Hydrogen Repulsion "Transition" in Co(OD)$_2$ at High Pressure?

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Neutron powder diffraction studies of β-Co(OD)$_2$ to 16 GPa show that the structural changes with pressure are continuous and reveal no evidence for the amorphization of the hydrogen sublattice at 11 GPa previously proposed on the basis of light-scattering and x-ray diffraction studies [Nyugen *et al.,* Phys. Rev. Lett. **78**, 1936 (1997)]. Instead, the changes in the deuterium packing with pressure suggest that the observed anomalies in Raman and infrared data at 11 GPa are the result of structural frustration due to H$\cdots$H repulsion.

Pressure is an excellent variable for probing the nature of bonding in condensed matter since the effects of variation of interatomic distances can be followed continuously in a single system, avoiding the ambiguities inherent in comparisons of different structures at ambient pressure. Furthermore, increasing density is an ideal means of exploring the balance between attractive and repulsive interactions. The hydrogen bond is one of the most studied interactions in the physical and biological sciences [1–3]. Some recent work has highlighted the significant role that H$\cdots$H repulsion [3] may play in H-bonded systems at high pressure [4]. The layered hydroxides with structures related to that of CdI$_2$ provide model systems for the study of this and the O$\cdots$H attraction. Their unique structure (Fig. 1) has hydrogen atoms isolated between layers of the MO$_6$ octahedra, in which the *M* sites are occupied by divalent metal ions (Mn, Fe, Co, Ni, Cd, Mg, Ca). Thus, the dominant interlayer interactions are H$\cdots$O and H$\cdots$H which will vary as the interlayer separation is changed by pressure. The recognition of this has prompted a number of spectroscopic [5–10] and crystallographic studies [9–12].

Spectroscopic studies of *M*(OH)$_2$ hydroxides reveal wide differences in behavior. In Mg(OH)$_2$ the O-H stretching mode remains distinct and its width changes smoothly with pressure [10]. Both Ca(OH)$_2$ [8] and β-Co(OH)$_2$ [6] show strong broadening of this mode at 11 GPa. In Ca(OH)$_2$, the spectroscopic anomaly is accompanied by the loss of the x-ray diffraction pattern, indicating full amorphization of the sample [13]. However, in β-Co(OH)$_2$ *no* sudden change is observed in the x-ray diffraction pattern at 11 GPa [6], which suggests that the process responsible for the broadening of the O-H stretch involves only the hydrogen atoms. As a result, Nguyen *et al.* [6] proposed that β-Co(OH)$_2$ amorphizes

in the H sublattice alone (Fig. 1). We have now studied β-Co(OD)$_2$ under pressure using neutron diffraction, a probe which is much more sensitive than x-ray diffraction to the position of hydrogen or deuterium [14] in the crystalline lattice. [The differences in behavior between H and D forms is known to be very small in systems, such as these, with long H bonds [15], and data were collected up to 16 GPa—well beyond the pressure of the anomalies in β-Co(OH)$_2$ [6].]

Powder diffraction data were obtained from a freshly prepared sample [12] using the Paris-Edinburgh pressure cell [16] at the UK pulsed-neutron source ISIS at the Rutherford Appleton Laboratory. Two loadings with sintered-diamond anvils were used to collect data at 300 K between 0 and 16 GPa on the PEARL beam line. In one loading (loading 1) 5 mol % of NaCl was incorporated into the sample to act as an intensity calibrant. In a second loading (loading 2) a pure sample was used. In addition,
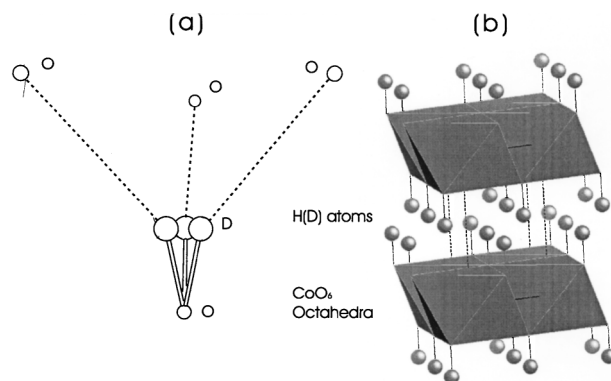

FIG. 1. (a) Hydrogen bond geometry in (b) the layered structure of the CdI$_2$-related β-Co(OD)$_2$. The D atoms in (a) are disordered over the three sites shown. This detail is omitted in (b).

data collected previously on the POLARIS beam line [12] with tungsten-carbide anvils (loading 3) were analyzed by the same procedure. For loadings 1 and 2 some data were taken with the thrust axis of the cell turned 90° to the incident beam. The lack of change in relative intensities between this and the standard cell orientation demonstrates that both samples were well randomized powders [17]. Care was taken to correct the data for the absorption of the cell and the anvils [18], and the data were used for Rietveld refinement [19] using the program GSAS [20].

The crystal structure refinement started from the accepted model for the CdI_2-related hydroxides [21] at ambient pressure (Fig. 1) with Co at $(0, 0, 0)$, and O and D at $(\frac{1}{3}, \frac{2}{3}, z)$ in space group $P\bar{3}m1$, with $z \sim 0.2$ for O and ~ 0.4 for D. The parameters varied were the z coordinates of O and D, the D site occupancy, and two anisotropic displacement (thermal) parameters for D, one perpendicular and one parallel to the c axis, to model both the anisotropy of the D thermal motion and the expected movement of D off the $2d$ (threefold) sites [Fig. 1(a)] with increasing pressure [12]. This gives the simplest unconstrained description of the D-atom distribution. The thermal parameters of Co and O were fixed to their ambient pressure values; this is physically reasonable and was shown in tests not to bias the results. Figure 2 shows the D-site occupancies obtained to 16 GPa [22]. There is a slight overestimate of $\sim 10\%$ on average, attributable to small uncertainties in the deuteration level and attenuation corrections, but the occupancy is clearly constant across the whole range. This conclusion can also be deduced from simple inspection of the raw data. Figure 3 shows the excellent fits obtained with the standard model at 8 GPa and, in the lower inset, at 16 GPa; the upper inset shows the clear misfits in relative peak intensities if the D-atom scattering is removed from the (coherent) diffraction pattern, as amorphization would require. Also, in those cases where NaCl was used as an intensity calibrant, the intensity ratios of peaks arising from the sample and the NaCl do not change to 16 GPa, indicating no loss of overall scattering from the β-Co(OD)$_2$. Thus, the standard model with fully occupied deuterium sites fits equally well above and below the spectroscopic discontinuity, and the principal structural change with pressure is a smoothly increasing displacement of the D atoms from the three-
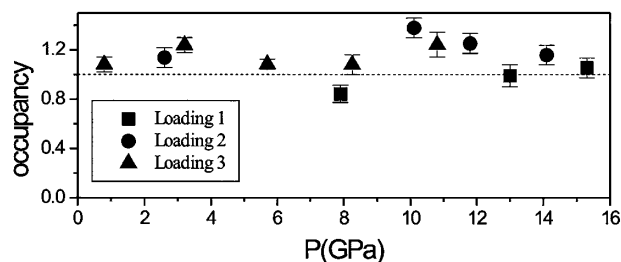
fold axes (Fig. 4)—as reported in previous investigations up to 10 GPa [11,12] and found in recent *ab initio* studies of Ca(OH)$_2$ and Mg(OH)$_2$ [23]. Our primary conclusion is thus that the D-site occupancy remains constant through the spectroscopic discontinuity, which rules out the H(D) sublattice amorphization previously proposed. True amorphization would require the occupancy to fall to zero.

What else could be the cause of the strong broadening of the OH stretching bands of β-Co(OH)$_2$ at ~ 11 GPa in both the infrared and Raman experiments? As Nguyen *et al.* [6] observe, the changes in the Raman and IR spectra are too large to be due to increases in hydrogen bond strength or lengthening of the O-H bond; at ~ 11 GPa the H$\cdots$O distance is about 2.2 Å, a distance not associated with strong hydrogen bonds [1,2]. But our results show no structural discontinuity (Figs. 2 and 4). Nguyen *et al.* [6] observe that the rapid increase in IR-band width is associated with the flattening of the c/a ratio above 11 GPa. [This flattening is also observed in deuterated β-Co(OD)$_2$ at about the same pressure (Fig. 4) and at the same value of c/a; this is further strong evidence that the H and D materials display very similar behavior.] The abrupt changes in the spectroscopic data thus contrast with a continuous variation of the structure with pressure. Consideration of the placement of the H(D) atoms on sites around the threefold axis, their packing, and the changes in packing with pressure suggest a plausible mechanism to reconcile this difference.

Two different configurations for H(D) sites displaced from the threefold axis have been proposed at ambient pressure, both of which use threefold disordered $x, 2x, z$ sites. Megaw *et al.* [24] argued for a location with $x < \frac{1}{3}$ (x less than a third, XLT, sites, shown as filled squares
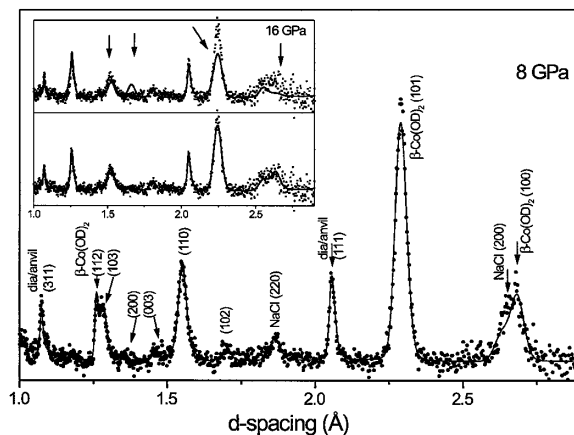

FIG. 3. Results of Rietveld structural refinements. The dots represent the observed data and the solid lines the best fit. The main figure shows the fit obtained at 8 GPa using the standard model described in the text. The lower plot in the inset shows a fit with the same model to data collected at 16 GPa. The upper inset plot shows the best "fit" to the same data with the D occupancy fixed at zero to model the proposed sublattice amorphization [6]. The arrows mark the largest misfits.
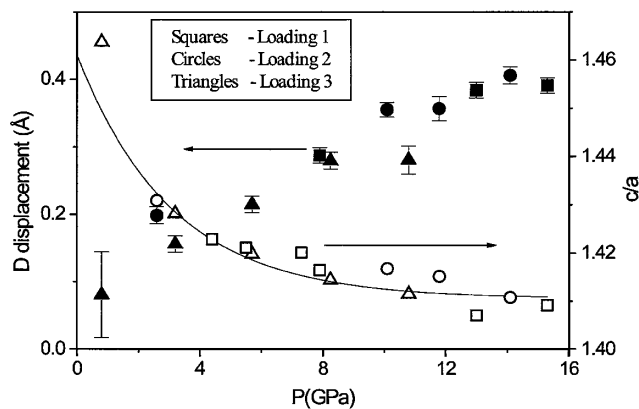

FIG. 2. Variation in the occupancy for the D sites in β-Co(OD)$_2$ determined by Rietveld structural refinement.

FIG. 4. The pressure dependence of the c/a ratio of β-Co(OD)$_2$ (open symbols, right hand scale) and the displacement of the D atoms from the threefold axis as a function of pressure (filled symbols, left hand scale). The line is a guide to the eye for the variation of c/a.

in the inset of Fig. 5) which gives the most favorable Co-O-H(D) tetrahedral angles. Alternatively, sites with $x > \frac{1}{3}$ (x greater than a third, XGT, sites, shown as open squares) minimize the H(D)$\cdots$O distances and give the strongest hydrogen bonding. Recent single-crystal neutron diffraction studies of Ca(OH)$_2$ and Mg(OH)$_2$ suggest that at ambient pressure the H(D) atoms are located on these XGT sites [21].

There is known to be a minimum contact distance for nonbonded H(D) atoms. In molecular systems the value is around 2 Å [3]. In ionic systems it may be as low as 1.8 Å [3,25]. At ambient pressure, we find that the only D$\cdots$D distances longer than 1.8 Å in the XGT model
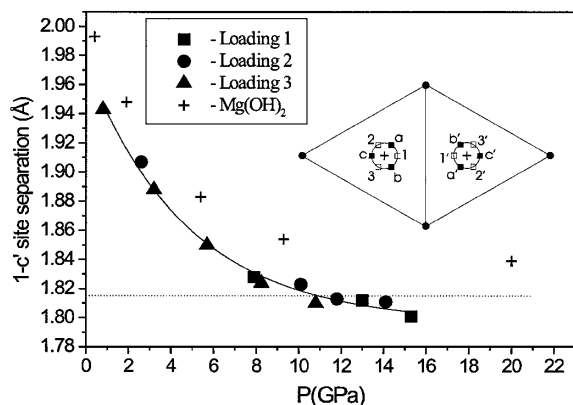

FIG. 5. The inset shows the structure of β-Co(OD)$_2$ projected along the c axis. The cobalt atoms are shown as small filled circles. The crosses show the location of the oxygen atoms on the threefold axes. The XGT sites (see text) are shown as open squares and the XLT sites as filled squares. The circles through these sites represent the loci of constant deuterium atom displacement from the threefold axes. The main plot shows the pressure dependence of the distance from XGT site 1 to XLT site c' for β-Co(OD)$_2$ and Mg(OH)$_2$. The solid line is a guide to the eye for β-Co(OD)$_2$, and the dashed line represents the most plausible minimum H(D)$\cdots$H(D) distance.

are from sites 1 to 2' and 3' (1.87 Å), 2 to 3' or 3 to 2' (2.17 Å), and 2 to 2' or 3 to 3' (2.2 Å). However, each XGT site is displaced off the threefold axis directly towards one of the three nearest-neighbor groups of D sites (Fig. 5, inset). Thus, any arrangement of XGT sites *must* involve a substantial number of the 1 to 2' type contacts with the short 1.87 Å lengths—even at ambient pressure the H atoms in β-Co(OD)$_2$ are densely packed.

The deuterium displacement from the threefold axis and its rate of increase with pressure (Fig. 4) are independent of the site model used. A displacement of D from the threefold sites tends to decrease the 1 to 2' (or 3') type of contacts over and above the effect of the general compression of the lattice and so this distance reduces rapidly and reaches 1.8 Å by ~3 GPa. Since the exclusive use of XGT sites must involve 1 to 2' (or 3') contacts, an arrangement with only XGT sites is thus not possible above 3 GPa if we take 1.8 Å as the minimum possible D$\cdots$D distance. The XLT model, where the direction of D displacement is between two adjacent groups of D sites, allows longer D$\cdots$D distances. The only possible D$\cdots$D distances for this model are from a or b to c' (2.06 Å) and from c to c' (2.35 Å). These distances are almost pressure independent—the increasing displacement of the deuterium from the threefold axis (Fig. 4) approximately compensates for the overall compression of the structure. However, the greater length of these distances results in inefficient D packing, and accurate drawings of possible networks show that exclusive use of XLT sites cannot give an extended structure with D$\cdots$D distances greater than 1.8 Å. Instead, a mixture of XLT and XGT sites is required, and the drawings show they can be linked only by contacts of the type 1 to c'.

The pressure dependence of the 1 to c' distance is shown in Fig. 5. The values were obtained from the measured lattice parameters and the D displacements from the three-fold axis, based on the assumption that the O-D distance remains constant at the value found at ambient pressure (0.95 Å). This assumption is in line with expectation for long H bonds and is supported by experimental studies of ice VIII and NaOD [26]. As can be seen, the 1 to c' distance approaches the minimum value of ~1.8 Å by 10 GPa, and so it is no longer possible for the mixed XLT and XGT model to give *any* arrangement with acceptable D$\cdots$D distances at pressures beyond this limit. Instead, to achieve an extended arrangement, the deuterium atoms must—we suggest—be distributed over a range of positions lying on circles of constant displacement from the threefold axis (see Fig. 5). In such an arrangement the location of the D atoms is determined by the need to maintain D$\cdots$D distances above the minimum value and D$\cdots$D repulsion overcomes effects such as H bonding and ion-dipole interactions, which favor the XGT and XLT sites. Positioning of the D atoms anywhere around the circles in Fig. 5 leads to a range of D$\cdots$O distances and Co-O-D angles, and such a variation of local hydrogen

environments would be expected to produce a broadening of the O-H(D) stretch mode.

Hence, it appears probable that the reported spectroscopic anomaly [6] is the result of the H atoms being forced to be distributed over a range of general sites by the need to achieve sufficiently large $H \cdots H$ distances. Further support for this interpretation comes from molecular dynamics studies by Raugei *et al.* [23] which conclude that structural frustration of the H atoms is the cause of the broadening of the O-H stretch mode. The change in the H(D) location to general sites provides a plausible explanation of the spectroscopic anomaly at 11 GPa, and a minimum $H \cdots H$ distance in $Co(OH)_2$ of ~ 1.81 Å appears to allow a unified interpretation of the spectroscopic and diffraction data.

Nguyen *et al.* [6] contrast the behavior of $Co(OH)_2$ with that of icostructural $Mg(OH)_2$ whose O-H stretch shows no sudden increase in width up to 30 GPa [8,10]. Figure 5 shows the pressure dependence of the 1 to c' distance in $Mg(OH)_2$, calculated using the same procedure as for $Co(OD)_2$. It remains above 1.81 Å up to 20 GPa, and falls to ~ 1.8 Å only somewhere above 30 GPa—the maximum pressure currently explored [8,10]. A spectroscopic transition similar to that found in $Co(OH)_2$ may thus occur in $Mg(OH)_2$ above this point.

Our data and the spectroscopic studies [6–9] provide indications of the importance of repulsive effects at high pressure. We conclude that these effects induce a highly disordered (but crystalline) proton arrangement at high pressure in $Co(OD)_2$ which can account for its observed spectroscopic anomalies. The family of CdI_2-structure layered hydroxides are particularly good systems in which to study such effects since $H \cdots H$ and $O\text{-}H \cdots O$ dominate the interactions between layers, and the level of frustration experienced by the structure will vary strongly with unit cell size and compressibility. Our conclusions invite further experimental and modeling work to explore the effects of hydrogen repulsion and understand the balance between the $H \cdots H$ and $O\text{-}H \cdots O$ interactions.

[1] W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids* (W. A. Benjamin, Inc., New York, 1968).

[2] G. A. Jeffrey, *An Introduction to Hydrogen Bonding* (Oxford University Press, Oxford, 1997).

[3] H. Savage, Water Sci. Rev. **2**, 67–148 (1986).

[4] S. K. Sikka, In. J. Pure Appl. Phys. **35**, 677 (1997); S. K. Sikka, Curr. Sci. **73**, 195 (1997).

[5] Q. Williams and L. Guenther, Solid State Commun. **100**, 105 (1996).

[6] J. H. Nguyen, M. B. Kruger, and R. Jeanloz, Phys. Rev. Lett. **49**, 1936 (1997).

[7] J. H. Nguyen, M. B. Kruger, and R. Jeanloz, Phys. Rev. B **49**, 3734 (1994).

[8] M. B. Kruger, Q. Williams, and R. Jeanloz, J. Chem. Phys. **91**, 5910 (1989).

[9] M. Catti, G. Ferraris, and A. Pavese, Phys. Chem. Miner. **22**, 200 (1995).

[10] T. S. Duffy *et al.,* Am. Mineral. **80**, 222 (1995).

[11] J. B. Parise *et al.,* Am. Mineral. **79**, 193 (1994).

[12] J. B. Parise *et al.,* Phys. Chem. Miner. **25**, 130 (1998); J. B. Parise *et al.,* Rev. High Pressure Sci. Technol. **7**, 211 (1998).

[13] C. Meade and R. Jeanloz, Geophys. Res. Lett. **17**, 1157 (1990).

[14] Deuteration eliminates the high background given by incoherent neutron scattering from hydrogen atoms.

[15] H. D. Lutz *et al.,* J. Mol. Struct. **351**, 205 (1995); H. D. Lutz, *Hydroxide Ions in Condensed Materials—Correlation of Spectroscopic and Structural Data* (Springer-Verlag, Berlin, Heidelberg, 1995); H. D. Lutz and C. Jung, J. Mol. Struct. **404**, 63 (1997).

[16] J. M. Besson *et al.,* Physica (Amsterdam) **180+181B**, 90 (1992); R. J. Nelmes *et al.,* Trans. Am. Crystallogr. Assoc. **29**, 19 (1993).

[17] ISIS 1996 Annual Report, Vol. I, p. 61; Rutherford Appleton Laboratory Report No. RAL-TR-96-050, 1996.

[18] R. M. Wilson *et al.,* Nucl. Instrum. Methods Phys. Res., Sect. A **3354**, 145 (1995).

[19] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).

[20] A. C. Larson and R. B. von Dreele, Los Alamos National Laboratory Report No. LAUR-86748, 1986 (unpublished).

[21] L. Desgranges, G. Calvarin, and G. Chevrier, Acta Crystallogr. B **52**, 82 (1996); L. Desgranges *et al.,* Acta Crystallogr. B **49**, 812 (1993).

[22] Pressures for loadings 1, 2, and 3 were calculated from the measured unit cell volume of $Co(OD)_2$ and the measured equation of state [12] extrapolated beyond the measured range (0–10 GPa) where appropriate.

[23] S. Raugei, P. L. Silvestrelli, and M. Parrinello (private communication).

[24] H. D. Megaw, *Crystal Structures: A Working Approach* (W. B. Sanders Company, Philadelphia, 1973); Rev. Mod. Phys. **30**, 96 (1958).

[25] W. H. Baur, Acta Crystallogr. B **48**, 745 (1992).

[26] R. J. Nelmes *et al.,* Rev. High Pressure Sci. Technol. **7**, 1138 (1998); J. S. Loveday *et al.,* J. Phys. Condens. Matter **41**, 597 (1996).