Low-temperature infrared spectroscopic study of OH-stretching modes in kaolinite and dickite

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ABSTRACT

The powder-transmission infrared spectra of OH-stretching modes in well-ordered samples of kaolinite and dickite are recorded from 270 to 10 K. Effective medium modeling of the kaolinite spectrum confirms the coupled motion of non-equivalent OH groups in the inter-layer OH-stretching modes. A full assignment of OH-stretching bands in dickite is proposed. In particular, the band observed at 3685 cm^{-1} in room-temperature spectra is attributed to a kaolinite-like defect, whereas that at 3706 cm^{-1} is related to OH3 groups of the dickite structure. The changes in phonon frequency and line shape are analyzed as a function of temperature. The results evidence the quasi-harmonic nature of the OH-stretching modes in kaolinite-group minerals. Coupling of OH-stretching modes to each other can be related to the macroscopic electrostatic properties of the composite medium, made of mineral particles and KBr matrix, and not to microscopic anharmonic mechanisms. The low saturation temperatures of vibrational frequencies and linewidths indicate that the OH-stretching modes probe the average thermal bath of the crystal, without coupling to a specific decay channel.

Keywords: Infrared spectroscopy, kaolinite, dickite, thermodynamic, phonons

INTRODUCTION

The stretching vibrational modes of OH groups are commonly used to probe the structural order of hydrous minerals (Farmer 1974). They are sensitive to the occurrence of defects such as cationic substitutions and planar defects, and to the structural changes associated with phase transitions. This is particularly true for hydrous layered minerals, such as kaolinite group minerals, serpentines, or aluminum hydroxides that display significant modifications under pressure (e.g., Johnston et al. 2002). These minerals also display a great variability of their defective structure that can be used to gain information about the physical-chemical conditions that prevailed during their formation (Muller et al. 1995). In particular, infrared spectroscopy of OH-stretching modes has been used to unravel the transformation of kaolinite group minerals in natural environments (e.g., Beaufort et al. 1998; Balan et al. 2007a) and can be applied to optimize the use of kaolin-based materials (e.g., Fourdrin et al. 2009). It has also been shown that the narrowing and differential shift of OH-stretching infrared absorption bands at low temperature can be used to improve the identification of stacking faults in disordered varieties of kaolinite-group minerals (Prost et al. 1989; Brindley et al. 1986; Bish and Johnston 1993; Johnston et al. 2008). In addition, the high quality of some kaolinite-group mineral samples together with the relatively small size of their unit cell make them important model compounds to investigate the bulk and surface properties of hydrous minerals by theory and experiment (Geysermans and Noguera 2009).

The OH-stretching modes are usually considered as significantly anharmonic (e.g., Tosoni et al. 2005; Prencipe et al. 2009). However, first-principles harmonic calculations in hydrous, layered minerals contradict this view and have provided a description of OH-stretching vibrations, which is fully consistent with experiment (e.g., Balan et al. 2001, 2002a, 2005, 2006). In fact, previous investigations of anharmonicity in hydrous minerals mostly focused on the frequency shift observed between harmonic and anharmonic calculations. From an experimental point of view, the shift can be assessed by comparing the frequency of fundamental and overtone bands (Petit et al. 2004) or by analyzing the frequency changes induced by D/H isotopic substitution (Berglund et al. 1978). Perturbation theory applied to OH-stretching modes evidences that the large frequency shift mostly results from the small effective mass of the stretching modes related to the small mass of hydrogen; whereas the potential energy profile associated with stretching modes is only very weakly anharmonic (Balan et al. 2007b). In this article, we re-examine the anharmonic character of OH-stretching modes in kaolinite and dickite, the most common polymorphs of aluminous phyllosilicates, by analyzing the changes in phonon frequency and line shape as a function of temperature. Our results evidence the quasi-harmonic nature of the OH-stretching modes in these kaolinite-group minerals and provide an interpretation for all OH-stretching absorption bands observed in the infrared spectrum of kaolinite and dickite.

EXPERIMENTAL MODES

Infrared spectra were recorded on well-ordered samples of kaolinite (GB1) from St. Austell (Great Britain) (Cases et al. 1982; Balan et al. 2000) and dickite (S1) from El Berrocal, Spain (Allard et al. 2003; Balan et al. 2005). Additional

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spectra were recorded on two well-ordered dickite samples from St. Claire, Pennsylvannia (Ward's Natural Science Establishment Inc.; Bish and Johnston 1993; Johnston et al. 1998; Shoval et al. 2001), and Nowa Ruda, Poland (Balan et al. 2002b). Approximately 2 mg of dried sample were gently ground with 300 mg of dried KBr. The mixture was pressed at 10 ton/cm², oven-dried overnight to remove adsorbed water, and pressed again to produce a KBr pellet. The transmission IR spectrum of the pellet was recorded using a FTIR spectrometer Nicolet 6700 with a resolution of 1 cm⁻¹. Low-temperature measurements were performed using an ARS CS-204 SI cryo-cooler fitted with KRS-5 windows.

RESULTS

The structure of kaolinite and dickite is based on the regular stacking of dioctahedral layers related to each other by a simple translation in kaolinite or by a glide plane in dickite (Bish 1993; Bish and Johnston 1993; Neder et al. 1999). These hydrous minerals display two different types of OH groups. The intra-layer OH groups, also referred to as inner-OH groups (e.g., Giese and Datta 1973), are located within the layers and are weakly affected by changes in the stacking pattern. In contrast, the three non-equivalent inter-layer OH groups, also referred to as inner-surface OH groups, are located on top of the dioctahedral aluminous sheet. They share weak hydrogen bonds with the oxygen atoms of the basal plane of the next layer and react strongly to changes of the stacking sequence.

As commonly observed in kaolinite samples, the low-temperature infrared spectrum of the GB1 sample in the frequency range of OH-stretching modes display four intense band at 3616, 3660, 3678, and 3711 cm⁻¹ (Fig. 1). The interpretation of these bands in terms of vibrational stretching modes can be found in Farmer (1974) and was recently confirmed by first-principles calculations (Balan et al. 2001). The 3616 cm⁻¹ band corresponds to the stretching of the intra-layer OH group. The three other bands involve the coupled motion of the three inter-layer OH groups. The band at 3711 cm⁻¹ corresponds to the in-phase motion of the three OH groups, whereas the two weaker bands correspond to out-of-phase motion. A very weak band is also observed at 3595 cm⁻¹. It is ascribed to OH groups bonded to Al^{3+} and Fe^{3+} cations, indicating the occurrence of minor amounts of Fe for Al substitution in the investigated sample. A low amount of structural trivalent iron in this sample was previously observed using electron paramagnetic resonance (Balan et al. 2000).

The lowering of temperature from 270 to 10 K leads to significant changes in the frequency, width, and intensity of OH-stretching bands (Figs. 2 and 3). The intra-layer OH-stretching band shifts toward lower frequencies, whereas the inter-layer OH bands are shifted to higher frequencies. The frequency of the four bands varies almost linearly with temperature at high temperature (> ~100 K) but becomes temperature-independent at low temperature (< ~100 K). This behavior is consistent with the observations of Johnston et al. (2008) on the Wilkinson County kaolinite. The low-temperature quantum saturation of mode frequency is a general phenomenon in crystals. It can be analyzed using a function of the form (Salje et al. 1991a):

$$\omega(T) = A + B \coth(\Theta_S/T) \qquad (1)$$

where T is the temperature and A, B, and Θ_S are fitted parameters. The "temperature-independent" domain extends from 0 to T_S with $T_S = \Theta_S/2$. In kaolinite, Θ_S ranges between 118 and 163 K
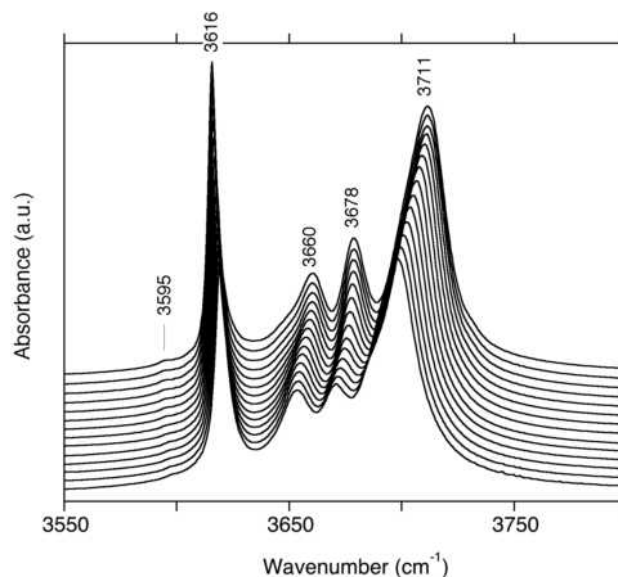

FIGURE 1. Powder transmission infrared spectra of kaolinite (GB1 sample) from 10 K (top) to 270 K (bottom) by steps of 20 K.

for the OH-stretching bands (Table 1).

An overall decrease in linewidth is observed as a function of temperature. The evolution of the linewidth with temperature can be efficiently analyzed using an autocorrelation approach initially developed to investigate phase transitions in minerals using hard mode spectroscopy (Salje et al. 2000). This method is particularly suited to investigate the transformations of low-symmetry minerals such as kaolinite, whose spectrum displays several overlapping bands. Compared with a fitting procedure, it does not require any assumption on the number of components, a point that has been previously debated for the kaolinite spectrum (Farmer 1998, 2000). The self-convolution of the IR spectrum with an offset ω′ in the frequency leads to the autocorrelation function

$$corr(\alpha, \omega') = \int_{-\infty}^{+\infty} \alpha(\omega + \omega')\alpha(\omega)\,d\omega \qquad (2)$$

where $\alpha(\omega)$ is the spectrum after baseline subtraction in absorbance units. The main information on the linewidth of the IR spectrum ($\Delta corr$) is then obtained from the shape of the autocorrelation function in the limit $\omega' \rightarrow 0$ (Salje et al. 2000). It relates to the average linewidth and mode splitting in the relevant spectral region and proves to be rather more robust with respect to changes of baselines and instrumental noise than the usual line fitting procedure. Practically, the method implies to choose some segments of the IR spectra and subtract a linear baseline in such a way that the intensity falls to zero on the limits of the segments, i.e., $\alpha(\omega) = 0$ beyond these limits. For kaolinite, two domains have been selected, 3550–3640 and 3640–3750 cm⁻¹, corresponding to the intra-layer OH and inter-layer OH bands, respectively. At low temperature, the linewidth becomes also temperature independent and the fit using Equation 1 leads to Θ_S of 208 and 223 K for the intra-layer OH and inter-layer OH bands, respectively.

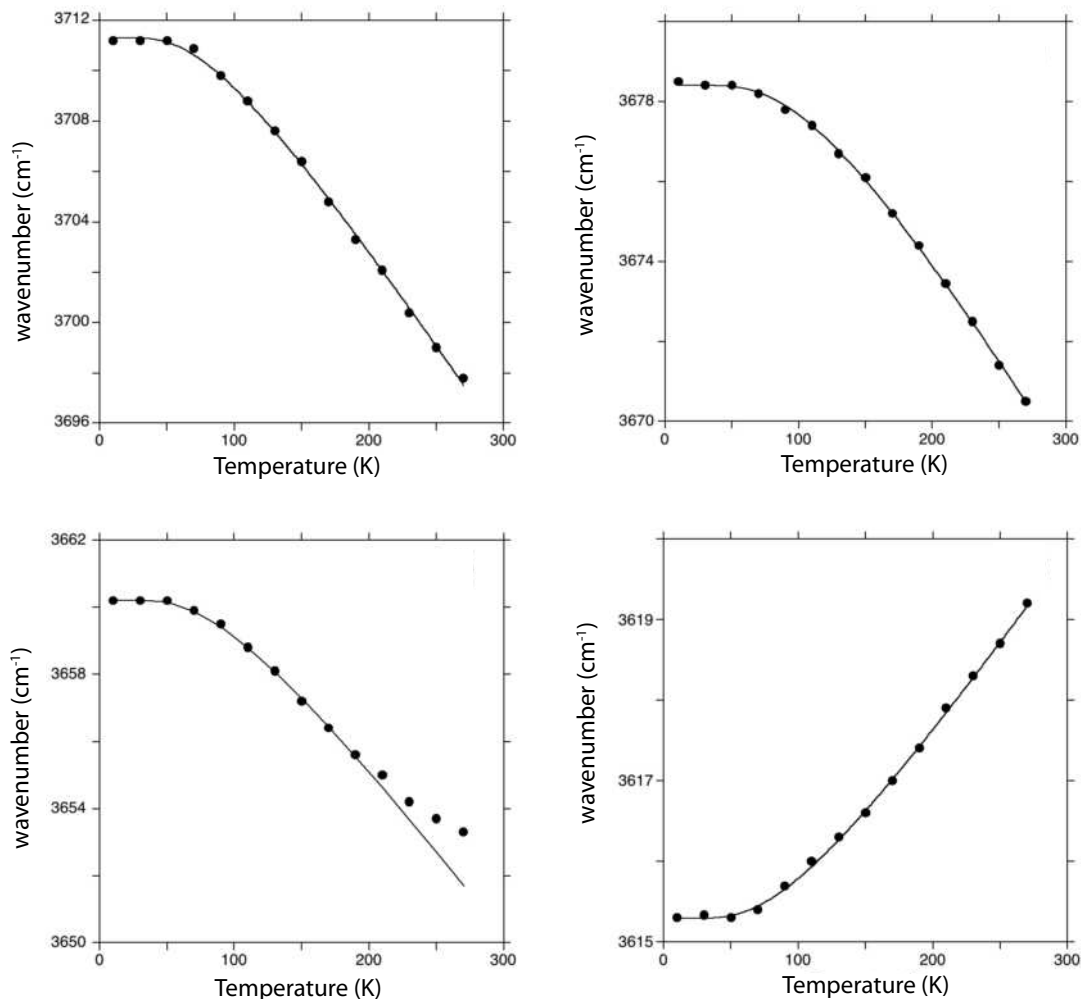Finally, the total absorbance obtained after subtraction of

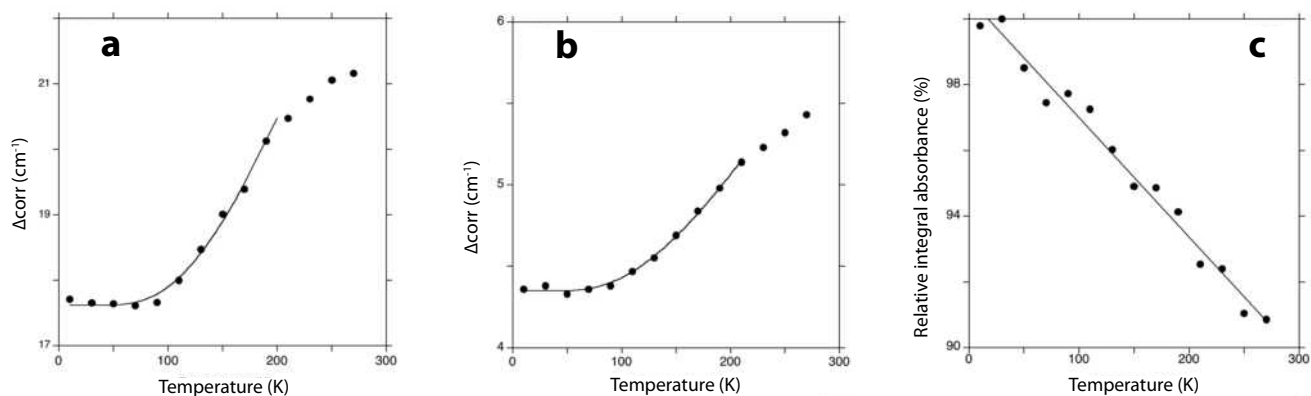**FIGURE 2.** Temperature dependence of the frequency of the major OH-stretching bands of kaolinite.

FIGURE 3. Temperature dependence of the linewidth of OH-stretching bands in kaolinite obtained from autocorrelation: (**a**) inter-layer OH bands, (**b**) intra-layer OH band. (**c**) Relative variation of the integrated absorbance of OH-stretching bands with temperature.

a linear baseline and integration from 3550 to 3800 cm^{-1} decreases by about 10% between 10 and 270 K. Such a variation of the absorbance with temperature is consistent with previous observations on hydrous minerals, including phyllosilicates,

by Zhang et al. (2007).

In dickite, the three non-equivalent inter-layer OH groups have a different orientation from that in kaolinite (Bish and Johnston 1993). Instead of being almost perpendicular to the

TABLE 1. Saturation temperatures in kaolinite and dickite

	Frequency (cm⁻¹) at 10 K	Nature of stretching mode	Θ_S (K)	A (cm⁻¹)	B (cm⁻¹)
Kaolinite	3616	Intra-layer OH	131	3612	3.2
	3660	Out-of-phase stretching of inter-layer OH groups	131	3667	−7.0
	3678	Out-of-phase stretching of inter-layer OH groups	163	3688	−9.3
	3711	In-phase stretching of inter-layer OH groups	118	3721	−9.6
Width (intra-layer OH)			208	1.8	2.5
Width (inter-layer OH)			223	5.7	12
Dickite	3612	Out-of-phase stretching of OH2 and OH4	n.d.	n.d.	n.d.
	3620	Intra-layer OH	55	3620	0.23
	3649	In-phase stretching of OH2 and OH4	56	3647	2.2
	3690	"kaolinite" defect	325	3721	−30
	3716	OH3 (out-of-plane)	106	3721	−5.4
	3730	OH3 (in-plane)	43	3733	−3.2

Note: Parameters A and B refer to Equation 1 (see text).
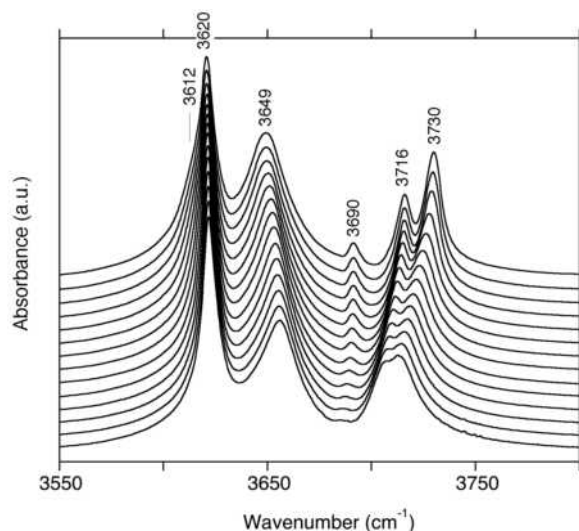

FIGURE 4. Powder transmission infrared spectra of dickite (S1 sample) from 10 K (top) to 270 K (bottom) by steps of 20 K.
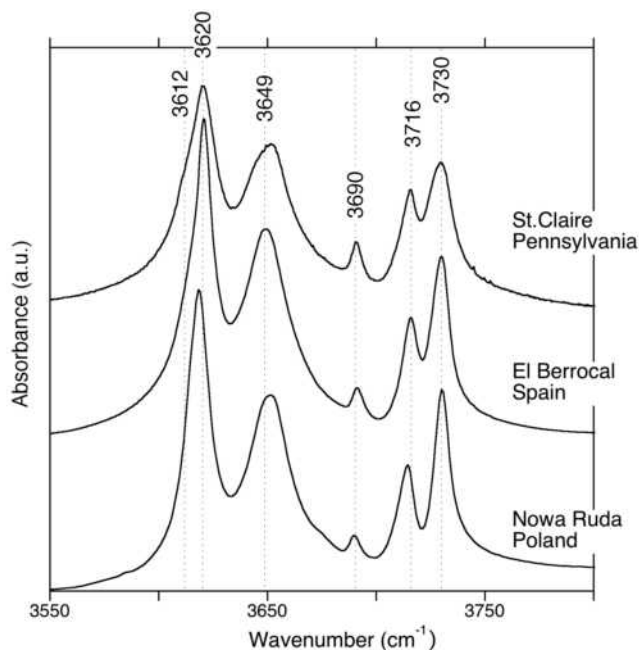

FIGURE 5. Low-temperature (10 K) powder transmission infrared spectrum of well-ordered dickite samples. Note the presence of the bands at 3690 and 3716 cm⁻¹ in the three samples of different origin. Note the splitting of the bands at 3620 and 3649 cm⁻¹ in the St. Claire sample.

layers, one OH group (OH3) is inclined and shares a longer H-bond with the next layer. The two other inter-layer OH groups (OH2 and OH4) remain perpendicular.

The dickite spectrum at 270 K displays five absorption bands at 3621, 3656, 3685, 3706, and 3712 cm⁻¹ (Fig. 4). These bands are classically observed in ordered dickite samples such as those from St. Claire, Pennsylvania (Beaufort et al. 1998; Shoval et al. 2001), Nowa Ruda, Poland (Balan et al. 2002b), Wisconsin (Prost et al. 1989), and Schuylkill, Pennsylvania (Brindley et al. 1986). They display significant shifts and narrowing with temperature and six bands can identified at low temperature at 3612, 3620, 3649, 3690, 3716, and 3730 cm⁻¹ in well-ordered samples (Fig. 5). The band observed at 3620 cm⁻¹ is unambiguously ascribed to intra-layer OH groups. It corresponds in fact to two almost degenerated vibrational bands, related to the doubling of unit-cell size in dickite compared with kaolinite. Following the interpretation proposed from first-principles calculations (Balan et al. 2005), the band at 3612 cm⁻¹ corresponds to the two almost degenerated out-of-phase vibration of OH2 and OH4 groups. The band at 3649 cm⁻¹ contains two components corresponding to the in-phase vibration of OH2 and OH4 groups, split by inter-layer coupling. Note that the two components are resolved in the low-temperature spectrum of the St. Claire dickite (Fig. 5). Finally the high-frequency band at 3730 cm⁻¹ corresponds to the vibration of the inclined OH3 group. The origin of the bands observed at 3685 and 3706 cm⁻¹ in the 270 K spectrum is more controversial. They are usually ascribed to defects in the dickite structure, although observed in the spectrum of well-ordered samples from different origin (Fig. 5). The band at 3706 cm⁻¹ in St. Claire dickite has also been ascribed to the OH3 group, from Raman and photo-accoustic IR spectroscopy (Shoval et al. 2001).

The spectral changes as a function of temperature have been analyzed with the same approach as for kaolinite (Fig. 6). The frequency of absorption bands becomes also temperature independent at low temperature, but the values of Θ_S are more scattered in dickite, ranging from 43 to 325 K (Table 1). The linewidth was analyzed by autocorrelation on four frequency domains: 3575–3635, 3635–3680, 3680–3701, and 3701–3765 cm⁻¹. Except for the high-frequency domain that displays a significant decrease in linewidth at low temperature, other domains display smaller variations in linewidth with a more complex behavior (Fig. 7). The increase of the linewidth with decreasing temperature observed for the bands at 3620 and 3655 cm⁻¹ is a clear indication of line splitting. In fact, the splitting
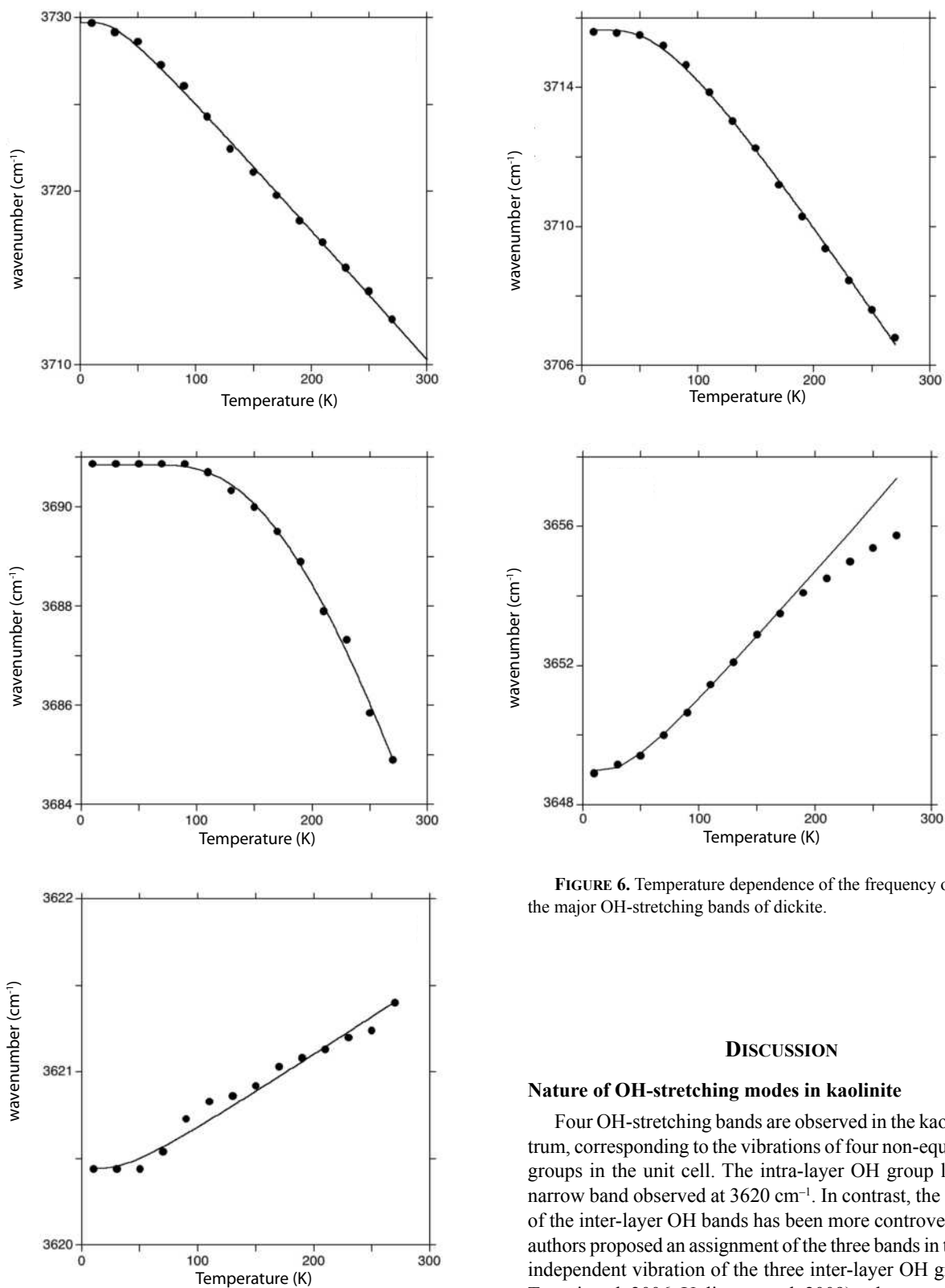
FIGURE 6. Temperature dependence of the frequency of the major OH-stretching bands of dickite.

DISCUSSION

Nature of OH-stretching modes in kaolinite

Four OH-stretching bands are observed in the kaolinite spectrum, corresponding to the vibrations of four non-equivalent OH groups in the unit cell. The intra-layer OH group leads to the narrow band observed at 3620 cm^{-1}. In contrast, the assignment of the inter-layer OH bands has been more controversial. Some authors proposed an assignment of the three bands in terms of the independent vibration of the three inter-layer OH groups (e.g., Tosoni et al. 2006; Ugliengo et al. 2009), whereas other assignments were based on vibrational modes involving the coupled motion of the inter-layer OH groups (e.g., Farmer 1964, 1974; Balan et al. 2001).

Considering the similar bond length and orientation of inter-layer OH groups in kaolinite (Bish 1993), the one-to-one

is particularly evident in the spectrum of St. Claire dickite (Fig. 5). Finally, a 5% decrease of the integrated absorbance is observed from 10 to 270 K.
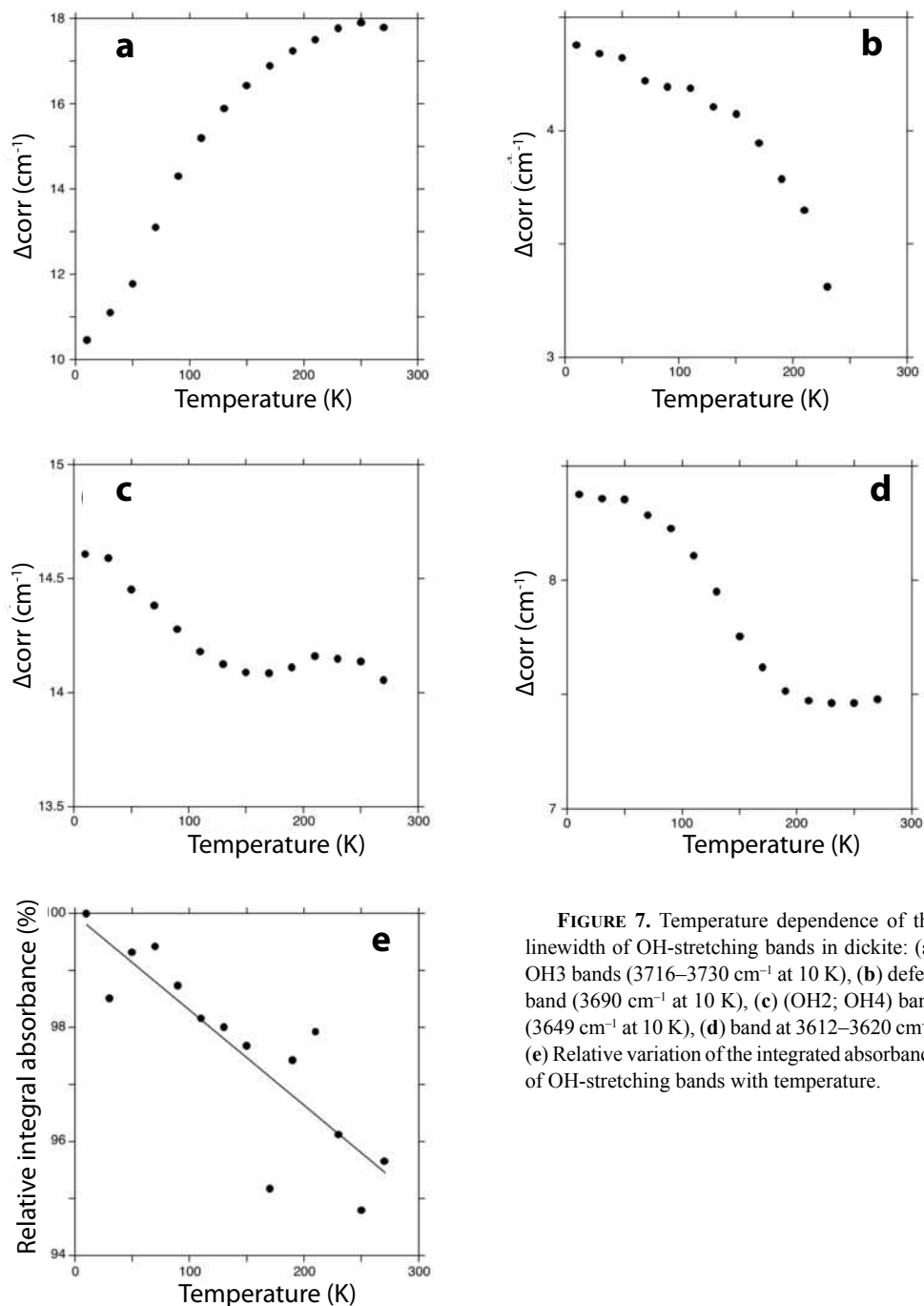
FIGURE 7. Temperature dependence of the linewidth of OH-stretching bands in dickite: (**a**) OH3 bands (3716–3730 cm^{-1} at 10 K), (**b**) defect band (3690 cm^{-1} at 10 K), (**c**) (OH2; OH4) band (3649 cm^{-1} at 10 K), (**d**) band at 3612–3620 cm^{-1}. (**e**) Relative variation of the integrated absorbance of OH-stretching bands with temperature.

assignment implies that the three absorption bands correspond to three vibrational-modes with similar oscillator strengths (or effective charges) and polarization properties. As discussed by Farmer (1974), this is not consistent with the dichroic character experimentally observed on oriented preparations or single crystals of kaolinite (Farmer 1974; Johnston et al. 1990). A fit of the kaolinite spectrum based on effective-medium theory (Yagil et al. 1995; Salje and Bismayer 1997; Zhang and Salje 2001) can be used to gain independent information on the mode-oscillator strength related to these bands. In the present case, the anisotropy of the dielectric tensor of kaolinite is neglected and the total absorbance computed by considering the complex dielectric tensor of a composite medium made of spherical kaolinite particles inserted in a KBr matrix. In that case, the depolarization factors are 1/3 and the absorbance of the effective medium is proportional to

$$A(\omega) \propto \frac{\omega \, \text{Im}[\varepsilon(\omega)]}{\left[2\varepsilon_{KBr} + \text{Re}[\varepsilon(\omega)]\right]^2 + \left[\text{Im}\big[\varepsilon(\omega)\big]\right]^2} \qquad (3)$$

where ε_{KBr} is the dielectric constant of the matrix ($\varepsilon_{KBr} = 2.25$) and $\varepsilon(\omega)$ the dielectric function of the pure material. For kaolinite, this function is defined by:

$$\varepsilon(\omega) = \varepsilon(\infty) + \sum_{j=1}^{4} \frac{A_j^{\,2}}{(\omega_j^{\,2} - \omega^2 - i\omega\gamma_j)} \qquad (4)$$

where $\varepsilon(\infty)$ is the electronic contribution to the dielectric function, taken equal to $\varepsilon(\infty) = 2.5$ (Balan et al. 2001). The transverse optical mode frequencies ω_j, the mode effective charges A_j, and the damping parameters γ_j are fitted parameters. The effective medium theory thus makes it possible to extract physically meaningful, vibrational-mode parameters from absorbance spectra recorded on composite samples. It does not involve any structural parameter nor require any assumption about the microscopic nature of the vibrational modes. Use of effective medium theory is better suited to fit the infrared spectra of mineral/KBr mixtures than simple decomposition procedures based on Gaussian or Lorentzian line shape, because it accounts for the line shifts and intensity changes related to electrostatic interactions within the absorbing sample.

Application of the effective medium model to kaolinite evidences that, beside a shift of absorption bands with respect to transverse optical mode frequencies (Table 2), energy can be transferred from one mode to the other through electrostatic coupling, leading to a relative increase of the intensity of the high-frequency band at the expense of the other bands (Fig. 8). Note

that the neglect of the dielectric tensor anisotropy maximizes the energy transfer, which should be smaller in actual samples. However, even with such energy transfer, the observed intensities cannot be reproduced by using three similar mode effective charges for the inter-layer OH-stretching modes. Considering that the three inter-layer OH groups are structurally similar, the different effective charges of the inter-layer OH modes (Table 2) constitute further evidence that these modes do not involve the vibration of independent OH groups. Although weak, the coupling between inter-layer OH groups cannot be neglected in the interpretation of spectroscopic observations, confirming the attribution proposed from experimental observations (Farmer 1964, 1974) and first-principles modeling (Balan et al. 2001, 2005).

Nature of OH-stretching modes in dickite

Coupled motion of OH groups explains the variations observed between the kaolinite and dickite spectrum. The observation of the band at 3612 cm^{-1} confirms the interpretation based on a previous first-principles modeling (Balan et al. 2005). Indeed, it was predicted that the dickite spectrum contains a low-frequency band related to out-of-phase coupling of OH2 and OH4. This band is very weak and hard to observe at room temperature because of the strong overlap with the intra-layer

TABLE 2. Results of the effective medium modeling of kaolinite infrared spectrum

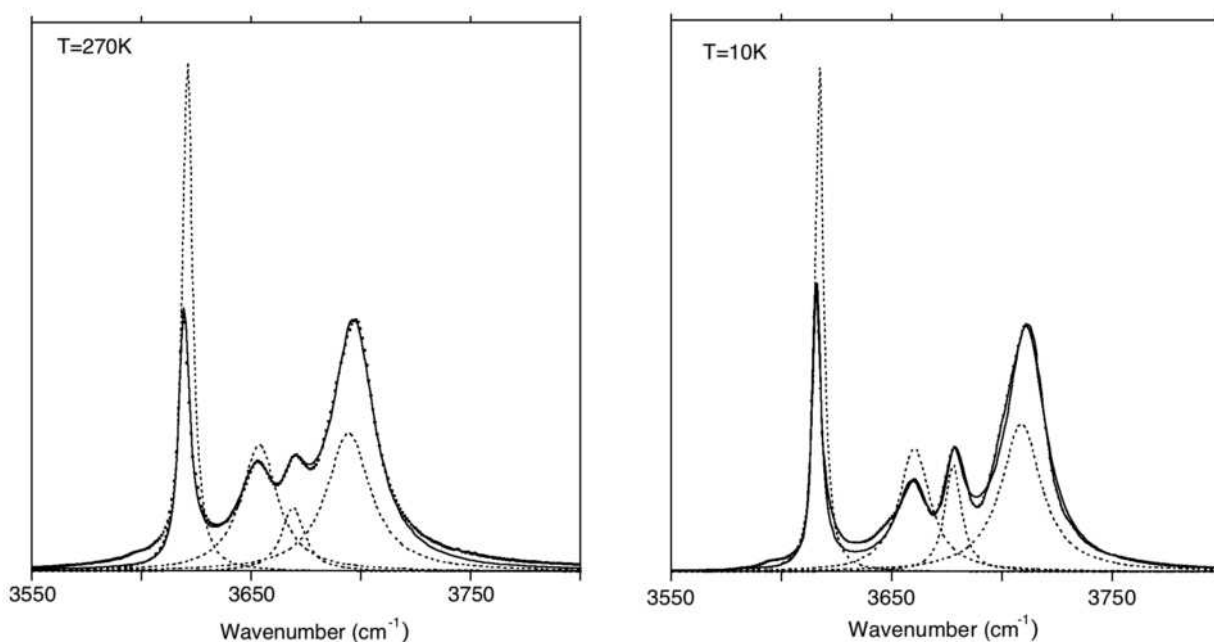| 270 K			10 K		
Transverse frequency (cm^{-1})	Effective charge (arbitrary units)	Damping parameter (cm^{-1})	Transverse frequency (cm^{-1})	Effective charge (arbitrary units)	Damping parameter (cm^{-1})
3614.1	580	5.5	3611.0	550	4.5
3647.5	550	20.0	3654.5	530	17.0
3667.0	310	12.5	3675.0	360	9.0
3686.5	630	24.0	3700.0	660	22.0

FIGURE 8. Fit (continuous line) of the powder transmission infrared spectra of kaolinite (points) using effective medium theory (see text) at 270 K (**left**) and 10 K (**right**). The dotted lines correspond to the effective absorption of isolated oscillators. Note the energy transfer between the bands due to the macroscopic electrostatic coupling between the modes (the spectrum differs from the sum of isolated oscillator absorptions).

OH absorption band. A splitting of the high-frequency OH band was also predicted by first-principles calculations, due to the doubling of dickite unit cell (Balan et al. 2005). The significant intensity of the band observed at 3716 cm^{-1} in the 10 K spectrum of well-ordered dickite samples thus suggests that the two bands at 3716 and 3730 cm^{-1} in fact correspond to the two modes predicted for the OH3 group. The occurrence of two OH3 bands in the dickite spectrum is consistent with the small but significant shift of the high-frequency band observed in the Raman spectra recorded with the a(c'c')$\bar{\text{a}}$ and c'(bb)$\bar{\text{c'}}$ geometrical configurations on the St. Claire dickite (Johnston et al. 1998; Shoval et al. 2001). From these single-crystal Raman observations, the band at 3730 cm^{-1} is in-plane polarized, whereas that at 3716 cm^{-1} display a perpendicular polarization. Therefore, we suggest that the intensity of the band at 3716 cm^{-1} was reduced in the low-temperature spectra recorded by Bish and Johnston (1993) because of orientation effects related to the sample preparation by sedimentation.

In contrast, the band observed at 3690 cm^{-1} in the low-temperature spectra of well-ordered samples of dickite cannot be understood within the same framework. The two OH3 modes, the split mode corresponding to the broad band at 3649 cm^{-1} and the almost degenerated modes leading to bands at 3612 and 3620 cm^{-1} correspond in total to the eight vibrational modes expected from the dickite crystal structure. In fact, the frequency of the band at 3690 cm^{-1} (3685 cm^{-1} at 270 K) matches that of the transverse frequency of the in-phase motion of the three inter-layer OH groups in kaolinite. Therefore, this band is likely related to "kaolinite-like" stacking defects in dickite. In that case, the corresponding intra-layer OH vibration almost coincides with that of dickite, whereas the two out-of-phase vibrations of inter-layer OH group are not observed because of their significantly lower intensity. The occurrence of "kaolinite-like" stacking defects in well-ordered dickite samples is consistent with the HRTEM observations of Kogure and Inoue (2005). Comparatively, the occurrence of "dickite-like" stacking defects is commonly observed in well-ordered kaolinite samples (e.g., Johnston et al. 2008).

Phonon coupling and quantum saturation effects in kaolinite group minerals

The successful fit of experimental spectra using a simple model based on effective medium theory indicates that OH-stretching modes behave approximately as independent Einstein oscillators. Direct coupling of phonons is indeed known to lead to asymmetric line shapes, usually referred to as Breit-Wigner or Fano line shape (Scott 1974). In the present case, such coupling mechanism is not required to reproduce the weak asymmetry observed on the intra-layer OH band at 270 K. Note that the difference between the fit and the experimental curve at ~3640 cm^{-1} in the low-temperature spectrum (Fig. 8) is in fact related to the occurrence of a minor proportion of "dickite-like" defects in the GB1 kaolinite sample.

The treatment of OH-stretching modes as Einstein oscillators is consistent with the fact that weakly dispersive hard modes at high frequency display very short correlation lengths (Salje 1992). The anharmonic damping of otherwise harmonic oscillators leads to the frequency shift and line broadening observed with increasing temperature. Both effects can be described by

introducing a complex damping constant α in equation describing a damped harmonic oscillator driven by an oscillating electric field of pulsation ω:

$$m\ddot{X} + \alpha \dot{X} + kX = Z^* E_0 \exp(i\omega t) \tag{5}$$

where $\alpha/m = \Gamma + i\Delta$ and m, k, and Z^* are effective mass, force constant, and charge, respectively.

The real parameters Δ and Γ thus account for the shift in absorption band position and change in linewidth observed as a function of temperature, respectively. Both Γ and Δ are proportional to the density of final states into which the harmonic phonon is decaying. Thus, they depend on temperature and follow the Bose-Einstein occupation n_i of the phonon states produced in the decay (Scott 1974):

$$n_i = \frac{1}{\exp(\hbar\omega_i / kT) - 1} \tag{6}$$

where ω_i is the phonon frequency and k the Boltzmann constant. This dependence leads to the quantum saturation behavior observed at low temperature, which is conveniently fitted using Equation 1. The values of Θ_S can be compared to the Einstein temperature Θ_E at $T_S = \Theta_S/2$, obtained by fitting the calorimetric data of Robie and Hemingway (1991) (Fig. 9). The Einstein temperature reflects the characteristic frequency of optical phonons contributing to the crystal thermal properties at a given temperature. It can be observed that Θ_S ranges from $\Theta_E/2$ to $\Theta_E/4$ (Fig. 9). The low Θ_S values observed for the OH-stretching modes in kaolinite group minerals thus indicate that the OH vibrations probe the average thermal bath of the crystal, without coupling to a specific decay channel (Salje et al. 1991b).

Leading terms in the frequency shifts are related to the third and fourth derivatives of the total energy with respect to atomic displacements and to the thermal expansion of the lattice, described by the mode Gruneisen parameter (e.g., Lazzeri et al. 2003). The differential shift of the bands related to the intra- and inter-layer OH groups (B parameter, Table 1) is likely related to different H-bond geometry (e.g., Libowitzky 1999; Winkler et al. 2008a). The weakening of intra-layer OH-stretching vibration with decreasing temperature and structure contraction indicates some H-bonding. In comparison, the strengthening of inter-layer OH vibrations suggests almost no H-bonding. Noteworthy, OH-stretching frequencies above 3650 cm^{-1} weakly depend on "H-bond" lengths (Libowitzky 1999) and likely involve other parameters, such as electrostatic interactions between OH groups and the surrounding crystal structure (e.g., Mitev et al. 2009). Together with the coupled motion of OH groups, this casts some doubts on the straightforward use of the OH···O distance in the assignment of the OH-stretching bands in kaolinite-group minerals (Johnston et al. 2008). The anisotropic thermal expansion of kaolinite (Bish 1993) also explains the larger frequency shift observed for inter-layer OH bands compared with the intra-layer OH band. In dickite, the inter-layer OH2 and OH4 groups appear as more strongly H-bonded than the OH3 group, which is consistent with the H-bond lengths inferred from low-temperature structure refinement (Bish and Johnston 1993).

The absorption profile of high-frequency vibrational modes is usually the convolution of an intrinsic line profile, depending
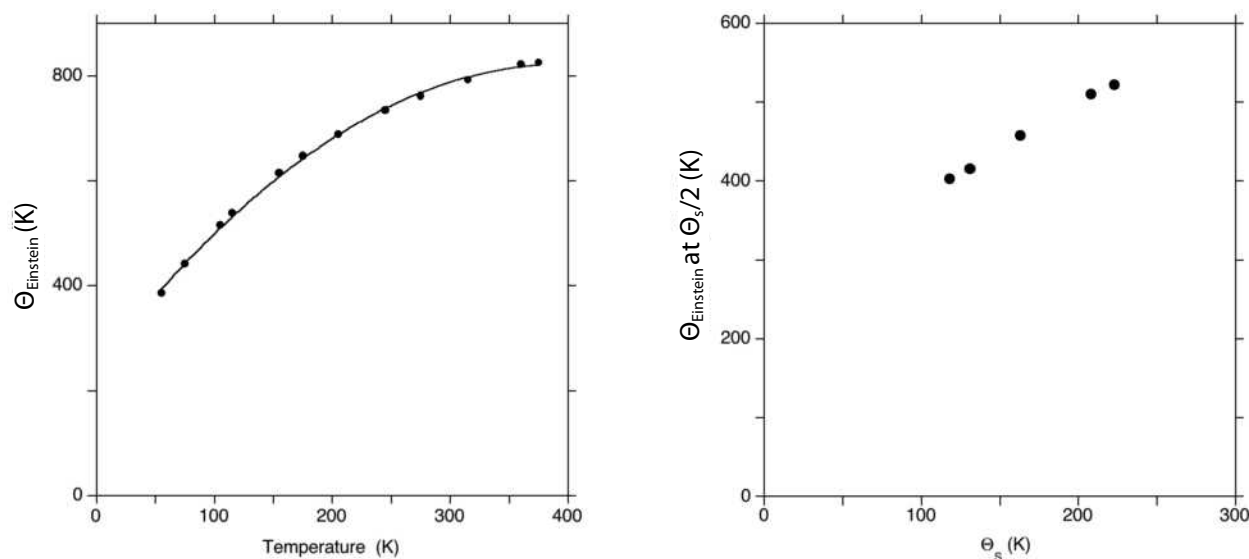
FIGURE 9. (left) Einstein temperature of kaolinite from calorimetric data of Robie and Hemingway (1991). The Einstein temperature is obtained by fitting the experimental data at a given temperature using an Einstein function. **(right)** Einstein temperature at $\Theta_S/2$ as a function of Θ_S.

on the real part of the damping coefficient Γ, with a distribution function of phonon frequencies related to the system heterogeneity. The damping term is related to the decay of the phonon into two phonons of lower energy and only involves the third derivative of the total energy with respect to atomic displacements (e.g., Menéndez and Cardona 1984). Accordingly, the linear extrapolation to low temperature of the linewidth, i.e., the neglect of quantum saturation, should intercept the origin at 0 K (provided that the instrumental linewidth is much smaller than any of the phonon linewidths). The significant departure observed for OH-stretching modes in kaolinite thus indicates that their linewidth is in fact dominated by inhomogeneous broadening, either from defects or from distribution of the depolarization factors in the composite sample. Note that the increased value of Θ_S for the linewidth can be understood in the quasi-harmonic approximation to stem from the same heat bath as the temperature evolution of the mode frequencies.

Interestingly, the absorption line related to kaolinite-like stacking defects in ordered dickite displays a higher saturation temperature. This distinct behavior can be ascribed to the planar nature of the defect, restricting the dispersion of vibrational frequencies in two dimensions. This defect also corresponds to a narrow band at low temperature, which can be explained by the fact that isolated defects are less affected by depolarization effects and absorb light at frequencies close to the transverse optical frequency. This is a way to distinguish kaolinite-like stacking defects in dickite from an admixture of well-ordered kaolinite and well-ordered dickite.

To conclude, the temperature dependence and effective medium fit of the kaolinite spectrum does not reveal any strong anharmonicity in the OH-stretching modes. Anharmonic effects seem therefore to be mostly related to a rigid shift of the bands, whose magnitude is dominated by the effect of the small H mass. The quasi-harmonic behavior of OH-stretching modes explains the successful harmonic modeling of vibrational properties of hydrous minerals using density functional perturbation theory (e.g., Balan et al. 2001; Winkler et al. 2008b).

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