant and non-resonant data, dealing with charge quadrupolar and structural changes in the system, respectively. Both sets of data show qualitatively the same result, the appearance of new Bragg peaks below T_Q which are then by symmetry assigned to ordering of certain charge quadrupoles and deformations of the lattice, where oxygen ions move away from their high-symmetry, high-temperature positions. Crucially, the size of those deformations is only $\sim 1/3$ of those associated with the Jahn-Teller effect. At high temperatures ReO_6 octahedra are dynamically distorted at the level of 1-2 % of the equilibrium Re - O distances. There is no coherence between the neighbours and therefore both resonant and non-resonant elastic scattering reports a high-symmetry, cubic structure, with a unique oxygen ion site. Below T_Q , the charge quadrupolar interaction couples the quadrupoles and forms a long-range ordered state. The asymmetric charge distribution around Re ions affects the equilibrium positions of oxygen ions and leads to several oxygen positions within the unit cell. Importantly, new equilibrium positions are much smaller than the distortions caused by the dynamical JT effect. The charge redistribution on Re ions effectively distorts the local potential for oxygen ions, leading to a small renormalization of PES (potential energy surface, presented in Fig3e for a non-distorted case).

So when one discusses distortions in $\text{Ba}_2\text{MgReO}_6$, one needs to be careful to clearly distinguish the two. The JT type is a dynamical one, larger, and is not observed in elastic scattering experiments. The one occurring below T_Q is smaller, and comes about as a consequence of a ferro-type charge quadrupolar order. Note that in parallel there is an antiferro-type charge quadrupolar order which causes a rhombohedral type of distortion of oxygen ion positions but there is no cumulative effect on the unit cell dimensions like for the ferro-type.

Reviewer 2

The authors presented Re-L and O-K edge RIXS measurement of the rhenium electronic excitations in Ba₂MgReO₆. The most important discovery of the present work is a small splitting of the Re⁶⁺ $j_{\text{eff}}=3/2$ level resolved by the high resolution oxygen K edge measurement, that suggests the existence of non-cubic local distortion in Ba₂MgReO₆ well above the magnetic/quadrupolar ordering temperatures. This is explained by a dynamical JT effect. The present work seems to provide an explanation for the missing electronic entropy seen in Ba₂MgReO₆ and other double perovskite material. I think this is an interesting work that potentially has wide implication in the study of 5d double perovskite, and hence suitable for nature communications. However, I cannot recommend its publication in the current form as there are some important questions that were not properly addressed as I explain below. However, once the authors address them, I am willing to consider recommending it for publication.

We are happy that the referee recognizes the wider implications of our work.

1) My most important comment is the following: RIXS measurement of the Re⁶⁺ electronic excitation only provides part of the evidence for a dynamical JT scenario, the current work lacks a direct structural evidence for it.

According to the calculations, the observed splitting is consistent with a structural distortion about 1-2% that does not change up to 200K. This should be quite observable by PDF measurement. Including such a measurement will greatly strengthen the current manuscript.

Moreover, based on the current measurement (even combined with the PDF measurement), it is difficult distinguish between a dynamical JT scenario versus a scenario where the local distortions are random but static. Since the time-scale for lattice fluctuation is much slower than the electronic time scale, both will give the same electronic excitations. Complementary phonon measurements showing softening at appropriate Q's are necessary for this purpose.

Here Referee 2 raises an important question, how to distinguish between a dynamical JT scenario (scenario 'A') and a random distribution of static distortions (scenario 'B'). The approaches suggested by Referee 2 sound reasonable but are in no way smoking-gun revelations. For instance, PDF measurements (we assume this stands for a pair-distribution function) are plagued with an unfavorable mass difference between rhenium and oxygen ions, meaning that the contribution of oxygen to the PDF intensity is very small. Combined with small distortions (10x smaller than the corresponding distortions observed in 3d oxides), PDF does not represent a clear cut solution (which is actually recognized by Referee 2 in the first sentence of the last paragraph above). Similarly, we aimed to obtain EXAFS data, which is also used to acquire information about the local environment. Again, the differences between the short and long Re-O distances were deemed too small to be able to guarantee a revealing result and no beamtime was awarded. On the other hand, there are plenty of reports with EXAFS data on 3d oxides, so one should be very careful in extending the reasoning towards 5d oxides. At the end, for x-rays both 'A' and 'B' scenarios are 'frozen', so distinguishing eventual tiny difference between a dynamic and a static version is definitely not a routine experiment/analysis.

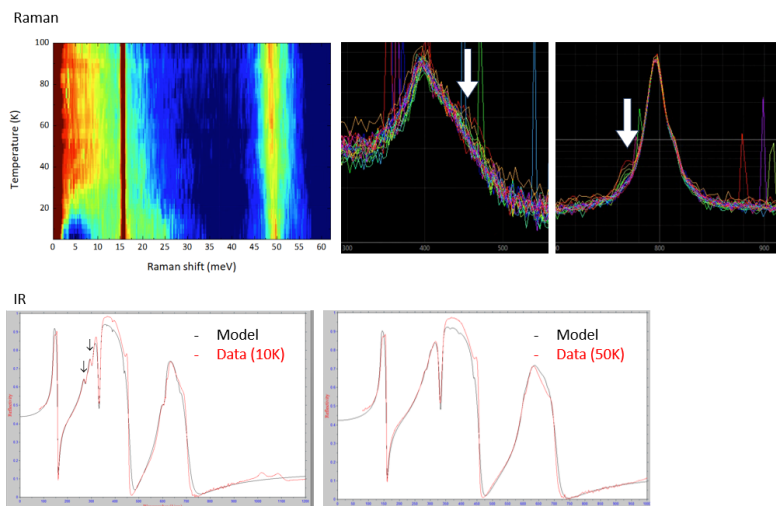
Concerning phonon measurements, here Referee 2 implies that there should be softening of some phonons, at appropriate Q's. It is not completely clear to us which phonons should go soft (or not) in order to distinguish between 'A' and 'B'. Here we would also like to bring into focus a sentence written by Referee 2 under point (5):

On the other hand, the distortion of the octahedra should take the form of a collective lattice distortion.

In the first approximation the distortions on one ReO₆ octahedron do not influence the distortion on its neighbors (in both 'A' and 'B' scenarios). Each ReO₆ octahedron is an independently distorted unit (whether dynamically or statically) due to the fact that in a double-perovskite structure individual octahedra do not share ligands. The effect of these distortions on acoustic phonons is practically negligible. The optical phonons around Q=0 could indeed be renormalized and in the case of 'B' one could imagine that a transition from a high-temperature, undistorted structure

(above T_{JT}) to a low-temperature, distorted one (with random distribution of distortions) could go via phonon softening (but again on an individual octahedron level, not as a collective mode). If this is the intended meaning of referee's comment, then there are several issues that again make this approach questionable. First, the softening occurs around T_{JT} , and from our data it is easy to estimate that T_{JT} is very high, most likely above material's decomposition temperature. Second, even if the phonons are measured at high(er) temperatures, it is not clear to us how would the eventual softening distinguish between 'A' and 'B'. Note that the PES for oxygen ions is identical in both cases so the instability would presumably exist also in scenario 'A'. We are not aware of a model system where this dichotomy has been demonstrated and resolved so again this approach does not sound like an adequate/sufficient way to address the question raised by Referee 2.

The phonons definitely change across T_Q but only very slightly, there is no softening since the quadrupolar order only slightly changes the effective spring constants, similar to many magneto-elastic materials. We have recently obtained Raman and IR spectroscopy data, which are still under analysis, where very weak features can be seen developing *below* T_Q :



These include small shoulders appearing around well defined modes, as well as opening of a gap in spin susceptibility seen in Raman spectroscopy. Again, those weak features are in no way smoking-gun proof of what is going on in the system. They indicate weak lowering of the symmetry at T_Q but that is already known from high-resolution x-ray diffraction. The analysis of phonon properties is afflicted by strong $d - p$ hybridization which is clearly seen in the comparison of Raman spectra between Ba₂MgReO₆ and a non-magnetic BMWO (J.Am.Ceram.Soc. 96, 2898 (2013)). The strongest Raman mode seen in BMWO around 440 cm^{-1} gets slightly renormalized to 400 cm^{-1} but also significantly reduced in intensity and acquires an asymmetric shape. We note that with charge quadrupoles ordering at T_Q (of two types, $\mathcal{T}_x$ and $\mathcal{T}_z$) it is very far from trivial to address those features from a simple dynamic vs. static JT scenario.

We argue that in general any lattice-related method will not be sufficient to clearly distinguish between 'A' and 'B', especially with 5d oxides sporting significantly smaller distortions than in 3d cases. We emphasize again that distortions on individual octahedra are independent from each other due to the lack of shared ligands.

On the other hand, we regret to see that Referee 2 completely disregarded the results of our local cluster calculations, which are unambiguously supporting the dynamic JT scenario. The achieved agreement between calculated results and experimental RIXS data falls within 10 % for the relevant low-energy region. The calculated wave function is clearly equally distributed across all three local minima *and* there is no visible impact of energy barriers on $|\Psi|^2$. Crucially, $E_1 - E_0$, which determines the characteristic time (t_0 in our manuscript), is of the right order of magnitude, ensuring that the system is dynamic for NMR experiments (single line observed in Ba₂NaOsO₆ at high temperatures) while being static for scattering experiments. To freeze individual octahedra, t_0 would need to be several orders of magnitude longer, which implies $E_1 - E_0$ needs to be several

orders of magnitude smaller, and for that the PES valleys need to be much larger and broader, with much higher barriers between, to allow the zero-point motion energy E_0 to fall in a single valley (see PRR 4, 033020 (2022) for a detailed discussion of the topic). We argue that the changes in the charge environment around Re ions would need to be so severe that the resultant crystal field scheme would be vastly different from the one observed in RIXS experiments. We point out that we did calculations for a fictitious tetragonal structure elongated by 0.1 % and the JT gap is strongly renormalized, indicating that the calculations based on the experimental structure obtained at 40 K faithfully reflect the local Re environment.

Furthermore, Referee 2 also did not take into account additional arguments presented in the discussion. From the structural point of view, the scattering experiments alone are insufficient to address the difference between a dynamic and a static case, especially with distortions at the level of 1 % and smaller. However, Ba₂MgReO₆ and similar systems (especially Ba₂NaOsO₆) exhibit additional features at low temperatures, namely long-range charge quadrupole and magnetic dipole ordering, which are also accompanied by small *coherent* lattice distortions. Due to a strong coupling between vibronic and orbital degrees of freedom, and a strong spin-orbit coupling, the static JT scenario is completely incompatible with ferroic types of order observed below T_Q and T_M . We have expanded the existing discussion, and even added a new figure (Figure 5) in order to highlight those arguments.

We have also explicitly added a discussion about the NMR experiment on Ba₂NaOsO₆ which undoubtedly shows a highly symmetric charge environment above T_Q , again incompatible with the static scenario.

A third argument which we also added into the discussion section concerns the inevitable stress which would be generated in the static JT scenario. As shown for double perovskite structures with $3d^9/5d^0$ and $3d^9/5d^{10}$ (J.SolidStateChem. 147, 291 (1999)), this stress is relieved by having all local static distortions aligned along a single principal axis, which turns the symmetry of the unit cell from cubic to tetragonal, and the static JT effect into a cooperative JT effect.

We hope Referee 2 will accept our arguments that there is no single smoking-gun experimental result which would somehow undoubtedly select between a dynamic and a static JT scenario. We also hope that the already presented arguments, as well as the additional ones, which are all incompatible with a static JT scenario, will be sufficient to recommend the publication of the manuscript.

2) Can the authors provide an explanation for the long tail of the inelastic features observed in the K-edge spectrum. The tail is clearly longer than the instrumental resolution as seen from Fig S5-S6 and hence represent a real broadening of the inelastic features. Is it consistent with a distribution of Delta-JT shown in Fig3g?

The question of the long tail in RIXS K-edge spectra has been answered in detail in our response to Referee 3. Here we mention that according to our analysis the tail is composed of several modes which are linked to main $d-d$ excitations across Δ_{JT} and Δ_{SO} energy gaps via simple relations $E_n^\alpha = E_\alpha + n \cdot E_{mode}$ and $A_n^\alpha = A_0^\alpha e^{-n \cdot B}$. The interpretation of those modes is beyond the scope of our manuscript but they could be linked to vibronic modes which have been predicted in a recent contribution (arXiv:2311.01621). At the first glance the line-shape does resemble the distribution of Δ_{JT} in Fig3g but at the closer look it is clear that the distribution is much broader around its maximum and the exponential tail appears at much larger values of Δ_{JT} , while on the other hand the RIXS data show a quasi-exponential decay immediately above its maximum.

3) In TABLE 1, the agreement between the calculated/observed values for Delta-JT seems pretty good (10% discrepancy). On the other hand, there is a large discrepancy between theory and experiment for the splitting of Delta-O (teg-eg excitation): the observed splitting is about 250meV whereas the calculated one is about 385meV (50% larger). Do the authors have an explanation for this? It is useful to include a temperature dependence of Delta-O alongside Delta-SO/Delta-JT in Fig 2d/2e to show that they have the same temperature dependence.

Although it is true that the calculated splitting of Δ_O seems to be rather disparate from the experimental value, a closer look at the source of this discrepancy reveals that the individual e_g levels are overestimated by (only) 20 - 25 % and that the small difference in the overestimation

factor leads to the $\sim 50\%$ difference in splitting. As we described in the Methods section, the calculations are taking into account 21-atom cluster, with core potentials and basis functions given within the package. As we have also elaborated when discussing Raman spectroscopy data, the strong $d - p$ hybridization seems to be the main culprit, where e_g levels are strongly σ -bonded with oxygen orbitals and are particularly susceptible to small changes of wave functions. Our local cluster calculations also do not take into account the effects of long-range order, particularly of two types of charge quadrupoles.

Since we have measured Re RIXS data only at those two temperatures (8 K and 45 K), there is not much of a temperature dependence to be revealed. Besides, the energy scales are significantly different so a direct comparison with Δ_{JT} and Δ_{SO} seems to us rather impractical. Since we do not find this aspect a crucial issue, we would prefer to leave the plots as they are.

4) The existence of electronic symmetry breaking due to dynamical JT effect provides an interesting explanation for the missing entropy in the specific heat data in Fig 4. However, if the additional entropy (other than that guaranteed by the time reversal symmetry (TRS)) is already removed well above T_Q (according to Fig 2e, there is no change in Delta-JT below 200K), what is the driving force for the quadrupolar ordering?

We are happy to see that Referee 2 recognizes one of the most important questions which stems from our work. Indeed, so far all theoretical studies have considered that each transition (T_M and T_Q) releases one $R\ln 2$, reflecting the expected four-fold degeneracy at high temperatures. With $S_{tot} = R\ln 2$ across both transitions it is not clear at the moment why the apparent order-parameter-like increase of intensity at T_Q is accompanied with (only) a broad feature in specific heat. At the moment we can only speculate that strong SOC is behind this behavior, entangling magnetic dipoles and charge quadrupoles in a single quantum-mechanical entity whose projections get successively ordered at two transitions. So to answer the question, a quadrupolar interaction is driving the quadrupolar ordering, but since quadrupoles are strongly entangled with magnetic dipoles, a part of entropy gets released across T_Q . It remains for future work to address all the details of this interesting problem.

5) Since I am an experimentalist, this question is perhaps intended more for clarifications. The authors calculation in Fig 3e appears to be for a single octahedra sitting in a background of fixed ions (please correct me if I am wrong). On the other hand, the distortion of the octahedra should take the form of a collective lattice distortion. How is the latter accounted for in the calculation?

Referee 2 is correct in the first half of this paragraph. Fig3e represents a potential energy surface (PES) obtained by calculating the total energy of a cluster for different *static* combinations of Q_2 and Q_3 modes around the central Re ion. Then, the total wave function is calculated based on PES which leads to the conclusion about the dynamic JT state.

The next statement, 'the distortion of the octahedra should take the form of a collective lattice distortion', we have already addressed under point (1). Here we repeat that each ReO₆ octahedron is an independent Jahn-Teller active unit that minimizes its energy by a distortion of oxygen positions. Since there are no shared ligands, in the first approximation, distortions of one ReO₆ octahedron do not affect neighbouring octahedra. How these localized modes are mixed into 'regular' phonon modes (collective lattice distortions) will be the subject of future work, part of which we already sketched by showing preliminary Raman and IR results.

Since local cluster calculations deal with static charge configurations, they are ill-posed to take on the problem of dynamic effects and their interactions. We do not state that there is none but since the dominant energy scale is set by the Jahn-Teller effect, some corrections might occur at low(er) temperatures, similar to what is seen when charge quadrupolar order sets in. Therefore, the main conclusions of our work will not be affected.

Reviewer 3

The authors propose a demonstration of dynamic Jahn-Teller effect in Ba₂MgReO₆ by combining RIXS, transport measurements (susceptibility and specific heat) and embedding multi-reference quantum chemistry calculations where SOC is taken into account.

While the manuscript is well structured, the main idea is very appealing and the interest of the topic is well contextualized and presented in the introduction, the analysis of the RIXS data show some important deficiencies that questions the main conclusion and therefore the paper itself.

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Based on the above, I cannot recommend the publication of the paper in its current form. Instead, a detailed analysis of the O K-edge data is required in order to ambiguously proof the main conclusion of the manuscript. Since these data seem to be more critical to understand the system, I think they shall be central in the manuscript.

We have followed the suggestion of Referee 3 and performed a detailed analysis of O K-edge data. The full evolution of how we arrived at the presented model is shown in the supplement, with main results also incorporated in the manuscript.

The main problem in describing such an asymmetric line-shape is a burgeoning number of free parameters. Without a theoretical guidance, we reverted to a phenomenological description, noting that the intensity of the line-shape in the relevant region of energies follows a simple exponential decay. This then lead to a simple model where additional modes are equidistant in energy starting from main $d-d$ excitations. We note that this approach successfully describes the double peak structure flagged by Referee 3.

In doing so we also obtained the energies of main $d-d$ excitations across Δ_{JT} and Δ_{SO} . The extracted values, as well as their temperature dependence, is effectively unchanged from the approach we used in our first submission. Additionally, the energy of the additional mode, whose origin is not completely clear but potentially can be associated with vibronic modes calculated recently (arXiv:2311.01621), also seems to be very much temperature independent. Therefore, all the conclusions and implications that we established previously still hold.

We are hopeful that the presented analysis is convincing and that Referee 3 will find the current version of our manuscript acceptable for publication.

One further suggestion: the symbols used in the transport measurements makes it very difficult to compare the evolution of the different curves. This is especially inconvenient in figure 4a.

We changed the symbols in Figure 4 from all circles to three different ones for three values of magnetic fields. We hope this helps with apprehension of the evolution.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors provided convincing answers to all of my questions.

I recommend the publication of the present version in Nature Communications.

One minor comment: References [27], [28], [S1] are now published in Physical Review Letters. Their data should be updated.

Reviewer #2 (Remarks to the Author):

The authors have competently addressed my concerns. I am happy to recommend the publication of the present manuscript!

Reviewer #3 (Remarks to the Author):

Dear authors,

I thank you for the updated version of the manuscript and in particular for the detailed analysis of the RIXS data at the O K-edge. The connection to reference 27 to explain the asymmetry is convincing. The authors may want to relate the energies obtained to fit their structures with the values from reference 27 for the same compound before the manuscript is published.

In this submission we address the final remarks from reviewers.

Reviewer 1 suggested to update the two arXiv references, which we did.

Reviewer 2 did not have any objections.

Reviewer 3 indicated that 'The authors may want to relate the energies obtained to fit their structures with the values from reference 27 for the same compound before the manuscript is published.' Here we are inclined not to follow the advice, for three reasons: 1) our main focus is on the JT excitation, going into more details about the line-shape is diluting the main story; 2) Ref[27] discusses the rhenium line-shape, while we are analyzing the oxygen one; 3) the resolution is simply not appropriate for a more quantitative approach and comparisons with theory. We have just applied for a new beamtime with a much better resolution which will allow us to address which theory is more suitable, so a more detailed analysis will be the core of a follow-up publication.

We have added one more reference in the introduction (now Ref [24]).