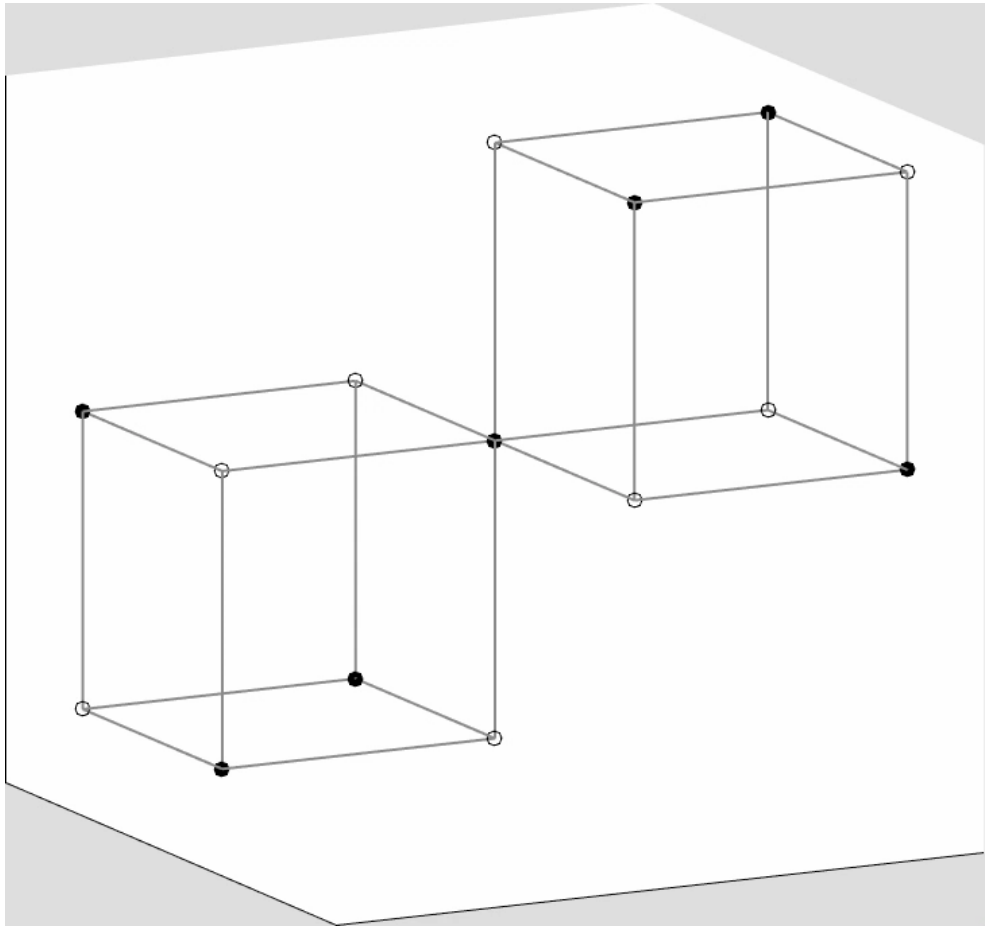
Revealing the atomic motion composing the B1-B2 structural transformation of MgO under high pressures



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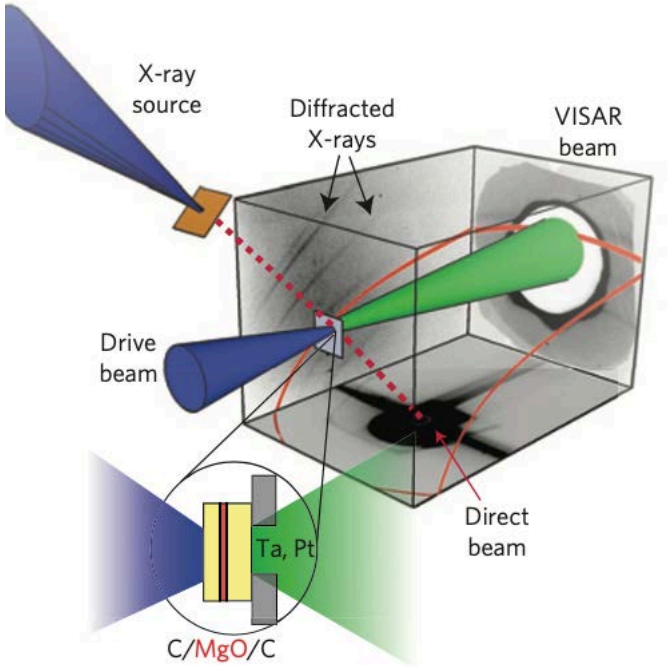
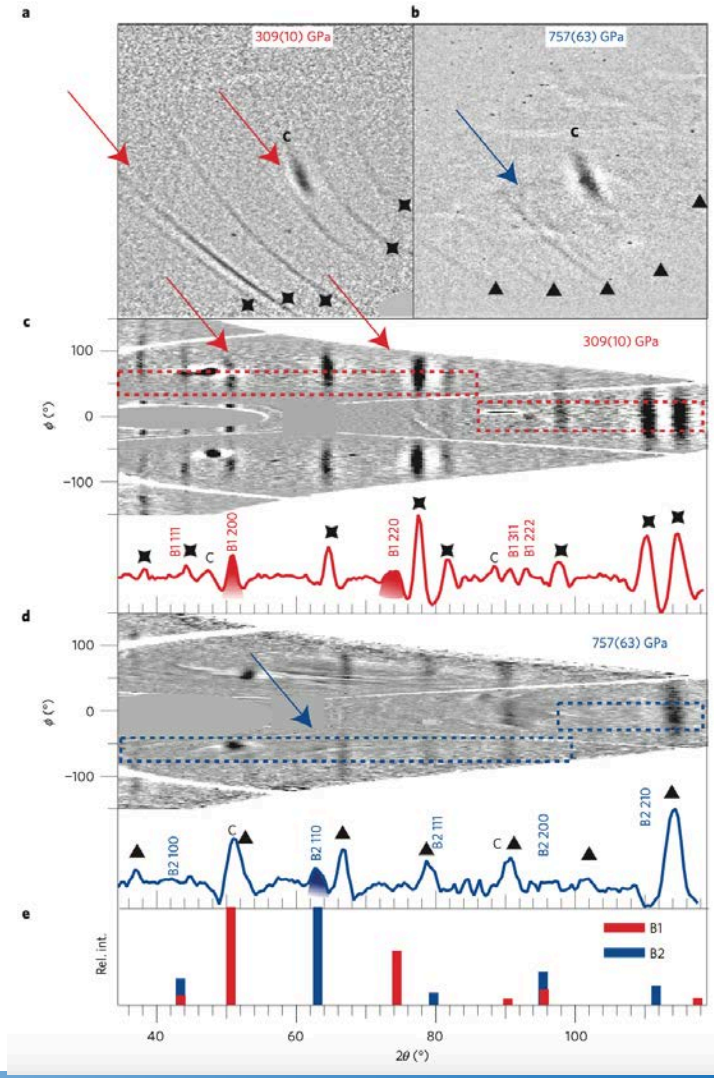
The B1 to B2 phase transition of MgO has been observed in dynamic compression experiments.

Experimental analysis of images of
X Ray diffraction peaks indicate
the most stable structure of ramp compressed MgO at
(independent) variable pressures, and low roughly
constant Temperatures.





F. Coppari, et al. *Nature Geoscience* 6, 926 (2013).

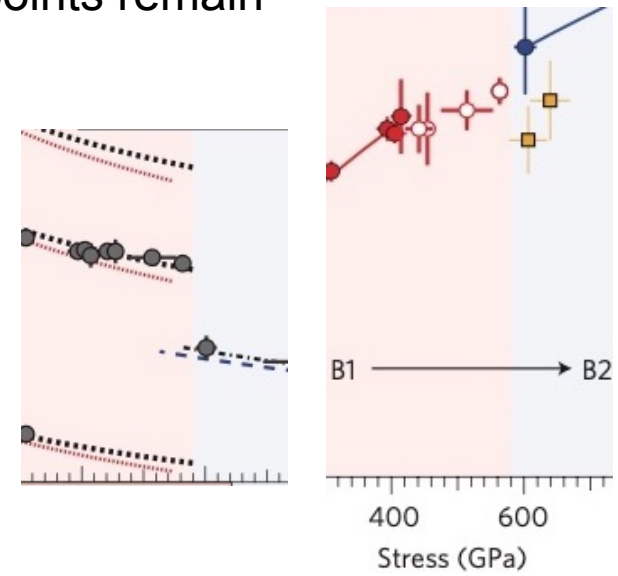
Motivation

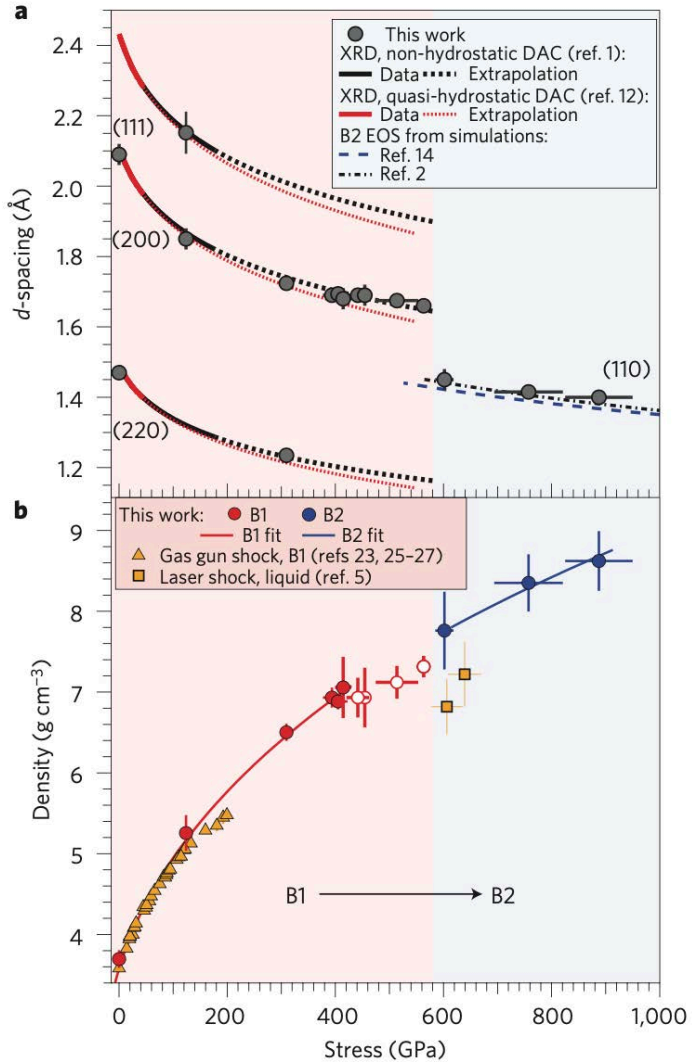
The high pressure MgO B1 to B2 structural transition pathway is unknown.

Ramp compression experiments result in a transion at the following Thermodynamic conditions:

- Temperature near 4,000 K
- Pressure in 400 to 600 GPa range

Ramp compression experiments have shown direct evidence of the MgO B1 to B2 transformation, intermediate data points remain unexplained.





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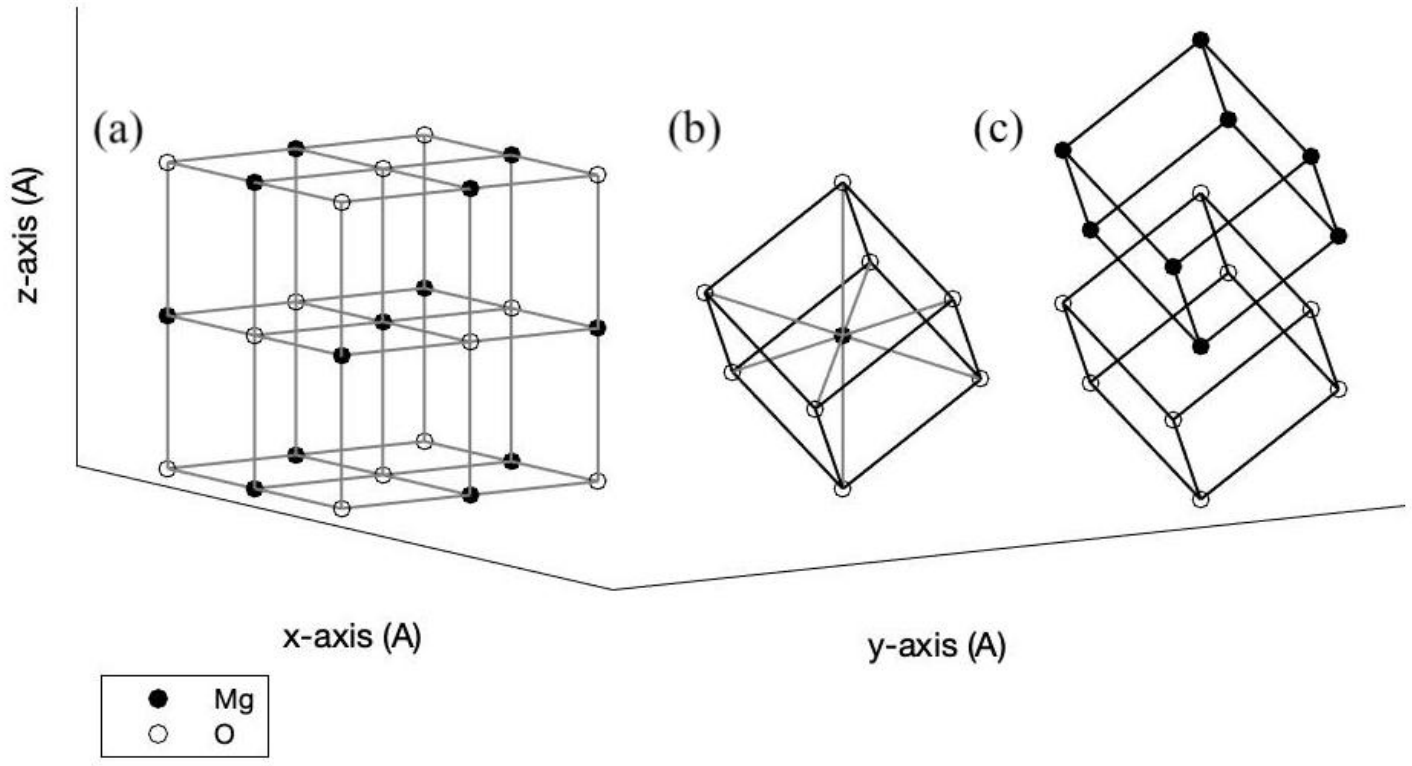
The atomic positions of crystalline MgO are represented by crystallographic unit vectors.

$$\mathbf{x}_{Mg[\mathtt{X}][i,j,k]} = (-0.2+i)\boldsymbol{v}_{1[\mathtt{X}]} + (0.2+j)\boldsymbol{v}_{2[\mathtt{X}]} + (0.2+k)\boldsymbol{v}_{3[\mathtt{X}]}$$

$$\mathbf{x}_{O[\mathtt{X}][i,j,k]} = (0.3+i)\boldsymbol{v}_{1[\mathtt{X}]} + (0.3+j)\boldsymbol{v}_{1[\mathtt{X}]} + (-0.3+k)\boldsymbol{v}_{1[\mathtt{X}]}$$

$$i,j,k \in \mathbb{Z}, \mathtt{X} = B1, B2$$



$$\boldsymbol{v}_{1[B1]}(a) = a/2(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$$

$$\boldsymbol{v}_{2[B1]}(a) = a/2(\hat{\boldsymbol{z}} + \hat{\boldsymbol{x}})$$

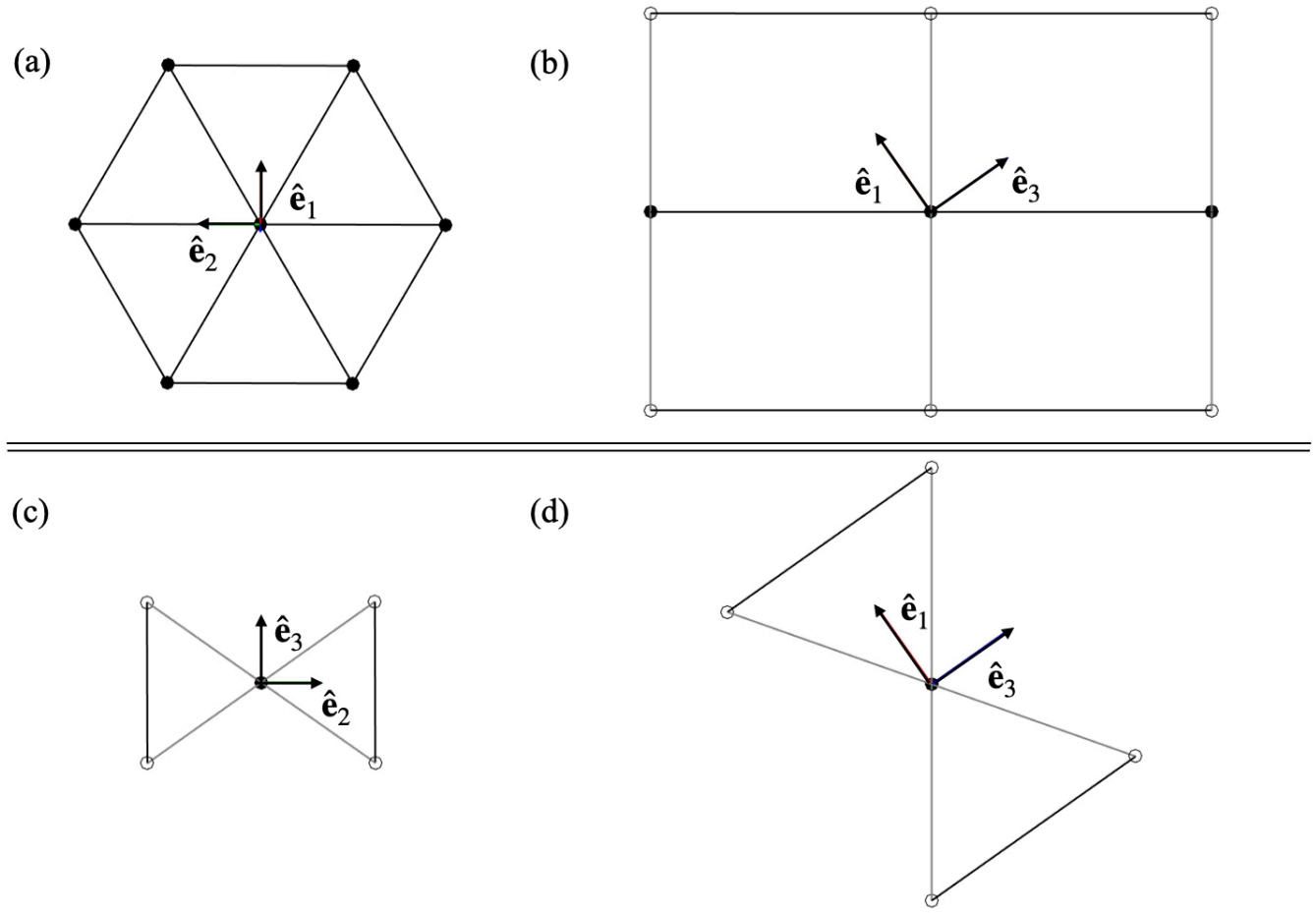
$$\boldsymbol{v}_{3[B1]}(a) = a/2(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})$$

$$\boldsymbol{v}_{1[B2]}(a) = a/6\left((\sqrt{3}-1)\hat{\boldsymbol{x}} + (\sqrt{3}+1)\hat{\boldsymbol{y}} + 2\hat{\boldsymbol{z}}\right)$$

$$\boldsymbol{v}_{2[B2]}(a) = a/6\left((\sqrt{3}+1)\hat{\boldsymbol{x}} + (\sqrt{3}-1)\hat{\boldsymbol{y}} + 2\hat{\boldsymbol{z}}\right)$$

$$\boldsymbol{v}_{3[B2]}(a) = a/\sqrt{3}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})$$

The transformation matrix for the B1 to B2 transition has been derived in this study.



$$\hat{\boldsymbol{e}}_1 = 1/\sqrt{6}(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + 2\hat{\boldsymbol{z}})$$
$$\hat{\boldsymbol{e}}_2 = -\hat{\boldsymbol{x}}/\sqrt{2} - \hat{\boldsymbol{y}}/\sqrt{2}$$
$$\hat{\boldsymbol{e}}_3 = \hat{\boldsymbol{x}}/\sqrt{3} - \hat{\boldsymbol{y}}/\sqrt{3} + \hat{\boldsymbol{z}}/\sqrt{3}$$

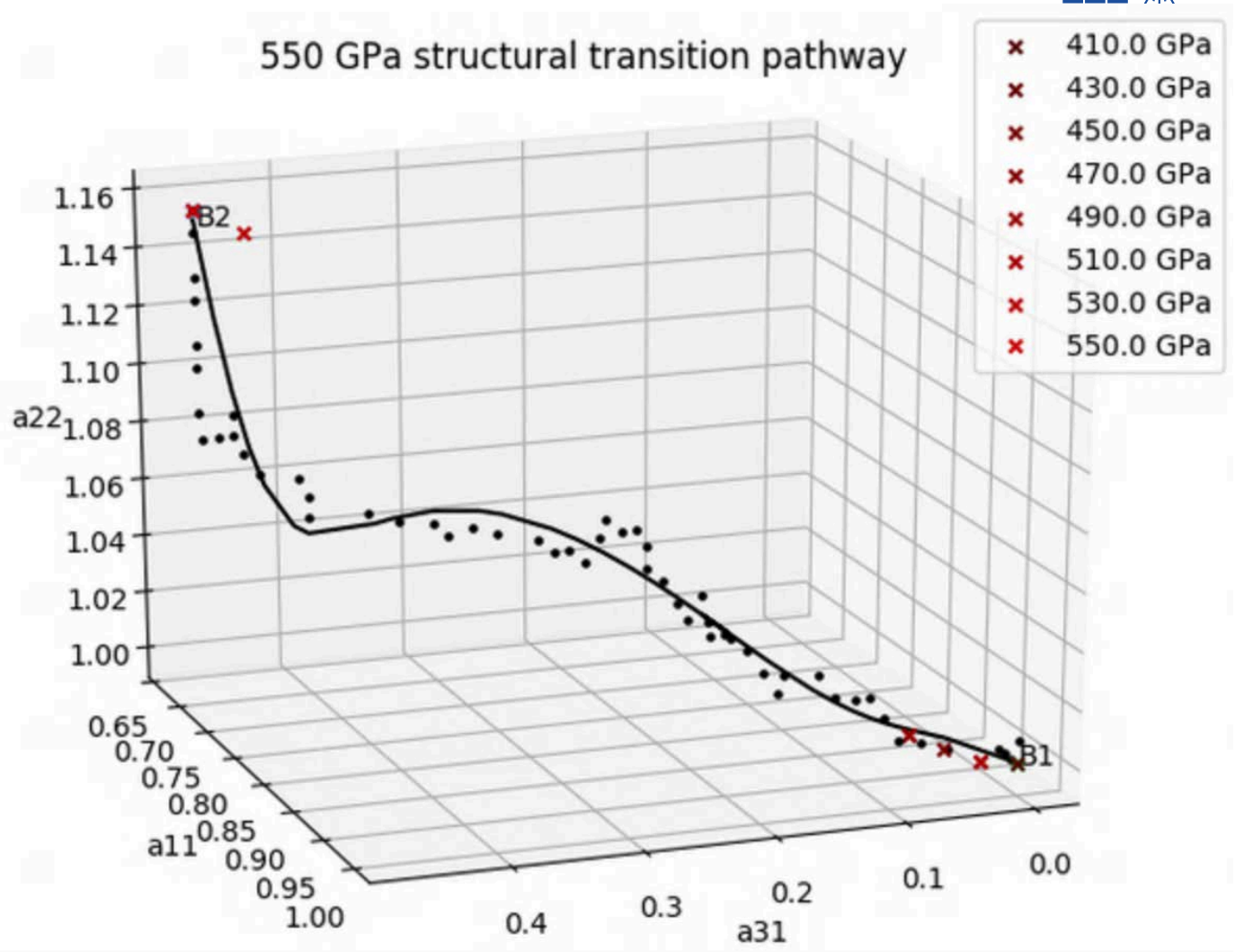
$$\mathbf{A} = a_{11}\hat{\boldsymbol{e}}_1\hat{\boldsymbol{e}}_1 + a_{31}\hat{\boldsymbol{e}}_1\hat{\boldsymbol{e}}_3 + a_{22}\hat{\boldsymbol{e}}_2\hat{\boldsymbol{e}}_2 + \hat{\boldsymbol{e}}_3\hat{\boldsymbol{e}}_3$$

$$\boldsymbol{v}_{i[\mathrm{X}]}(a) = \mathbf{A}\boldsymbol{v}_{i[B1]}(a), i = 1, 2, 3$$

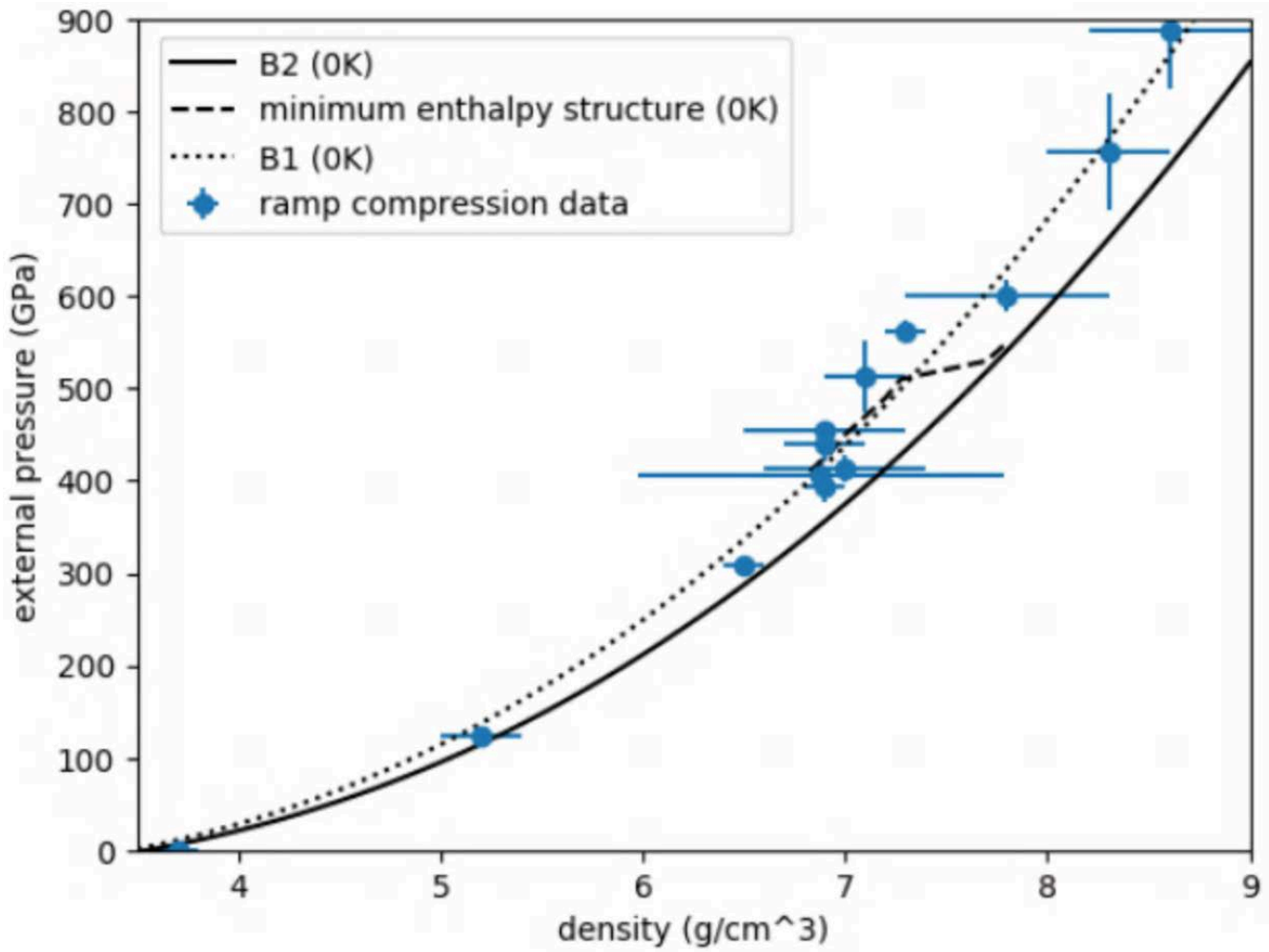
The transition pathway can be expressed by the structural coordinates.

The transition pathway is determined by a program that analyzes DFT data for a set of parametric structural coordinates.

- The transition pathway for the 550 GPa contour is shown in black.
- The pathway is determined by looking at the minimum enthalpy in a limiting radius around each point between the boundary structures.
- The minimum enthalpy point for contours below the transition pressure are labeled red x's. They are along the calculated pathway.



Zero temperature DFT calculations agree reasonably well with ramp compression experiments.



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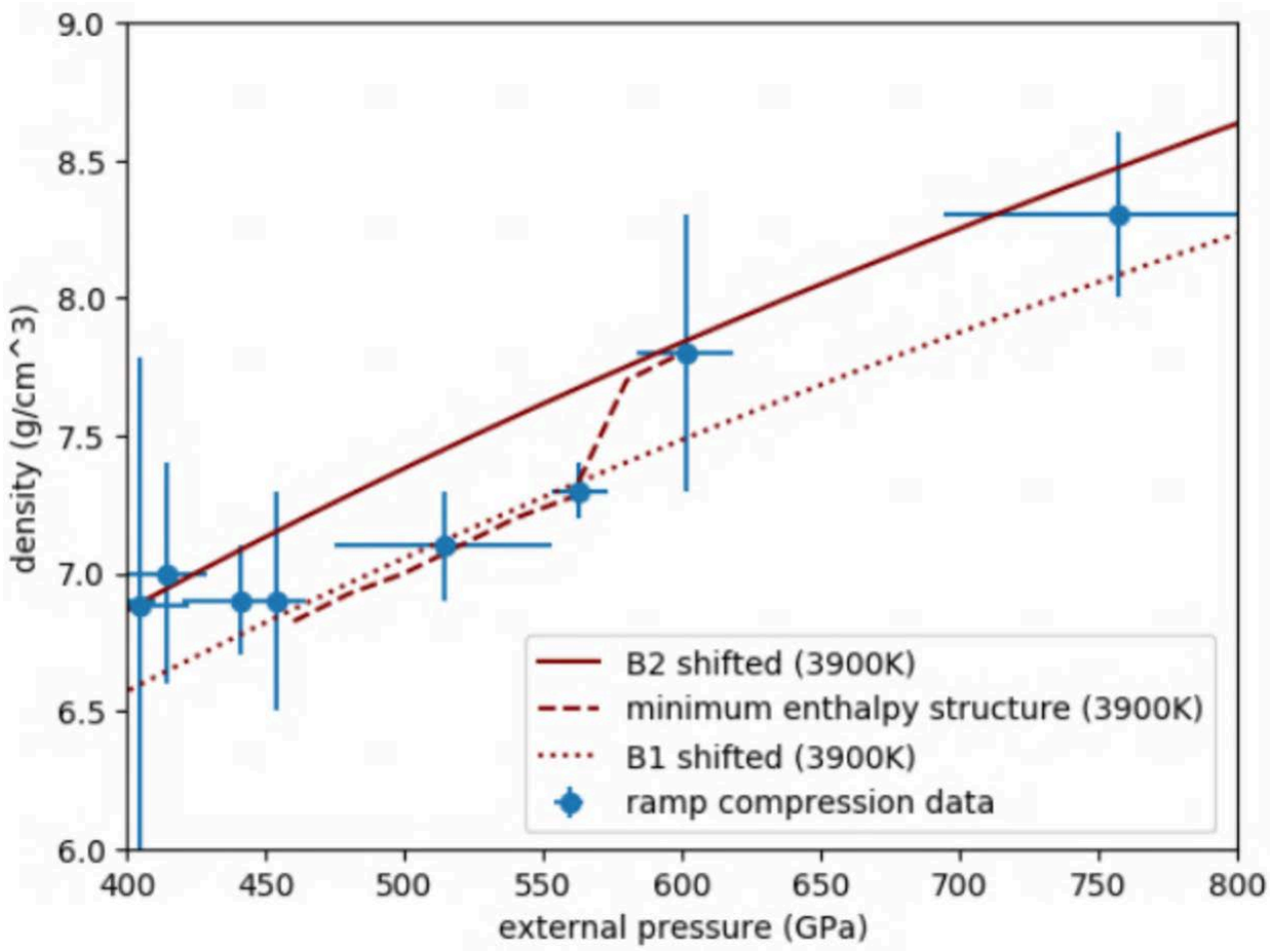
The density v. pressure curves near the transition pressure have been shifted according to uncertainty in pressure due to temperature.



The uncertainty in pressure due to temperature was calculated using the transition temperature and transition pressure of the cited reference.

$$P \approx P_{transition}$$

$$\Delta P = \frac{\partial P}{\partial T}\Delta T$$

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Summmary

The B1 to B2 structural transformation pathway of MgO has been calculated.

- The atomic positions of crystalline MgO are specified by crystallographic unit vectors.
- A transformation matrix connecting the B1 and B2 structures has been derived and utilized to define a set of structures across the transition.
- The energies and thermodynamic quantities of MgO has been calculated with DFT software (VASP) for the set of structures across the transtion.
- The data was then sorted into pressure contours and the transition pathway of minimum enthalpy was determined.
- When the DFT calculated density v. pressure curves are adjusted to estimate the effect of temperature on pressure, within the range of uncertainty in pressure due to temperature, ramp compression experimental data matches the DFT data of this study.

thank you