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High-pressure structural study of MgCl_2 up to 1 Mbar: Extensive pressure stability of the $\beta\text{-MgCl}_2$ layered structure.



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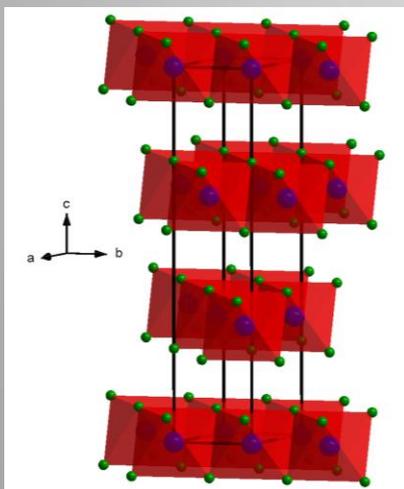
Crystal structure of AX₂ compounds- MgCl₂

Application of High pressures results to structural phase transitions towards :

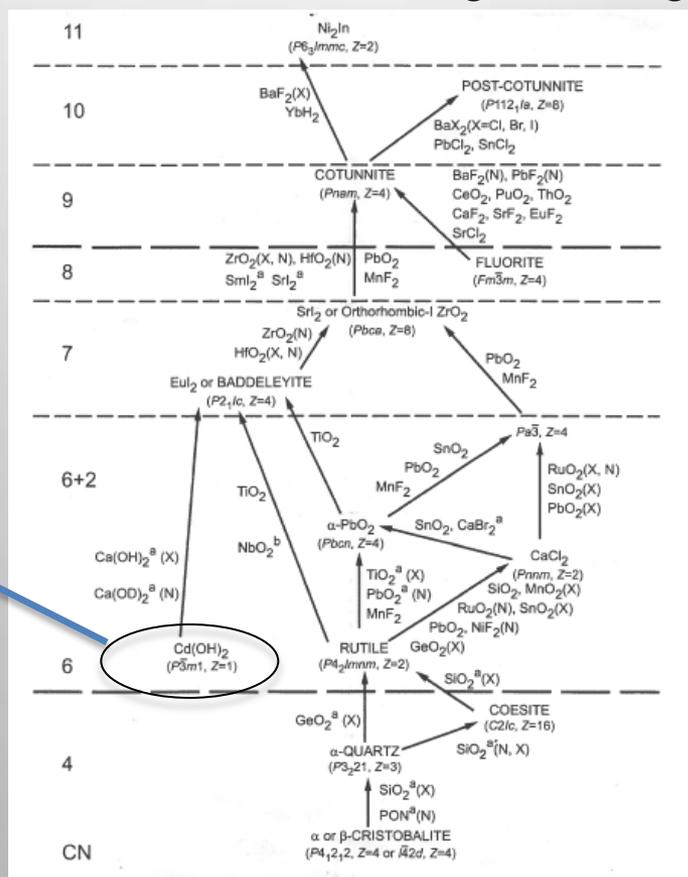
- increase of coordination number of cations (from 4-11)
- Structural types representative of higher $R=r_+/r_-$

Coordination number and R values are related through Pauling's first rule.

Lawrencite -type $R < 0.41$

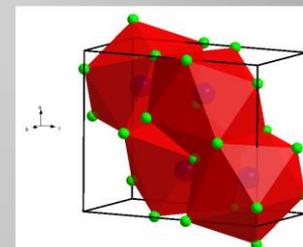


6-fold coordination
2D layered structures

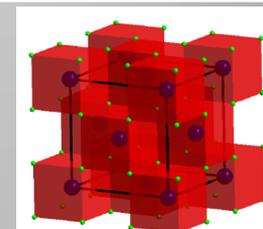


Courtesy of K. Syassen

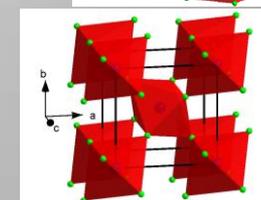
$R > 1$



$R > 0.73$



$R > 0.41$



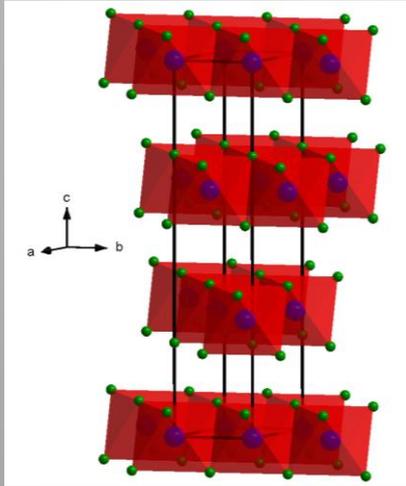
$R > 0.225$

Crystal structure of MgCl_2

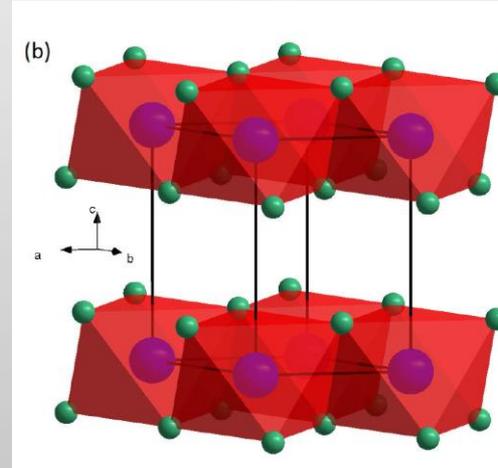
Two polymorphs at ambient conditions, **edge shearing AX₆ octahedra** forming sandwich of **X-A-X layers**. Staking of halide atoms maybe:

- cubic-closed packed ABCABC along c-axis (e.g. rhombohedral CdCl_2 -type)
- hexagonal close-packed ABABAB along c-axis (e.g. hexagonal CdI_2 -type)

$\alpha\text{-MgCl}_2$ (CdCl_2 -type)



$\beta\text{-MgCl}_2$ (CdI_2 -type)

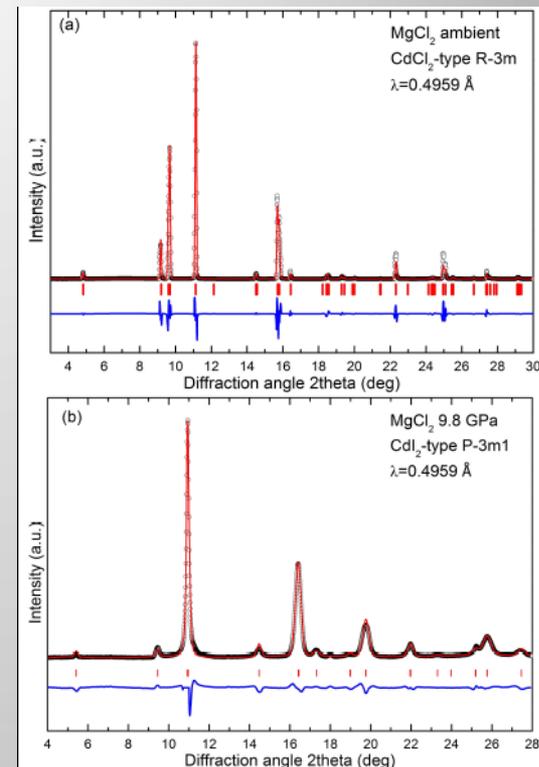
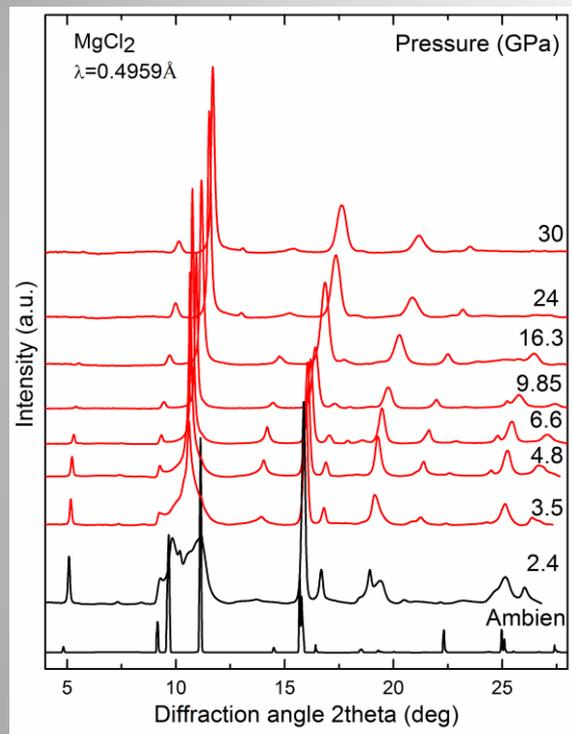


These layered structures hold a very interesting position in the AX_2 phase diagram: Intermediate between 3D structures with 4-fold coordinated cations for $0.35 < R$ (quartz- SiO_2) and rutile-type (stishovite- SiO_2).

Previous studies and motivation

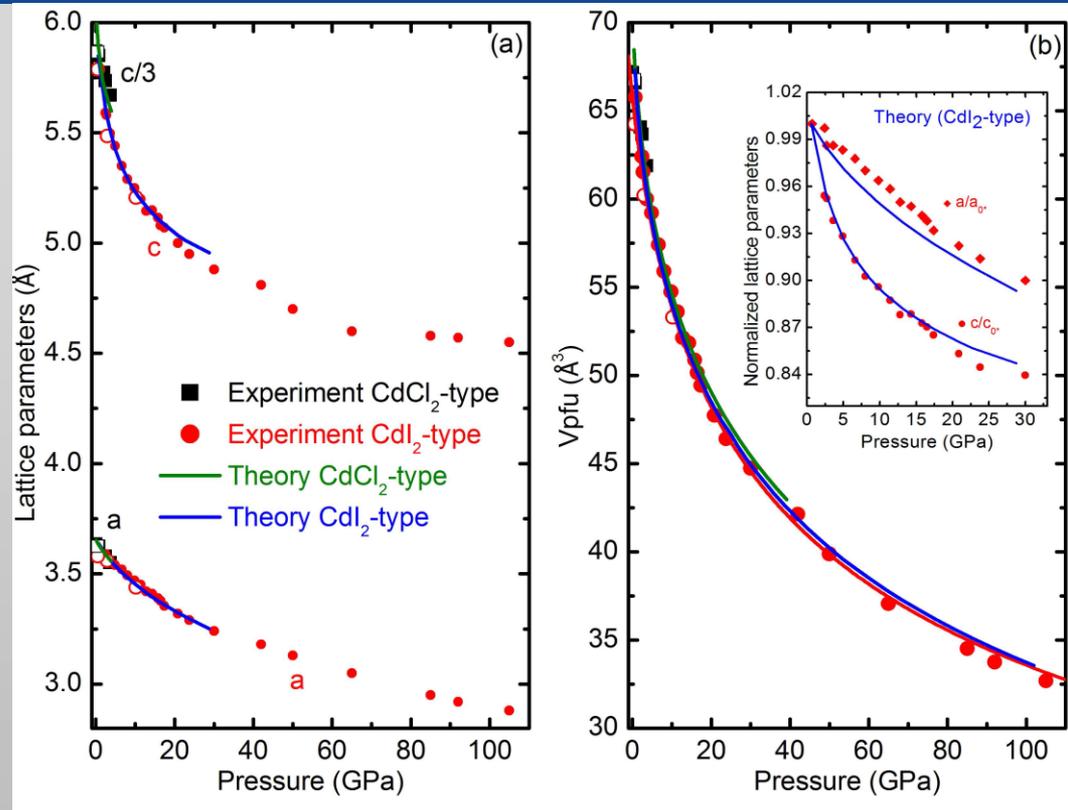
- No high pressure experimental structural study exists on MgCl_2
- According to a [previous theoretical study](#) (Barrera1997) MgCl_2 (α or β phases) will transform to [rutile at 17 GPa](#) and [fluorite at 77 GPa](#).
- In the case of FeCl_2 , a second order phase transition from the ambient CdCl_2 -type phase to the CdI_2 -type has been observed at very low pressure (0.6GPa)
 - This phase remains stable up to 65 GPa (Rozenberg2009)
- Halogen, interhalogen, and halogen oxide oxidize and disrupt the bacterial cells.
 - Use in energetic formulations targeted at destroying/neutralizing bio-agents is requires knowledge of their behavior at detonation and post-detonation conditions
 - Confident semi-empirical thermochemical calculations under extreme pressure-temperature conditions are made using equations of state data.

XRD under pressure



XRD data shows **discontinuous changes** starting at about 0.7 GPa,.
Bragg peaks of the HP phase can be indexed with the **hexagonal CdI₂-type structure**.
Above 50 GPa Bragg peaks lose intensity and become broader
We manage to trace the most intense Bragg peaks of HP phase up to 100 GPa
without **any sign of a subsequent phase transition**.

MgCl₂: Structural properties under pressure

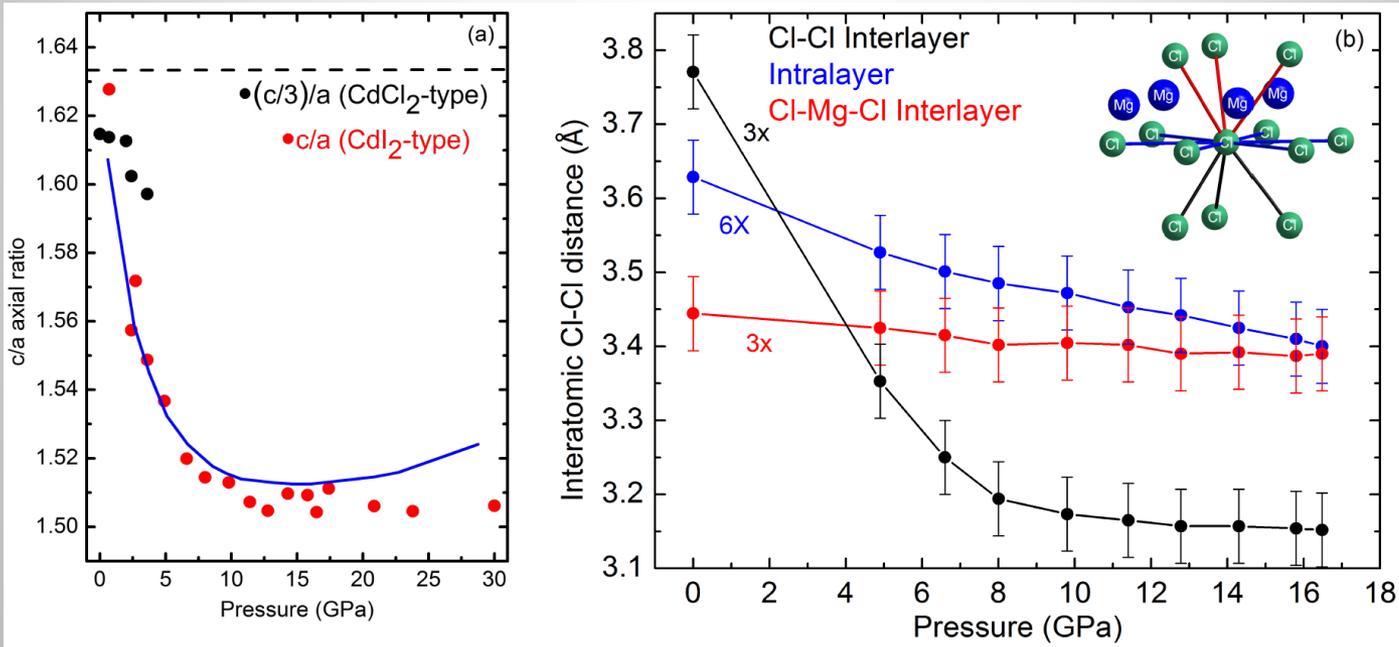


Continuity of the values of the lattice parameters and $V_{p.f.u.}$ indicates a second-order phase transition.

Experiment and theory agree well for both phases.

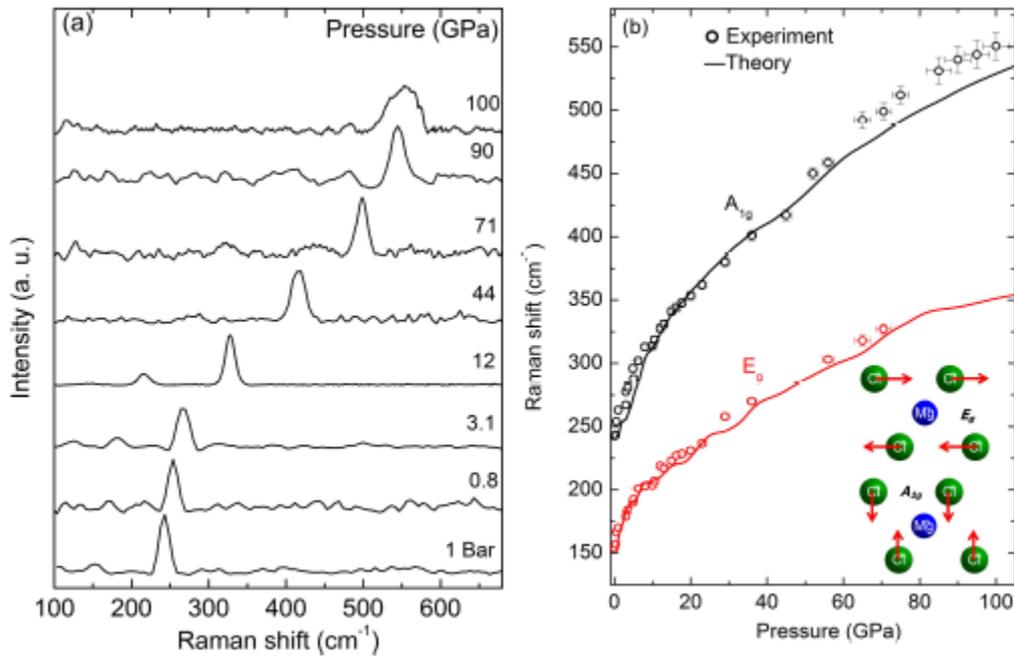
Compressibility of the c-axis is higher than the a-axis during initial compression
Higher compressibility perpendicular to the layers that reduces the free interlayer space

MgCl₂: Structural properties under pressure



c/a strongly decreases with increasing pressure reaching a constant value ~ 10 GPa. Lower compressibility of c -axis above this pressure which becomes equal to a -axis. This effect can be understood in terms of the difference Cl-Cl interatomic distances. Initial compression mainly affects the interlayer Cl-Cl distance while the Cl-Cl distances inside the same Cl-Mg-Cl “sandwich” are slightly affected. At 10 GPa the interlayer Cl-Cl distance becomes shorter than the intralayer ones. Repulsion between interlayer Cl-Cl anions \rightarrow decrease of the c -axis compressibility.

MgCl₂: Raman spectroscopy under pressure



Two Raman-active modes for both α -MgCl₂ and β -MgCl₂ phases: A_{1g}+E_g

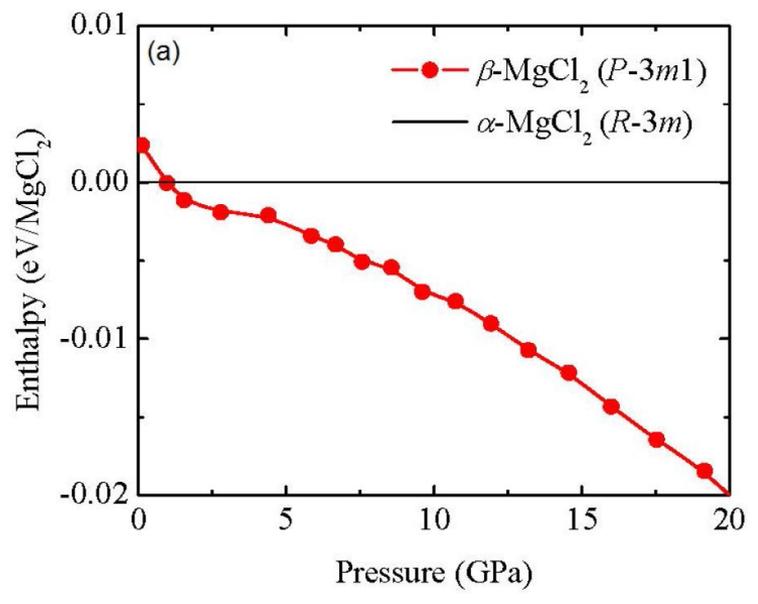
Above 1 GPa the number of observed Raman modes remains the same and no discontinuity of the Raman frequencies has been observed .

In agreement with a second-order α -MgCl₂ \rightarrow β -MgCl₂ phase transition.

A_{1g} mode can be observed up to 100 GPa with a smooth variation with pressure

The continuity of the A_{1g} together with the absence of any new intense Raman peak further justifies the argument that the β -MgCl₂ phase remains stable up to 100 GPa.

MgCl₂: Enthalpy calculations



β -MgCl₂ structure becomes more stable than α -MgCl₂ at 0.9 GPa (exp= 0.7 GPa)

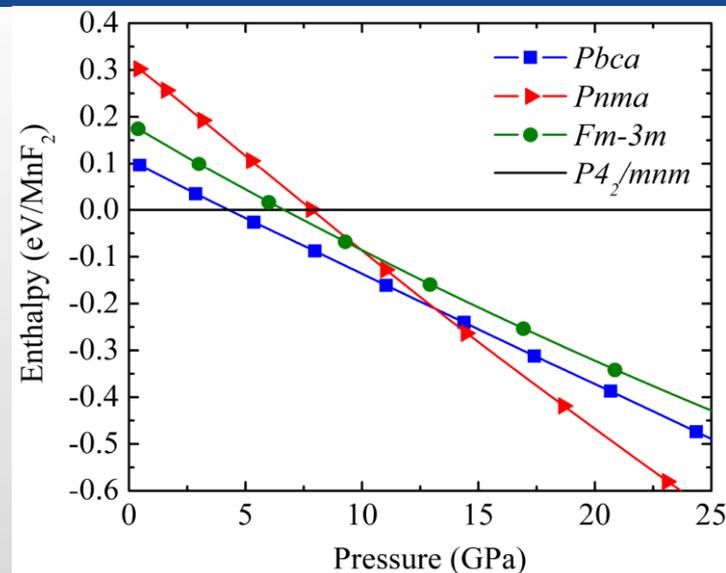
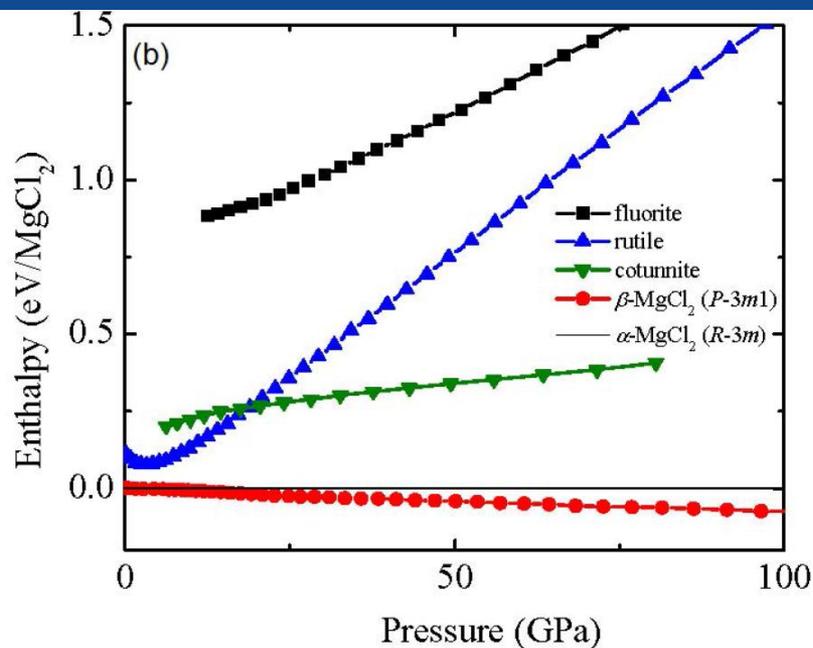
Experimental results: MgCl₂ remains in the β -MgCl₂ 2D layered structure up to 1 Mbar. Kinetic barrier that prevents a phase transformation?

e.g. SiO₂, phase transition α -PbO₂-type \rightarrow PdF₂-type > 268 GPa (Kuwayama2005).

CaF₂ and SrF₂, phase transition cotunnite-type \rightarrow Ni₂In-type (Dorfman2010)

Higher temperatures, using laser heating, were needed to overcome the kinetic barriers.

MgCl₂: Enthalpy calculations



MnF₂ Stavrou et al. 2016

- First principle enthalpy calculations for the β -MgCl₂ phase and the hypothetical rutile, fluorite and cottunnite phases: β -MgCl₂ remains the more stable phase up to 100 GPa. The enthalpy difference between the β -MgCl₂ and the candidate phases increases. These structures will not become energetically favorable even above 100 GPa. Slight modifications of the prototypical candidate structures might have lower enthalpies:
- The difference should be much lower than the difference with β -MgCl₂
 - The enthalpy difference will also increase with pressure

Conclusion

- The high-pressure structural behavior of α -MgCl₂ has been explored by a combined experimental and first-principles study up to 100 GPa.
- A second-order phase transition to the β -MgCl₂ has been observed at 0.7 GPa.
- Full structural analysis including detailed determination of the interatomic distances
 - β -MgCl₂ remains stable up to the highest pressure of this study according to experimental observations and the first-principle calculations.
- Our study provides a better understanding in the near empty field of the high-pressure structural behavior of the CdCl₂-type and CdI₂-type compounds.
- MgCl₂ doesn't follow the general structural behavior of highly compressed AX₂ compounds up to the maximum pressure of this study.
- Agreement between Cheetah thermochemical calculations and experimental data

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Thank you for your attention

