Evidence for "Partial" (Sublattice) Amorphization in $Co(OH)_2$

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Infrared absorption and Raman spectroscopy under pressure document that the O-H bonds of crystalline $Co(OH)_2$ become disordered when the sample is compressed to 11.2 (±0.3) GPa at room temperature. The disorder is reversible on decompression, but involves only the H sublattice: x-ray diffraction shows that the Co-O sublattice of $Co(OH)_2$ retains long-range order between 0 and 30 GPa. The results document a novel form of pressure-induced disordering, sublattice amorphization, and imply that amorphization transitions can be staged, with the crystal → glass transition being achieved through the successive disordering of sublattices. [S0031-9007(97)02520-9]

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Since its discovery in SnI_4 and H_2O ice [1,2], pressure-induced amorphization has been documented for a wide variety of crystalline materials [3–6]. The disordering process is distinct from thermally induced disorder, such as melting and superionic conduction, and is of fundamental interest for understanding order-disorder phenomena in condensed matter, including solid-state amorphization (e.g., radiation induced, or chemical), the stability of crystals, and the nature of dislocation cores [7–9]. The detailed mechanism responsible for pressure-induced (or strain-induced) amorphization remains elusive, however, and more than one type of transition may be involved depending on the initial crystal structure and its stress history. For this reason, it is useful to compare the amorphization achieved in several isostructural compounds [3,5,10].

In the case of $Ca(OH)_2$ portlandite, a reversible crystal → glass transition is observed by x-ray diffraction at 13 (±2.5) GPa [4,11]. At virtually the same pressure, 12 (±2) GPa, the width of the O-H infrared-absorption band increases dramatically and the amplitude of the O-H Raman mode essentially vanishes [11,12]. This broadening is hardly unexpected, as the changes in O-H vibrational modes simply record the disordering of the hydrogen sublattice associated with the amorphization of $Ca(OH)_2$. In contrast, the isostructural $Mg(OH)_2$ brucite does not amorphize, based on a combination of x-ray diffraction, infrared absorption, and Raman spectroscopy to peak pressures of 30–78 GPa [12–16]. Neutron diffraction gives evidence of a decrease in symmetry of the H (or D) sites in $Mg(OH)_2$ and $Mg(OD)_2$ starting at about 5–10 GPa [17,18], but no evidence of pressure-induced amorphization has been found in brucite to date. Because of the small ionic radius of Mg relative to Ca, it is perhaps not surprising that $Mg(OH)_2$ fails to amorphize below 80 GPa.

$Co(OH)_2$ is isostructural with $Mg(OH)_2$ and $Ca(OH)_2$, all having the CdI_2 structure ($P\overline{3}m1$, $Z = 1$) at ambient conditions [19]. The smaller radius of Co, relative to the Mg ion, might lead one to expect that $Co(OH)_2$ should amorphize at pressures above 80 GPa. However, infrared absorption spectra exhibit a rapid (and reversible) broadening of the O-H stretching vibration at 11 (±1) GPa, similar to that observed for $Ca(OH)_2$ [20]. By combining results from x-ray diffraction and Raman spectroscopy with those of infrared spectroscopy, we show that there is indeed a transition in $Co(OH)_2$ near 10 (±2) GPa, but it does not involve disordering of the entire crystal structure.

Experiment.—Polycrystalline $Co(OH)_2$ (Johnson-Matthey Company, Ward Hill, Massachusetts) was loaded into Mao-Bell and Merrill-Bassett diamond cells with anvils having 350 μm culets [21]. Each sample was contained in a 200 μm diameter hole drilled into a spring-steel gasket, and pressure was calibrated via the ruby-fluorescence method [22]. All experiments were carried out at room temperature.

Bomen DA3.02 and Bruker IFS 66V Fourier transform infrared (FTIR) spectrometers, each with a KBr beam splitter and a liquid-N_2 cooled InSb detector, were used for absorption spectroscopy under pressure. In some of the FTIR experiments, an Ar pressure-transmitting medium was used to reduce shear stresses across the sample, with maximum pressure variations of ~1 GPa being found at 50 GPa. Other experiments used CsI as a pressure medium, and exhibited larger pressure gradients, so are described only for pressures below 12 GPa [20]. Complementary high-pressure Raman spectra were obtained with a Dilor OMARS 89 spectrometer. An Ar^+ laser operating at 514.5 nm wavelength and a power of ~20 mW served as the excitation source, focused to a spot ~2 μm in diameter at the sample. Low-fluorescence diamonds and spatial filtering were used to minimize noise, and there was no pressure transmitting medium in these runs.

X-ray diffraction (XRD) patterns of $Co(OH)_2$ were collected at pressure with a Rigaku 12 kW/mm^2 rotating anode source (monochromatized Mo K_α radiation). Diffraction patterns were collected in an angular-dispersive mode using film and analyzed by methods described elsewhere [23]. No pressure medium was used in the XRD experiments, but ≤5% Au, Fe, or Re included with the

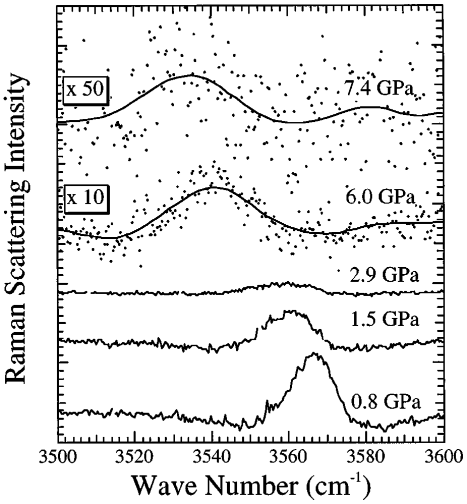

FIG. 1. Representative Raman spectra of the A_{1g} O-H vibrational mode of $Co(OH)_2$ at high pressures and room temperature. All spectral intensities have been normalized. The spectra at 6.0 (±0.2) and 7.4 (±0.3) GPa are shown on an expanded scale for clarity. Smoothed lines were added as visual guides.

sample served as additional calibrants of the pressure and diffraction geometry [24–26].

Results.—Raman spectra, collected both on compression and decompression, show that with increasing pressure the A_{1g} O-H mode decreases rapidly in intensity and increases in width at pressures between 6 and 8 GPa (Fig. 1). We were unable to observe this mode in spectra collected at 8.4 (±0.4) and 9.4 (±0.4) GPa, the highest pressure at which it was observed being 7.4 GPa. Therefore, in terms of the present experiment, the Raman-active O-H mode of $Co(OH)_2$ vanishes near 7.9 (±0.5) GPa.

These results are in good agreement with our observations of the A_{2u} (infrared-active) O-H mode [20], which is found to increase ~(4–5)-fold in width starting at 8–10 GPa (Figs. 2 and 3). The full width at half maximum (FWHM) of the IR mode changes most rapidly around 11.2 (±0.3) GPa, and reaches nearly 200 cm^{-1} by 30 GPa (beyond the range shown in Fig. 3).

The apparent difference in the transition pressures inferred from the disappearance of the Raman mode (~8–10 GPa) and the broadening of the infrared mode (~10–12 GPa) is due to at least two effects. First, Raman scattering is intrinsically a higher-order process than is IR absorption, and can therefore be especially sensitive to changes in bonding character [27]. Second, the IR experiments were carried out under more nearly hydrostatic conditions than were the Raman experiments. Careful work by Duffy *et al.* on a variety of hydroxides (and deuteride) has shown that the O-H Raman intensities tend to be degraded by nonhydrostatic stresses, and the pressure at which Raman modes decrease rapidly in amplitude depends on loading conditions as well as details of spectrometer sensitivity [13]. Therefore, both for intrinsic reasons and because of experimental differences, it is not surprising that the Raman mode vanishes at a pressure slightly lower than that at which the ir band changes most rapidly in width.

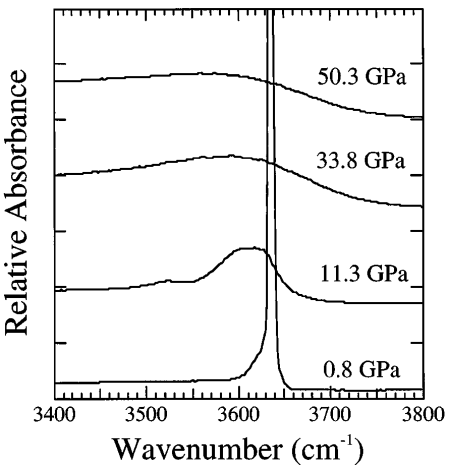

FIG. 2. Representative infrared absorption spectra of the A_{2u} O-H vibrational mode of $Co(OH)_2$ at high pressures and ambient temperature. All spectra have been taken from the same set of experiment on decompression.

Both the broadening of the ir mode and the intensity loss (and broadening) of the Raman mode are indicative of disordering of the O-H bonds within $Co(OH)_2$ [4,11,13,20]. Indeed, the FWHM of the ir mode is

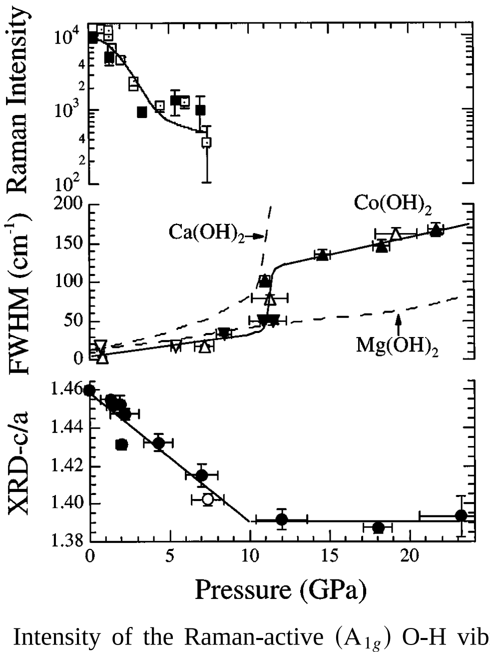

FIG. 3. Intensity of the Raman-active (A_{1g}) O-H vibrational mode in $Co(OH)_2$ are shown as a function of pressure at the top (squares). Full width at half maximum of the absorption due to the infrared-active (A_{2u}) O-H vibrational mode in $Co(OH)_2$ are shown in the middle (triangles) [20]; dashed lines summarize the corresponding infrared absorption-band widths for $Ca(OH)_2$ and $Mg(OH)_2$ which, respectively, do and do not amorphize over the indicated pressure range [12]. The c/a lattice-parameter ratio for $Co(OH)_2$ is displayed as a function of pressure at the bottom (circles). In all cases, closed and open symbols indicate data collected on compression and decompression, respectively.

comparable with values observed for hydrogen-bearing oxide glasses, and for the O-H and O-D vibrations in water [28–30]. At pressures below 11.2 GPa, the FWHM of the IR mode is similar to that of crystalline ice Ih, 20–30 cm^{-1} [29,30]. Above this pressure, however, the FWHM surpasses that of the O-D vibrational width (160 cm^{-1}) and approaches that of the O-H vibrational width (250 cm^{-1}) in liquid water [29,30]. The FWHM of the O-H vibration in $Co(OH)_2$ is presumably lower than that in water because the oxygen atoms are constrained by the ordered Co-O framework. In fact, the spectroscopic changes found for $Co(OH)_2$ at 8–12 GPa are similar to those observed for $Ca(OH)_2$ as the latter undergoes pressure-induced amorphization; there is a dramatic contrast with $Mg(OH)_2$ and $Mg(OD)_2$, which show no such changes in spectra up to ~30 GPa (Fig. 3) [12,13]. Overall, the present Raman spectra reinforce the interpretation of the IR results as indicating that $Co(OH)_2$ undergoes pressure-induced disordering at about 8–12 GPa [20]. Our best estimate of the disordering pressure is 11.2 ($\pm$0.3) GPa based on the quasi-hydrostatic infrared-absorption experiments (Figs. 2 and 3).

X-ray diffraction reveals a different story. As illustrated in Fig. 4, the diffraction patterns show that $Co(OH)_2$ retains crystalline order to pressures of at least 20–30 GPa. Nonhydrostaticity in these runs should only have lowered the amorphization pressure, relative to hydrostatic experiments [10]. Therefore, we can conclude only that, like $Mg(OH)_2$ but unlike $Ca(OH)_2$, $Co(OH)_2$ does not become fully disordered at pressures below 30 GPa.

X-ray diffraction intensities are insensitive to the crystallographic location of the hydrogen ions, however, and only document ordering of the Co-O sublattice. Consequently, the diffraction and vibrational-spectroscopy experiments are not in conflict, as they probe different aspects of the structure of $Co(OH)_2$. Our interpretation of the results is that while the H sublattice becomes disordered at ~11 GPa, the Co-O sublattice remains ordered to much higher pressures. Thus, while the x-ray data show no evidence of disorder, the spectroscopic measurements clearly show that the CdI_2 structure of $Co(OH)_2$ becomes amorphous under pressure via H disordering.

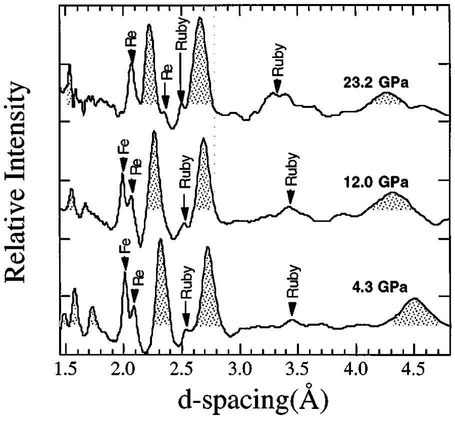

FIG. 4. Representative x-ray diffraction patterns for $Co(OH)_2$ at three different pressures (shaded peaks). Pressure calibrants, ruby and rhenium, and the α phase of iron from the gasket are identified and shown without shading. All patterns are normalized with respect to the $Co(OH)_2$ peaks.

In detail, the x-ray diffraction measurements do show that the relative compression of the unit-cell parameters changes significantly at the disordering transition (Fig. 3). Initially, the c direction is most compressible, due to rapid shortening of the hydrogen bonds between the (c-normal) sheets of Co-O octahedra. This observation is in agreement with the results of a recent neutron diffraction study of $Co(OD)_2$, showing that the O-D bond length remains constant up to 10 GPa and that the c-lattice parameter decreases with increasing pressure [31]. Above 10 GPa, however, this compression mechanism is saturated; apparently, the structure becomes more isotropically compressible as the hydrogen ions are forced into disordered positions between the octahedral sheets. Similar compression behavior has been documented for other hydroxides, with initially rapid compression of the c axis being followed by a more constant value of the c/a ratio as a function of increasing pressure [13].

Disordering of the hydrogen sublattice is compatible with the results of previous studies on other hydroxides [4,11–16]. Neutron diffraction clearly shows that the effect of pressure is to shift H (and D) ions in $Mg(OH)_2$ [and $Mg(OD)_2$] off the threefold site-symmetry axis in the CdI_2 structure [17,18]. There is some controversy about the details, but the existing data suggest the possibility that the O-H (and O-D) bonds take on disordered orientations as the site-symmetry is broken [12,13,17,18]. Similarly, Duffy *et al.* have interpreted spectroscopic measurements as providing evidence for hydrogen disordering in $Mg(OH)_2$ and $Mg(OD)_2$ [13]. In all cases, however, the observed changes for the Mg-hydroxides are minor, and the inferred degree of disordering is thus much less than is documented here for $Co(OH)_2$.

Using Reitveld refinement of $Co(OD)_2$ neutron diffraction data up to 10 GPa, Parise *et al.* showed that the D atoms move from a single threefold symmetric site $2d$ at $(\frac{1}{3}, \frac{2}{3}, z)$ to three equivalent sites $6i$ at $(x, 2x, z)$ with occupation factor $\frac{1}{3}$ with increasing pressure [31]. Parise's model also suggests that the O-D bond length decreases from 2.291 ($\pm$0.005) Å at ambient pressure to 1.95 ($\pm$0.02) Å at 9.5 GPa. The increase in hydrogen bond strength, or decrease in O-H bond length, with increased pressure was also inferred from infrared absorption data [20]. Since the neutron diffraction study was limited to pressures below our proposed hydrogen disordering pressure, it does not record the actual deuterium disordering. However, the shift off the threefold symmetry site appears to herald the initiation of the sublattice disordering documented by our spectra.

In our experiment, there is no evidence for a volume decrease at the disordering transition (Fig. 5). A fit to the second-order Birch-Murnaghan equation of state yields an initial bulk modulus $K_0 = 73.3$ ($\pm$9.5) GPa, assuming

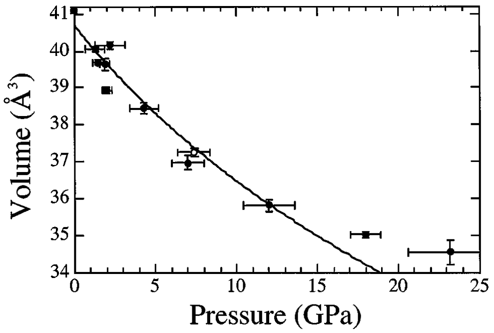

FIG. 5. Co(OH)$_2$ unit-cell volume as a function of pressure, with the solid line being calculated using the second-order Birch-Murnaghan equation of state ($K'_0 = 4$). The deviation of the highest-pressure points from the curve suggests either (or both) that nonhydrostatic effects are important [26] or that a higher-order equation of state may be justified.

a pressure derivative $K'_0 = 4$ [32], with corresponding linear incompressibilities $K_{0a} = 333\ (\pm 74)$ GPa and $K_{0c} = 120\ (\pm 24)$ GPa [4]. These values are self-consistent, in that $K_0^{-1} = 2^*K_{0a}^{-1} + K_{0c}^{-1}$ [33], and are in general agreement with those of other hydroxides [4,14–17,34] in showing that the unit cell of Co(OH)$_2$ is almost three times as compressible along the *c* direction as along the *a* direction. The scatter above 10–15 GPa (Fig. 5) is likely caused by the effects of inhomogeneous and nonhydrostatic stresses across the sample, due both to the conditions under which the sample was loaded and to the effect of the pressure-induced transformation itself.

In the case of Ca(OH)$_2$, the disordering of Ca-O and O-H lattices takes place simultaneously at the amorphization transition (within experimental resolution). However, our new results for Co(OH)$_2$ show that this need not always be the case. Instead, successive disordering of sublattices can take place, ultimately leading to complete amorphization in many cases but not always (as in the present instance). Indeed, pressure-induced amorphization may generally consist of the more-or-less simultaneous occurrence of sublattice disorder. The lack of an observed volume change in the present work suggests that pressure-induced disordering of the hydrogen sublattice need not be a first-order transition. Whether or not sublattice amorphization is generally first order, we note that previous studies have documented the first-order character of some pressure-induced amorphization transitions [1,2,35].

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