

Hydrogen Thermal Motion in Calcium Hydroxide: Ca(OH)₂

BY L. DESGRANGES,* D. GREBILLE AND G. CALVARIN

Laboratoire de Chimie-Physique du Solide, URA CNRS 453, Ecole Centrale de Paris,
92295 Châtenay-Malabry CEDEX, France

G. CHEVRIER

Laboratoire Léon Brillouin, CEA-CNRS, CEN Saclay, 91191 Gif-sur-Yvette CEDEX, France

AND N. FLOQUET AND J.-C. NIEPCE

Laboratoire de Réactivité des Solides, URA CNRS 23, Université de Bourgogne BP 138,
21004 Dijon CEDEX, France

(Received 25 March 1993; accepted 7 April 1993)

Abstract

Calcium hydroxide, Ca(OH)₂, $M_r = 74$, trigonal, $P\bar{3}m1$, $a = 3.589$ (8), $c = 4.911$ (14) Å, $V = 54.8$ (4) Å³, $D_x = 2.26$ g cm⁻³ at room temperature, $Z = 1$, $\lambda = 0.8330$ (5) Å, $\mu = 1.195$ cm⁻¹, $F(000) = 9.028$ fm, final $R = 0.018$, $wR = 0.019$, for 105 unique reflections, at 80 K; $R = 0.025$, $wR = 0.027$, for 211 unique reflections, at room temperature. The structure of calcium hydroxide has been refined using neutron data collected at 80 K and at room temperature. Thermal motion of the H atom has been refined with anharmonic thermal-motion parameters at room temperature and at 80 K. Corresponding probability-density functions have been calculated. A three-site disordered model for the H atom is also proposed and discussed. These new structural models allow us to give a new interpretation of the apparent shortness of the O—H distance reported in the literature.

Introduction

The structure of calcium hydroxide has been refined by Busing & Levy (1957) by neutron diffraction on the basis of a first model proposed by Bernal & Megaw (1935). The positions of Ca, O and H atoms are respectively 1(*a*) (0, 0, 0), 2(*d*) (1/3, 2/3, $z_O = -0.2341$) and 2(*d*) (1/3, 2/3, $z_H = -0.4248$) in space group $P\bar{3}m1$ (trigonal symmetry) (Fig. 1*a*). Ca(OH)₂ is a layered compound; the layers are built with distorted edge-sharing CaO₆ octahedra. Each hydroxyl group is linked to three Ca atoms in its layer and surrounded by three other hydroxyl groups belonging to the adjacent layer (Fig. 1*b*).

* On leave from Laboratoire de Réactivité des Solides, URA CNRS 23, Université de Bourgogne, France.

However, the above authors reported an unusual thermal motion for the H atom. At room temperature as well as at 130 K, the values of the anisotropic thermal parameters β_{ij} of the H atom are very large in the (*xy*) plane and consequently, thermal motion exhibits a large anisotropy; moreover, the calculated O—H distance is short (0.936 Å) compared with usual values. More recently, another neutron single-crystal diffraction study was reported from room temperature to 570 K (Chaix-Pulchery, Pannetier, Bouillot & Niepce, 1987); it confirmed the large

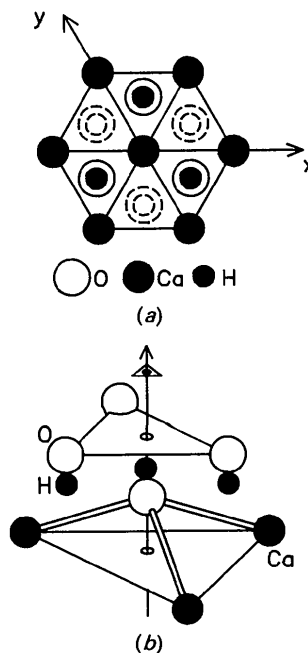


Fig. 1. Schematic representation of the structure of calcium hydroxide Ca(OH)₂. (*a*) Projection along the *c* axis. (*b*) Environment of a hydroxyl group OH.

values and the anisotropy of thermal parameters of the H atom. Some other studies on isostructural compounds also reported the same behaviour: $\text{Mg}(\text{OH})_2$ (Zigan & Rothbauer, 1967), $\text{Ni}(\text{OD})_2$ (Greaves & Thomas, 1986).

In order to interpret why the calculated O—H distance is too short, Busing & Levy (1957) suggested, referring to Hexter & Dows (1956), that the H atom undergoes a 'riding motion': it moves on a portion of a sphere centred on the O atom by keeping a constant O—H distance. Thus, in this model, the calculated O—H distance from the mean atomic coordinates of O and H atoms does not correspond to the actual O—H distance, but to the mean projection on the *c* axis of this distance. These authors also proposed a mathematical expression for the H-atom distribution with an 'umbrella' shape. Until now, this model has never been confirmed by means of a structural refinement.

The purpose of this work is to improve the description of H-atom thermal motion by means of anharmonic parameters. Classical harmonic thermal parameters are not adequate to take into account an umbrella-shaped distribution. In contrast, an anharmonic description makes it possible; however, the data collection has to be of high quality (Kuhs, 1992). Thermal motion can then be described by probability density function (PDF) maps calculated from the refined thermal parameters (see, for example, Zucker & Schultz, 1982).

From optimized neutron data collections at 300 and 80 K, structural refinements of $\text{Ca}(\text{OH})_2$ were carried out, using anharmonic thermal parameters. The calculated PDF's show preferential directions of thermal motion and suggest a split-atom model. Refinements in this last model were also carried out and the results obtained are discussed and compared.

Experimental

$\text{Ca}(\text{OH})_2$ single crystals were prepared by slow diffusion of calcium chloride solution into a sodium hydroxide solution (Ashton & Wilson, 1927). The crystals are transparent hexagonal prisms (axis of the prism = *c*) with sizes up to 8 mm. A well shaped crystal with height 2.78 mm and a hexagonal base with sides of 1.7 mm was selected for the neutron experiment.

Neutron four-circle P110 diffractometer, Orphee Reactor (CEN-Saclay), Cu(220) monochromator, $\lambda = 0.8330(5) \text{ \AA}$; 20 centred reflections for lattice parameters and orientation matrix ($32.5 < 2\theta < 48.5^\circ$), space group $P\bar{3}m1$.

Data collection: $3 < 2\theta < 75^\circ$, ω scans; $75 < 2\theta < 120^\circ$, ω - θ scans. 41 steps, 2.5 or 5 s step^{-1} as a function of $1/\sigma(I)$ of scan widths according to

the instrumental resolution ($17.3 - 58.4 \tan \theta + 95.9 \tan^2 \theta$)°; index range: *h* - 8 to 8, *k* - 8 to 8, *l* 0 to 10.

Two sets of data were measured: room temperature (standard reflections 004 and 122 stable over 4 d within 2.2%, no decay or crystal movements, 945 reflections measured); and 80 K (standard reflections 122 and 113 stable over 4 d within 4.1%, no decay or crystal movements, 772 reflections measured of which 442 reflections retained, $2\theta < 80^\circ$, because of the intensity fluctuations of the background created by the cryostat).

Integrated intensity determined from resolution-adapted profile measurement of the peaks; background determined with an average of the first and the last six steps of each side; 211 unique reflections ($R_{\text{int}} = 0.026$), of which 188 with $F^2 > 3\sigma(F^2)$ considered observed at room temperature; 105 unique reflections ($R_{\text{int}} = 0.033$), of which 88 with $F^2 > 3\sigma(F^2)$ considered observed at 80 K.

Lorentz-polarization and absorption corrections; anisotropic correction assuming secondary-extinction type I with Lorentzian distribution (Becker & Coppens, 1974*a,b*, 1975); Full-matrix least-squares refinement, computer program *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983), neutron-scattering lengths: 4.90, 5.805 and -3.7409 fm for Ca, O and H atoms, respectively.

Refinements

The data were found to be strongly affected by extinction as already reported (Busing & Levy, 1957; Chaix-Pulchery *et al.*, 1987) and as expected from the crystalline quality of the sample. (001) reflections were preferentially affected by extinction, which can be assigned to an anisotropic distribution of mosaic spread in relation with the layered structure of $\text{Ca}(\text{OH})_2$. Various extinction models were tested with the formalism of Becker & Coppens (1974*a,b*, 1975). The best results were obtained by assuming a Lorentzian anisotropic mosaic distribution (type I). In an initial stage, the six parameters of the extinction tensor were refined; the results showed that the tensor is nearly isotropic in the *ab* plane with only two independent parameters g_{11} and g_{33} . Final structural refinements were performed with fixed values for g_{11} and g_{33} . These values slightly differ at 80 K and at room temperature: $g_{11} = 0.32$ (2), $g_{33} = 0.010$ (1) and $g_{11} = 0.28$ (2), $g_{33} = 0.020$ (3), respectively.

Harmonic thermal-motion refinements

The atomic coordinates z_{O} and z_{H} of the structural model of Bernal & Megaw (1935) and anisotropic harmonic thermal parameters were refined (nine

refinement parameters). Results are given in Table 1 and compared with those of the literature. The agreement between the different studies is rather good, except for some discrepancies for thermal parameters. These differences can be explained by different treatments of extinction, which is strongly correlated to thermal motion; it must also be noted that the data-collection quality, particularly the $(\sin\theta_{\max})/\lambda$ range, takes a prominent part in the accurate determination of these values.*

Anharmonic thermal-motion refinements

The refined anharmonic parameters were developed in a Gram-Charlier expansion up to fourth order. Since the site symmetry of the H atom is $3m$, there are three third-order and four fourth-order independent anharmonic parameters. The number of refined parameters is 16. Results are given in Table 2. The only statistically meaningful anharmonic parameters (value $>3\sigma$) are c_{113} , c_{333} , d_{1111} and d_{3333} at 80 K, and c_{111} , c_{113} and d_{1111} at room temperature.

The corresponding PDF's at 80 K and at room temperature were calculated. A section of the PDF at room temperature in the xz plane and at $y = \frac{2}{3}$ is illustrated in Fig. 2(a). It shows one maximum located on the ternary axis at $z = -0.434$. This value differs from the refined value of the z_H parameter (-0.4224), indicated by a cross on the figure. This difference is due to third-order anharmonic parameters which displace the maximum of the PDF from the centre of the ellipsoid associated with harmonic thermal motion. Consequently, one may understand that the actual O—H distance is not given by the classical formula $(z_O - z_H)c$ [$0.927(5)$ Å], but must be calculated from the location of the maximum of the PDF [$0.98(1)$ Å]. The convex shape of the PDF in the xz plane is due to the c_{113} parameter.

A section of the PDF at room temperature in the xy plane and at $z = -0.43$ is represented in Fig. 2(b). In this plane, the c_{111} and d_{1111} parameters slightly modify the isotropic harmonic PDF, giving it three directions of preferential thermal motion, symbolized by arrows in Fig. 2(b). These three directions are the $(x, -x, z_H)$ and symmetry-related directions. They point towards the O atom of the adjacent layer.

The calculated PDF of the H atom at 80 K exhibits large negative areas at the centre of the distribution and abnormal and important fluctuations along the z axis. These results do not allow us

Table 1. Results of the structural refinement for the model of one harmonic site for the H atom and comparison with previous studies

Thermal parameters are given in $\text{Å}^2 \times 10^{-4}$.

	80 K		130 K		Room temperature	
	This work	(a)	(a)	(b)	This work	(b)
z_O	-0.2341 (1)	-0.2346 (2)	-0.2341 (3)	-0.2340 (3)	-0.2337 (1)	-0.2337 (1)
z_H	-0.4285 (3)	-0.4280 (2)	-0.4248 (6)	-0.4256 (6)	-0.4256 (1)	-0.4256 (1)
Ca	u_{11} 16 (2)	38 (5)	89 (9)	83 (4)	42 (1)	42 (1)
	u_{33} 62 (4)	78 (6)	158 (11)	193 (13)	145 (2)	145 (2)
O	u_{11} 32 (2)	49 (4)	92 (6)	106 (3)	82 (1)	82 (1)
	u_{33} 49 (3)	66 (4)	117 (6)	149 (6)	106 (2)	106 (2)
H	u_{11} 346 (4)	419 (10)	536 (17)	528 (10)	510 (5)	510 (5)
	u_{33} 107 (5)	103 (8)	170 (12)	205 (16)	157 (3)	157 (3)
R	0.019	0.033	0.048	0.038	0.028	0.028
wR	0.020	—	—	0.027	0.029	0.029
Independent reflections	105	53	53	103	211	211

References: (a) Busing & Levy (1957); (b) Chaix-Pulchery *et al.* (1987).

Table 2. Results of the structural refinement for the model of one anharmonic site for the H atom at 80 K and at room temperature

Thermal parameters are given in $\text{Å}^2 \times 10^{-4}$.

	80 K	Room temperature
	z_O	-0.2336 (2)
z_H	0.4293 (7)	-0.4224 (4)
Ca	u_{11} 0.0012 (2)	0.0044 (1)
	u_{33} 0.0060 (3)	0.0146 (2)
O	u_{11} 0.0031 (1)	0.0083 (1)
	u_{33} 0.0030 (4)	0.0106 (1)
H	u_{11} 0.0338 (9)	0.0480 (9)
	u_{33} 0.0013 (16)	0.0160 (8)
	c_{111} -0.003 (5)	-0.041 (6)
	c_{333} -0.017 (6)	0.004 (1)
	c_{113} 0.012 (2)	0.024 (2)
	d_{1111} -0.040 (17)	-0.068 (14)
	d_{3333} -0.030 (4)	-0.001 (2)
	d_{1113} -0.007 (3)	-0.008 (3)
	d_{1133} 0.003 (3)	-0.001 (2)
R	0.016	0.025
wR	0.018	0.026

to give any physical significance to the set of refined parameters at 80 K. This can be assigned to an instability of the thermal parameters in the z direction.

At room temperature as at 80 K, the anharmonic treatment highlights the limits of the riding-motion model in describing the H-atom thermal motion. At room temperature, the calculated PDF presents a curvature towards the corresponding O atom, as predicted by the riding motion model, but it is not isotropic in the xy plane as expected from the corresponding 'umbrella' shape distribution. At 80 K, the riding motion cannot be refined satisfactorily. For this reason, a disordered three-site model was tested at both temperatures in order to describe the H-atom thermal motion.

Three-site split-atom model

In this model, the H atom occupies with an equal probability three symmetry-related positions around the $2(d)$ average position. These positions have been chosen on the three preferential directions of thermal motion evidenced in the anharmonic description at

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71071 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [(CIF reference: DU0369)]

room temperature (Fig. 2). One of these positions is schematically represented in Fig. 3. Refinements were performed with the data collected at room temperature and at 80 K and with anisotropic harmonic parameters for all atoms. The number of structural parameters was 12. The results are given in Table 3.

The PDF's were calculated at room temperature and at 80 K by summing the three thermal-motion ellipsoids of each site.

Sections of the PDF at room temperature in the xz plane at $y = \frac{2}{3}$ and in the xy plane at $z = -0.43$ are represented in Figs. 4(a) and 4(b), respectively. The corresponding PDF's appear to be similar to those calculated with the anharmonic thermal-motion model (Fig. 2). These results prove the validity of the calculated PDF, which is equally reproduced with

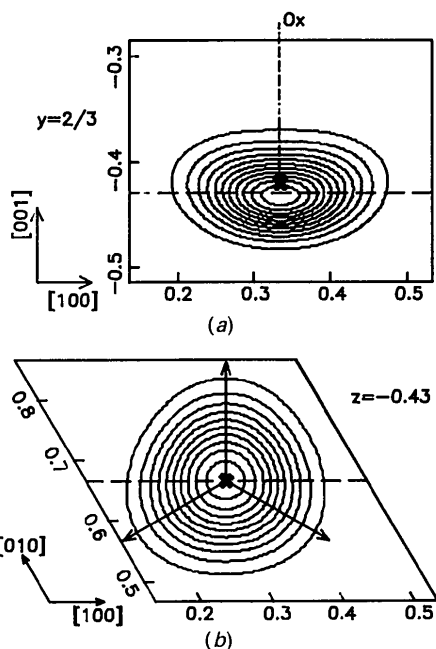


Fig. 2. Sections of the PDF of the H atom in the anharmonic thermal-motion model. (a) In the xz plane. (b) In the xy plane.

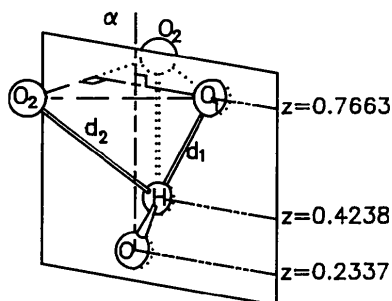


Fig. 3. Schematic representation of a disordered site for the H atom in a split-atom model.

Table 3. Results of the structural refinement for the model of three harmonic sites for the H atom at 80 K and at room temperature

Thermal parameters are given in $\text{\AA}^2 \times 10^{-4}$.			
		80 K	Room temperature
O	z_O	-0.2342 (1)	-0.2337 (1)
H	$x_H, y_H/2$	0.3599 (12)	0.3606 (9)
	z_H	-0.4275 (3)	-0.4238 (2)
Ca	μ_{11}	0.0015 (2)	0.0041 (1)
	μ_{33}	0.0061 (3)	0.0145 (2)
O	μ_{11}	0.0031 (1)	0.0083 (1)
	μ_{33}	0.0044 (4)	0.0105 (1)
H	μ_{11}	0.0204 (16)	0.0353 (11)
	μ_{33}	0.0113 (5)	0.0162 (3)
	μ_{12}	0.0136 (6)	0.0187 (6)
	μ_{13}	0.0014 (3)	0.0025 (5)
R		0.018	0.025
wR		0.019	0.027

two different models (one anharmonic site or three harmonic sites).

Sections of the PDF at 80 K in the xz plane at $y = \frac{2}{3}$ and in the xy plane at $z = -0.43$ are represented in Figs. 5(a) and 5(b), respectively. These are different from those at room temperature. The general shape is still convex, but now the maximum of the PDF, which is on the $2(d)$ ($\frac{1}{3}, \frac{2}{3}, z_H$) position at room temperature, splits into three symmetry-related maxima around this average position. These maxima do not correspond exactly to the three H-atom sites defined by the x_H and y_H parameters; this is because of the overlap of the PDF's associated with each independent site. It is interesting here to note that the three sites for the H atom in this split-atom model are the same at room temperature and at

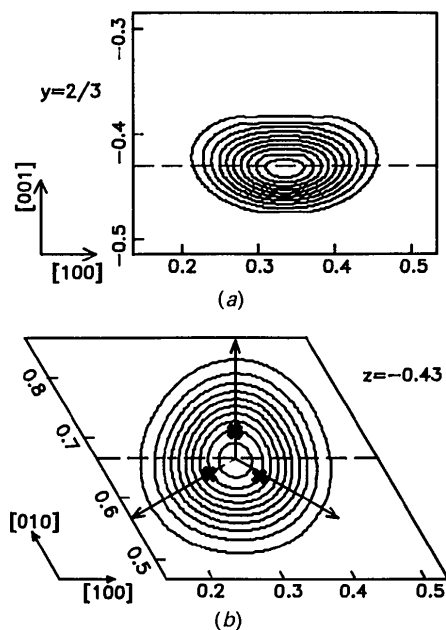


Fig. 4. Sections of the PDF of the H atom at room temperature in the disordered harmonic model. (a) In the xz plane. (b) In the xy plane.

80 K, as proved by the value of the x_{H} parameter at both temperatures (Table 3).

A comparison of the respective agreement factors R and wR obtained with an anharmonic model or with a split-atom model cannot allow us to discriminate between the two hypotheses. They are similar in both cases. The first model has a slightly larger number of refinement parameters. But among these parameters, the results prove that only three are really significant, which reduces the number of effective refinement parameters. Under these conditions, an accurate interpretation of the R factors is questionable and cannot be a sufficient criterion.

Discussion and conclusions

All the models tested provide us with a new description of the thermal motion of the H atom in calcium hydroxide.

First, our results show that the 'riding motion' proposed by Busing & Levy (1957) is a good approximation, but is not sufficient to describe the actual PDF's of the H atom.

The corresponding 'umbrella-shape' distribution implies a convex PDF which should be compatible with a constant O—H distance: This distance is now bigger than the apparent O—H distance calculated from the results of a classical harmonic description of the structure. Moreover, this PDF should be

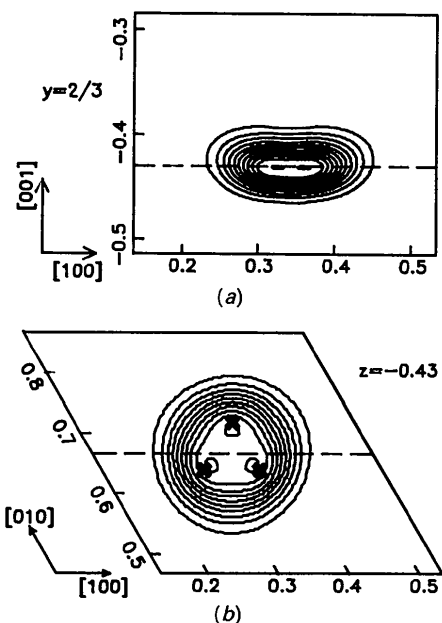


Fig. 5. Sections of the PDF of the H atom at 80 K in the disordered harmonic model. (a) In the xz plane. (b) In the xy plane.

isotropic in the xy plane, with a maximum on the $2(d)$ ($\frac{1}{3}, \frac{2}{3}, z_{\text{H}}$) position. This model should be valid whatever the temperature.

However, the calculated PDF's at room temperature and at 80 K differ from these predicted features. At room temperature the curvature of the PDF towards the related O atom is confirmed, but three directions of preferential thermal motion are demonstrated in the xy plane by two different and independent models: an anharmonic thermal motion model and a disordered three-site model. At 80 K, the only significant PDF was obtained with the disordered model and exhibits a relative minimum on the $2(d)$ site with three maxima around this average position, and consequently a trigonal anisotropy in the xy plane.

Second, our results show that an anharmonic description of thermal motion is not sufficient to explain the evolution of the H-atom thermal motion between room temperature and 80 K.

In a classical interpretation of an anharmonic behaviour, thermal motion should be characterized by smaller displacement amplitudes and by decreasing anharmonic parameters with decreasing temperature. The anharmonicity should be enhanced only for higher temperatures and should be a correction of the basic harmonic motion of the fundamental levels of vibration (see, for example, Zucker & Shulz; 1982). We have seen that the anharmonic description is available at room temperature and gives a satisfactory image of the PDF of the H atom with the c_{111} , c_{113} and d_{1111} anharmonic parameters. But the same model should also be available at 80 K with smaller values of these same parameters, or even with only harmonic parameters. Our results do not confirm this analysis; the concerned anharmonic parameters decrease, but new parameters c_{333} and d_{3333} are now necessary for the convergence of the refinement, and are responsible for the physically meaningless corresponding PDF. The behaviour of these parameters can be interpreted by comparison with the PDF's derived from a three-site disordered model. The existence of an absolute maximum of the PDF on the $2(d)$ site at room temperature and of a relative minimum of the corresponding PDF on the same site at 80 K means two different qualitative distribution shapes. At room temperature, the anharmonic model can satisfactorily describe the shape of the PDF; it does not work at 80 K. A harmonic description is possible but with a very large and unsatisfactory value of the u_{11} parameter.

Consequently, the H-atom motion is shown to be more satisfactorily described by a three-site disordered model both at room temperature and at 80 K. The site location is found to be the same at both temperatures. The only difference is the larger value of the amplitudes of thermal motion at room

temperature. The decrease of these values with decreasing temperature allows a better discrimination of the three sites at 80 K. Nevertheless, these sites are very close to each other (0.30 Å) and it is not possible to conclude from our results on a static or dynamic occupation of the sites, even at low temperature. The calculated O—H distance is almost constant whatever the temperature. The relatively short value of this distance (0.95 Å) implies a strong O—H bond and is compatible with the high value of the O—H stretching frequency observed by infrared and Raman spectroscopy (Dawson, Hadfield & Wilkinson, 1973).

Thus, our structural results show that a three-site model for the H atom is able to describe the H-atom thermal motion between room temperature and 80 K. Such a model has already been suggested by Megaw (1958). According to this author, the tendency of oxygen to form tetrahedral bounds would force the CaOH angle to a value around 109°. However, the three corresponding sites are not those obtained in the present study, but would be located in the opposite direction of the preferential thermal-motion directions shown in Fig. 2(b). Using our data sets, Megaw's model has also been tested, and has been proved to be less satisfactory than the present model (Desgranges, 1992). A new argument can be given to vindicate the three-site model. In this model, each H-atom site has a nearer O atom in the adjacent layer (see Fig. 3). The position of such a site may be the result of a compromise between the covalent bonding of the H atom with the O atom in the O—H bond, and the Coulombic interaction of the electro-positive H atom and the electronegative O atom of the adjacent layer.

The existence of three sites for the H atom should also have specific consequences for the physical properties and characterizations of calcium hydroxide. This model can also be tested by other experimental methods. Studies are now in progress to determine the possible influence of this disorder on the infrared and Raman spectra of Ca(OH)₂.

The authors are indebted to Professor F. Holuj of the Department of Physics, University of Windsor, Canada, for kindly providing Ca(OH)₂ single crystal samples. We wish to express our gratitude to the CNRS and the Région Bourgogne for a stipend granted to one of us (LD).

References

- ASHTON, F. W. & WILSON, R. (1927). *Am. J. Sci.* **5**, 209–218.
 BECKER, P. J. & COPPENS, P. (1974a). *Acta Cryst.* **A30**, 129–147.
 BECKER, P. J. & COPPENS, P. (1974b). *Acta Cryst.* **A30**, 148–153.
 BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
 BERNAL, J. D. & MEGAW, H. D. (1935). *Proc. R. Soc. London Ser. A*, **151**, 384–420.
 BUSING, W. R. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.
 CHAIX-PULCHERY, O., PANNETIER, J., BOUILLOT, J. & NIEPCE, J. C. (1987). *J. Solid State Chem.* **67**, 225–234.
 DAWSON, P., HADFIELD, C. D. & WILKINSON, G. R. (1973). *J. Chem. Phys.* **34**, 1217–1225.
 DESGRANGES, L. (1992). Thesis, Univ. de Bourgogne, France.
 GREAVES, C. & THOMAS, M. A. (1986). *Acta Cryst.* **B42**, 51–55.
 HEXTER, R. M. & DOWS, D. A. (1956). *J. Chem. Phys.* **25**, 504–509.
 KUHS, W. H. (1992). *Acta Cryst.* **A48**, 80–98.
 MEGAW, H. D. (1958). *Rev. Mod. Phys.* **30**, 96–99.
 ZIGAN, F. & ROTHBAUER, R. (1967). *Neues Jahrb. Mineral. Monatsh.* pp. 137–143.
 ZUCKER, U. H., PERENTHALER, E., KUHS, W. H., BACHMANN, R. & SCHULZ, H. (1983). *J. Appl. Cryst.* **16**, 358.
 ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* **A38**, 568–576.

Acta Cryst. (1993). **B49**, 817–822

Phase Transition of Zeolite NH₄-Rho to a High-Temperature but Low-Volume Form

BY ANNA BIENIOK AND WERNER H. BAUR

Institut für Kristallographie und Mineralogie, Johann Wolfgang Goethe-Universität, Senckenberganlage 30, D-60054 Frankfurt/Main, Germany

(Received 28 August 1992; accepted 7 April 1993)

Abstract

An *in situ* X-ray powder diffraction experiment evaluated by a Rietveld-type refinement shows that NH₄-Rho zeolite, Cs(NH₄)₁₁Al₁₂Si₃₆O₉₆, exists in two forms when heated in vacuum. The high-temperature

form has at 573 K: $a = 14.4803(1)$ Å, $D_x = 1.688$ g cm⁻³, and when quenched at 295 K: $a = 14.4024(6)$ Å, $D_x = 1.716$ g cm⁻³; the low-temperature form after prolonged cooling in vacuum at 295 K gives $a = 14.8168(2)$ Å, $D_x = 1.576$ g cm⁻³. For all three cases: space group $\bar{I}43m$, $Z = 1$, $M_r =$