RIETVELD REFINEMENT AND FOURIER-TRANSFORM INFRARED SPECTROSCOPIC STUDY OF THE DICKITE STRUCTURE AT LOW TEMPERATURE

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Abstract—The full structure of dickite from St. Claire, Pennsylvania, including hydrogen atoms, was refined in space group Cc using time-of-flight neutron powder diffraction data obtained at 12 K and Rietveld refinement/difference-Fourier methods ($R_{wp} = 2.62\%$, reduced $\chi^2 = 1.915$, 113 variables, $a = 5.1474(6)$Å, $b = 8.9386(10)$Å, $c = 14.390(2)$Å, and $\beta = 96.483(1)°$). The non-hydrogen structure is essentially identical to published structures for dickite, but the hydrogen positions are distinct. The inner hydroxyl group is approximately parallel to the (001) plane, inclined by 1.3° towards the tetrahedral sheet. Contrary to published low-temperature infrared (IR) spectra, there is no evidence that dickite possess lower symmetry at low temperatures although there is tentative evidence for statistical occupancy of H3 on more than one site. Low-temperature IR spectra of St. Claire and Wisconsin dickites do not show evidence for more than four hydroxyl groups and are consistent with the reported structure. Upon cooling from 300 to 15 K, the position of the OH3 stretching band increased from 3710 to 3731 cm^{-1}. This large, positive shift in frequency was attributed to the increase in the internuclear O-H3$\cdots$O distance upon cooling. The frequency of the 3655 cm^{-1} band initially decreased by 2 cm^{-1} to 3653 cm^{-1} upon cooling from 300–125 K; however, the band increased in frequency by 1 cm^{-1} upon further cooling to 15 K. This unusual change in frequency upon cooling is consistent with the assignment of this band to OH2 and OH4. The position of the OH1 stretching band decreased from 3622 to 3620 cm^{-1} upon cooling, which was attributed, in part, to the observed increase in the Al-O(H1)-Al angle at low temperature.

Key Words—Dickite, FTIR, Infrared spectroscopy, Low temperature, Neutron powder diffraction, Rietveld refinement.

INTRODUCTION

The basic structure of the kaolin minerals was first described by Pauling (1930), and an analysis of the structure of dickite, $Al_2Si_2O_5(OH)_4$, followed shortly thereafter (Gruner, 1932). The first refinement of the structure was undertaken in space group Cc, using single-crystal X-ray data, by Newnham and Brindley (1956). This study, and the subsequent results of Newnham (1961), showed that dickite exhibits significant distortions from the ideal kaolin layer, including the now well-known rotation of the silicate tetrahedra and distortion of the octahedral sheet. They were, however, unable to locate the hydrogen atoms unambiguously.

Several subsequent studies of the dickite structure have been performed. In the first application of the Rietveld (1969) method to a clay mineral or layer silicate, Adams and Hewat (1981) used neutron powder diffraction data in an attempt to determine the positions of the hydrogen atoms in the dickite structure. Although Adams and Hewat unambiguously located the hydrogen atoms using Fourier methods, their unusually long oxygen-hydrogen bond distances and the reported presence of two-dimensional diffraction effects in their dickite powder pattern make their detailed

conclusions suspect. Subsequent structure refinements using single-crystal X-ray diffraction data have been reported by Rozhdestvenskaya *et al.* (1982), Sen Gupta *et al.* (1984), and Joswig and Drits (1986).

As Joswig and Drits pointed out, the orientations with respect to the basal plane of the inner-surface hydroxyl groups determined in all studies are similar, but large differences exist in the published orientations of the inner hydroxyl group. Their data suggested that the inner hydroxyl group is approximately parallel to the basal plane, and they concluded that the results of Adams and Hewat (1981) and Sen Gupta *et al.* (1984) were in error. Recently, Johnson *et al.* (1990) summarized the available data on hydroxyl group orientations in dickite and emphasized the large variability in oxygen-hydrogen bond distances and orientations of the inner surface hydroxyl groups with respect to the *b* axis. Although Johnson *et al.* could not determine the orientation of the hydroxyl groups with respect to the basal plane, they determined their locations with respect to the *b* axis using polarized infrared (IR) spectroscopy. Their results were in relatively poor agreement with all previously published orientations. Clearly, there is no consensus regarding the orientation of the hydroxyl groups in dickite.

Low-temperature IR spectroscopy provides a useful

tool to probe the nature of the environment around the hydroxyl groups. Upon cooling to near liquid-helium temperatures, the ν(O-H) bands narrow in line width and shift in position. The decrease in line width, in particular, significantly improves resolution of overlapping bands. Low-temperature IR spectra of several dickite specimens from Ouray, Colorado, and Wisconsin were reported by Prost (1984) and Prost et al. (1987, 1989). In addition, a low-temperature IR spectrum of a dickite sample collected from Schuylkill, Pennsylvania, was reported by Brindley et al. (1986). These published low-temperature IR spectra of dickite share the common feature of three strong, distinct bands at $\sim$3615, 3642–3649, and 3711–3726 cm^{-1}. There are surprising differences, however, in the intensities of two weaker bands at $\sim$3685 and $\sim$3712 cm^{-1}, depending upon the sample treatment and sample presentation method used. To date, the IR spectrum of dickite has not been reconciled with the accepted crystal structure. At present, it is not clear if dickite has only three OH-stretching bands and the two weaker bands at 3685 and 3712 are due to defects or another crystalline phrase (e.g., kaolinite or nacrite), or if dickite has five distinct OH-stretching bands. Based upon the accepted crystal structure of dickite in space group Cc, with four crystallographically distinct hydroxyl groups, one would expect to observe no more than four OH-stretching bands. Taken at face value, the Prost et al. (1987, 1989) data suggest that dickite may have a lower space group symmetry based upon the observation of more than four OH-stretching bands.

Because of the apparent discrepancy between observed low-temperature IR spectral data for dickite and the accepted structure and the lack of agreement in the literature on the orientations of the hydroxyl groups, a neutron powder diffraction measurement of dickite was performed at 12 K to evaluate the possibility of a lower space symmetry or split hydrogen positions and to provide further information on the orientation of the hydroxyl groups. In addition, IR spectra were obtained from 18 K to room temperature for both the dickite specimen used by Prost et al. and the sample (St. Claire, Pennsylvania) used in the present neutron diffraction study. The low-temperature IR data provide information complementary to the neutron diffraction data and illustrate the sensitivity of the ν(O-H) bands to minor changes in the dickite structure as a function of temperature.

EXPERIMENTAL METHODS

The <325-mesh fraction (<44 μm) of a sample of dickite from St. Claire, Pennsylvania, obtained from Wards Natural Science Establishment Inc., was used in this study, and no impurities were detected in this fraction by powder X-ray diffraction measurements. Other than sieving, the dickite sample was not treated or ground in any way, and the fully hydrogenated sample
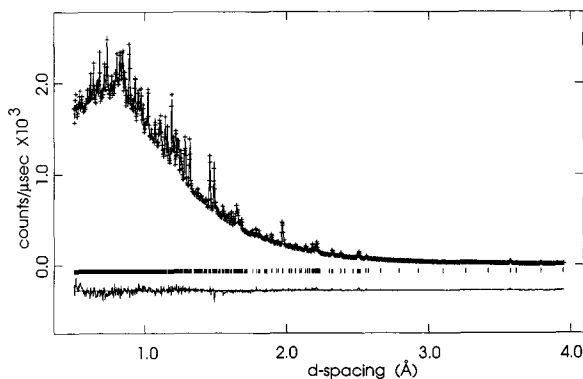

Figure 1. Observed (pluses) and calculated (solid line) TOF neutron powder diffraction pattern (–90° bank) for dickite. Tick marks indicate positions for allowed reflections, and the bottom curve is the difference between observed and calculated profiles. The elevated background at low d values is due to a combination of the incident spectrum and incoherent scattering from H.

was used. Powder time-of-flight (TOF) neutron diffraction data were obtained on the high-resolution Neutron Powder Diffractometer (NPD) at the Los Alamos Neutron Scattering Center (LANSCE). The sample was placed in a ⅜" V can and sealed under dry He, and data were collected at $\sim$12 K in four detector banks ($\pm$148° and $\pm$90°) for approximately 24 hr (Figure 1). No chemical analysis of the transparent crystals was performed, and subsequent structure refinement assumed the ideal composition.

The Rietveld refinement program GSAS (Larson and Von Dreele, 1988) was used for all crystal structure refinements and difference-Fourier calculations. The non-H atom positions determined by Joswig and Drits (1986) were used as the starting model, with the z coordinate of their Si1 atom changed to 0.0407 (to correct what is apparently a typographical error). The convolution function described by Von Dreele et al. (1982), considering anisotropic broadening, was used to model the experimental profiles, and a six-term Fourier series modeled the backgrounds.

Initially, refinement of lattice parameters and scale factors and profile parameters for the four sets of data were performed, with the positions of the non-hydrogen atoms fixed and no hydrogen atoms included. Difference-Fourier maps were then calculated to locate the missing hydrogen atoms. The Fourier maps consistently indicated the existence of four significant negative regions of neutron density, with other minor negative and positive regions. No significant anisotropy was evident in any of the hydrogen density, unlike the maps obtained for kaolinite (Bish and Von Dreele, 1990), although H3 showed very minor anisotropy (Figure 2). The four apparent hydrogen atoms were then added to the asymmetric unit, and refinement proceeded with the application of "soft" distance constraints and variation of all atomic positions. A total
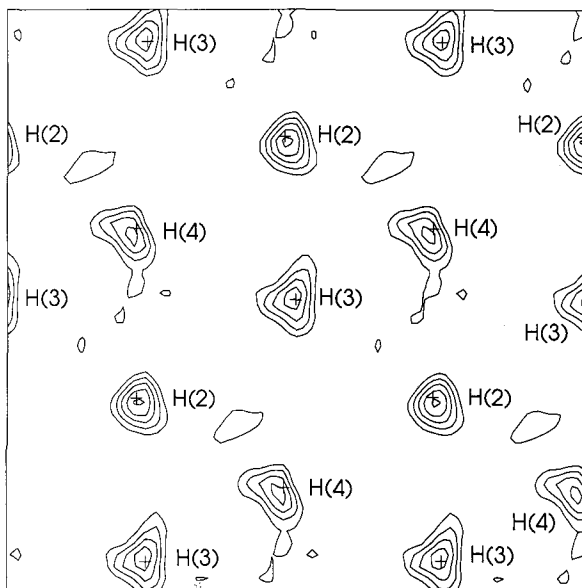
Figure 2. Difference-Fourier map in the interlayer region (z = 0.352, x horizontal, y vertical) showing the positions of the inner-surface hydrogens. Map was calculated with all hydrogens removed from the structure. Contours are drawn at -0.5, -0.4, -0.3, -0.2, and -0.1. Plus ($+$) symbols represent the final refined positions for each hydrogen atom.

of 59 constraints was used: eight tetrahedral distances of 1.61 Å; 12 octahedral distances of 1.91 Å; four O-H distances of 0.98 Å; and a variety of O-O distances. The constraints were weighted so that they made up 9% of the total minimization function [$M = \Sigma W_i(y_o - y_i)^2$] for all four banks of data. Anisotropic profile coefficients and a preferred orientation correction (Dollase, 1986), using [001] as the special axis, were varied in the later stages of refinement. The preferred orientation correction consistently refined to a value of 1.29 $\pm$ 0.01. This value is consistent with the type of platy preferred orientation normally expected with dickite in transmission geometry.

Subsequently, isotropic temperature factors were varied for groups of similar atoms (all O atoms, all hydroxyl O atoms, all H atoms, all Al atoms, and all Si atoms grouped together, respectively). These parameters were followed by refinement of an absorption correction, which apparently did not function properly, probably due to the large absorption cross section of the fully hydrogenated sample; diffraction may have occurred only near the outside of the V can. Although the sample contained a large amount of hydrogen and would be expected to absorb neutrons to a much greater extent than the V can, the refined absorption correction was negative. The correction was fixed to zero in subsequent refinement cycles because it was obvious that problems with its refinement led to inaccurate values for atomic temperature factors, some of which were negative. Although the temperature factors are inac-

curate, the relative values should be useful. Changing the absorption correction had little effect on the atom positions. A full isotropic refinement (26,048 observations, including 59 soft constraints), with different temperature factors allowed for each H atom, yielded an overall $R_{wp} = 2.62\%$ and a reduced $\chi^2 = 1.915$ for 113 variables. A final set of cycles (overall $R_{wp} = 2.55\%$, reduced $\chi^2 = 1.82$, 133 variables) with anisotropic H atoms revealed some anisotropy in the H positions, but some values were non-positive-definite. Final refined lattice parameters from the isotropic refinement were: $a = 5.1474(6)$ Å; $b = 8.9386(10)$ Å; $c = 14.390(2)$ Å; $\beta = 96.483(1)°$; and volume $= 657.9(2)$ Å^3.

Low-temperature infrared spectra were obtained for the St. Claire, Pennsylvania, and the Wisconsin dickites with a Bruker 113v Fourier-transform infrared (FTIR) spectrometer. A mercury-cadmium-telluride (MCT) detector was used with a measured D* value of 3.13×10^9 cmHz0.5 and a low-frequency cutoff of 400 cm^{-1}. The unapodized optical resolution was 1.0 cm^{-1}, and all spectra were transformed using a Hamming apodization function. The number of scans co-added varied between 150 and 250, depending on the signal-to-noise ratio. FTIR spectra of dickite were obtained in the transmission mode for dried deposits on a AgCl window and were ratioed against a clean AgCl window. Deposits were prepared by placing a 0.5 ml aliquot of an aqueous dickite suspension on the AgCl window. After the suspension had dried, the window was mounted on the cold finger of an Air Products D200 displex using an indium gasket. A drop of mineral oil was placed on the dried deposit prior to IR analysis to minimize the difference in the index of refraction between dickite and its surrounding medium. The oil did not contribute to any absorption features in the ν(OH) region. The displex was operated under a vacuum of 10^{-6} torr and could control temperatures in the range of 330 to 15 K. FTIR spectra were analyzed with the Siemens DIFFRAC 5000 software package, using the regular Pearson VII profile function with a refinable background and Pearson VII exponent. Only three bands, of predominantly Lorentzian character, were required to represent the dickite spectra in the OH-stretching region.

RESULTS AND DISCUSSION

The resulting non-hydrogen structure in space group Cc (Table 1) is very similar to those previously published, taking into consideration the low-temperature at which these data were collected (and thermal contraction). In general, the estimated standard deviations for the atomic positions are smaller than other published values, although several authors have argued that standard deviations resulting from Rietveld refinements are unrealistically small (e.g., Scott, 1983). Si-O and Al-O bond lengths (Table 2) are all reasonable, and the octahedral shared edges are significantly

Table 1. Final atomic parameters for dickite at 12 K.

Atom	x	y	z	$100 \cdot U_{iso}$ (Å)[1]
Si(1)	0.0126(4)[2]	0.3992(2)	0.0398(2)	0.03(2)
Si(2)	0.9977(4)	0.0692(2)	0.0403(2)	0.03(2)
Al(1)	0.9127(5)	0.2489(2)	0.2283(2)	0.27(3)
Al(2)	0.4133(5)	0.4149(3)	0.2276(2)	0.27(3)
O(1)	0.9550(3)	0.2352(2)	0.9938(1)	0.15(1)
O(2)	0.2577(3)	0.4695(2)	0.9932(2)	0.15(1)
O(3)	0.7663(3)	0.5054(2)	0.0086(2)	0.15(1)
O(4)	0.0786(3)	0.3880(2)	0.1516(1)	0.15(1)
O(5)	0.0052(4)	0.0790(2)	0.1523(1)	0.15(1)
OH(1)	0.5814(4)	0.2722(2)	0.1564(2)	0.32(1)
OH(2)	0.2442(4)	0.2761(2)	0.2976(2)	0.32(1)
OH(3)	0.2447(4)	0.8914(2)	0.2990(2)	0.32(1)
OH(4)	0.3191(4)	0.5813(2)	0.2974(2)	0.32(1)
H(1)	0.4795(9)	0.1848(4)	0.1549(5)	1.84(9)
H(2)	0.2957(8)	0.2558(5)	0.3627(3)	1.41(9)
H(3)	0.326(1)	0.9456(5)	0.3515(4)	2.3(1)
H(4)	0.2891(9)	0.5813(6)	0.3605(3)	1.9(1)

[1] $U_{iso} = B_{iso}/8\pi^2$.

[2] Values in parentheses are estimated standard deviations in the last place.

Table 2. Si–O and Al–O bond lengths for dickite.

Si(1)–O(1)	1.621(2) Å	Si(2)–O(1)	1.632(2) Å
–O(2)	1.620(2)	–O(2)	1.609(2)
–O(3)	1.607(2)	–O(3)	1.608(2)
–O(4)	<u>1.610(2)</u>	–O(5)	<u>1.611(2)</u>
	1.615(4)		1.615(4)
Al(1)–O(4)	1.925(3) Å	Al(2)–O(4)	1.948(3) Å
–O(5)	1.961(3)	–O(5)	1.914(3)
–OH(1)	1.904(3)	–OH(1)	1.904(3)
–OH(2)	1.892(3)	–OH(2)	1.874(3)
–OH(3)	1.902(3)	–OH(3)	1.901(3)
–OH(4)	<u>1.899(3)</u>	–OH(4)	<u>1.889(3)</u>
	1.914(7)		1.905(7)

shortened, as shown previously. Soft constraints had only a minor effect on the apparent accuracy of the bond lengths. The tetrahedral rotation, 7.25°, is slightly larger than the values of 6.7° found by Joswig and Drits (1986) and 6.8° by Sen Gupta et al. (1984), perhaps a subtle result of the low temperature of measurement.

The refined lattice parameters show that most of the thermal contraction to 12 K occurs along the c direction, consistent with results reported by Bish (1989) for kaolinite. Rietveld refinements using room-temperature X-ray powder diffraction data (Cu Kα) for the St. Claire dickite yielded lattice parameters of a = 5.1500(3) Å; b = 8.9410(6) Å; c = 14.4255(2) Å; β = 96.739(2)°; and volume = 659.64(5) Å³. Thus, from 294 K to 12 K, a decreased by 0.05% and b decreased by 0.03%, whereas c decreased by 0.25%. The β value decreased by 0.256° and the volume decreased by 0.26%. The changes in a and b are not significant at the 3σ level. As previously shown by Bookin et al. (1989), these data show that the lattice parameters reported by Sen Gupta et al. (1984) and Joswig and Drits (1986) are unreasonably short, shorter than our low-temperature parameters. Comparison of the low-temperature structure with either the Joswig and Drits (1986) or the Sen Gupta et al. (1984) structures, assuming the room-temperature lattice parameters for the St. Claire dickite, shows that the primary reason for the decrease along the c direction is a decrease in the interlayer thickness. The thickness of an individual 1:1 layer did not change significantly from 294 to 12 K.

There is fairly good agreement in the literature concerning the orientation of the hydroxyl groups with respect to the (001) plane and the angle of the OH1 group with respect to the b axis. In contrast, the reported angles of OH2, OH3, and OH4 with respect to

the b axis vary considerably, probably due to their orientations at relatively high angles with respect to the (001) plane. The hydrogen positions and hydroxyl orientations found in this study (Table 3) are significantly different from most published values, although, in general, our results agree most closely with those of Joswig and Drits and, surprisingly, differ most from the neutron diffraction results reported by Adams and Hewat (1981). In particular, the O-H bond distances are more reasonable than any other published values, lying between 0.94 and 0.96 Å, although they were affected by the use of soft distance constraints. The hydrogen bonding geometries in the interlayer are similar to literature values summarized by Johnston et al. (1990), namely that OH2 and OH4 are more strongly hydrogen bonded than OH3. However, the OH···O distances obtained in this study do not agree perfectly with literature results, which are all consistent. The OH(2)···O(1) distance, 2.911 Å, is ~0.035 Å shorter; the OH(4)···O(2) distance, 2.906 Å, is ~0.05 Å shorter; and the OH(3)···O(3) distance, 3.145 Å, is ~0.02 Å longer than the room-temperature values. These differences appear to be due to the effects of temperature. The decreases in the two shorter hydrogen bonds agree well with the decrease in the c lattice parameter with temperature, and the increase in the OH(3)···O(3) distance appears due to the change in the β angle.

Although the absolute values of the temperature factors determined in this study are probably inaccurate due to errors in the absorption correction, the U_{iso} values for the hydrogen atoms are in general agreement with those obtained by Joswig and Drits (1986). In particular, the H(3) atom has the largest temperature factor, and this large value of U_{iso} at 12 K probably represents positional disorder rather than thermal vibration. The existence of positional disorder is consistent with H(3) having the weakest interlayer hydrogen bonding of the three inner-surface hydroxyl groups and with OH(3)'s smaller angle with respect to the (001) plane. The isotropic temperature factors do not provide evidence of significant smearing of the hydrogen positions, which would suggest split positions, that may

Table 3. Structural parameters for OH groups in dickite.

Atom	O-H (Å)	Angle of OH with b-axis	Angle of OH with (001) plane	Distance O-H··O (Å)		Al-O-Al angle
OH(1)	0.940(4)	33.8°	−1.3°			102.4(2)°
OH(2)	0.963(4)	41.3°	75.5°	··O(1)	2.911(3)	104.4(2)°
OH(3)	0.954(4)	34.6°	51.9°	··O(3)	3.145(3)	102.7(2)°
OH(4)	0.937(4)	89.9°	74.1°	··O(2)	2.906(3)	104.3(2)°

occur if the structure were refined in an incorrect space group. These results are not inconsistent with a statistically split H3 site, which is suggested by the low-temperature FTIR data. Although anisotropic temperature factors can provide information on the nature of any positional disorder or anisotropic thermal vibration, the values refined for the four hydrogens were

Figure 3. FTIR spectra between 3575 and 3775 cm⁻¹ for a) St. Claire and b) Wisconsin dickites as a function of temperature from 18 to 300 K.

not all positive-definite and are suspect. Perhaps the best evidence that the hydrogen atoms all occupy single, well-defined sites comes from the difference-Fourier maps used to locate the hydrogen atoms. Neutron density for all four hydrogens was fairly symmetric, and the maps did not reveal evidence of significant anisotropy or split sites (Figure 2).

The neutron powder diffraction data do not support the presence of more than four distinct hydrogens at low temperature or the need for considering a lower space group symmetry for St. Claire dickite. However, one is left with the compelling argument, provided by the low-temperature infrared spectra of Prost *et al.* (1989), for more than four distinct hydrogen atoms in the Wisconsin dickite.

FTIR spectra of the St. Claire and Wisconsin dickites in the OH stretching region are shown in Figure 3 as a function of temperature between 8 and 300 K. In contrast to the four distinct, IR-active OH-stretching bands for highly crystalline kaolinite (Prost *et al.,* 1989), the low-temperature IR spectra of the dickites are characterized by three strong bands at 3620, 3655, and 3731 cm⁻¹. Less intense bands appear in the low-temperature spectrum of the St. Claire dickite at 3691 and 3717 cm⁻¹ and are much more distinct in the Wisconsin dickite spectrum. These results are in qualitative agreement with published low-temperature IR data for dickite (Table 4). Low-temperature FTIR data have been reported for dickite specimens collected from Ouray, Colorado; Wisconsin; and Schuylkill, Pennsylvania. But no data have been reported for the St. Claire, Pennsylvania, dickite sample. Although the tabulated values of our results obtained for the St. Claire and Wisconsin dickites do not appear to agree well with the published data of Prost *et al.* (1989), the fit can be significantly improved if a positive 5 cm⁻¹ offset is applied to the published values. This correlation is not unreasonable since the published data were obtained on a dispersive IR spectrometer.

3620 cm⁻¹ band

The 3620 cm⁻¹ band of dickite was unambiguously assigned to the inner hydroxyl, OH1, by Farmer and Russell (1964) and Farmer (1974). Support for this assignment comes from the observed shift in band position as a function of temperature (Figure 4) and from the change in the Al-O-Al angle for this OH group
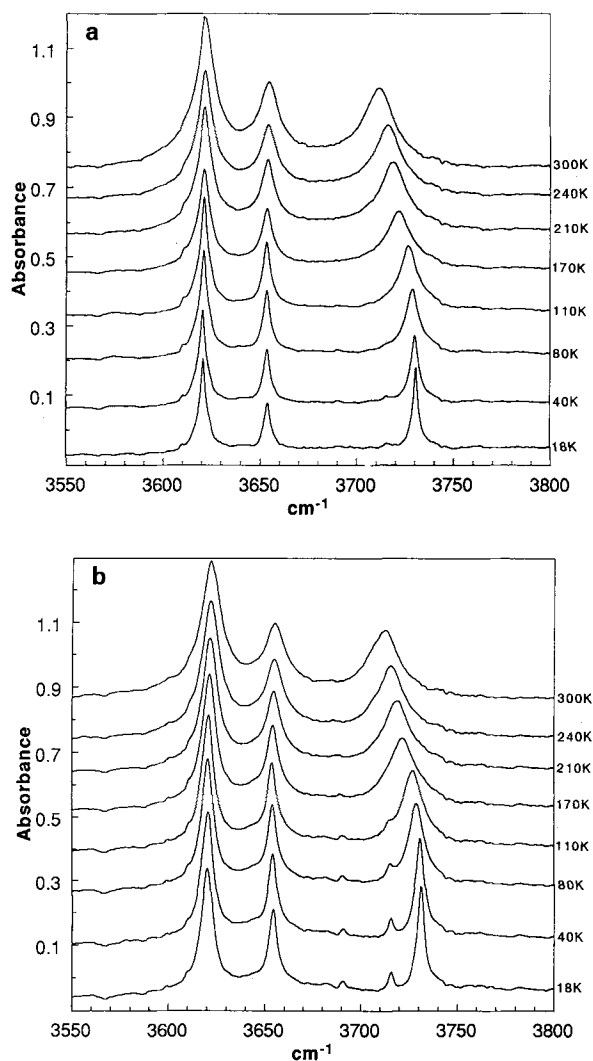
Table 4. Positions (cm^{-1}) of ν(OH) bands in low-temperature IR spectra of dickite.

OH Group	St. Claire	Wisconsin	Prost[1]	Prost[2]
OH1	3619	3621	3620	3620
OH2, OH4	3655	3655	3647	3654
Defect	3691	3691	3690	3690
OH3?	3717	3717	3716	3717
OH3	3731	3732	3731	3731

[1] Prost *et al.* (1989), KBr pellet sample, 5 cm^{-1} added to positions, 5 K.

[2] Prost *et al.* (1987), deposit on CaF$_2$ window, 5 cm^{-1} added to positions, 5 K.

(Table 3). This ν(OH) decreases in frequency only slightly upon cooling, which contrasts sharply with the observed frequency shift of the 3731 cm^{-1} band of dickite. The frequency of the OH-stretching band is expected to be influenced, in part, by the angle of the Al-O-Al group to which the hydrogen atom is attached. The Al-O-Al angle increases for OH1 upon cooling compared with a decrease for the OH2, OH3, and OH4 groups consistent with a decrease in frequency of the ν(OH1) vibration (Johnston *et al.*, 1990). The shift in frequency of OH1, however, is minimal and is consistent with the minimal change in the overall structure of the dickite 1:1 layer upon cooling.

3655 cm^{-1} band

In a single-crystal FTIR study of kaolinite and dickite, Johnson *et al.* (1990) assigned the 3655 cm^{-1} band to the OH2 and OH4 groups on the basis of their similar internuclear O-H$\cdots$O distances, O-H$\cdots$O angles, angles of the OH group with respect to the (001) plane, and the Al-O-Al angles for the OH2 and OH4 groups (Table 3). It is expected that the internuclear O-H$\cdots$O distance and the O-H$\cdots$O angle, in particular, will have a large influence on the position of the OH-stretching band, and the dependence of the OH-stretching frequency on the hydrogen-bond distance is well documented. The most direct evidence to support this assignment comes from comparing the observed dichroic behavior of the OH stretching bands upon tilting at low temperature (Prost *et al.*, 1987) with the angle of the OH2 and OH4 groups with respect to the (001) plane. Because most of the dickite particles are oriented with their (001) faces parallel to the deposition surface, it follows that the closer to 90° the angle of the OH group with respect to the (001) plane is, the higher the dichroic ratio will be. The 3655 cm^{-1} band has the highest dichroic character of any of the dickite OH bands, consistent with observed angles of 75.5° and 74.1° for (001) *vs* OH2 and OH4, respectively. These angles are considerably closer to 90° than are the angles for OH3 (51.9°) or OH1 (1.3°). The shift in position of this band is unusual in that its position decreases upon cooling to 120 K followed by a slight increase on further cooling. A monotonic change in frequency is observed
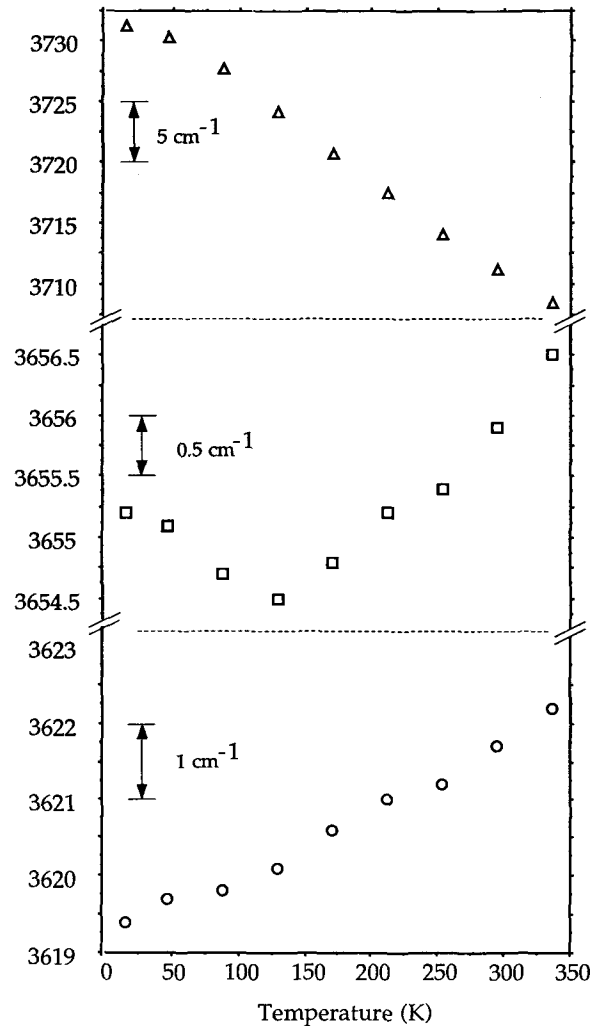

Figure 4. ν(OH) band positions for the St. Claire dickite as a function of temperature from 18 to 300 K.

for the 3620 and 3631 cm^{-1} bands. The anomalous frequency shift of the 3655 cm^{-1} band may be indicative of two nearly degenerate bands that have slightly different positions at low temperature. Further evidence for two closely overlapping bands comes from analysis of the profiles in terms of the percent Lorentzian character. For a "pure" vibrational transition, a band of high Lorentzian character is expected (Wilson *et al.*, 1955; Bellows and Prasad, 1979). This is observed for the 3620 and 3731 cm^{-1} bands. The profile of the 3655 cm^{-1} band, however, takes on a strong Gaussian character at low temperature. If two closely spaced Lorentzian bands are fit with a single profile of variable Lorentzian character, the composite band will increase in Gaussian character. These observations suggest that the OH2 and OH4 groups are in a very similar environment at room temperature. Upon cooling, these bands narrow considerably until the two bands are
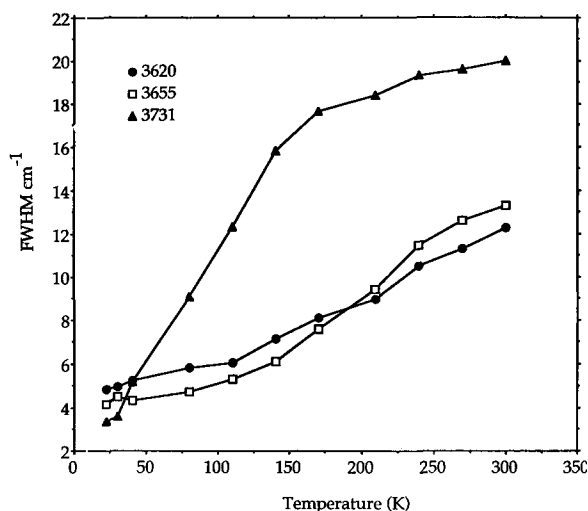
Figure 5. FWHM for the St. Claire dickite ν(OH) bands as a function of temperature from 18 to 300 K.

almost resolved, giving rise to the increase in Gaussian character.

3731 cm⁻¹ band

The 3731 cm⁻¹ band was assigned to OH3 by Johnston et al. (1990) on the basis of its unique polarization behavior. Unlike the other dickite ν(OH) bands, the intensity of the 3710 cm⁻¹ band (room-temperature) is strongly attenuated upon rotation of the electric vector away from the b-axis, consistent with its orientation. Additional support for this assignment is provided by two observations. First, this OH group has the longest O-H···O distance of the three inner-surface OH groups and should exhibit the highest frequency ν(OH) band. Second, the O-H···O distance increases upon cooling as opposed to decreasing for the OH2 and OH4 groups, indicative of weaker hydrogen bonding for the OH3 group at low temperature. This decrease in O-H···O distance is mirrored in the increase in the frequency of the ν(OH3) band as temperature is decreased. In other words, the intermolecular interactions of this group with the opposing siloxane surface decrease, and the position of this band becomes more consistent with that of an isolated Al-O-H group as temperature is decreased. The ν(OH) band position of a completely isolated Al-O-H group is expected to be near 3750 cm⁻¹. As noted by Prost et al. (1987), this band does show some dichroic character, which is consistent with the observed angle of the OH3 group with respect to the (001) plane of 51.2°. In addition to the large shift in frequency upon cooling, this band narrows significantly upon cooling, going from a 21 to a 3 cm⁻¹ full-width-at-half-maximum (FWHM) (Figure 5). The large decrease in FWHM of OH3 as a function of temperature indicates either that the environment around

OH3 becomes significantly more symmetrical at low temperature or that it exhibits less positional disorder.

3691 and 3717 cm⁻¹ bands

The assignment of these two bands in the St. Claire and Wisconsin dickites is currently only speculative. It is unlikely that either band corresponds to an additional structural OH group because of their low intensity and lack of dichroic character (Prost et al., 1987). A possible explanation for the two bands is that they are due to defects and/or stacking faults within the dickite or to a separate mineral phase present in the sample. The former hypothesis is supported by the observation that the band intensities relative to the other three dickite bands depend on the origin and treatment of the sample. For example, the intensities of these two bands appear to increase upon grinding the sample. The intensities of these bands in the KBr-pellet spectra (Prost et al., 1987) where the sample was ground are significantly greater than their corresponding intensities in a deposit on a CaF_2 window where no grinding was involved. Similarly, the intensities of these bands are large in the low-temperature, KBr pellet IR spectrum of the dickite from Schuylkill, Pennsylvania, where the sample was ground (Brindley et al., 1986). It is distinctly possible that the 3717 cm⁻¹ band is a component of OH3, representing a split position and positional disorder of the OH3 hydrogen atom. Evidence to support this hypothesis includes the large temperature factor determined for H3 in this study and difference-Fourier maps showing some anisotropy of the H3 site (Figure 2).

SUMMARY

Neither the neutron powder diffraction data nor the low-temperature FTIR spectra for the St. Claire sample provide evidence that ideal dickite possesses more than four crystallographically distinct hydrogen sites or has a space group symmetry lower than Cc. After refinement in space group Cc, there were no significant discrepancies between the observed and calculated powder patterns, and, importantly, there were no observed reflections violating space group Cc. However, there are indications from the low-temperature FTIR spectra that additional, minor, defect-related, statistically occupied OH sites may be present. The OH orientations obtained in this study are not in good agreement with those obtained by Johnston et al. (1990) and may represent changes due to the low temperature of the current study and/or difficulties in interpreting the single-crystal FTIR spectra of Johnston et al.

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