

Pressure-Induced Frustration and Disorder in $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$

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Using *ab initio* molecular dynamics we study pressure-induced hydrogen sublattice amorphization in $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$. Our calculations reproduce the experimental behavior of these two systems, with $\text{Ca}(\text{OH})_2$ showing significantly more marked effects. We find that the interplay of short-range repulsion and electrostatic forces explains the amorphization process. This is due to a frustration phenomenon and has a dynamical character at room temperature, but it can be frozen in at low temperatures.

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The pressure-induced transition from crystalline to amorphous state is currently the subject of intense study [1]. Particularly intriguing is the observation of the recovery of the crystalline state upon decompression (memory effect). Among the systems that are believed to show pressure-induced amorphization, the hydroxides of the type $M(\text{OH})_2$, where M is a divalent metal like Ca, Co(II), and Mg, have received considerable attention [2–11]. These minerals have relevant geological interest since they serve as simple model systems for the complex hydrogen-bearing silicates of the earth's crust and mantle and for structurally bound hydrogen; in addition $\text{Ca}(\text{OH})_2$ (portlandite) finds widespread application in cement. These compounds have a hexagonal layered structure (space group $P\bar{3}m1$, see Fig. 1a) with weak interlayer forces. The OH groups from different interlayers face each other and form an antiferromagnetic arrangement, where each OH is surrounded by three oppositely oriented OH groups coming from the neighboring layers, as shown in Fig. 1b. As the system is subjected to an external pressure the interlayer distance decreases considerably more than the intralayer one. In this condition the OH groups interact more strongly, and this is believed to lead to a reversible disorder in the H sublattice. Most of the evidence comes from IR experiments which show a broadening of the antisymmetric OH stretching peak and a down-shift of its frequency [2,5,10]. A more direct probe of the H sublattice structure comes from neutron diffraction. The available neutron experiments on the effects of pressure on these compounds confirm rather clearly the amorphization picture for $\text{Co}(\text{OH})_2$ [11], whereas the situation is less clear for $\text{Mg}(\text{OH})_2$ (Brucite) [4,6]. Theoretical studies have examined only the question of the nature of the interlayer interaction forces in the ordered crystal and come to the conclusion that it is dominated by Coulomb and dispersion interaction [12]. This contradicts speculation that hydrogen bonds play an important role [2,4,5,10,13]. Furthermore, there is no understanding of the nature of the disordered state and its causes.

To this effect we present here a Car-Parrinello molecular dynamics (MD) simulation [14] on $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$. These have been chosen on the basis of computer cost considerations, which discourage the study of $\text{Co}(\text{OH})_2$, and because $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ are representative of weak and strong disordered situations [2]. Our results are in agreement with the experiments and show that the amorphization is the result of a frustration phenomenon not dissimilar from that which occurs in 2D

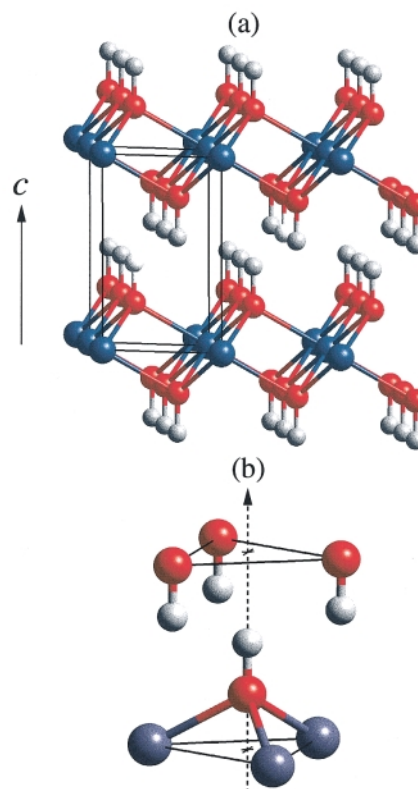


FIG. 1. (color). (a) Schematic representation of the structure of $M(\text{OH})_2$ hydroxides (black lines mark the unitary cell). (b) Environment of a hydroxyl OH group.

triangular antiferromagnets. The analysis of the interaction between hydroxyl groups reveals that Coulomb forces play a crucial role in the transition and that the notion of the H bond is not applicable to these systems.

A series of constant volume, constant temperature simulations at values of the experimental lattice constants, corresponding to pressures in the range 0–14 GPa, have been performed. Our MD box is hexagonal and contains 90 atoms and two independent layers. We used the Becke, Lee, Yang, and Parr (BLYP) exchange and correlation functional [15] that has been shown to describe well the formation of hydrogen bonds [16], the Γ -point sampling of the supercell Brillouin zone, and soft pseudopotentials of the Troullier-Martins type [17]. For Ca the semicore $3s$ and $3p$ states were included in the valence, whereas for Mg nonlinear core corrections were taken into account. The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 70 and 80 Ry for $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, respectively. This choice gives structural parameters within about 1% of the experimental values. We used D rather than H in order to increase the integration time step, which was 0.14 and 0.10 fs, with fictitious electronic mass of 700 and 400 a.u. for $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, respectively. Experiments on Brucite [4,6, 18] do not exhibit significant dependence on the isotopic mass, and we expect that the quantum effects are only of quantitative relevance. Nosé thermostats were used throughout to keep the ionic temperature constant.

The computed structure factor for $\text{Mg}(\text{OH})_2$ at low and high pressure gives Bragg's plane sequences in very good agreement with the experimental ones [6]. Another support to the reliability of our model comes from the study of the IR spectrum (see Fig. 2), which we have calculated from the ionic position and the electronic wave functions using the Berry phase method [19]. Since these calculations are computationally demanding, the IR spectra have been evaluated only at ambient pressure and at the high-

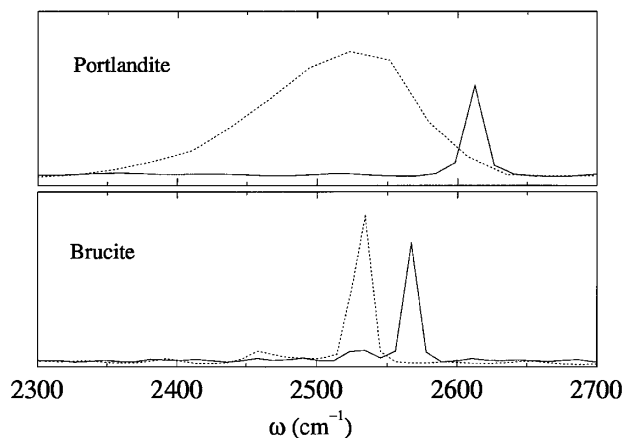


FIG. 2. Computed infrared spectra for deuterated Brucite and Portlandite in the internal stretching region at 0 (solid line) and 14 GPa (dotted line). The intensity is in arbitrary units.

est pressure considered. The experimental behavior, under pressure, of the A_{2u} OH stretching mode in $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ is rather different [2]. In fact a broadening and a downshift of the peak is observed, which are small in $\text{Mg}(\text{OH})_2$ and much larger in $\text{Ca}(\text{OH})_2$. Our calculations reproduce the pressure-induced down-shift and broadening of the peak in $\text{Ca}(\text{OH})_2$, whereas the effects on $\text{Mg}(\text{OH})_2$ are within our error bars, as shown in Fig. 2.

Reassured by these findings we now turn to the analysis of our results. We find that, at all the pressures studied, the metals and hydrogens undergo large anharmonic motions. In agreement with experiments, the metal moves mostly along the c axis, whereas the hydrogens have their largest displacements in the ab plane [13,20]. In Fig. 3 we plot the hydrogen probability distribution function (PDF) in the ab plane. As can be seen, the pressure changes the character of this distribution from having a single peak at the origin to one having three equivalent maxima oriented towards the three neighboring O of the adjacent layer. In crystallographic terms the average H position moves from a $2d$ site at $(1/3, 2/3, z)$, where the OH group are aligned along the c axis, to a $6i$ site at $(x, 2x, z)$ with occupation factor $1/3$, where the OH group are tilted towards one of their neighbors. This is much more pronounced for $\text{Ca}(\text{OH})_2$ than for $\text{Mg}(\text{OH})_2$. Note that the PDF have a complex structure which cannot be expressed simply in terms of a few Gaussians functions,

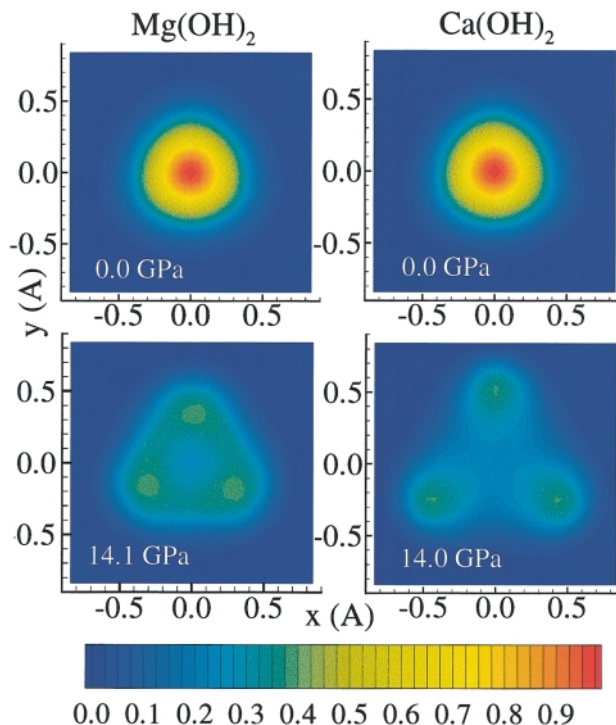


FIG. 3. (color). Probability distribution function (PDF) of the proton around the $2d$ crystal sites. The color contour level scale has been normalized to the $\text{Mg}(\text{OH})_2$ distribution at 0 GPa.

as is normally done in the analysis of neutron scattering diffraction experiments. This is particularly true at low pressures and might be one of the causes of the difficulties in the assignment of the $\text{Mg}(\text{OH})_2$ structure.

In order to quantify the trend towards destabilization of the $2d$ site, we measured the order parameter $c_3 = \langle \cos 3\theta \rangle$ where θ is the angle between the OH axis projection on the ab plane and a fixed direction in the plane. Also c_3 exhibits a different behavior in $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, as shown in Fig. 4. As the pressure is increased, c_3 increases slowly in $\text{Mg}(\text{OH})_2$, whereas in $\text{Ca}(\text{OH})_2$ its variation is much larger and apparently discontinuous. We notice the very strong similarity between the behavior of c_3 and that of the bandwidth of the A_{2u} mode (inset of Fig. 4).

One current interpretation of the amorphization process is in terms of the formation of interlayer hydrogen bonds between OH groups. These would cause the broadening and the down-shift of the A_{2u} peak. However, the latter is not necessarily related to the formation of the H bond, as recently demonstrated [21]. In our simulations we do not find evidence for H bonds. In fact, if we use the conventional geometrical criteria in terms of distances and angles to define the H bonds, we find that their lifetime is very short (about 100 fs), indicating at most very weak H bonds. At a deeper level we have investigated the bonding properties of the system by examining its electronic orbitals. To this effect we use the recently introduced maximally localized Wannier functions [22] which, for a periodic system, are the analog of the Boys localized orbitals [23]. They define for each OH group a set of three lone pairs. As a function of pressure the arrangement of these lone pairs does not change. We can therefore rule out a charge transfer between different OH groups and the formation of genuine H bonds.

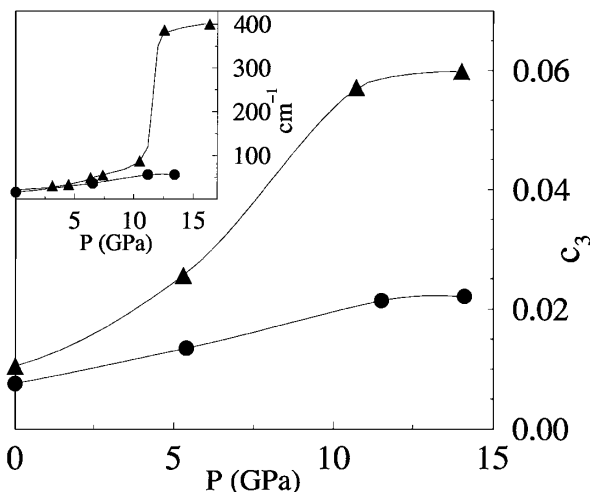


FIG. 4. Orientational order parameter, c_3 (see text for the definition). In the inset the experimental [2] full width at half maximum of O-H infrared-active stretching mode is shown. Circle: $\text{Mg}(\text{OH})_2$; triangles: $\text{Ca}(\text{OH})_2$. The solid curves are only a guide for the eye.

Rather it is a combination of electrostatic and short-range repulsion that explains the amorphization process. Using the Wannier functions we can separate the charge of the hydroxyl groups from that of the metal ions. We find that due mostly to charge-dipole interaction, it is energetically favorable for a hydrogen atom to move closer to a neighboring O atom of the nearest layer. In fact, for both the systems studied, the position $2d$ is a maximum for the electrostatic energy.

With increasing pressure, the interlayer distance decreases and the effect of the charge-dipole interaction is enhanced. Once the $2d$ position is destabilized, as is clearly the case for $\text{Ca}(\text{OH})_2$ above 11 GPa, then any form of long-range order is necessarily lost due to the geometrical arrangement of the two sets of OH anions. In Fig. 5 it is seen that any attempt at forming an ordered array, in which the hydrogens are moved to a $6i$ position in order to minimize the electrostatic interaction, is frustrated due to the topology of the honeycomb lattice. In $\text{Ca}(\text{OH})_2$ an amorphization (possibly metastable [3]) of the Ca sublattice has been reported in the range of pressure in which the IR line broadening takes place [3]. The phenomenology reported makes it compatible with pressure induced softening of incommensurable mode. Clearly, in our simulation the small size and the constant-shape boundary conditions will prevent the softening of this mode to take place. Our finding that even with an ordered Ca sublattice the IR line broadening takes place indicates that IR line broadening and metal sublattice disorder are not necessarily coupled as it is the case for $\text{Ca}(\text{OH})_2$. The different behavior of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ can then be ascribed to the different size of the two ions. Mg is smaller than Ca and thus the OH groups are much closer. Steric interactions between neighboring hydroxyls limit the displacement from the $2d$ positions and therefore the possible gain of electrostatic energy. In $\text{Ca}(\text{OH})_2$ the OH anions are much farther apart and this effect is strongly

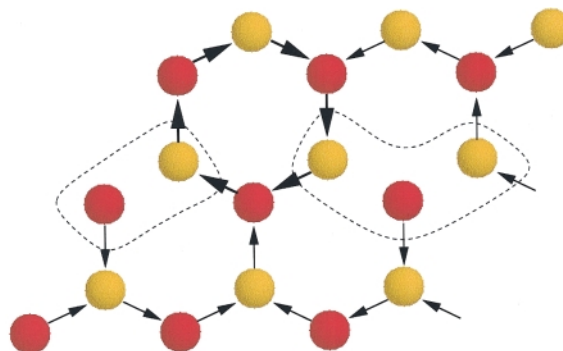


FIG. 5. (color). Ring structure in a typical high-pressure disordered layer conformation. Yellow and red spheres indicate the ideal positions of the two different sets of OH groups belonging to different layers and the arrows the displacement of the hydrogen atom. A close six-term ring is indicated by heavy arrows. The closure defects are enclosed by dashed curves.

enhanced. However, we are aware that other effects, such as the presence of the d electron in Co(OH)_2 and the ionic polarizability, can play an important role. We would also remark that, at room pressure, the nature of the disorder is strongly dynamical, with the OH groups executing fast rotational motions in both the systems studied. In Ca(OH)_2 at 14.0 GPa, although still fast, the rotational diffusion appears to be jump-diffusion-like. This indicates that the potential energy surface is rather flat and the system moves easily from one minimum to the other. Upon cooling, however, it is possible that the dynamical disorder is quenched and turned into static disorder [as experimentally suggested for Ca(OH)_2 by Desgranges *et al.* [24]], this effect being enhanced by pressure. Particularly intriguing in this respect would be the study of very low-temperature behavior where frustration and quantum effects could mix together. We plan in the near future to investigate this possibility by making use of a two-dimensional honeycomb lattice model.

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Note added.— During the preparation of this manuscript we became aware of the paper by Parise *et al.* [25] in which our picture is experimentally confirmed.

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