

High-pressure structural phase transitions in magnesium fluoride studied by electronic structure calculations

V. Kanchana, G. Vaitheeswaran, M. Rajagopalan*

Department of Physics, Anna University, Chennai 600 025, India

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Abstract

The present work employs the self-consistent tight binding linear muffin tin orbital method (TB-LMTO) to calculate the electronic structure and the relative stability of MgF_2 . MgF_2 is found to undergo a series of structural phase transitions under high pressure. The sequence of the structural phase transition is rutile \rightarrow CaCl_2 \rightarrow PdF_2 \rightarrow cotunnite that occurs around 10, 14.1 and 36.8 GPa, respectively. The calculated transition pressures are in fairly good agreement with the experimental results. The ground state properties of this compound are calculated in all the phases. The band structures are plotted at ambient as well as at high pressures. This compound is a wide band gap insulator with a gap of 6.45 eV at ambient conditions. The band gap tends to increase continuously even in the final high-pressure phase in contrast to other alkaline earth fluorides [45,46] wherein metallisation has been predicted for CaF_2 , SrF_2 and BaF_2 . The possible reason for this behaviour in MgF_2 is also discussed.

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1. Introduction

The structure of the AX_2 compounds can be divided into four main groups based on the constituent cation-centered anion polyhedra: the quartz group, the rutile group, the fluorite group and the cotunnite group, in which the coordination number is four (tetrahedra), six (octahedra), eight (cube) and nine (elongated tricapped trigonal prism), respectively [1]. Among the alkaline-earth fluorides, MgF_2 crystallises in the rutile-type structure [2–5], whereas CaF_2 , SrF_2 and BaF_2 crystallise in the fluorite-type structure [6–9]. The effect of pressure and temperature on the dielectric properties of these alkaline-earth halides has been extensively studied by Samara [9]. Ionic conductivity studies on the fluorite-type compounds have been reported by Voronin et al. [10]. Relatively little attention has been paid to pressure-induced phase transitions in the group II halides in contrast to the volume of work on the B1 \rightarrow B2 transition in the alkali halides and alkaline-earth oxides.

Because of the technological importance a number of authors have investigated the properties of MgF_2 , such as

elastic [11–16], chemical bondings [17], optical and equilibrium properties [18,19]. Molecular dynamics studies on the shock-induced phase transition of MgF_2 crystal was performed by Nishidate et al. [2]. They found that the rutile structure of the MgF_2 crystal gets transformed to cubic fluorite structure. The rutile to fluorite transformation in MgF_2 has also been reported by Nga and Ong [20] by molecular dynamics simulation. A similar transition from rutile to fluorite structure was reported by Allan et al. [21] based on the two-body potential. The high-pressure behaviour of magnesium fluoride is of considerable interest, as this material is a simple ionic solid, which makes it particularly suitable as a test case for theoretical studies. Previous theoretical studies mentioned above indicate that rutile-type MgF_2 should transform to a fluorite type structure ($Fm-3m$, $Z=4$) at high pressures. A recent experimental study using angle dispersive X-ray powder diffraction and the density-functional plane wave method showed that the high-pressure behaviour of MgF_2 is quite different. A second order transition from the tetragonal rutile-type to an orthorhombic CaCl_2 -type structure is observed at 9.1 GPa prior to the transformation at close to 14 GPa to the cubic phase, which is found to have a modified fluorite structure of the PdF_2 -type. A denser cotunnite-type ($\alpha\text{-PbCl}_2$) phase is observed at pressures

*Corresponding author. Tel.: +91-44-235-1265x3153; fax: +91-44-235-216.

E-mail address: mrajagopalan@lycos.com (M. Rajagopalan).

above 35 GPa. The results of the density functional calculations yield the following sequence of the stable phases: rutile \rightarrow α -PbO₂ \rightarrow PdF₂ \rightarrow PbCl₂ and indicate that the fluorite-type structure always has a higher energy than the PdF₂-type structure and is never stable for MgF₂ [4]. Since MgF₂ is a wide band gap insulator, it is necessary to have an idea about the band structure. But there is no band structure available even at ambient conditions. Hence efforts have been taken in the present case to obtain the electronic band structure, ground state properties and structural phase transitions of MgF₂ using the tight binding linear muffin tin orbital method (TB-LMTO). The rest of the paper is organised as follows. Section 2 gives the computational details. Section 3 deals with the structural aspects. Results are elaborated in Section 4. Finally Section 5 gives the conclusions of this paper.

2. Computational details

The electronic structure and the basic ground state properties of these fluorides are calculated using the TB-LMTO method [22,23]. The von-Barth and Hedin parameterisation scheme has been used for the exchange correlation potential [24] within the local density approximation (LDA). Atomic sphere approximation (ASA) has been used in the present work [25], which divides the crystal into space filling spheres centred on each of the atomic sites. Combined correction terms are also included which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere to minimize the errors in the LMTO method. The sphere radius is chosen in such a way that the sphere boundary potential is minimum and the charge flow is in accordance with the electronegativity criteria. 's', 'p' and 'd' partial waves are included. The tetrahedron method of the Brillouin zone integration has been used to calculate the density of states. The '2p' states of magnesium and '2s' states of fluorine are treated as fully relaxed valence states in the present calculation.

3. Structural aspects

At ambient conditions, MgF₂ crystallise in the rutile type structure [2–5] with the space group $P4_2/mnm$ ($Z=2$). Mg occupies the (0 0 0) position and the Fluorine atoms are positioned at ($x x 0$) with $x=0.3027$ [4,5,17]. MgF₂ is reported to undergo a series of transitions and the structural details of the high-pressure phases are as follows:

At a pressure of around 9 GPa, orthorhombic distortion of the unit cell occurs, which is similar to that observed in many other rutile-type compounds [26–29]. The high-pressure orthorhombic phase is found to have a CaCl₂ type structure with the space group $Pnmm$ ($Z=2$). Mg and F

ions occupy the (0 0 0) and ($x y 0$) positions respectively, where $x=0.306$ and $y=0.294$ [4]. The next high-pressure phase is found to have a modified fluorite-type structure with space group $Pa-3$ ($Z=4$). This is similar to the high-pressure phases of difluorides and di-oxides such as PdF₂, MnF₂, RuO₂ and PbO₂ [26–34]. The position of Mg and F are (0 0 0) and ($x x x$), respectively, with $x=0.3451$. The major difference between the modified fluorite and fluorite-type structure concerns the fractional atomic coordinates of the anion which is 0.25 for the latter and 0.34–0.35 for the former. In both the structures, the cations occupy a face centred cubic sub-lattice. The difference in the anion position results in the co-ordination polyhedra being a rhombohedron rather than a cube in the case of the modified fluorite-type structure. The cation co-ordination number is 6+2 in the PdF₂-type structure and 8 in the fluorite-type structure. Thus there is an increase in the co-ordination number from 6 to 8 in MgF₂ at high pressures [28]. The final high-pressure phase of MgF₂ is of the cotunnite (α -PbCl₂)-type structure with the space group $Pnam$ ($Z=4$). Mg and F ions occupy the positions (0.259 0.120 0.250), (0.361 0.423 0.250), (0.039 0.332 0.750), respectively.

Since the LMTO method works well for closely packed structures, either two, or three or one or five empty spheres are put in the appropriate positions in the rutile, CaCl₂-type, modified fluorite and cotunnite structures, respectively, without breaking the crystal symmetry. In the rutile structure, the experimental value of c/a (0.6589) is used whereas in the CaCl₂- and cotunnite-type structures, the axial ratios c/a and b/a are minimised at the equilibrium volume and those values are used in the calculations.

4. Results

4.1. High-pressure structural phase transitions

To study the structural phase transitions of these compounds, total energies were computed in a manner similar to our earlier works [35–37] by reducing the cell volume from V_0 to $0.5 V_0$ where V_0 is the experimental equilibrium volume. The calculated total energies are fitted to the Birch equation of state [38] to obtain the pressure–volume relation. The graphs connecting the total energies and relative volume are shown in Fig. 1. From the graphs, it can be clearly seen that the rutile-type structure is the most stable phase at ambient conditions for MgF₂. A second order phase transition from rutile-type \rightarrow CaCl₂-type is reported around 9 GPa [4]. As the energy difference between the rutile- and the CaCl₂-type structure is much less, the structures are resolved separately and given along with Fig. 1 as an insert. The above transition, which is reported experimentally, is observed at about 10 GPa using the TB-LMTO method. The graph connecting the pressure–volume in all the phases of MgF₂ is shown in Fig. 2.

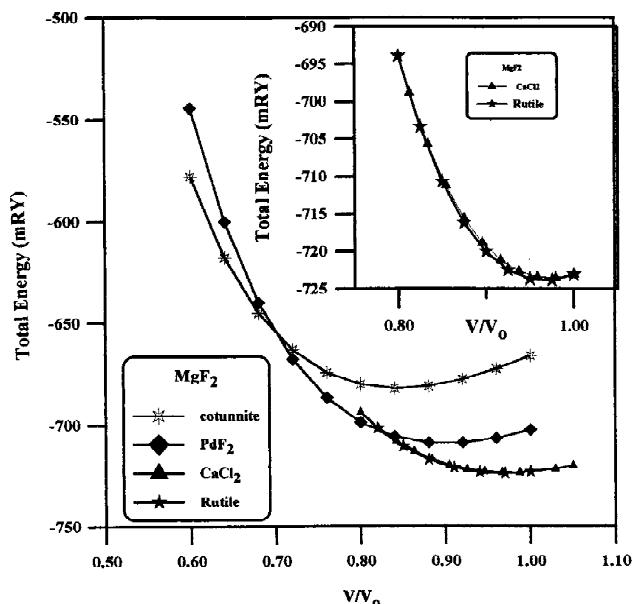


Fig. 1. Calculated total energy ($-1595.00 +$) Ry V_0 relative volume in the rutile, CaCl_2 -type, modified fluorite and cotunnite phases of MgF_2 .

The bulk modulus of MgF_2 in the rutile-type structure is found to be 101 GPa which is in good agreement with the experimentally reported value of 101(3) GPa [4]. This is also in good agreement with the values reported by ultrasonic studies of 101.7 GPa [39]. The calculated lattice constants in the rutile type phase are, $a=4.572 \text{ \AA}$ and $c=3.019 \text{ \AA}$. The calculated lattice constant agrees well with that of the experimental values, which is tabulated in Table 1. It is well known that the rutile-type compounds undergo a series of phase transitions at high pressure with

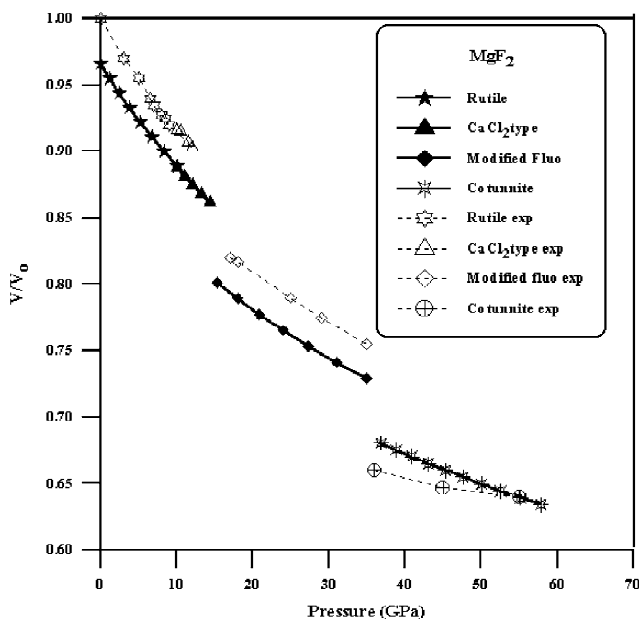


Fig. 2. Calculated pressure–volume relation in the rutile, CaCl_2 -type, modified fluorite and cotunnite phases of MgF_2 .

an increase in the co-ordination number, leading eventually to the formation of cotunnite-type structure [27,40]. In the rutile-type structure, the typical sequence of the high-pressure phases is rutile \rightarrow $\text{CaCl}_2 \rightarrow \alpha\text{-PbO}_2 \rightarrow \text{PdF}_2 \rightarrow \text{SrF}_2$ / orthorhombic-I- $\text{ZrO}_2 \rightarrow \alpha\text{-PbCl}_2$ with an overall increase in the cation co-ordination number from 6 to 9. $\alpha\text{-PbO}_2$ phase is reported to be formed only upon decompression in MgF_2 [4]. The results of density–functional calculations yield the following sequence of stable phases: rutile $\rightarrow \alpha\text{-PbO}_2 \rightarrow \text{PdF}_2 \rightarrow \alpha\text{-PbCl}_2$ and indicate that the fluorite-type structure is never stable for MgF_2 [4]. The above-mentioned results for MgF_2 are confirmed using the TB-LMTO method in the present case. As stated earlier MgF_2 undergoes a second order phase transition from rutile to the CaCl_2 -type structure around 10 GPa. Following this, a first order transition to the modified fluorite-type structure occurs around 15.4 GPa, which is in fairly good agreement with the experimentally reported transition pressure of 14 GPa. The final transition to the cotunnite-type structure is found to be around 36.8 GPa, which agrees quite well with the experimental value of 36 GPa [4]. The calculated transition pressures of MgF_2 are tabulated in Table 2 along with the volume collapse associated with each transition. The calculated equilibrium lattice constants, bulk modulus, interatomic distance and cohesive energies are tabulated in Table 1 for all the phases of MgF_2 . The bulk modulus in the high-pressure phases is overestimated by around 40%, which is due to the limitation of LDA. This extent of error is similar to that observed in other semiconductors and insulators [41].

4.2. Band structure

The self-consistent band structures plotted at ambient as well as at high pressures are shown in Fig. 3a, b. The Mg ‘p’-like states mainly contributes the lowest lying bands. The next higher lying bands arise from F ‘s’-like states. The bands lying close to the Fermi level are the F ‘p’-like states. The top of the valence band occurs at the Γ point. The bands lying above the Fermi level are those arising mainly from the Mg ‘s’-like and ‘d’-like states. The gap existing between the top of the valence band and the bottom of the conduction band at the Γ point is around 6.45 eV. This direct gap underestimates the earlier reported values by around 40% [42]. In MgF_2 the gap is between F ‘p’-like states and Mg ‘s’-like states, whereas in other alkaline–earth fluorides the gap lies between the halogen ‘p’-like states and the ‘sd’-like states of the metal atom. The under estimation of band gap is similar to that observed in many other semiconductors [43,44] which may be due to the inherent limitation of LDA. This behaviour is also observed in CaF_2 , SrF_2 , BaF_2 and some of the alkaline–earth fluoro halides [41,45,46].

At ambient conditions, the band structure of MgF_2 is compared with that of BaF_2 (Fig. 3a, c). The fat bands indicated in these figures denote the ‘d’-like states of the

Table 1
Calculated ground state properties of MgF₂

Properties	Rutile		CaCl ₂ -type		Modified fluorite		Cotunnite	
	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.
Lattice parameter (Å)	$a=4.572$	$a=4.625^a$	$a=4.419$	–	$a=4.702$	–	$a=5.104$	–
	$c=3.017$	$c=3.052^a$	$b=4.640$	–		–	$b=5.716$	–
			$c=2.828$	–		–	$c=3.045$	–
Bulk modulus (GPa)	101	101(3) ^a	134	–	170.1	123(3) ^a	259	163(35) ^a
Energy gap (eV)	6.45	10.8 ^b	7.29	–	7.10	–	8.24	–
Mg–F (a.u.)	1.946	–	1.909	–	1.926	–	1.864	–
F–F (a.u.)	2.537	–	2.568	–	2.520	–	2.483	–
Cohesive energy	13.86	–	13.66	–	13.31	–	12.50	–

^a Ref. [4] experiment.

^b Ref. [42].

metal atom. It can be clearly seen that the bands lying above the Fermi level are the hybridised bands of ‘s’ and ‘d’-like states of the metal atom in BaF₂, whereas the bands are only ‘s’-like in the case of MgF₂. The ‘d’-like states lie far apart from the ‘s’-like states of the Mg atom in MgF₂.

The band gap increases on application of pressure and it is around 7.29 eV in the CaCl₂-type structure at the Γ point. The gap increases continuously and reaches a value of 1 Ry in the final cotunnite phase for $V/V_0=0.45$. In contrast to MgF₂, the gap increases initially and then decreases upon compression in CaF₂, SrF₂, and BaF₂. The possible metallisation of these compounds are predicted to be around 210, 91, 33 GPa for CaF₂, SrF₂ and BaF₂, respectively. A similar attempt was made for MgF₂, but the gap increases up to $V/V_0=0.45$. Hence it may be difficult to attain metallisation in MgF₂. One possible reason could be that the ‘d’-like states of the metal atom are lying around 0.5 Ry in BaF₂, whereas they are located around 1.2 Ry in MgF₂ (Fig. 3a, c). In MgF₂, the bands lying close to the Fermi level are mainly ‘s’-like states of

Mg. In all other fluorides these bands are constituted by the ‘s’ and ‘d’-like states of the metal cation. Generally upon compression the ‘d’-like states tend to drop down and the ‘s’-like states move up. In MgF₂, as stated above the ‘d’ states are far away from the Fermi level (Fig. 3b) in the cotunnite phase even for the $V/V_0=0.45$ leading to the very slow movement of the ‘d’-like bands of the metal atom towards the Fermi level. In the other alkaline–earth fluorides, the ‘sd’ states of the metal atom drop down faster towards the Fermi level on application of pressure and the ‘p’-like states of the anion move up above the Fermi level leading to the band overlap metallisation. In MgF₂, there is no shift in the ‘p’-like states of the anion and the ‘d’ and ‘s’-like states of the metal atom are also moving down very slowly leading to the insulating behaviour of MgF₂ even at very high pressures. The band structure at the metallisation pressure of BaF₂ is shown in Fig. 3d. As the ‘d’ states are situated close to the Fermi level the possible metallisation could be achieved in BaF₂ and other fluorides. A similar trend is also observed in alkaline–earth oxides where the possible metallisation of MgO is not observed till $V/V_0=0.55$. At that compression, the band gap is found to be 6.3 eV. As far as MgF₂ is concerned, this is the first ever reported band structure at ambient as well as at high pressures. As there are no photoemission spectroscopic studies available for these compounds the above band structures could not be compared. The band gap values at all the high-pressure phases are tabulated in Table 1.

4.3. Calculation of cohesive energy

The cohesive energy is a measure of the strength of the forces, which binds atoms together in the solid state. In this connection, the cohesive energy of MgF₂ is calculated

Table 2
Calculated transition pressures of MgF₂

Transitions	Transition pressure (GPa)		Volume collapse (%)	
	Present	Expt.	Present	Expt.
Rutile→CaCl ₂	10	9.1 ^a	0	0 ^a
CaCl ₂ →modified fluorite	15.4	14 ^a	6.97	6 ^a
Modified fluorite →cotunnite	36.8	36 ^a	6	≈10 ^a

^a Ref. [4].

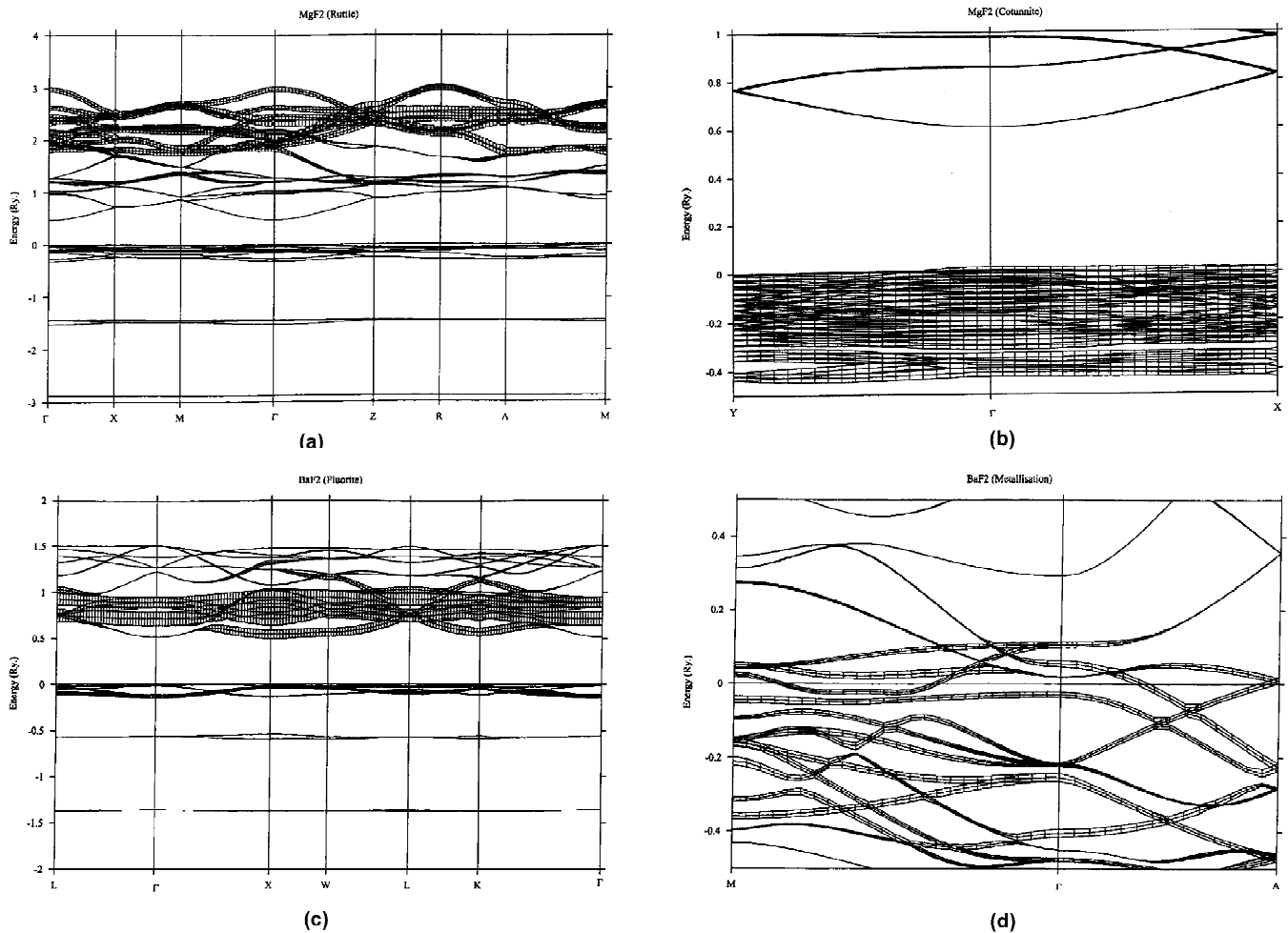


Fig. 3. (a) Band structure of MgF_2 in the rutile phase. (b) Band structure of MgF_2 in the cotunnite phase. (c) Band structure of BaF_2 in the fluorite phase. (d) Band structure of BaF_2 in the orthorhombic phase at the metallisation.

at ambient as well as at high pressures. The cohesive energy (E_{coh}) in a given phase is defined as the difference in the total energy of the constituent atoms at infinite separation and the total energy of the particular phase

$$E_{\text{coh}}^{\text{AB}} = [E_{\text{atom}}^{\text{A}} + E_{\text{atom}}^{\text{B}} - E_{\text{total}}^{\text{AB}}]$$

where $E_{\text{atom}}^{\text{AB}}$ refers to the total energy of the compound and $E_{\text{atom}}^{\text{A}}$ and $E_{\text{atom}}^{\text{B}}$ refer to the atomic energies of the pure constituents. The cohesive energies of MgF_2 in all the phases are tabulated in Table 1. From the results it can be seen that the cohesive energy decreases as we go to the high-pressure phases indicating the rutile-type structure to be the stable phase at ambient conditions.

5. Conclusion

In agreement with the experimental and the pseudo potential work, the present LMTO work also indicate that the high-pressure behaviour of MgF_2 is much more

complicated and there is no direct transformation between the rutile to fluorite-type structure. The fluorite-type structure is not stable for MgF_2 . The high-pressure phase transition sequence for this compound is rutile \rightarrow $\text{CaCl}_2 \rightarrow$ $\text{PdF}_2 \rightarrow$ cotunnite, with an overall increase in the co-ordination number of Mg^{2+} from 6 to 9. The transition pressures for the above mentioned sequence are 10, 14.1, 36.8 GPa, respectively. Our calculations are in reasonable agreement with the experimental results [4]. The basic ground state properties are calculated in all the phases. The calculated bulk modulus in the high-pressure phases overestimates the experimental values by approximately 30–40%, which is due to the usage of LDA.

The band structures are plotted at ambient as well as at high pressures. The band gap at ambient conditions is found to be 6.45 eV, which earlier reported value by under 30%. Even in the compressed conditions, since the ionic character still remains, MgF_2 is found to be insulating in all the phases. The band gap tends to increase continuously even in the final high-pressure phase in contrast to other alkaline earth fluorides [45,46] wherein metallisation

pressures have been predicted for CaF_2 , SrF_2 and BaF_2 . The possible reason could be that the Mg 's'-like states are the lower lying states above the Fermi level and the 'd'-like states are far away from the Fermi level and lie around 1.2 Ry, whereas in other alkaline–earth fluorides mentioned above the bands lying above the Fermi level are the hybridised bands of 's' and 'd'-like states of the metal atom and lie around 0.5 Ry. Hence on application of pressure, the 'sd'-like states of the metal atom could approach the Fermi level faster and the anion 'p'-like states also moves up, leading to the band overlap metallisation. In MgF_2 , neither the 's' and 'd'-like states of the metal atom nor the anion 'p'-like states are moving faster and the compound is found to be insulating even at very high pressures. A similar trend is observed in alkaline–earth oxides also [41] in which, there is no possibility of band overlap metallisation in MgO .

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