

Jan 2015 Writing Exercise analysis

Note: My submission for this offering was actually quite similar to Hambali's; hence, I got a zero score.

This paper was about J.-E. Jorgensen et al., Order parameter and critical exponent for the pressure-induced phase transitions in ReO₃, Phys. Rev. B33, 4793 – 4798 (1986). However, I don't currently have the questions or rubric, only the 16 peers that I evaluated in that offering.

What is notable is that failing to have enough words/ATOMS drawing would **not** be necessarily a zero score, unlike later offerings; also, there was **no** plagiarism check. This shows who would have gotten a zero score under Jan 2016 Writing Exercise rules.

Peer	Name	Word Count	Originality	ATOMS drawing
1		94	100%	
2		1,394	92%	?
3	Chua Mi Gin	847	100%	✓
4	Hambali	21	N/A	
5	Cheryl Chon Xue Ting	1,321	98%	
6	Wee Hui Wen	416	100%	
7		320	100%	
8	Tan Jia Hui Sherina	406	100%	
9	Yukino	539	100%	
10	Tan Yan Ling	1,053	98%	✓
11	Mok Yan Rong Hilary	0	N/A	
12		201	82%	
13	Christina Wang	375	82%	✓
14	Daphne Huang Kaiyun	1,378	92%	✓
15	Pearlyn Au Fang Wei	812	95%	
16	Lee Si Hui	1,311	93%	

Hambali and Hilary would have gotten zero even in the Jan 2015 offering as no attempt was made to answer the questions at all. Only Tan Yan Ling can score any marks (and with the increased weight, have any chance of passing the course); Cheryl could also score marks in the Aug 2015 offering.

The 16 Writing Exercises have been included below.

Peer 1's Writing Exercise

Paragraph 1

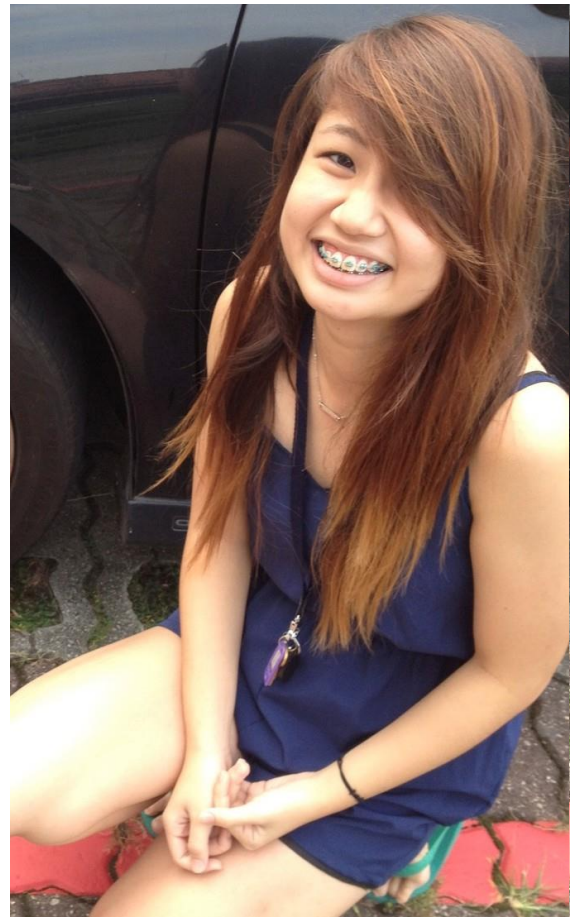
Rhenium trioxide, ReO_3 has a similar structure to perovskite, but they have A sites that are unoccupied at the center of the unit cell. At applied pressure, they appear as cubic structures. However, at 5.2Kbar, it has a tetragonal structure.

Paragraph 2

The pressure applied determines the structures of the polymorph. The bond length of Re-O decreases as pressure increases. This also means that there is greater compressibility and the rotational angle increases as well.

Paragraph 3

There will be a transition from PM3M to P4/MBM to I4/MMM to IM3 . ReO_6 will change continuously from $[100]$ to $[111]$.



Peer 2's Writing Exercise

Paragraph 1

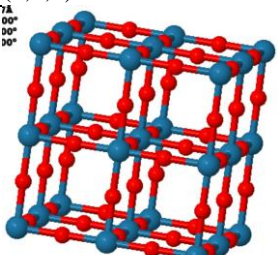
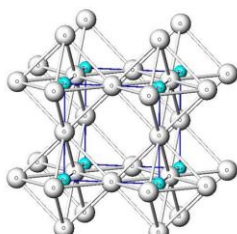
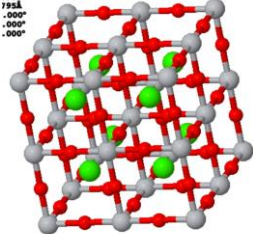
ReO₃ undergoes a series of phase transitions at difference pressures^β and this is in line with the condensation of M₃ phonons. For instance, it has a cubic Pm3m structure at ambient pressure, tetragonal P4/mbm at 5.2kbar and lastly, cubic Im3 at 7.3kbar and beyond. As pressure increases from 5.0 to 27.4 kbar, the rotation angle changes according to (P-P_C) and β= 0.322(5). β signifies a large critical region compared to its usual size with rotation angles exceeding 14°. Analysis of ReO₃ at ambient pressure reveals that it demonstrates a nondistorted perovskite structure. Perovskites have a general formula of ABO₃, but however ReO₃ deviates from this as its A site are empty instead of being occupied. “Compressibility collapse” accounts for the pressure-induced phase transition at the critical pressure P_C of 2.4kbar at 2 K. High-pressure phase produce a large volume strain proportionate to (P-P_C)^{2/3}. This is attributed by the buckling of Re–O–Re bonds while the ReO₆ octahedra maintaining its rigid shape. This is made possible by the condensation of M₃ phonons due to the fact that coordinated rotations of the octahedral around [100] axes are the primary constituents of the atomic displacement of the phonons. In addition, M₃ phonons are triply degenerate and hence it is able to undergo transformations from its Pm3m structure into P4/mbm, I4/mmm or Im3 structures via condensation of one, two, or three M₃ phonons. The time-of-flight Laue method revealed that the structure of the high-pressure phase at 15 kbar was cubic Im3. However, only limited result can be obtained because the data was only derived at a single pressure. Therefore, the pressure dependence of the structural distortion is unable



to be derived. The Rietveld method of structural refinement with high-resolution powder data provides a high degree of precision for atoms position which allows the pressure dependence of the distortion to be measured and as well as the establishment of the order parameter exponent where $\varnothing \propto (P-P_C)^\beta$ demonstrates the pressure dependence of the rotation angle. It is useful to note that its structure at 15 kbar was ascertained recently by single-crystal neutron diffraction measurements. The results of powder neutron diffraction asserts that phase transition highly dependent on pressure and confirmed the existence of at least two high-pressure phases which are P4/mbm and Im3. The only distortion associated with the transition is revealed to be the M-point rotation, with the rotation angle \varnothing varying continuously through both phases despite the varying axis of rotation which changes discontinuously from [100] to [111]. The significance of neutron diffraction is that its usefulness is amplified due to the relatively large cross section of oxygen which results in a clearer picture of the rotations of the ReO₆ octahedra. The tetragonal p4/mbm phase in ReO₃, which is identified as a high-pressure phase, has a 300 bar wide region just above 5.0 kbar.

Paragraph 2

Table 1: Pressures and geometrical and structural relationships

Pressure	Ambient Pressure	5.2 kbar	7.3 kbar and higher
Structure	Pm3m	P4/mbm	Im3
Unit cell structure	Cubic	Tetragonal	Cubic
Lattice Position	Re: Special position 1a (0,0,0) O: Special position 3d (2,0,0)	Re: 2b positions O: 4h and 2a positions	Re: Special position 8c (1/4,1/4,1/4) O: Special position 24g (O, y, z)
Drawing of ATOMS			

Geometric	a=b=c	a=b ≠ c	a=b=c
relationship	α= β= γ= 90°	α= β= γ= 90°	α= β= γ= 90°
Lattice	a= 3.7504 Å	a=5.2968Å, c=3.7415Å	a=7.4882Å

The various crystal lattice structures assert that the geometry hinges on the amount of applied stress, more specifically, increased stress will engender a sequence of phase transitions. Referring to Figure 1, at ambient pressure, ReO₃ has a cubic Pm3m with a lattice parameter of a=3.7501. When the stress increases to 5.2 kbar, a phase transition will take place and ReO₃ will obtain a tetragonal structure with lattice parameter a=5.2968Å, c=3.7415Å. Lastly, with increased stress of 7.3 kbar or higher, another phase transition will occur and the structure will transform into Im3 consisting of lattice parameter a=7.4882Å. Any higher stress applied has no impact on the crystal lattice and the structure remains at Im3. It can be established that the relevant space groups relating to high-pressure phases of ReO₃ are P4/mbm and Im3, and both are in line with M₃ phonon condensation. It is important to acknowledge the significant reduction of the anisotropy of the oxygen thermal ellipsoid in the Im3 phase, while holding it in contrast with the observation in the Pm3m at ambient pressure. Distortion of the ReO₆ octahedron is present in both the P4/mbm as well as the Im3 structures. In p4/mbm, two symmetry inequivalent Re–O bond lengths are allowed. On the other hand, only a single Re–O bond length exists in the Im3 structure. Both structures consist of two inequivalent O–O distances and they provide a measure of the irregularity of the ReO₆ octahedron. As pressure increases, the rotation angle ϕ increases until it reaches a value of 14.0(3)° at 27.40kbar. In this pressure range, deviations in Re–O bond lengths and O–O distances across the edges of the ReO₆ octahedra are within the standard deviations. Hence, the structural distortion is first order as a rigid rotation pertaining to the ReO₆ octahedra. This is because of the change in bond distances. The compression of ReO₃ is due to the shortening of Re–O bond length. The high stability of ReO₆ reinforces the assumption that the ReO₆ octahedra rotate as rigid bodies. A positive strain is produced by rigid-body rotations in the P4/mbm structure, while a negative strain is produced by high pressure and this signals a slight distortion of the octahedron. The Re–O bonds that lie in 90° to the c axis are longer than the corresponding bond at the x axis. This is because during the rotation of the ReO₆ octahedron, the Re–O remains being compressed. On the other hand, the compression of the Re–O bond perpendicular to the x axis is being relaxed. In both the P4/mbm and Im3 structure, the Re–O bond lengths in the bent Re—O—Re bonds are not affected by pressure while the Re–O that is parallel to the rotation axis decreases in bond length in the p4/mbm structure. In the Im3 structure, all Re–O are bent. This underscores the bending of the Re—O—Re bonds with negligible involvement of bond shortening that produced an anomalously large volume strain in the Im3 phase.

Paragraph 3

Powder neutron diffraction measurements reveal the angle of rotation of the ReO₆ octahedra. The Rietveld method yields a high degree of precision regarding the position of atoms and it is a reliable method for the pressure dependence to be measured with sufficient accuracy. Phase transition in ReO₃ results in the rotation of the ReO₆ octahedra around the [100] axis, and subsequently at higher pressures, it rotates around the [111] axis. Rigid-body rotations give rise to a positive strain in the p4/mbm structure. On the other hand, the negative strain which is supported by the Rietveld refinement of the P4/mbm structure signals a small degree of distortion of the octahedron. The negative strain suggests that the Re–O bonds that lie at 90° to the c axis has a longer length compared to the corresponding bond along the c axis. This result is unusual and may be attributed by the fact that the Re–O bond along the c axis is compressed when the ReO₆ is undergoing rotation, while the rotation causes the relaxation of the compression of the Re–O bond perpendicular to the c axis. A three-component order parameter provides an explanation for the pressure-induced phase transition.

Condensation of one, two, or three M₃ phonons precipitate the sequence of phase transitions as follows: Pm3m → P4/mbm → I4/mmm → Im3. There is a discontinuity in the lattice parameter at 5.3kbar where the p4/mbm to Im3 transition occurs and this is reinforced by the nonzero tetragonal strain observed for ReO₃ at 5.20 kbar. The rotation angle ϕ in ReO₃ is larger than normal at 14.0(3)° and it occurs at the peak pressure of 27.4 kbar. By making the assumption that the octahedron undergoes rotation in rigid units, the volume strain for small rotations is very likely to be proportional to ϕ . The ϕ in Im3 structure is calculated by the projection of the oxygen atoms into a plane that lies perpendicular to the [111] axes. The rotation angle ϕ is a function of pressure, and it increases smoothly with increasing pressure above the transition of 27.40 kbar.

Chua Mi Gin's Writing Exercise

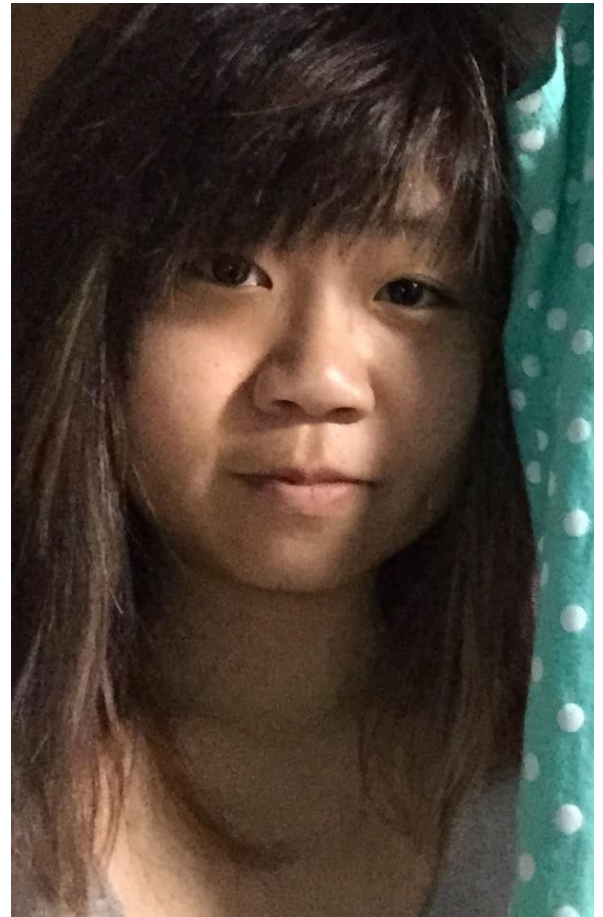
Paragraph 1

ReO₃ has a perovskite structure, which follows the general formula of ABO₃. It is undistorted and has an empty A site. At ambient pressure, ReO₃ has a cubic structure, tetragonal structure, as well as a cubic Im3. It should be noted that at room temperature is different from critical pressure, which is referred to as "compressibility collapse". A large strain volume is exhibited in the high-pressure phase, proportional to $(P - P_c)^{2/3}$. The buckling of Re-O-Re bonds is likely to be caused by the large strain volume, with ReO₆ rigid octahedral structure. The condensation of M3 phonons make the rotations possible since the atomic displacements are made up of rotations of octahedral around 100 axes in a coordinated manner. Through three levels, M3 phonons are degenerated. Hence, the cubic Pm3m structure can thus form into three varying structures. They are I4/mmm, P4/mbm or Im3 structure, which occurs with the condensation of one, two or three M3 phonons.

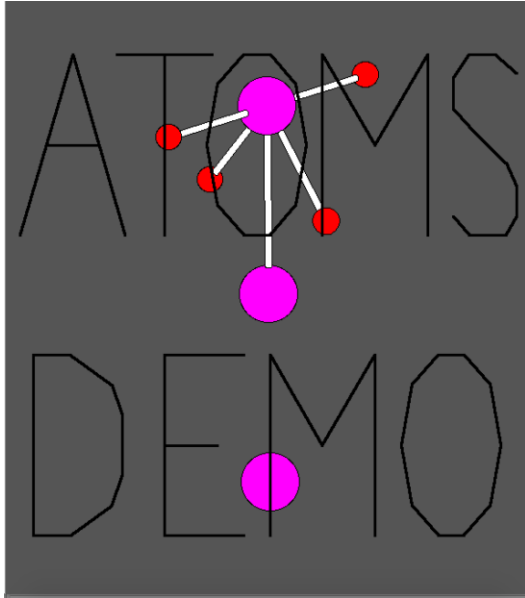
From the high-pressure phase of ReO₃, Im3 was the first suggested space group. The time-of-flight Laue method helped establish this structure. The data obtained, however, was collected from only pressure value. Hence the pressure dependence in this structural distortion was unable to be established. $\phi \propto (P - P_c)^\beta$, or the rotation angle's pressure dependence. The value of β is representative of an anomaly large critical region that reaches to the rotation angles of over fourteen degrees. The high-pressure phases of ReO₃ are defined as Im3 and P4/mbm, in line with M3 phonon condensation.

Paragraph 2

The Pm3m structure can allow us to deduce how distorted perovskite structures are when the octahedral is tilted around the cubic axes. With various tilt arrangements, different possible high-pressure phases, which are able to be formed are illustrated. The structure is cubic Pm3m at atmospheric pressure. In the space group of cubic Pm3m, structural parameters for ReO₃ are such that O lies in special position 3d (2, 0, 0) and Re lies in special position 1a (0, 0, 0). For high-pressure phases of ReO₃, the relevant space groups are P4/mbm and Im3, both of which are in line with M3 phonon condensation. O is in the 4h as well as 2a positions, while Re is in the 2b positions, following the conventional tetragonal P4/mbm space group setting. Re is in the special position of 8c with $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in the Im3 space group, and O is in the special position of 24g (0,y,z). The anisotropy of what is seen as the oxygen thermal ellipsoid is greatly decreased in the Im3 phase compared to the Pm3m phase at ambient pressure. ReO₆ octahedra is rotated around the [111] direction in the Im3 unit cell, corresponding to the condensing of all the three M3 phonons. Distorting of the ReOs octahedron can happen in both Im3 and P4/mbm structures. In P4/mbm, only one Re-O bond length is in the Im3 structure although there are two symmetrical though inequivalent Re - O bond lengths. In both structures, there are two inequivalent O-O



distances which are at the edges of the octahedron ReO_6 , creating a some irregularities in the ReO_6 octahedron. The extent of how much tilt there is in ReO_6 octahedra varies by pressure. The interatomic distances between O and Re and angles in ReO_3 changes as pressure increases.



Paragraph 3

Powder neutron diffraction measurements have allowed for a quantitative analysis of ReO_6 and establish the rotation angle of the octahedra ReO_3 , which is also valid for the transition in terms of order parameter in the large oxygen cross section. Using the Rietveld method allows for a precise method to position atoms and allow the distortion from pressure dependence to be measured sufficiently accurately to show that the order parameter exponent β , in which $\phi \propto (P - P_c)^\beta$, the pressure induced phase change causes a sequence of transitions in phases.

The difference of rigid body rotations is the positive strain that lies in the $P4/\text{mbm}$ structure. Negative strains that the Rietveld refinement favoured in the $P4/\text{mbm}$ structure shows slight distortion in the octahedral, and tilt of it along the cubic axes. This could be due to the $\text{Re}-\text{O}$ bond at the c axis staying compressed in the rotating of the ReO_6 octahedra while it is perpendicular to the c axis. The rotation along axis with low-pressure conditions is because of the phase transition in ReO_3 . This can be condensation of M -point phonons and also since at higher pressure, around the axis of the phase $\text{Im}3$. Still, at high pressure, phase change is seen to tilt arrangements. Relevant space groups in the original distorted perovskite in ReO_3 structures can be drawn from cubic $\text{Im}3$ and tetragonal $P4/\text{mbm}$. Both of these are in line with the $M3$ phonon condensation through tilting the octahedral around its cubic axes. Should the octahedral rotate with fixed units, small rotations' volume strains are likely to be proportional to the rotation angle. This angle is directly derived from the $\text{Re}-\text{O}-\text{Re}$ angle bond in the structure of $P4/\text{mbm}$. By projecting oxygen atoms on a perpendicular plane to the axes in the $\text{Im}3$ structure, the angle can be obtained. The angle increases as pressure increases from here.

Hambali's (lack of) Writing Exercise

Didn't have time to do this assignment. I cannot ask for any marks. So do what you must. No hard feelings.



Mok Yan Rong Hilary's (lack of) Writing Exercise

(A blank pdf was submitted.)



Cheryl Chon Xue Ting's Writing Exercise

Paragraph 1

A perovskite is a structure that has the same crystal structure as calcium titanium oxide with a general formula of ABO_3 . ReO_3 is such a structure but with a slight difference, the structure of ReO_3 is undistorted at ambient temperature due to the empty A site at the center of the structure. Each Rhenium atom is able to form an octahedral structure, the octahedral structure is formed by six oxygen atoms that surround it.



This structure remains rigid while there is a buckling of bonds between the rhenium and oxygen atoms. This buckling of bonds causes a large volume strain. This large volume strain is seen during a high-pressure phase. At pressures of 3kbar with relatively low temperatures, it is observed that there is a non-linear behavior in the Fermi-surface of the cross section of the ReO_3 structure. This non-linear behavior is said to be a pressure-induced phase which is also known as the “compressibility collapse”. This pressure-induced phase is said to be due to the large compressibility in the high-pressure phase. The high-pressure phase showed that there was a large volume strain that was proportional to the formula $(P-P_c)^{2/3}$. The critical pressure (P_c) of this phase was determined to have a pressure of 2.4kbar at temperatures of 2 kelvins. The transition pressure of the critical pressure (P_c) was found to be 5kbar at ambient temperature. The rotations that is achieved due to the buckling of the bonds is due to the condensation of M_3 phonons. There is an atomic displacement of the phonons, it primarily contains coordinated rotations of the octahedral around $[100]$ axes. It is assumed that the octahedral rotates as rigid units, thus the angle of rotation (ϕ) of ReO_6 is a valid order parameter for transition. The pressure dependence of the rotation angle is expressed in the form of $\phi \propto (P-P_c)^\beta$ with the β value of $\beta = 0.322(5)$ between the pressures of 5kbar and 27.4kbar. β indicates the large critical regions that has rotation angles of more than 14° . By condensing either one, two or three M_3 phonons, the cubic structure of ReO_3 can transform into 3 structures: a tetragonal $P4/mbm$, a tetragonal $I4/mmm$ or a cubic $Im\bar{3}$. These structures are seen as high-pressure phases of ReO_3 . $Im\bar{3}$ is the first structure to be suggested as a high-pressure phase of

ReO₃. However, since the data collected is only at pressure, the pressure dependence on structural distortion cannot be obtained. It is also still a question as to if there is an intermediate phase in the ReO₃ structure.

Paragraph 2

By tilting the ReO₆ octahedra structure it can be seen that there is a distortion of the Pm3m structure. It was seen as the pressure increases, the ReO₃ structure goes through a phase transition where it transits from a cubic Pm3m to a tetragonal P4/mbm structure. At ambient temperature and atmospheric temperature, it was observed that the ReO₃ structure is a cubic structure Pm3m. As the pressure increases even more, the structure transits again into a tetragonal I4/mmm and then to a cubic Im3. It was seen that the bonds between the rhenium and oxygen bonds bend more and the bond length also decreased. And as calculated, It could be determined that the rotation angle increases as the pressure increases. The main reason for the transition in all the different phases is due to the shortening or increasing of the bonds which would change the distances of the bonds. As mentioned in the first paragraph, when the M3 phonons condenses, there were a few structures seen as high-pressure phases of the ReO₃ structure. As Rhenium is surround by 6 oxygen it forms a relatively stable structure that give a positive strain to the P4/mbm structure. This positive strain is due to the rotation of the rigid octahedral structure. There is however a negative strain in the structure at high pressure causing a distortion to the ReO₆ structure. The ReO₆ structure rotates around a [001] axis when there is a formation of P4/mbm tetragonal phase where the rhenium and oxygen bond which is perpendicular to the rotation axis. The bonds lengths are relaxed to the lengths during ambient pressure while those that are parallel to the axis are shortened. It was observed in the P4/mbm structure that the rhenium and oxygen bonds that are parallel to the axis of rotation are all shorten. Also, the rhenium and oxygen bonds in the Im3 structure are all entirely bent. This showed that the large volume strained as mentioned in paragraph one is based mainly on the bending on the bonds while the shortening of the bond does not really contribute to the large volume strain. The distortion of the ReO₆ structure is allowed in both the P4/mbm and Im3 structure. The distortion that we mainly observe in the P4/mbm and Im3 structure is due to the Rhenium and oxygen bond length. With P4/mbm possessing two identical but not equal bond length and the Im3 can only have one rhenium bond.

Paragraph 3

As mentioned in the first paragraph, the condensation of the M3 phonons causes a phase transition of the structure. Since the rotation exist around a given axis, a transition from one rotational axis to another involves the discontinuous motion of atoms. The pressure-induced phase transition changes the structure of ReO₃ from Pm3m to P4/mbm to I4/mmm to Im3. There is a change in the direction of the rotation which is discontinuous from [100] to [111] when there was a phase transition from P4/mbm to Im3. All of these transitions are the subgroups of the Pm3m structure. The phase transitions of the structure are all first order in nature that is due to the rotation of the structure on an axis. There is however, a second order during the phase transition of all the phase groups. This second order is mainly due to the transition to another rotation axis need to involve a discontinuous motion of the atoms. It was determined that there were 2 different strains that contribute to the distortion of the ReO₃ structure, the positive strain and the negative strain. The positive strain is mainly due to the rotation of the ReO₆ octahedral structure around the [100] or [111] axis as the pressure increases. The negative strain on the other hand is caused by the change in the length of the bond between the rhenium atom and the oxygen atom. The negative strain is also due to the bending of the bond between the rhenium and oxygen atom. From the power neutron diffraction, it was determined that there was a few different phases as the pressure increases. It was observed that as the rigid body of the ReO₆ structure rotates, there is a positive strain of the I4/mbm structure. The negative strain is observed when there is a tilt in the octahedral structure along the cubic axis. The power law with the form $\phi \sim (P - P_c)^\beta$ expresses the pressure dependence of the rotation angle. The power law when ln produces a logarithm curve when plotted, β is determined through the linear regression of the slope which give a value of $\beta = 0.322(5)$ between the pressures of 5 kilobar and 27.4 kilobar. The ϕ represents the angle of rotation, it is determined by projecting the oxygen atoms in a plane which is perpendicular to the axis, the calculated using the coordinates of the oxygen atoms. This measurement will be able to determine if the structure is distorted or tilted. The distortion of the structure and the rotation of the structure is due to either is changing of the bond length or the bending of the bond between the rhenium and oxygen atoms. The rotation angle of the ReO₆ octahedra structure that would describe the distortion in the high- pressure phase. It was observed that the distortion during the transitions were mainly sure to the rotation angle which varied through the phases although the axis has changed discontinuously.

Wee Hui Wen's Writing Exercise

Paragraph 1

ReO₃ is known as a unique type of perovskite because of the absence of atoms at the A sites, which are usually filled. It has a critical pressure of 2.4kbar at 2K and has been given the name of “compressibility collapse”. Its transition pressure was found to be 5kbar under room temperature. Under high pressure phase, the structure experienced a large volume strain and this is due to the inflexible buckling of the Re- O-Re bonds with the ReO₆ octahedral. Such rotations were possible due to the condensation of M3 phonons. Reason being, the atomic displacement of these phonons includes rotations coordination of the octahedral around [100] axis. Under ambient pressure, ReO₃ structure is a cubic Pm3m while under 5.2kbar, it is a tetragonal P4/mbm. Above 7.3kbar, it is a cubic Im3 structure. Through the condensation of M3 photons that are triply degenerate, the structure of cubic Pm3m can transform into P4/mbm and Im3 structures.



Paragraph 2

By tilting the octahedral around the cubic axis, Pm3m structure will be distorted. Different tilt arrangements such as P4/mbm and Im3 structure are resulted from different high pressure phases. Im3 structures experience a refinement where the Re and O are placed in 8c and 24g special position. Furthermore, the anisotropy of the oxygen thermal ellipsoid is significantly decreased in its structure as compared to the structure of Pm3m. On the other hand, the refinement in the tetragonal P4/mbm structure used the common setting where Re in the 2b position while O in the 4h and 2a positions. They both allow the distortion of ReO₆ octahedron. There are two inequivalent symmetry of Re-O bond length in P4/mbm while there is only one Re-O bond length in Im3. Therefore, these allow the irregularity of the ReO₆ octahedron to be quantified due to the inequivalent O-O distance.

Paragraph 3

M-point phonons condensation is used to describe the phase transition of ReO₃. As mentioned above, the main reason that results in rotation of ReO₆ octahedral around the [100] and [111] axis under high pressure is M-point phonons condensation. In P4/mbm phase, a negative strain represents that the perpendicular Re-O bonds to the c-axis are longer than the corresponding c-axis bond; while the rotation of rigid-body will result in a positive strain. The occurrence of negative strain may due to the compression and relaxation of Re-O bonds when the octahedral structure rotates along the c-axis and perpendicular to the c-axis respectively. Im3, on the other hand, have all Re-O bonds bending and hence, resulting in significantly large volume strain.

Peer 7's Writing Exercise

Perovskites have the general formula of ABO_3 , which usually have occupied A sites. However, ReO_3 is special as it has empty A sites. At ambient pressure, ReO_3 has a nondistorted perovskite structure. At room temperature, the transition pressure, P_c is found to be 5.0 kbar. Being termed "compressibility collapse", the critical pressure, P_c is determined to be 2.4 kbar at 2 K. High pressure phase exhibits a large volume strain proportional to $(P - P_c)^{2/3}$. This exceptionally large volume strain is due to the buckling of Re-O-Re bonds with the rigid ReO_6 octahedral structure.



Since atomic displacements of M_3 phonons consist principally of coordinated rotations of the octahedra around $[100]$ axes, the rotation is possible as it is achieved by the condensation of the M_3 phonons. If the octahedra ReO_6 structure rotates as rigid units, the volume strain for small rotations should be proportional to ϕ^2 where ϕ is the rotation angle. The angle of rotation of the ReO_6 octahedra is a valid order parameter for the transition. Through condensation of one, two, or three M_3 phonons, the triply degenerate M_3 phonons and the cubic $Pm\bar{3}m$ structure could transform into $P4/m\bar{3}m$, $I4/m\bar{3}m$ or $Im\bar{3}$ structures. In attempts to find out the structure of the high-pressure phase(s) in ReO_3 , the $Im\bar{3}$ structure has been identified. However, the pressure dependence of the structural distortion could not be established as data were collected at only one pressure. Also, there may be existence of more than one high pressure structure, but it all depends on the condensation of M_3 phonons. The rotations of the ReO_6 octahedra are much more easily seen with neutrons than with x ray as a result of the large cross section of oxygen. The Rietveld method allows the pressure dependence of the distortion to be measured with sufficient accuracy to establish the order parameter exponent β where $\phi \propto (P - P_c)^\beta$ expresses the pressure dependence of the rotation angle.

Tan Jia Hui Sherina's Writing Exercise

Paragraph 1

Rhenium trioxide, ReO_3 , has a crystal cubic structure of space group $\text{Pm}\bar{3}\text{m}$, and a space group equivalent of 221. The structure of ReO_3 is similar to most perovskites only without the large A cation in the centre. It was first found at pressure close to 3kbar at lower temperatures.



The critical pressure P_c was then found to be 2.4 kbar at 2K and 5.0 kbar at room temperature. The high pressure phase exhibits a large volume strain, which is proportional to $(P - P_c)^{2/3}$. The larger volume strain of ReO_3 was attributed to the buckling of Re-O-Re bonds with the octahedral structure of ReO_6 forms strong covalent bonds which does not break. The rotations are caused by the condensation of M_3 phonons along the octahedra axis [100]. The $\text{Pm}\bar{3}\text{m}$ space group is attributed to the triply degenerate M_3 phonons and can form two tetragonal structures: $\text{P4}/\text{mbm}$, $\text{I4}/\text{mmm}$, or a cubic $\text{Im}\bar{3}$ structure by condensation.

The first established structure was $\text{Im}\bar{3}$ at pressures of 15kbar. Another high pressure phase established is $\text{P4}/\text{mbm}$ at pressures just above 5.0kbar.

Paragraph 2

At different stress levels of pressure, the geometry of ReO_3 changes due to the extent of rotation along the octahedral axis and undergoes different phases. At low pressure of 100MPa, the crystal structure is a tetragonal $\text{Pm}\bar{3}\text{m}$ and has a lattice parameter of $a = 3.704\text{\AA}$. As it increases to 730MPa, the crystal changes its phase to a cubic $\text{Im}\bar{3}$ with lattice parameter $a = 7.4882\text{\AA}$. As pressures continue to increase from 1285MPa

to 2740MPa, the crystal will not undergo a phase transition but remain as $Im\bar{3}$. However, the angle of rotation and the extent of tilt of the ReO_6 octahedra will increase, and the parameter decreases to $a = 7.4265\text{\AA}$ to 7.3426\AA . This is because at higher pressures, the Re-O-Re bond will bend more and decrease in length. Hence, at with high pressures, the ReO_6 structure will condense and change its shape.

Paragraph 3

The distortion of ReO_6 is attributed to the decrease in Re-O-Re bond due to the condensation of structure, while the tilt is due to the rotation along the ReO_6 Octahedra axis. In the experiment, it was found that ReO_3 can experience a series of transitional and non-definite phases, for example $Pm\bar{3}m-P4/m\bar{3}m$. Both the positive and negative strain of tetragonal $P4/m\bar{3}m$ can be observed at a range of pressures from 5kPa-5.3kPa. The positive strain is due to the rigid body ReO_6 rotation while the negative strain is due to the condensation of Re-O bond.

Yukino's Writing Exercise

Paragraph 1

Describe the symmetry characteristics of the ReO₃ polymorphs and their relationship to applied pressure

Rhenium trioxide (ReO₃) has a similar structure to perovskite (ABO₃) at ambient pressure. However ReO₃ has empty A sites in the center position of the structure. For its unique characteristic, many had studied the pressure-induced phase transition in ReO₃, and the first observation at low temperatures and at close to 3kbar pressure was the non-linear behaviour of the Fermi-surface cross sections. Then, “compressibility collapse” was named for the measurements of critical pressure P_c at 2.4kbar and temperature at 2K as the compressibility is in an order of magnitude larger in high pressure phase shown at room temperature. Later, transitional pressure P_c to be 5kbar at room temperature was determined through high-precision measurements, exhibiting large volume strain proportional to $(P - P_c)^{2/3}$ at high pressure phase. This is due to the buckling of Re – O – Re bonds in the remaining ReO₆ octahedra rigid through the condensation of the M_3 phonons. The coordinated rotations of the octahedra around [100] axes accounts for the displacement of the phonons. Given that Φ is the rotation angle, the volume strain for small rotation should be proportional to square of rotational angle (Φ^2). M_3 phonons can be degenerated three degrees transforming the cubic Pm3m structure into P4/mbm, I4/mmm or Im3 structures, through condensation of one, two or three M_3 phonons. The first suggestion as the space group of ReO₃ in the high pressure phase was Im3 structure on the basis of several non-structural studies. In consistent with the M_3 phonon condensation, P4/mbm and Im3 were the space group for the high pressure phases of ReO₃. Pressure dependence of rotation angle, $\Phi \propto (P - P_c)^\beta$, where β is the order parameter exponent and when over a pressure range of 5kbar to 27.4kbar is equal to 0.322(5). The value of β indicates an anomaly huge critical region extending to rotation angles more than 14°.

Paragraph 2

Describe the metrical relationships between the polymorph unit cells and ReO₆ octahedral tilting. Use the CIF files to create ATOMS drawings that support your analysis

Paragraph 3

Explain the distortion of the ReO₆ octahedra with pressure and quantify the ReO₆ octahedral tilting.

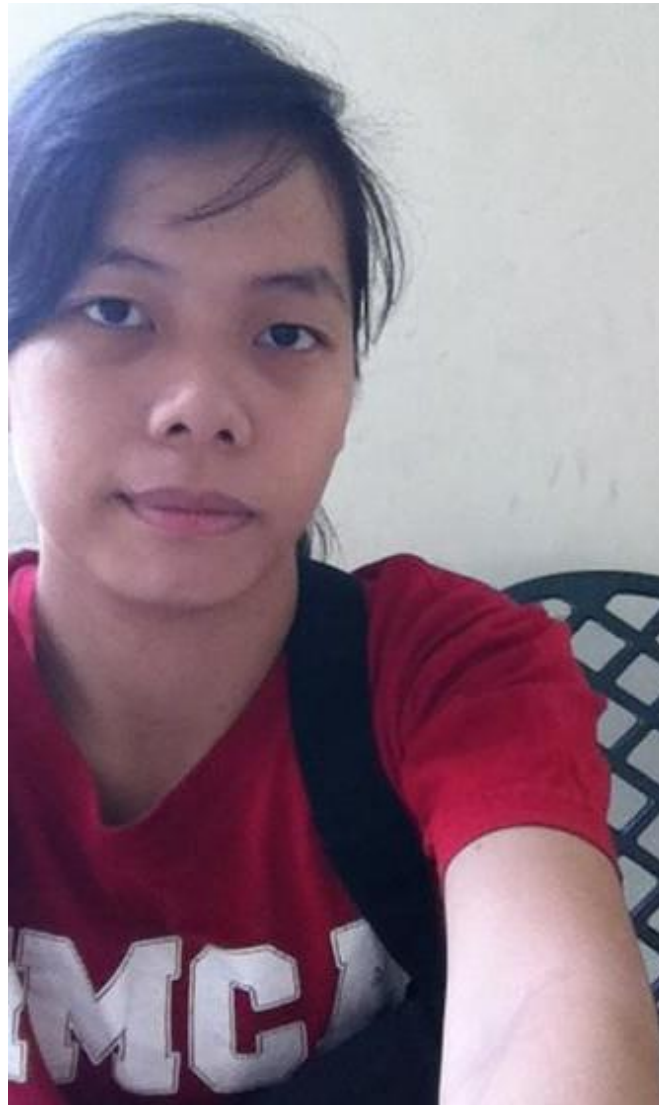
By tilting the octahedra of the Pm3m structure around the cubic axis, the distorted perovskite structures were achieved. Using powder neutron diffraction through the angle of rotation of octahedral ReO₆, the nature of distortion of ReO₃ can be quantitatively measured. While Rietveld method offers precision for atom positions which is comparable to previously reported single-crystal



neutron diffraction studies. Also, through establishing the order parameter exponent, β , it allows the pressure dependence of the distortion to be measured. ReO_3 shows polymorph formation undergoing pressure induced phase transition from $\text{Pm}\bar{3}\text{m}$ to $\text{P4}/\text{mbm}$ to $\text{I4}/\text{mmm}$ to $\text{Im}\bar{3}$, where $\text{P4}/\text{mbm}$, $\text{I4}/\text{mmm}$ and $\text{Im}\bar{3}$ are all subgroup of $\text{Pm}\bar{3}\text{m}$. Phase transition from $\text{Pm}\bar{3}\text{m}$ to $\text{P4}/\text{mbm}$ occurs at 5kbar pressure which is also observable at 5kbar to 5.3kbar as there are presence of positive strains in $\text{P4}/\text{mbm}$ structure which is what Rietveld refinement favours, detecting even the slightest distortion. As compression remained in the Re-O bonds along the cubic axes, the Re-O bonds bend when ReO_6 octahedra rotates at a perpendicular angle to the cubic axes. At 5.2Kbar high pressure, phase changes in ReO_3 are caused by a total of 23 possible tilted arrangements in the structure. The distortion was only observable in $\text{P4}/\text{mbm}$ and $\text{Im}\bar{3}$ structures, which are in agreeable with the condensation of M_3 phonon.

Tan Yan Ling's Writing Exercise

ReO₃ belongs to the perovskite structure and the structure is cubic Pm3m at normal surrounding pressure. It is different from other perovskites as the A sites in ReO₃ are missing compared to the other perovskites with the same general formula of ASO₃. ReO₃ has tetragonal P4/mbm when at 5.2kbar pressure and cubic Im3 at even higher pressures. When at higher pressures, the rotation angle of ReO₆ octahedra will describe the distortion which varies as $(P - P_c)^\beta$ with $\beta = 0.322(5)$. The origins of pressure-induced phase transition would trace back to Razavi *et al* who then noticed a non-linear behaviour of the Fermi-surface cross sections at low temperatures at pressure close to 3kbar. It was later concluded by Schirber and Morosin that the critical pressure P should be at 2.4kbar at 2K temperature. This transition was proposed to be “compressibility collapse” since the



x-ray diffraction at room temperature showed that compressibility is larger in magnitude in the high-pressure phase. Measurements also showed that the high-pressure phase exhibits a large volume strain which was found to be larger than other materials undergoing similar transformations. This is in consistent with the observation that large volume strain results from buckling of the Re-O-Re bonds with the ReO₆ octahedral remains rigid. Such rotations are obtained by condensation of M3 phonons as the atomic displacements for the phonons consist of coordinated rotations of the octahedral around [100] axes. The first suggested space group of the high-pressure phase for ReO₃ was then noted as Im3. Elastic neutron scattering measurements later revealed the super lattice reflections above P was consistent with the condensation of M3 phonons. On top of that, inelastic neutron scattering confirmed the existence of a phonon mode whose frequency decreases dramatically as pressure approaches P from below. The M-point rotations are often only shown as distortion associated with the transitions with rotation angle P varying continuously through both phases. While for such study of transitions, neutron diffraction would be particularly useful because of the relatively large cross section of the oxygen atom. Thus, the rotations of the ReO₆ octahedral are much

more easily seen with neutrons than with x-rays.

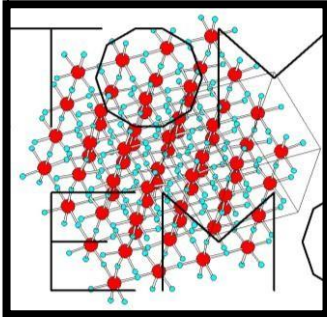
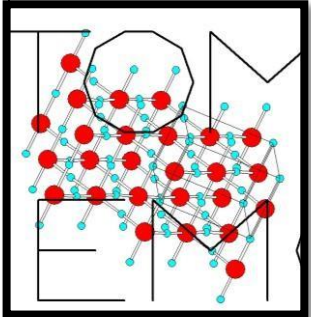
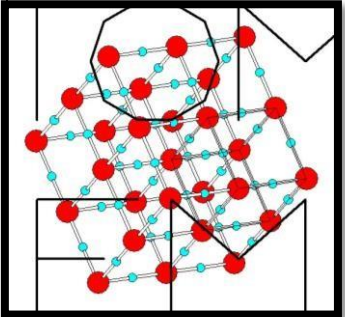
Structure	Im3	P4/mbm	Pm3m
Pressure	7.3 kbar	5.2kbar	Room Pressure
Unit cell structure	Cubic	Tetrahedral	Cubic
ATOMS drawing			

Table 1

From the Pm3m structure, we can tilt the octahedral around the cubic axes to obtain the distorted perovskite structures. From Table 1, we can see that the higher pressures (7.3kbar and 5.2kbar) belong to the space group Im3 and P4/mbm respectively where distortion of the ReO₆ octahedron is allowed. In P4/mbm, the two symmetry non-equivalent Re-O bond lengths are allowed. However, in the Im3 structure, only one Re-O bond length is allowed. In both structures, the non-equivalent O-O distances are present and provide the extent of the irregularity of the ReO₆ octahedron. When ReO₆ octahedral rotate around the [001] axis to form the P4/mbm tetragonal, the Re-O bonds perpendicular to the rotation axis ease down back to their room pressure lengths while the bonds which are parallel to the axis remain compressed and are slightly shorter than the Re-O bonds which exist in the cubic phase a pressure below 5.0kbar. This behaviour happens because the bond lengths are more likely to take up their room pressure values along those directions where compression is achievable by rotating the octahedral. This result also resonates with the fact that the Re-O bond length in the cubic Im3 phase at 7.30kbar is equal to that at room pressure as seen in the table of Principal interatomic distances in ReO₃ versus pressure in the paper by Jorgensen et al. This same table from the paper also included the figures for rotation angle of the bonds, which is also a function of pressure. In the P4/mbm structure, rotation angle Φ is calculated from the Re-O-Re bond while in the Im3 structure, Φ is calculated by projecting the oxygen atoms into a plane perpendicular to the [111] axes. In the same table from the paper, it shows that the

rotation angle Φ increases gradually from 0.0 degree to 14.0(3) degree with increasing pressure of 0.001kbar to 27.40kbar. Over this range of values, it can also be seen that the changes in bond lengths are typically small. Therefore, the structural distortion is described to be first order as rigid rotation of the ReO_6 octahedral.

The phase transition in ReO_3 is in the following sequence: $\text{Pm}3\text{m} > \text{P}4/\text{mbm} > \text{I}4/\text{mmm} > \text{Im}3$ whereby $\text{P}4/\text{mbm}$, $\text{I}4/\text{mmm}$ and $\text{Im}3$ are subgroups of $\text{Pm}3\text{m}$. The primary order parameter for the phase transition is written as $\Phi^- = \Phi e^-$ where Φ is the magnitude of the rotation angle and e^- is the unit vector defining the direction of the rotation axis. Transitions between $\text{P}4/\text{mbm}$, $\text{I}4/\text{mmm}$ and $\text{Im}3$ are of first order such that once a rotation is identified around a given axis, the transition to another rotation axis must involve a discontinuous motion of the atoms. In such manner, the nonzero tetragonal strain in ReO_3 at 5.2kbar exerts a discontinuity in the lattice parameter at 5.3kbar at which the $\text{P}4/\text{mbm}$ to $\text{Im}3$ transition occurred. The empty A sites in ReO_3 actually allows a less restricted and rigid rotation and accounts for the reason why ReO_3 has large compressibility. With the presence of phase transitions, positive and negative strains exist in the structure. Rigid body rotations give positive strain in $\text{P}4/\text{mbm}$ structure and the negative strain existing in $\text{P}4/\text{mbm}$ signifies a slight distortion in the octahedral. This negative strain implies that the Re-O bonds perpendicular to the c-axis are longer than the corresponding bond along the c-axis. This could be that the Re-O bond along the c-axis stays in compression during the rotation of the ReO_6 octahedral while the rotation relaxes the compression of the Re-O bond perpendicular to the c-axis. Results seen in the table have shown that for both $\text{P}4/\text{mbm}$ and $\text{Im}3$ structures, the Re-O (1) bond lengths in the bent Re-O-Re bonds are almost not affected by pressure. On the other hand, for the Re-O (2) bond which is parallel to the rotation axis, the bond length is shortened in the $\text{P}4/\text{mbm}$ structure. While for $\text{Im}3$ structure, all the Re-O-Re bonds are bent indicating that the anomalously large volume strain is achieved entirely through a bending of the Re-O-Re bonds with a minimal contribution from the bond shortening.

Peer 12's Writing Exercise

Polymorphism refers to the condition in which a solid chemical compound exists in more than one crystalline form. The forms differ physically and sometimes have varying chemical properties even though their solutions and vapours are identical. Polymorphs are most stable at high temperatures and high pressures, but there are exceptions where they are stable under low temperatures and pressures. Of all polymorphs, quartz is the only stable form at normal ambient conditions. At normal pressure, trigonal quartz (α -quartz) will transform into hexagonal β -quartz at 573°C . Upon further heating, the SiO_2 will transform into hexagonal β -tridymite at 870°C and later to cubic β -cristobalite at 1470°C . At 1705°C , β -cristobalite finally melts.



Changes in crystal structure result in changes in the specific density where an increasing temperature corresponds to increasing atomic vibrations in the crystal lattice, favouring more open crystal structures. The whole process is fully reversible if temperature changes very slowly. However, if temperature is increased or decreased more quickly, the processes become far more complex. When a quartz crystal is heated very quickly, it will still undergo a phase transition to β -quartz, but the β -quartz will then "skip" the transition to β -cristobalite and directly melt at 1550°C , a much lower temperature.

Christina Wang's Writing Exercise

ReO₃ has the A sites that are empty instead of being filled unlike the traditional perovskite (ABO₃). It has an octahedral structure, with rhenium atom in the centre and 6 oxygen atoms around it. A significant observation is the determination of the vital temperature P_c to be 2.4 kbar at 2K, which shows the nonlinear behaviour is observed by Razavi et al. Another experiment that was conducted later, established that P_c to be 5 kbar at room temperature and high pressure phase shows a large volume strain proportional to $(P-P_c)^{2/3}$.



This is due to the buckling of the Re-O-Re bonds with the ReO₆ octahedra remains fixed. Compacting the M₃ phonons will achieve rotations around the [100] axes. The angle of rotation of the ReO₆ is proportional to ϕ^2 . The pressure is depend of $\phi_\alpha(P-P_c)^\beta$ with $\beta = 0.322(5)$ over 5.0 to 27.4 kbar. Value of beta shows a huge critical region extending to rotation angles more than 14 degrees. The M₃ phonons will degenerate 3 times from cubic Pm3m to tetragonal P4/mbm, 14/mmm and cubic Im3 respectively.

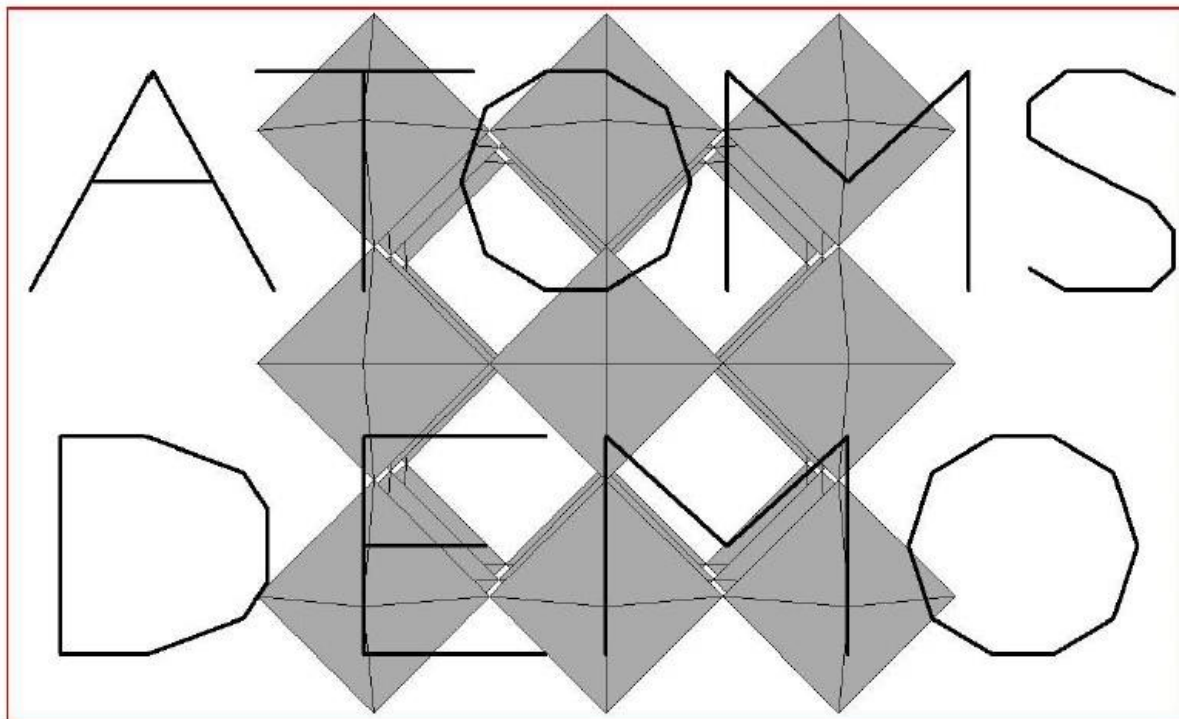


Figure 1 At ambient temperature

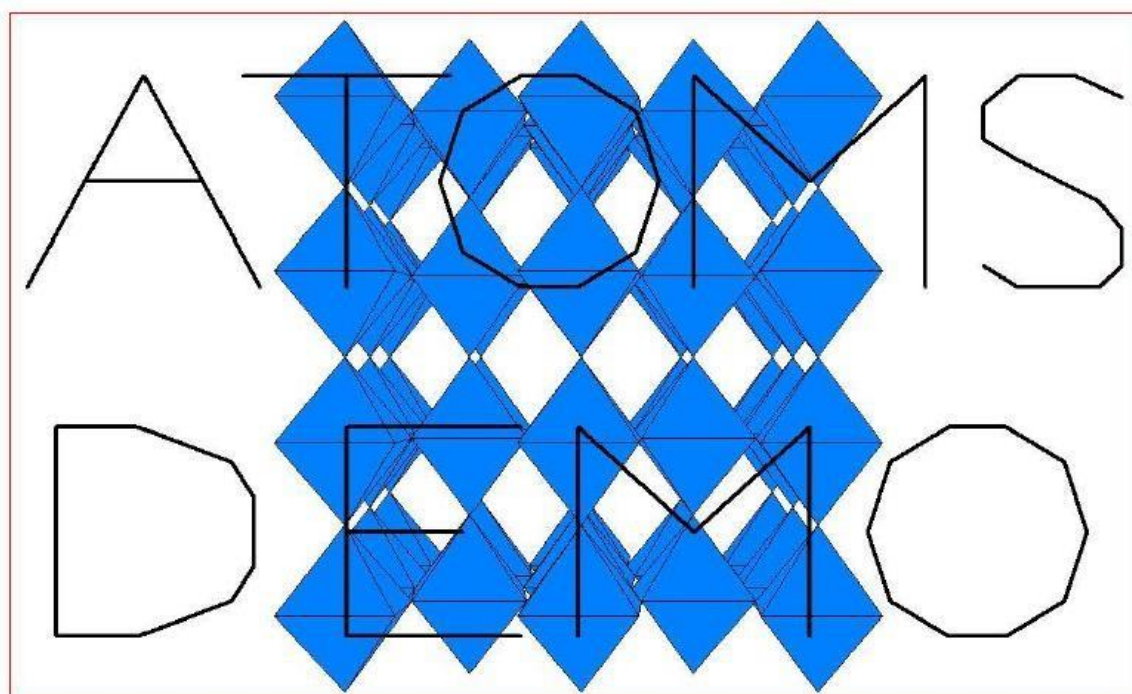


Figure 2 At 5.2 kbar

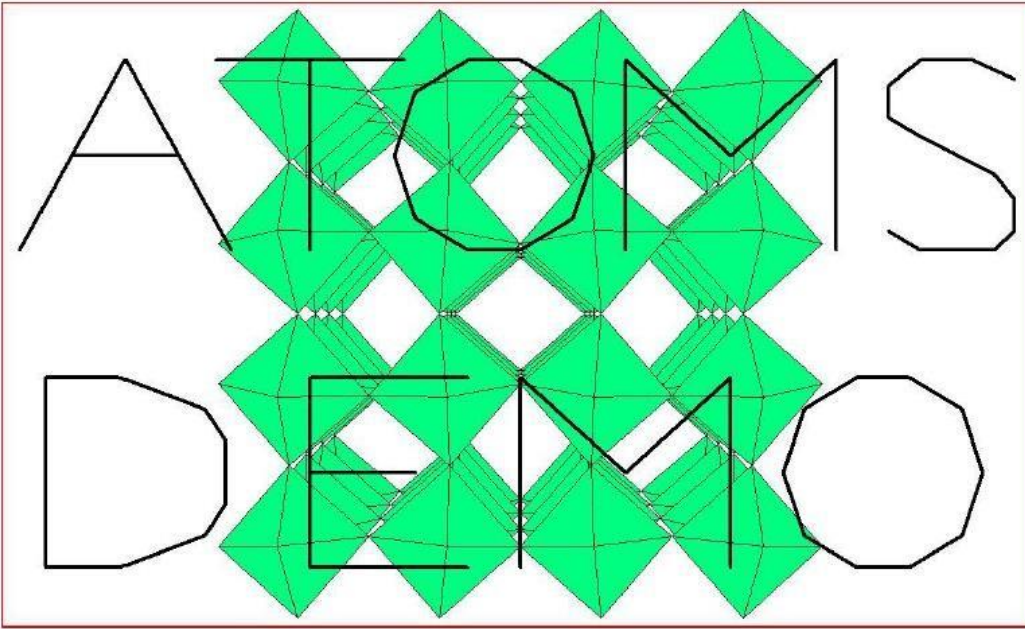


Figure 3 At 7.3 kbar

From the figures above, we can see the different structure due to the change in pressure. Additionally, the difference of tilting can also be observed throughout the change in pressure. Hence the distortion can be explained by tilting the $Pm\bar{3}m$ octahedral around the cubic axes. High pressure phases subsequently will present $P4/m\bar{3}m$ and $Im\bar{3}$ structures as pressure increases. These are all due to the condensation of the M_3 phonons, resulting in the distortion of the ReO_6 octahedron. There are two symmetry that are different, Re-O bond lengths and on Re-O bond length in $P4/m\bar{3}m$ and $Im\bar{3}$ respectively. It can be seen from the figure that Re-O length decreases as pressure increases. While for the O-O bonds do not change much and are considered negligible in our calculations. Hence, as pressure increases, rotation angle also increases smoothly.

We can see that rigid body rotations will gives us a postive strain in the $P4/m\bar{3}m$ structure while the negative strain is seen in the Rietveld refinement. This can be further expalined by the Re-O bond remaining compact perpendicular to the c-axis. Re-O-Re remains the same while Re-O (2) bond is affected by the compression.

Daphne Huang Kaiyun's Writing Exercise

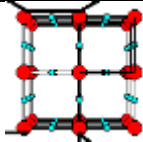
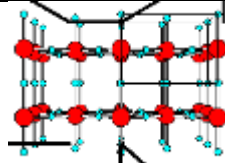
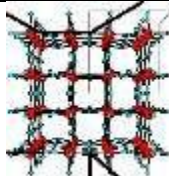
Paragraph 1

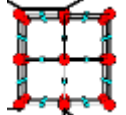
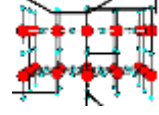



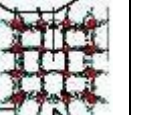

By reducing rhenium (VII) oxide with carbon monoxide, the inorganic rhenium trioxide (ReO_3) is formed. As the name suggest, rhenium trioxide is made up of rhenium and oxygen atoms. Rhenium trioxide has a structure close to that of perovskite (ABO_3), however it does not have the large cation A in its centre. Instead of the cation A, the rhenium atom in the centre is attached to six oxygen atoms and each oxygen atom is further attached to two rhenium atoms. With that being said, the rhenium atom and the six oxygen atoms form a 3D octahedral structure with the sharing of their corners. At different pressures, the rhenium trioxide structure is different. It can exist as a cubic structure and a tetragonal structure at ambient pressure and 5.2Kbar respectively. At relatively low temperatures and a pressure of about 3Kbar, the cross sections of the Femi-surface display non-linear behaviour. This concludes that there are phase changes when a certain pressure is applied to rhenium trioxide. This change is also known as “compressibility collapse”. The critical pressure at room temperature is determined to be about 5.0Kbar and that at 2K is about 2.4Kbar. In a high- pressure phase, the compressibility is about ten times more. The higher the pressure, the volume of the strain is relatively greater. The volume of the strain is proportional to $(P-P_c)^{2/3}$. This volume strain is due to the strong bonds between the rhenium and oxygen atoms (Re-O- Re) with the firm octahedral structure. The rotations are made possible due to the condensation of the M3 phonons. At high pressures, these phonons consists of coordinated rotations at the [100] axes and [111] axes.

The M3 phonons are triply degenerated. The condensed M3 phonon can be transformed from a cubic $\text{Pm}\bar{3}\text{m}$ structure into three different structures and it include cubic $\text{Im}\bar{3}$ or tetragonal I4/mmm or tetragonal P4/mbm by condensing 3, 2 or 1 M3 phonons respectively. The tetragonal P4/mbm and tetragonal P4/mbm are known as the high pressure phase of rhenium trioxide. There is a 300bar wide region just above 5Kbar in the tetragonal P4/mbm phase. As for the cubic $\text{Im}\bar{3}$, it was recently determined to have a cubic structure at 15Kbar using the single-crystal neutron diffraction measurement. It also exists in the high pressure phase established by time-of flight Laue method. Another parameter for the transition is the rotation angle (ϕ). The pressure dependency for the rotation angle is proportional to $(P-P_c)\beta [\phi \propto (P-P_c)\beta]$, where β is equal to 0.322(5) with a pressure range of about 5Kbar to 27.4Kbar. The β value determines the huge critical region extending to rotation angles of more than 14 degrees.



Paragraph 2

Pressure	Ambient pressure (1×10^{-3} kbar)	5.2Kbar	7.30Kbar
Structure	Pm3m	P4/mbm	Im3
Unit cell structure	Cubic	Tetrahedral	Cubic
Atoms drawing			

Pressure	100MPa	520MPa	730MPa	1285 MPa	1725 MPa	2270 MPa	2740 MPa
Structure	Pm3m	P4/mbm	Im3	Im3	Im3	Im3	Im3
Unit cell structure	Cubic	Tetrahedral	Cubic	Cubic	Cubic	Cubic	Cubic
Atoms drawing							

By using “ATOM” it allows us to observe the phase transitions of the rhenium trioxide structures. “ATOM” is a powerful program that displays atomic structures of all types, including molecules, polymers and crystals. In the previous paragraph, it was mentioned that the rhenium trioxide undergoes various phase transitions with an applied pressure or stress. By tilting the octahedral about its axes, it allows us to determine the distortion of the structure. High pressure phases can be form with different tilt patterns. As for the stress applied, it was observed that the crystal structure has a cubic Pm3m when a stress of about 100MPa was being applied to it. It was also observed that there was a phase transition in rhenium trioxide to a tetragonal P4/mbm when an increased stress of about 520MPa was being applied to it and it has an angle of about 3° . Another observation was that there was another phase transition to become an Im3 structure when a large stress of about 730MPa was being applied to it. This causes the rhenium-oxygen (Re-O-Re) bonds to bend. As the stress continues to increase to a range of 1285MPa to 2740MPa, there were not any phase transition observed (structure remains in Im3), however, the lattice parameter will start to decrease. This is caused by the further bending of the rhenium-oxygen (Re-O-Re) bonds when an increased stress is being applied. With this, it decreases the bond length. Besides the decrease in parameter, there was also a varying rotation angle. The rotation angle increases with increasing stress. It reaches up to 14° with a stress of 2740MPa being applied to it. The P4/mbm and the Im3 structures are the only ones that allow structural distortions. The changes in rhenium-oxygen (Re-O) bonds and oxygen-oxygen (O-O) distances in ReO₆ octahedral are insignificantly small and that can be known as a first order rotation (rigid). Due to the rigidity of ReO₆, it rotates as a rigid body as it is very stable. Positive strain in P4/mbm structure is caused by the rigid body rotation while negative strain is caused by high pressure. During the rotation of the ReO₆ octahedral, the rhenium-oxygen (Re-O) bond (along the c-axis) remains compressed. This causes the relaxed rhenium-oxygen (Re-O) bonds perpendicular to the e-axis to be longer than the bond along the c-axis. A large volume strain in the Im3 phase was

observed and the main reason for such observation is due to the bending of the rhenium-oxygen-rhenium (Re-O-Re) bonds and not due to the shortening of the bonds.

Paragraph 3

Rhenium trioxide undergoes phase transitions with increasing pressure. It starts off with a Pm3m phase to P4/mbm phase to I4/mmm phase to lastly the Im3 phase. The phase transitions occur at different elevated pressures. These pressures cause the rhenium trioxide structure to experience strains, negative strain or positive strain. As mentioned in paragraph two, the positive strain is caused by the rigid body rotation of ReO₆ octahedron and the negative is caused by high pressure. With pressure, rhenium trioxide will rotate along the [100] or [111] axis. Besides the rigid body rotation causing the positive strain, the ReO₆ octahedron also experience negative strain. The negative strain is caused by the octahedron having distortion due to varying rhenium-oxygen (Re-O) bond length, in addition to that, the rhenium-oxygen-rhenium (Re-O-Re) bonds also contributes to the negative strain. The distortion is caused by the change and bending in rhenium-oxygen (Re-O) bond lengths whereas tilt is caused by the rotation of the rigid body rotation of the ReO₆ octahedron. The rotation angle of the rigid body rotation of the ReO₆ octahedron is represented by ϕ . ϕ is an analysis of ReO₆ octahedron by using powder neutron diffraction measurements. The powder neutron diffraction measurement is a valid measurement for the change with a large cross section of oxygen. Precise atom positions and measurement of the distortion due to pressure can be measured using the Rietveld method. This method is sufficiently accurate to establish the order parameter, β . The rotation angle of the rigid body ReO₆ octahedron can be described by a power law in the form $\phi \propto (P - P_c)^\beta$, where β is equal to 0.322(5). The value of β was obtained using linear regression of the slope (slope of $\ln\phi$ versus $\ln(P - P_c)$). During the transition phase of P4/mbm phase to Im3 phase, the direction of the rotation axis changes discontinuously from [100] to [111] but the value of ϕ is still a continuous function above 5Kbar. This proves that rhenium oxide (ReO₃) undergoes a polymorph formation change due to phase transitions when a pressure is being applied to it. By condensing M3 phonons, we can obtain different phase transitions- Im3 or I4/mmm or P4/mbm by condensing 3, 2 or 1 M3 phonons respectively. The three phases namely P4/mbm phase, I4/mmm phase and Im3 phase are the subgroups of the original Pm3m phase. The transition from the Pm3m phase to its subgroup phases is second order. However, for symmetry, phase transitions must be in first order. The first order shows that transition to another rotation axis must involve discontinuous motion of the atoms at a given axis. The three-components primary order parameter phase transition is governed by $\vec{\phi} = \phi \vec{e}$. ϕ is the magnitude of the rotation angle (ϕ) and \vec{e} is the unit vector defined by the direction of the axis of rotation.

Pearlyn Au Fang Wei's Writing Exercise

Paragraph 1

The structure of ReO₃ is similar to perovskites which has a general formula ABO₃. However, the structure differs such that the ReO₃ is an undistorted perovskite with an empty A site. A non-linear behaviour of the Fermi-surface cross section is observed when temperature is low and pressure is close to 3kbar. This behaviour is a transition phase, known as compressibility collapse, in ReO₃ as a result of the exertion of pressure on the structure. There is a large volume strain at the high pressure phase which is proportional to $(P - P_c)^{2/3}$ where P_c is the transition pressure. At room temperature, the transition pressure is found to be 5kbar.

The large volume strain could be as a result of the binding of bonds in the Re-O-Re with the octahedral structure of ReO₆ remaining rigid. As the phonons are mainly made up by coordinated rotations of the octahedral around [100] axes, we can obtain the rotations by condensing the M3 phonons. By condensation, the M3 phonons degenerate and transform into three structures- P4/mbm, I4/mmm or Im3. The first space group suggested was Im3 which was established by the time of flight laude method. However, the data was only derived from only one pressure and hence, the pressure dependence of the structural distortion could not be established. The pressure dependence is shown as $\delta \propto (P - P_c)^\beta$ where $\beta = 0.322(5)$ and pressure ranging from 5kbar to 27.4kbar. The β value reflects an unexpected huge critical region extending to the rotation angles of more than 14 degrees. Apart from Im3, there exist more than one high pressure structure which is dependent on the number of phonons that condensed. The Rietveld refinement of powder data, single-crystal measurements of integrated intensities of (200) and (310) Bragg peaks, and the precise dilatometry P-V experiments have independently established that the tetragonal P4/mbm phase in ReO₆ also exists for a wide region just above 5.0kbar.

Paragraph 2

As observed from the tilting of the ReO₆ octahedral structure, different high pressure phases can be resulted as the arrangement of tilts differ. It is observed that the ReO₆ has a cubic Pm3m structure at atmospheric pressure, 100MPa. The lattice structure at atmospheric pressure for Re in special position is 1a (0, 0, 0) and for O the special position is 3d (2, 0, 0). As the pressure increases to 520MPa and 730MPa, there will be a transition in phase and experience structural changes to P4/mbm and Im3 respectively. As the pressure increases further, there will be no transition phase and the structure remains as the Im3 structure. However, the rotation angle increases as pressure increases due to the decrease in bond length of Re-O. Rotation in rigid structures will result in a positive strain in P4/mbm, however, the negative strain from the Rietveld redfinement indicates that the structure is distorted. The Re-O bond parallel to the c-axis is compressed during the rotation whereas the rotation loosen the compression of the Re-O bond perpendicular to the c-axis. As observed in the CIF files provided, the Re-O bond length decrease in the P4/mbm structure when pressure increases. Furthermore, it is suggested that the octahedral ReO₆ rotates as a rigid structure. In the Im3 transition phase, all the Re-O-Re bonds are bent which indicates that the huge strain in volume is due to the bending of the bonds rather than changes in the bond length.



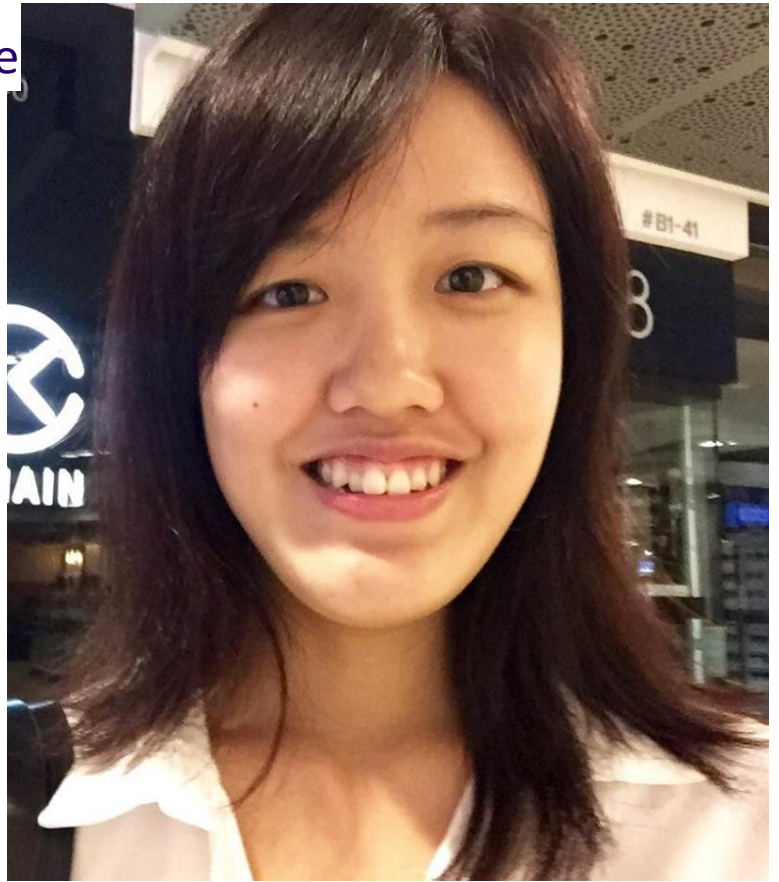
Paragraph 3

The distortion of the ReO₆ structure with pressure is closely related to the changes in bond length and the bending between bonds. On the other hand, the octahedral tilting of the ReO₆ structure is due to the rotation around the [100] axis and at [111] axis. As the M₃ phonons degenerate and transform, it undergoes a sequence of phase transition Pm3m → P4/mbm → I4/mmm → Im3. The tilting of ReO₆ is measure by the rotation angle which is obtained from the coordinates of the O atom. As the pressure increases above the transition phase and reaches 27.4kbar, the rotation angle P increases smoothly. The distortion of ReO₆ is not great under the pressure range hence, it can be said to be a rigid body rotation. The pressure and rotation angle is described by $\theta \propto (P - P_c)^\beta$. The value of β is found to be 0.322(5). Although the direction of the rotation axis changes from [100] to [111] at the transition phase, P is observed to be a continuous function with pressure above 5kbar. Also, the structural distortion is described as a first order as a rigid body rotation. The phase transitions between P4/mbm, I4/mmm and Im3 are associated with first order since the rotation angle is continuous despite the discontinuous changes in direction of the rotation axis, as mentioned. Whereas, phase transition from Pm3m to P4/mbm, I4/mmm and Im3 is of second order. The existence of intermediate phase I4/mmm in ReO₃, however, still cannot be determined.

Lee Si Hui's Writing Exercise

Paragraph 1

Rhenium trioxide (ReO_3) resembles perovskite, as it has a general formula of ABO_3 . However, there is a slight difference, as ReO_3 does not have an A cation at the center of the unit cell. It has a nondistorted perovskite structure at ambient pressure. Each rhenium center is surrounded by an octahedron of six oxygen atoms. The changes in symmetry with pressure also relates to different temperatures. A nonlinear behavior of the Fermi-surface cross-sections occurs at pressures around 3kbar under low temperatures.



Pressure- induced phase transition in ReO_3 had occurred. The critical pressure P_c is 2.4 kbar at 2K and 5.0 kbar at room temperature, which is known as the “compressibility collapse”. This is because compressibility is ten folds in the high-pressure phase. High pressure phase exhibits a large volume strain, proportional to $(P-P_c)^{2/3}$. This is due to the buckling of the Re-O-Re bonds with the ReO_6 octahedral structure remaining rigid. M_3 phonons condense, as the atomic displacements for these photons comprises mainly of coordinated rotations of the octahedral around [100] axes. It occurs around the [111] axis at higher pressures. The volume for small rotations is proportional to ϕ^2 , where ϕ is the rotation angle. ϕ is a valid order parameter for the transition. The M_3 phonons degenerate three times to form three different structures. The condensation of one M_3 phonon transforms $Pm3m$ to tetragonal $P4/mbm$. The condensation of two M_3 phonons converts to tetragonal $I4/mmm$. Lastly, the condensation of three M_3 phonons results in a cubic $Im3$ structure. The cubic structure of $Im3$ was initially identified as a high-pressure phase of ReO_3 by single-crystal neutron diffraction measurements performed by the time-of-flight Laue method. However, data were collected only at one pressure. Hence, it is not conclusive in terms of pressure dependence of the structural distortion. The

use of powder neutron diffraction suggests that there could be more than a single high-pressure phase. Neutron diffraction is especially effective, for the study of transitions with applied pressure, due to the relatively large cross-section of oxygen atoms. It is subsequently determined that $P4/mbm$ is also a high-pressure phase. The pressure dependency of the rotation angle of ReO_3 is $\phi\alpha(P-P_c)\beta$, where $\beta = 0.322(5)$ over the pressure range of 5.0 kbar to 27.4 kbar. This is established with the use of the Rietveld method of structural refinement with high-resolution powder data. It provides atom positions with similar precision to the single-crystal neutron diffraction measurement.

Paragraph 2

“ATOMS” allows us to visualize how the symmetry of ReO_3 transition from one crystal structure to another, depending on the amount of applied stress. Bond angles and principal interatomic distances between Re and O atoms change as pressure increases. These changes then result in phase transitions and rotation of the structure. At a pressure level of 1 kbar, ReO_3 exists as a cubic $Pm3m$ with lattice parameter of $a = 3.7504\text{\AA}$. Re atoms are found in special position of 1a (0, 0, 0) and O atoms in special position of 3d (2, 0, 0).

As pressure increases to 5.2 kbar, a phase transition occurs, resulting in a tetragonal $P4/mbm$. It has a lattice parameter of $a = 5.2968\text{\AA}$ and $c = 3.7415\text{\AA}$. The rotation angle ϕ around the c axis was identified to be 3.0° . The Re atoms are in the 2b positions, while O atoms are in the 4h and 2a positions. The Re-O bonds perpendicular to the e axis are longer than that parallel to the c axis. This will be further elaborated later. When pressure further increases to 7.3 kbar, another phase transition occurs and $Im3$ is obtained. It has a lattice parameter of $a = 7.4882\text{\AA}$. The Re atoms are located in special position of 8c (0.25, 0.25, 0.25) and O atoms are placed in special position of 24g (0, y, z). At this stress level, bond angle of Re-O-Re begins to change. If pressure is increased from around 12.8 kbar to 27.4 kbar, the crystal structure does not experience another phase transition. However, the lattice parameter decreases from $a = 7.4365\text{\AA}$ to 7.3426\AA . The Re-O-Re bond bends further and the bond length also decreases. Though the structure is still $Im3$, rotation angle ϕ has changed. It increases correspondingly to the increase in stress applied. At 27.4 kbar, rotation angle ϕ is 14.0° . When pressure increases beyond 27.4 kbar, the changes in Re-O bond lengths and O-O distances across the edges of the ReO_6

octahedra are insignificant.

ReO_6 has a stable structure, and can be assumed to rotate as a rigid body.

Rigid-body rotations exert a positive strain in $P4/mbm$ structure, while high pressure exerts a negative strain to the structure. This is indicated by a slight distortion of the octahedral structure. With reference to the earlier statement of differing Re-O bonds at pressure of 5.2 kbar, the reason is due to the rotation of ReO_6 octahedra. During the rotation, Re-O bond parallel to the c axis is under compression, while the compression of the Re-O bond perpendicular to the c axis is reduced. Re-O bond parallel to rotation axis is shorter in $P4/mbm$ structure. However, the Re-O bond lengths in the Re-O-Re bonds are unaffected by pressure in both $P4/mbm$ and $Im3$ structures. All Re-O-Re bonds are bent in $Im3$ structure. This implies that the anomalously large volume strain in the $Im3$ phase is mainly obtained through the bending of Re-O-Re bonds. Bond shortening does not appear to be involved.

Paragraph 3

As mentioned in previous paragraphs, ReO_3 undergoes phase transitions from $Pm3m$ to $P4/mbm$ to $I4/mmm$ to $Im3$. The phase transitions occur as a result of different pressure applied. The use of powder neutron diffraction measurements helps to identify the angle of rotation of the ReO_6 octahedra. Using the Rietveld method, atom positions can be observed precisely and the pressure dependence of distortion can be measured relatively accurately. The order parameter exponent β , where $\phi \propto (P - P_c)^\beta$, can then be established. As a result of phase transitions at higher pressures, the strain can be observed.

With reference to the $P4/mbm$ structure, there are positive and negative strains. The negative strain shows slight distortion of the octahedra, along with tilt of the structure along the cubic axes. This could result from the different compression on Re-O bond, as mentioned in paragraph 2. The rotation along [100] axis at low pressure is likely to be caused by phase transition of ReO_3 . It is due to the condensation of M3 phonons. At higher pressures, it is around the [111] axis of the $Im3$ phase. Conversely, under 5.2 kbar, phase change is due to tilting of the octahedral structure. In conclusion, distortion of ReO_6 octahedra is related to the change in the Re-O bond length. On the other hand, the ReO_6 octahedral tilting is due to the rotation of the ReO_6 octahedra. The different level of contribution of both factors result in the formation of positive and negative strains. To quantify the tilting, the rotation angle ϕ is used. It is identified by measuring the O atom coordinates. ϕ increases with pressure and plateaus off at pressure of 27.4 kbar. Beyond this pressure, the distortion is small and can then be

treated as a rigid body rotation. The pressure-induced phase transitions are an example of a polymorph function. The condensation of one, two, or three M3 phonons results in the phase transitions. The primary order parameter is a three- component order parameter, which is $\vec{\varphi} = \varphi \vec{e}$ where φ refers to the magnitude of the rotation angle and \vec{e} represents to a unit vector defining the direction of the rotation axis. Phase transition from $P3m3$ to $P4/m3m$, $I4/m3m$, or $Im3$ is of second order. This is because the other space groups are subgroups of $P3m3$. However, transitions between $I4/m3m$, $I4/m3m$, and $Im3$ are of first order. This is because once a rotation occurs around a given axis, a transition to another axis would involve a discontinuous movement of the atoms.