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First-principles study of the pressure-induced rutile–$CaCl_2$ phase transition in MgF_2

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Abstract

Ab initio calculations based on the density functional theory are performed to investigate the pressure-induced rutile–$CaCl_2$ phase transition in MgF_2. The phase transition is characterized as a second-order nature by evidence of the continuous changes of the cell volume and lattice constants at the transition, consistent with the experimental observation. Under compression, the B_{1g} Raman active mode in the rutile phase is predicted to soften, signifying the dynamical instability. The softening of shear modulus C_s with increasing pressure is also identified through the elastic constants calculation. The transition pressures derived from the free energy, soft mode, and elastic constants calculations are in satisfactory agreement with the experimental value. The current calculations have demonstrated that the rutile–$CaCl_2$ phase transition is driven by the coupling between the Raman active B_{1g} mode and shear modulus C_s.

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1. Introduction

As an archetypal simple ionic crystal, magnesium fluoride has both academical and technological importance; moreover, the ambient rutile-type structure ($P4_2/mnm, Z = 2$) [1] is isomorphic to SiO_2 (stishovite), which is one of the most important materials on Earth. From both experimental and theoretical points of view, there has been for decades a great degree of interest in the high-pressure behavior of MgF_2. Ming et al. [2] experimentally observed a transformation from the rutile to the cubic phase at ~30 GPa at room temperature, and at ~19 GPa at high temperature (~1300°C). Later, a number of theoretical researches [3–8] reported that the rutile MgF_2 would transform to the cubic fluorite phase ($Fm\overline{3}m, Z = 4$) under compression. Until recently, Haines et al. [9] observed a second-order transition from the rutile to the $CaCl_2$ ($Pnnm, Z = 2$) phase at 9.1 GPa by high-pressure angle-dispersive X-ray powder diffraction experiment. Under further compression, it was found that MgF_2 adopts the modified fluoride structure (PdF_2 type, $Pa\overline{3}$, $Z = 4$) at 14 GPa, and then the cotunnite structure (α-$PbCl_2$ type, $Pnam$, $Z = 4$) at 35 GPa.

The rutile–$CaCl_2$ phase transition has been observed in some dioxides (such as stishovite SiO_2 [10], GeO_2 [11], and SnO_2 [12], etc), and other difluorides (such as ZnF_2 [13]). According to the Landau theory [14] this phase transition should be ferroelastic and of second order. It involves the softening of the Raman active B_{1g} mode in the rutile phase, which transforms to an A_g mode for the $CaCl_2$ phase [10–13]. Moreover, the softened B_{1g} mode is coupled to the shear modulus C_s, which also softens with pressure, leading to an elastic instability [11,15]. For MgF_2, Pascual et al. [16] reported a linear softening dependence of the B_{1g} mode in rutile phase under uniaxial stress. Vassiliou et al. [17] observed that the shear modulus C_s softens with increasing pressure. However, the physical mechanism of the rutile–$CaCl_2$ phase transition in MgF_2 has not been clearly established yet, due to the very low applied stress and pressure (<1 GPa) and the unknown high-pressure $CaCl_2$-type phase at that time. Previous *ab initio* total-energy calculations [18] have confirmed the

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Table 1
Calculated equilibrium structural parameters, bulk modulus and its pressure derivative at zero pressure for rutile MgF_2

	a (Å)	c (Å)	c/a	u	B_0 (GPa)	B'_0
Present work	4.6912	3.0960	0.6600	0.3034	97	3.7
TB-LMTO[a]	4.572	3.017	0.6599	0.3043	101	
HFLCAO[b]	4.637	3.087	0.6657	0.3032	105.0	
Experiment[c]	4.6249	3.0520	0.6599	0.3027	101 ± 3	4.2 ± 1.1
Experiment	4.621[d]	3.052[d]	0.6604[d]	0.3029[d]	101.7[e]	3.85[e]

The other theoretical and experimental data are also shown for comparison.

[a] Reference [18].

[b] Reference [29].

[c] Reference [9].

[d] Reference [1].

[e] Reference [17].

relative phase stabilities of MgF_2 at high pressures [9], in good agreement with the experimental observation [9], but present few discussions on the mechanism of phase transitions.

In the present study, we have performed systemic first-principles calculations on the rutile–$CaCl_2$ transformation in MgF_2 to probe the physically driven mechanism of the phase transition. According to our results, the softening of B_{1g} Raman mode is clearly revealed to be strongly coupled with the shear modulus C_s, which is responsible for the phase transition.

2. Computational details

The *ab initio* calculations were performed within the density functional theory (DFT), using the plane-wave pseudopotential method as implemented in the Quantum-ESPRESSO package [19]. We used the generalized gradient approximation (GGA) of Perdew and Wang [20] for the exchange correlation functional. Ultrasoft Vanderbilt pseudopotentials [21] were used with the valence configurations of $2p^63s^2$ for Mg and $2s^22p^5$ for F. The total-energy convergence test gave the choice of kinetic energy cutoff as 30 Ry, and the Brillouin zone sampling with a grid of spacing $\sim 2\pi \times 0.041/\text{Å}$. We calculated the zone-center phonons based on the linear response method [22,23]. With the above choice of parameters, the phonon frequencies were found to be converged within 0.05 THz. Elastic constants of the rutile phase were calculated by performing six finite distortions of the lattice, and derived from the strain–stress relationship [24], using the all-electron projector augmented wave method [25,26] as implemented in the VASP code [27]. In these calculations, a kinetic energy cutoff of 435 eV was used to expand the electronic wave functions.

3. Results and discussion

We performed the full structural optimizations allowing simultaneous variations of unit cell and atomic positions at selected pressures. The theoretical equilibrium properties and equation of states (EOS) were determined by fitting the total energies as functions of volume to the Murnaghan EOS [28]. The calculated equilibrium structural parameters for the rutile MgF_2 are given in Table 1 to compare with other theoretical [18,29] and experimental data [1,9,17]. The slight overestimation of the lattice constants leads to a small underestimation of the bulk modulus, which is a typical characteristic of the DFT-GGA calculations. A good agreement within a 1.5% interval strongly supports the choice of pseudopotentials and GGA for the current study.

The rutile–$CaCl_2$ phase transition in MgF_2 can be clearly depicted from the pressure dependence of the enthalpies (zero-temperature free energy). For completeness, we also included the enthalpy calculations for the PdF_2 and α-$PbCl_2$ phases as shown in Fig. 1. It can be clearly seen that the $CaCl_2$ phase becomes energetically more favorable than the rutile phase over 9 GPa, and two further transitions to PdF_2 and α-$PbCl_2$ structures take place at 13.5 GPa and 40 GPa, respectively. Note that the predicted transition pressures agree with the experimental values of 9.1, 14, and 35 GPa [9], respectively. In Fig. 2, the calculated EOS and lattice constants for both rutile and $CaCl_2$ phases are also found to show good agreement with the experimental data [9]. It is clear that continuous changes in volume and lattice constants occur at the transition, characterizing the second-order nature observed in the experiment [9]. After the transition, the lattice constants (a and b) increasingly diverge, suggesting an improved degree of the orthorhombic distortion in the $CaCl_2$ phase under compression.

In Table 2, we calculated the zone-center Raman active phonons for the rutile phase of MgF_2 at zero pressure. A good agreement between the present calculation and experiment data [31] is evidenced by a largest difference of ∼0.87 THz in the A_{1g} mode. According to group theory, the space group *Pnnm* for the $CaCl_2$-type structure is a subgroup of $P4_2/mnm$ for the rutile structure; hence, the group–subgroup relationship of the rutile and $CaCl_2$ phases gives the direct mode correlations for the Raman active phonons. The pressure dependence of the Raman shifts for both the rutile and $CaCl_2$ phases are shown in Fig. 3. As one can see, the frequencies of Raman modes for the rutile phase all increase with pressure, except for the B_{1g} mode exhibiting softened behavior, whereas all Raman modes increase in the $CaCl_2$ phase. The softening of rutile-type B_{1g} mode with pressure is followed by a hardening of the $CaCl_2$-type A_g mode with which the B_{1g} mode is correlated. The transition pressure derived from the crossing of B_{1g}/A_g modes is ∼8.5 GPa, consistent with the enthalpy result. It should be pointed out that the hardening tendency of A_g mode for the $CaCl_2$ phase could not be observed, if