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 electropositive 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. (1974*a*). *Acta Cryst.* **A30**, 129–147.
BECKER, P. J. & COPPENS, P. (1974*b*). *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 NH_4-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 NH_4-Rho zeolite, $Cs(NH_4)_{11}Al_{12}Si_{36}O_{96}$, 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 $I\bar{4}3m$, $Z = 1$, $M_r =$

3087.48, Cu $K\alpha$, $\lambda = 1.54056$ Å. Thus the high-temperature form at 573 K has a volume 6.7% smaller than the low-temperature form at 295 K. At higher temperatures the framework contracts because the NH_4 groups which at lower temperatures block the collapse of the single-eight rings of TO_4 (T = Si, Al) tetrahedra assume new positions located in the larger pores of the framework. The transformation between the two forms is reversible and is of the reconstructive type.

Introduction

The crystal structure of zeolite Rho can be described as being built of interconnecting double-eight rings (D8R) of silicate and aluminate coordination tetrahedra of an average chemical composition $Si_{12}Al_4O_{32}$ (Robson, Shoemaker, Ogilvie & Manor, 1973). In the centrosymmetric form (space group $Im\bar{3}m$), the D8R is essentially round. In the non-centrosymmetric form of zeolite Rho (space group $I\bar{4}3m$), the two single-eight rings (S8R) within the D8R are approximately elliptical with their long axes at right angles to each other. Because this elliptical distortion of the D8R is allowed by the topology of the framework of zeolite Rho, the framework is not only very flexible, but it is also collapsible (Baur, 1992). The collapse can be blocked if a cation occupies the central position in the plane of the S8R. This has been observed in Sr-Rho, where the locations of the Sr atoms are responsible for the differences in the cell constants of the low- and high-temperature forms (Bieniok & Baur, 1991*a*,*b*).

Upon exchange with NH_4NO_3, an ammonium zeolite Rho of approximate composition $Cs(NH_4)_{11}Al_{12}Si_{36}O_{96}$ can be obtained from the prepared Na,Cs zeolite Rho (Robson, Shoemaker, Ogilvie & Manor, 1973). The ammonium form in turn is the precursor to the hydrogen form of zeolite Rho, obtained by calcination of ammonium Rho. The crystal structure of ammonium Rho was determined by McCusker (1984). It crystallizes in the non-centrosymmetric space group $I\bar{4}3m$ with a cell constant a of 14.821 Å (at 373 K). Subsequently, the crystal structures of two more samples of ammonium Rho were determined (Fischer *et al.*, 1989). These also crystallized in space group $I\bar{4}3m$, but their cell constants were clearly smaller than reported by McCusker (1984): 14.526 (at room temperature) and 14.425 Å (at 11 K). Both of these samples were deammoniated by calcination and the ammonium groups were at least partly replaced by deuterium atoms. One of the samples was reammoniated by reloading it with ND_3. Thus neither of these ammonium Rho zeolites represented a pure ammonium form. In NH_4-Rho zeolite with a large cell constant, the NH_4 group is located in the plane of the S8R, just as Sr ions are situated in the corresponding position of the S8R in the low-temperature form of Sr-Rho (Bieniok & Baur, 1991*a*,*b*). Therefore, could ammonium Rho with small cell constants simply be the quenched high-temperature form of ammonium Rho?

Experimental

The sample of zeolite Rho used for our work is from the batch of NH_4-Rho that was deep-bed calcined and studied by neutron diffraction by Fischer *et al.* (1986), where experimental details of the synthesis and cation exchange can be found. An evacuable heating device on a powder diffractometer was used for an *in situ* study of the crystal structure of dehydrated NH_4-Rho over the temperature range 573–150 K. Both the temperature and surrounding atmosphere (or vacuum conditions) were controlled during and between the collection of X-ray data. As known from NMR results, the dehydration is completed at 353 K in vacuum, while the deammoniation process begins at 423 and is completed only at 673 K (Vega & Luz, 1987). Upon heating in high vacuum (10^{-6} mbar) to 573 K two phases coexist in the sample. One disappears after heating the sample for 3 d at 573 K. Powder X-ray diffraction data were collected at this temperature (HT) and the crystal structure was determined using Rietveld methods. Following the nomenclature introduced by Fischer *et al.* (1986), the HT sample is called NH_4-Rho/573/573 (NH_4 exchanged Rho, no other molecules in the pores, heated to 573 K, measured diffraction data at 573 K). Upon cooling a new phase (LT) with larger cell constants appears and at room temperature (295 K) it is predominant in the sample. This LT sample is NH_4-Rho/573/295, because it was heated to 573 K and subsequently measured at 295 K (the diffraction data of this cooled sample were refined). The appearance of this phase after cooling shows that the coexistence of the two phases during heating is not due to the different ammonium content. It was impossible to transform all of the sample into the LT form. Even when cooling it to 150 K a small amount of the HT form remained. After several days the experiment was terminated and diffraction data were collected from a sample consisting of 92% of the LT phase and of 8% of the HT phase of NH_4-Rho (the percentages are based on volume % derived from the ratio of the scale factors in the Rietveld refinement). All measurements were performed during one long evacuation period in order to be certain that all water molecules had been evacuated and could not enter the sample again. The various treatments in terms of temperature and atmosphere to which our samples and those of McCusker (1984) and Fischer *et al.* (1989) were subjected are shown together with their unit-cell constants in Fig. 1.

Diffraction data were collected for both refinements from 5 to 105° in 2θ. The profile of the HT form was uneventful beyond 90° and was not used. Data below 16° (HT form) and 15° (LT form) were omitted because the shapes of the peaks could not be fitted with the functions available in our program. This is even visible up to about 30° in 2θ (Fig. 2). The structure refinements converged with the agreement factors of 9.83% for the weighted-profile R value and 2.74% for the structure (Bragg) R value of the HT form at 573 K, and 10.88 and 3.71% for the LT form at 295 K [the definitions of the R values are according to Hill & Howard (1986)]. In the case of the LT sample the 8% fraction of the HT phase was treated as a second phase. Only the scale factor, the cell constant and the fractional coordinates of the atomic positions of the second phase were varied, while the temperature factors and the occupancy factors were held constant in the refinement. For details of the experimental conditions and of the refinement see Table 1. The parameters resulting from the refinement and the interatomic distances and angles are listed in Tables 2 and 3. The observed and calculated powder diagrams are shown in Fig. 2.* The following computer programs were used in the course of the study: Hill & Howard's (1986) program for Rietveld-type refinements, *STRUPLO*90 (Fischer, le Lirzin, Kassner & Rüdinger, 1991) for the crystal structure plots and *SADIAN*90 (Baur & Kassner, 1991) for the calculation of bond distances and angles.

Table 1. *Experimental conditions, crystallographic data and definitions used in data refinement*

Sample designations	NH_4-Rho/573/573 (HT)	NH_4-Rho/573/295 (LT and HT)
Wavelength of radiation (Å)	Cu $K\alpha$, 1.54056, monochromatized on graphite (002) (secondary)	
Scan speed (° min^{-1})	0.15	0.10
Range in 2θ (°)	16–90	15–105
Step width (°)	0.02	0.02
Data-collection temperature (K)	573	295
Data-collection pressure (mbar)	10^{-6}	10^{-6}
Space group	$I\bar{4}3m$	$I\bar{4}3m$
Cell constant (Å)	14.4803 (1)	14.8168 (2) LT 14.4024 (6) HT LT/HT = 91.7%/8.3%
R values R_p (%)	7.52	8.66
R_{wp} (%)	9.83	10.88
R_{exp} (%)	2.06	1.76
R_I (%)	2.74	3.71 LT, 6.83 HT

Table 2. NH_4-*Rho*/573/573 (*HT, first line*) *and* NH_4-*Rho*/573/295 (*LT, second line*) *positional parameters in fractional coordinates, isotropic temperature factors* B (Å^2), *number of atoms per unit cell* N, *Wyckoff positions and site symmetry*

The e.s.d.'s are given in parentheses following the values in units of the least significant digit.

		x	y	z	B	N	Wyckoff position*	Site symmetry*
Si/Al	HT	0.2718 (2)	0.1220 (2)	0.4230 (2)	2.6 (1)	48	48(*h*)	1
	LT	0.2632 (2)	0.1136 (2)	0.4134 (2)	1.7 (1)	48		
O(1)	HT	0.2104 (3)	0.0364 (3)	0.3884 (4)	2.8 (2)	48	48(*h*)	1
	LT	0.2080 (4)	0.0222 (4)	0.3900 (4)	2.5 (2)	48		
O(2)	HT	0.2175 (4)	*x*	0.3983 (6)	3.5 (2)	24	24(*g*)	..*m*
	LT	0.2020 (4)	*x*	0.3827 (8)	2.1 (2)	24		
O(3)	HT	0.1292 (3)	*x*	0.6155 (5)	2.8 (2)	24	24(*g*)	..*m*
	LT	0.1392 (4)	*x*	0.6162 (6)	3.1 (2)	24		
Cs	HT	0	0	0.534 (1)	4.7	1.13 (2)	12(*e*)	2.*mm*
	LT	0	0	0.520 (4)	3.0	0.58 (3)		
N(1)	HT	−0.022 (2)	0.080 (4)	0.176 (4)	6.0	4.3 (5)	48(*h*)	1
	LT	0	0	0.399 (2)	3.0	10.0 (4)	12(*e*)	2.*mm*
N(2)	HT	0.212 (2)	*x*	0.161 (3)	6.0	6.2 (3)	24(*g*)	..*m*

* From *International Tables for Crystallography* (1983, Vol. A).

Results

Both the high-temperature and the low-temperature forms of NH_4-Rho crystallize in the non-centrosymmetric space group $I\bar{4}3m$. At 573 K the lattice constant of the HT modification is 14.4803 (1) Å. At 295 K the lattice constant of this phase is lowered to 14.4024 (6) Å (a volume reduction of 1.6%) while the predominant LT phase shows a large unit cell with a = 14.8168 (2) Å. The

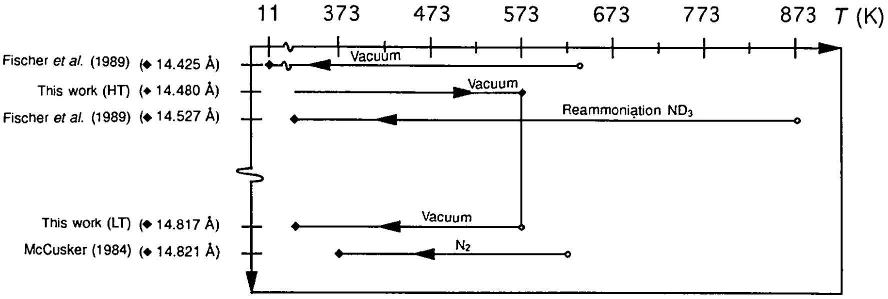

Fig. 1. Diagrammatic representation of the various pretreatment conditions in terms of temperatures and atmospheres (identified at the cooling lines) to which our sample and those of McCusker (1984) and Fischer *et al.* (1989) were subjected, shown together with their unit-cell constants at data-collection temperature (filled squares). All samples were heated (temperatures indicated by open circles) before diffraction data were collected.

---

* Lists of observed and calculated intensities have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71074 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH0025]

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *in* NH$_4$-*Rho*/573/573 (*HT*) *and in* NH$_4$-*Rho*/573/295 (*LT*)

	HT	LT
	T—O	*T*—O
T—O(1)	1.606 (5)	1.620 (7)
T—O(3)	1.623 (6)	1.643 (7)
T—O(2)	1.630 (7)	1.657 (7)
T—O(1)	1.669 (6)	1.668 (7)
⟨*T*—O⟩	1.632	1.647

	HT		LT	
	O—*T*—O	O—O	O—*T*—O	O—O
O(1)—O(3)	107.4 (3)	2.602 (6)	111.3 (3)	2.693 (8)
O(1)—O(2)	108.6 (3)	2.628 (7)	109.0 (4)	2.668 (8)
O(1)—O(1)	108.8 (3)	2.663 (7)	108.0 (3)	2.660 (8)
O(3)—O(2)	111.9 (3)	2.696 (7)	109.5 (4)	2.694 (9)
O(3)—O(1)	108.5 (3)	2.671 (6)	103.5 (4)	2.601 (8)
O(2)—O(1)	111.5 (4)	2.728 (8)	115.5 (5)	2.812 (10)
	T—O—*T*	*T*—*T*	*T*—O—*T*	*T*—*T*
T—O(1)—*T*	134.6 (3)	3.021 (4)	133.3 (4)	3.019 (4)
T—O(2)—*T*	140.3 (5)	3.068 (4)	142.2 (7)	3.135 (4)
T—O(3)—*T*	145.0 (3)	3.096 (4)	146.5 (4)	3.147 (4)
Weighted mean *T*—O—*T*	138.6		138.8	

	HT		LT
2 × Cs—O(3)	2.897 (8)	2 × Cs—O(3)	3.25 (3)
4 × Cs—O(1)	3.290 (7)	4 × Cs—O(1)	3.37 (2)
2 × Cs—O(3)	3.419 (11)	2 × Cs—O(3)	3.55 (3)
N(1)—O(3)	3.47 (5)	2 × N(1)—O(3)	2.926 (6)
N(1)—O(2)	3.51 (6)	4 × N(1)—O(1)	3.102 (6)
N(1)—O(1)	3.71 (6)		
2 × N(2)—O(2)	2.82 (3)		
2 × N(2)—O(1)	3.13 (3)		

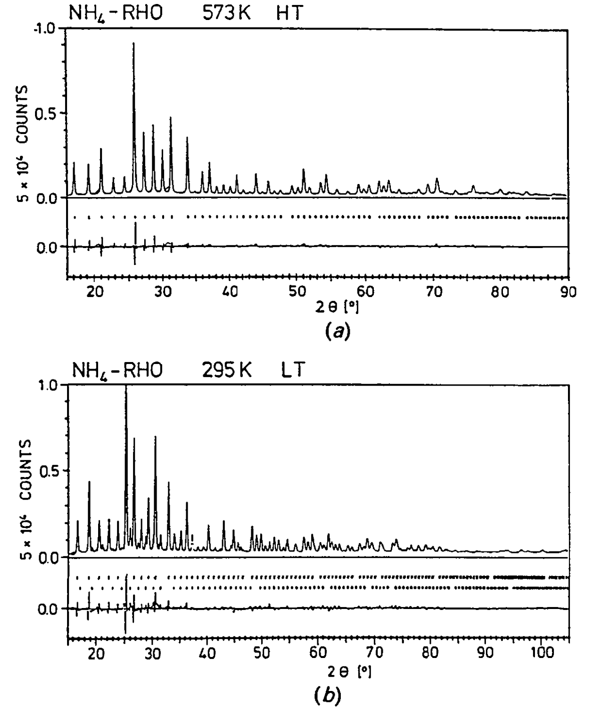

Fig. 2. Powder patterns, diagrams of the (*a*) HT form measured at 573 K in vacuum, observed and calculated intensities, tick marks at the positions of the Bragg peaks and difference plot; (*b*) LT form measured at 295 K in vacuum, observed and calculated positions, tick marks for the LT form (92% of sample, upper row) and for the HT form (8% of sample, lower row), and difference plot.

transformation is reversible. Both phases investigated here may be partly deammoniated when one keeps in mind the results of Vega & Luz (1987); however, the ammonium ion content as deduced from the refined population parameters, does not bear this out.

At room temperature, dehydrated NH$_4$-Rho has an aluminosilicate framework consisting of elliptically distorted double-eight rings (D8R) arranged on the faces of a cube. The long axes of the elliptical eight rings are perpendicular to each other within each D8R unit. The effective pore opening (PS) measures 3.13 Å and the ellipticity factor (EL) is 1.45 [for the definitions of PS and EL see Bieniok & Baur (1991*a*,*b*)]. Of the possible 12 positions in the plane of the single-eight rings, that is on the eight-sided faces of the D8R, a total of 10.0 (4) are occupied by NH$_4$ groups (the occupancy is derived from a refinement of the population parameters). Each NH$_4$ ion is surrounded within the plane of the S8R by two O(3) atoms at a distance of 2.926 (6) Å and by four O(1) atoms at 3.102 (6) Å. Nearly 10% of the centers of the D8R units are occupied by caesium ions, which had withstood all attempts at being exchanged. There should be 1.1 Cs atoms present per unit cell (Fischer *et al.*, 1986). We find the same number in the refinement of the HT data, but not in the refinement of the LT data (Table 2); we cannot explain the discrepancy. The fact that only ten instead of 12 NH$_4$ groups were located in our sample may be partly due to the residual Cs content and partly to incipient deammoniation of the sample. The model of the room-temperature (LT) structure as found here agrees essentially with the crystal structure of NH$_4$-Rho as described by McCusker (1984) and which is based on measurements at a temperature of 373 K and in an atmosphere of dry nitrogen.

In the high-temperature form, when compared with our low-temperature form, the ammonium groups are located in positions outside the D8R unit (Fig. 3). One part [6.2 (3) groups per unit cell, as determined by a refinement of the population factor] is located near the S6R unit with two distances each of 2.82 (3) to 3.13 (4) Å to the framework O atoms. The other 4.3 (5) NH$_4$ groups per unit cell are positioned in the α-cage of the Rho framework at distances of 3.47 (5), 3.51 (6) and 3.71 (6) Å (one each) to the framework O atoms. In both cases, the contacts to the framework are very one-sided. The elliptic deformation of the eight ring is stronger (EL = 1.68), the pore size measures only 2.59 Å. The highly distorted framework has a drastically reduced unit-cell volume, which is 6.7% smaller than the volume of the LT phase after cooling to room temperature. A similar transformation of the framework at high temperature was previously observed in zeolite Sr-Rho (Bieniok & Baur, 1991*a*,*b*).

Discussion

In the LT form the presence of the ammonium groups in the centers of the plane of the single-eight rings hinders their further deformation and a further collapse of the framework. In the HT form of zeolite Rho all the ammonium groups migrate out of the S8R and the blocking obstacle is removed. The Cs ions remaining in the centers of the double-eight ring may additionally contribute to the contraction of the D8R units in the HT form. Thus, we get the unusual result that a high-temperature modification has a distinctly lower unit-cell volume than the low-temperature form of the same chemical compound. It must be emphasized that the sample was kept in vacuum throughout the experiments. Thus, the phase transition is not connected with chemical changes, such as de- and rehydrations. The transformation is of the displacive type only as far as the framework is concerned. Since the coordinations around the ammonium groups are changing and N—H···O bonds must be broken and reformed, the transformation is really of the reconstructive type [we use here Buerger's (1972) terminology]. Usually one would expect large cations residing in a framework to have larger coordination numbers in the high-temperature form. In our case the NH_4 groups [position N(1)] are six coordinated in the LT form, and three [N(1)] and four coordinated [N(2)] in the HT form. However, here again the larger coordination number is associated with the larger unit-cell volume, which for NH_4-Rho happens to be the LT form.

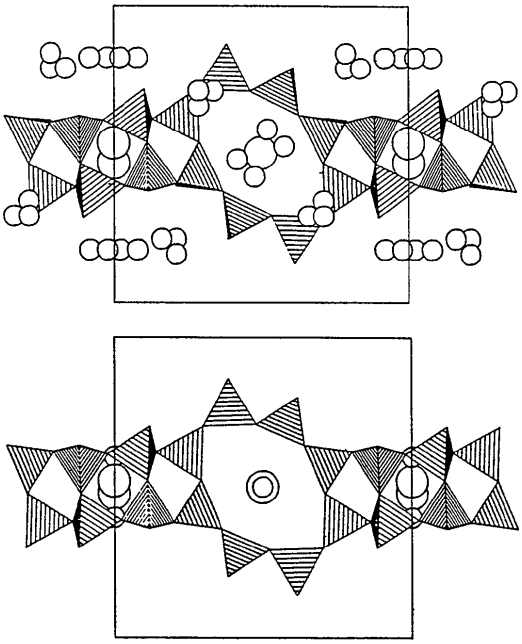
Fig. 3. Polyhedral representation of the D8R unit in the HT form (upper plot) and the LT form (lower plot) of NH_4-Rho. Each tetrahedron stands for a TO_4 group, with T (=Si, Al) in the center of the tetrahedron and O atoms at the corners. The large circles represent the Cs atoms, the small circles the locations of the NH_4 ions on the N(1) and N(2) positions. In the center is a view of one half of a D8R (just one ellipse is visible) seen from the top, while to the left and right are side views of the double-eight rings.

Similar to the HT structure of NH_4-Rho are the two crystal structures of reammoniated Rho and partly deammoniated Rho described by Fischer *et al.* (1989). In these two cases the different structures were believed to exist as a result of different conditions of preparation. The experiment described here may actually indicate that a quenched form of the HT structure was described in the case of the 14.42 Å structure of Fischer *et al.* (1989). This, however, is only a hypothesis since the chemical compositions of the samples studied by Fischer *et al.* were certainly different and no *in situ* experiments were performed by them.

The mean distance ($Si_{0.75}Al_{0.25}$)—O within the coordination tetrahedron around the T site (T = Si, Al) would be expected to have a length of about 1.648 Å. The mean distances observed for the HT and the LT forms are reasonably close to this value, especially if one considers the e.s.d.'s of the individual distances and the spread in individual T—O bond lengths. Similar values were found in the refinement of neutron powder diffraction data of an Na,Cs zeolite Rho (Baur, Bieniok, Shannon & Prince, 1989).

Concluding remarks

An *in situ* X-ray powder diffraction experiment shows that NH_4-Rho zeolite exists in two forms in vacuum. The HT form has at 573 K a volume 6.7% smaller than the LT form after cooling to 295 K. At higher temperatures the framework contracts because the NH_4 groups, which at lower temperatures block the collapse of the single-eight rings of TO_4 tetrahedra, assume new positions located in the larger pores of the framework. The transformation between the two forms is reversible and is of the reconstructive type.

We thank Dr D. Kassner for discussions and advice, Privatdozent Dr R. X. Fischer for a critical review of an earlier version of this paper, and Mrs A. Haake for drafting the figures.

References

Baur, W. H. (1992). *J. Solid State Chem.* **97**, 243–247.
Baur, W. H., Bieniok, A., Shannon, R. D. & Prince, E. (1989). *Z. Kristallogr.* **187**, 253–266.
Baur, W. H. & Kassner, D. (1991). *Z. Kristallogr.* (Suppl. 3), 15.
Bieniok, A. & Baur, W. H. (1991*a*). *Mater. Sci. Forum*, **79–82**, 721–726.

Bieniok, A. & Baur, W. H. (1991*b*). *J. Solid State Chem.* **90**, 173–177.

Buerger, M. J. (1972). *Sov. Phys. Crystallogr.* **16**, 959–968.

Fischer, R. X., Baur, W. H., Shannon, R. D., Parise, J. B., Faber, J. & Prince, E. (1989). *Acta Cryst.* C**45**, 983–989.

Fischer, R. X., Baur, W. H., Shannon, R. D., Staley, R. H., Vega, A. J., Abrams, L. & Prince, E. (1986). *J. Phys. Chem.* **90**, 4414–4423.

Fischer, R. X., le Lirzin, A., Kassner, D. & Rüdinger, B. (1991). *Z. Kristallogr.* (Suppl. 3), 75.

Hill, R. J. & Howard, C. J. (1986). Australian Atomic Energy Commission Report No. M112, p. 15. AAEC (now ANSTO), Lucas Heights Research Laboratories, New South Wales, Australia.

McCusker, L. (1984). *Zeolites*, **4**, 51–55.

Robson, H. E., Shoemaker, D. P., Ogilvie, R. A. & Manor, P. C. (1973). In *Molecular Sieves. Advances in Chemistry Series* No. 121, edited by W. M. Meier & J. B. Uytterhoeven, pp. 106–115. Washington, DC: American Chemical Society.

Vega, A. J. & Luz, Z. (1987). *J. Phys. Chem.* **91**, 365–373.

Acta Cryst. (1993). B**49**, 822–825

Determination of the Anharmonicity Constant of GaAs by Means of the Bijvoet Relation of the Weak (666) Reflection

By Ullrich Pietsch and Katrin Paschke

Fachbereich Physik der Universität Potsdam, Am Neuen Palais 10, *D-O-*1571 *Potsdam, Germany*

and Klaus Eichhorn

Institut für Kristallographie der Universität (*TH*) *Karlsruhe, Kaiserstrasse* 12, *D-W-*7500 *Karlsruhe, Germany*

(*Received* 18 *January* 1993; *accepted* 16 *April* 1993)

Abstract

As a result of the influence of anomalous dispersion the weak (*hhh*) and ($\bar{h}\bar{h}\bar{h}$) reflections of the zinc blende structure differ from each other. At large scattering vectors this difference, described by the Bijvoet relation B, depends solely on the size of the anharmonic force constant β. It can be determined by measuring B near the K-absorption edge of any constituent. This experiment was performed for the (666) and ($\bar{6}\bar{6}\bar{6}$) reflections of GaAs between $\lambda = 0.90$ and 0.97 Å using synchrotron radiation. Outside the extended X-ray absorption fine-structure spectroscopy region the integrated intensities decrease in a different manner with increasing λ for both reflections measured at '*umweganregung*' free azimuthal positions. Under the assumption of $\beta_{\rm Ga} = -\beta_{\rm As}$ and using the measured wavelength dependence of B, the anharmonicity constant is evaluated to $\beta = -1.75\,(0.15) \times 10^{-17}$ J Å^{-3} which is nearly the same as that for germanium.

Introduction

Because of its technological importance GaAs is one of the most thoroughly investigated semiconductors. It crystallizes in the zinc blende structure and its chemical bond is dominated by the covalent overlap of bonding orbitals and the electronic charge exchange between the valence shells (covalent–ionic bond). Since most of the ground-state properties are due to the valence electron density (VED) of the material, the latter has been studied by various theoretical and experimental methods. However, various discrepancies still exist between the calculated VED and the experimental density determined by Fourier transformation of highly accurate X-ray structure amplitudes (Pietsch, Tsirelson & Ozerov, 1986). This is due to the restricted consideration of the complicated many-electron system by various theoretical approaches and by experimental limits. The accuracy of the experimental VED is presently restricted by an incomplete data set, which is known up to the copper limit [$q = 4\pi(\sin\theta/\lambda) \leq 4\pi(0.64)$ Å^{-1}], and by the limited knowledge of the anharmonicity correction (Pietsch, 1993). Because of the close proximity of gallium to arsenic in the Periodic Table the weak reflections of the type $h + k + l = 4n + 2$ (*hkl* – Miller indices, $n = 0, 1, 2\ldots$) – which depend on the difference in scattering power of Ga and As – are very sensitive to the redistribution of valence electrons (bond charge) caused by the chemical bond. The weak scattering power of this type of reflection justifies the application of the kinematic scattering theory for the evaluation of the structure amplitude, $|F(hkl)|$, from the measured integrated intensity, $I(hkl)$ (Bilderback, 1975; Pietsch, 1981). Both the bond charge and the anharmonic

Acta Crystallographica Section B
ISSN 0108-7681 ©1993