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The effect of pressure on the intercalation of an ordered kaolinite

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ABSTRACT

Intercalation of an ordered kaolinite with potassium acetate (KCH_3COO) under a pressure of 20 bars and 220 °C, induced new Raman bands at 3590, 3603, and 3609 cm^{-1} in addition to the normal kaolinite bands. These bands are attributed to the inner surface hydroxyls hydrogen bonded to the acetate. It is proposed that the intercalation under 20 bars pressure at 220 °C caused the differentiation of the inner surface hydroxyl groups, resulting in the appearance of these additional bands. Diffuse reflectance infrared spectra of the potassium acetate intercalated kaolinite that was formed at 20 bars and at 220 °C showed new bands at 3595 and 3605 cm^{-1}. Upon formation of the intercalate at 2 bars and at 120 °C additional infrared (IR) bands were found at 3592, 3600, and 3606 cm^{-1}. These IR bands correspond well with the observed Raman spectra. It is proposed that the effect of intercalation of the highly ordered kaolinite under pressure caused the kaolinite to become disordered and this disordering was dependent on the temperature of intercalation. It is suggested that when pressure is applied to the kaolinite crystal in the presence of an intercalating agent, the hydrogen bonds between adjacent layers are broken to create space for the intercalating agent between the layers. A direct result is that the order of the kaolinite crystals shows a decrease resulting in more defect structures. This is evidenced by the additional spectroscopic bands in both the Raman and IR spectra.

INTRODUCTION

Structural disorder or degree of crystallinity is produced by either geological conditions of formation, transport, or deposition or by mechanical treatment, such as grinding (Brindley et al. 1986). Structural disorders in layer silicates, particularly in clay minerals are of many kinds including: thermal disorder, disorder in the distribution of cations, long-range and short-range order, disorder in layer stacking, order-disorder in mixed-layer systems, finite crystal size as a lattice disorder, structures with non-planar layers, and mechanically disordered structures (Brindley 1984). The most widely accepted and used method for the comparison of different kaolinites with regards to order and disorder is the Hinckley index (Hinckley 1963). Disorder due to layer stacking is common in clay mineral structures. For any particular type of layer structure and interlayer bonding mechanism, a great variety of theoretical polytype structures can be developed, for example, one- and two-layer kaolinite-type structures (Newnham 1961; Dornberger-Schiff and Durovic 1975). Clay minerals characteristically exhibit considerable variations in layer stacking order-disorder. Disorders arise commonly from the presence of variable amounts of intercalated material between the layers, such as variable hydration from layer to layer and from the presence of layers of other kinds irregularly distributed as in the many forms of interstratified structures.

Raman microscopy has proven most useful for the study of the kaolin structures (Frost and van der Gaast 1997) and for the determination of order-disorder relationships. In their work, kaolinites were classified according to the ratio of the intensities of the two types of inner surface hydroxyls at 3685 and 3695 cm^{-1}. The intensity of the 3650 and 3670 cm^{-1} bands were found to vary concomitantly with the 3685 and 3695 cm^{-1} bands. A relationship between the degree of defect structures and the intensity of the 3685 cm^{-1} band was found. In their work, correlation between the Raman spectrum of the hydroxyl stretching vibrations and the degree of disorder using the Hinckley Index was attempted and a linear relationship between this index and the ratio of the 3685 and 3695 cm^{-1} bands was found. Thus Raman spectroscopy provided a method for studying the defect structures of kaolinites. The application of Raman microscopy to the study of intercalated kaolinites also has proved most useful (Frost et al. 1997a; Frost and Kristof 1997; Frost et al. 1997b). An additional Raman band, attributed to the inner surface hydroxyl groups hydrogen bonded to the acetate, was observed at 3605 cm^{-1} for the potassium acetate intercalate with the concomitant loss of intensity in the bands at 3652, 3670, 3684, and 3693 cm^{-1}. In this paper, we report the changes in the defect structures of a

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highly ordered kaolinite induced through intercalation under pressures of 20 and 2 bars and at the two temperatures of 220 and 120 °C, respectively.

Experimental methods

Intercalation under pressure

The kaolin polytype used in this study is a low defect kaolinite from Kiralyhegy, Hungary. Intercalation under high pressure and temperature was carried out in a high-pressure asher (Anton-Paar, Austria). Kaolinite (200 mg), potassium acetate (16 g, KCH_3COO), and water (20 cm^3) were measured in the quartz bomb of the HPA equipment and closed by a quartz lid. A teflon gasket between the bomb and the lid ensured the gas-tight sealing of the bomb. Then the bomb, with the lid, was placed in the metal heating block of the equipment and a nitrogen pressure of 80 bars was applied over the lid to prevent escape of vapors from the bomb. After 30 min the temperature was increased to 220 °C and kept constant for 8 h. During this treatment the temperature and the external pressure were recorded by the computer controlling the process. At 220 °C the nitrogen pressure increases to 120 bars. It is not possible to measure the pressure inside the bomb but it does not exceed 23 bars. The pressure in this paper is considered to be 20 bars. In addition, a parallel experiment was conducted in which the same kaolinite and potassium acetate mixture was heated to 120 °C only. In this case the internal pressure did not exceed 2 bars. After cooling to room temperature, the external pressure was released and the clay was separated from the solution by centrifugation. The pH of the solution was 8.9. At this pH, the solution contains potassium acetate only.

Spectroscopy

Small amounts of the untreated kaolinite or the intercalated clay mineral were placed on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system, and a charge-coupled device (CCD). A Spectra-Physics model 127 He/Ne laser (633 nm) was used to record Raman spectra at a resolution of 2 cm^{-1} and were acquired in sections of approximately 1000 cm^{-1}. Repeated acquisitions using the highest magnification were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The best method of placing the kaolinites on this metal surface was to take a very small amount on the end of the spatula and then tap the crystals on to the metal surface. Further details on this spectroscopic technique have been published elsewhere (Frost and van der Gaast 1997; Frost and Shurvell 1997; Frost et al., 1997b). Diffuse reflectance Fourier transform (DRIFT) IR spectroscopy analyses were undertaken using a Bio-Rad 60A spectrometer where 512 scans were obtained at a resolution of 2 cm^{-1}. In DRIFT spectroscopy, the intensity of the bands is displayed as Kubelka-Munk (K-M) units. The K-M function is the relationship between absorbance and intensity of reflected radiation (Griffith and Fuller 1981).

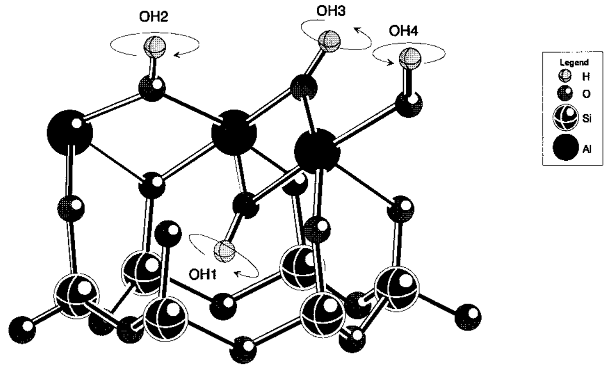

Figure 1. Computer-generated model of the unit cell of kaolinite showing the theoretical hydroxyl orientations of the four hydroxyl groups.

Spectral manipulation such as baseline adjustment, smoothing, and normalization was performed using the GRAMS Spectracalc software package (Galactic Industries Corporation, New Hampshire, U.S.A.). Band component analysis was undertaken using the Jandel ''Peakfit'' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Peaks were fitted with a mixture of Gaussian and Lorentzian shapes using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian ratio was maintained at values >0.7 and fitting was repeated until reproducible results were obtained with squared correlations of r^2 >0.995.

Results and discussion

Intercalation expands the *c* axis of the kaolinite by the insertion of various intercalating molecules or atoms. This intercalation process may be observed in the XRD pattern and the appearance of a new (001) peak at ~14 Å instead of the original 7.2 Å (001) peak. The unit cell of kaolinite contains four hydroxyl groups (Fig. 1). OH1 is the internal hydroxyl group commonly referred to as the inner hydroxyl and gives rise to the ν_5 band centered at 3620 cm^{-1}. OH2, OH3, and OH4 are the three inner surface hydroxyls with differing orientations. These three hydroxyls give rise to the ν_1, ν_4, ν_2, and ν_3 Raman modes at 3695, 3685, 3670, and 3645 cm^{-1} (Frost and van der Gaast 1997). Intercalation on a molecular scale is observed by changes in the IR and Raman spectra of both the kaolinite and intercalating molecule. Intercalation with potassium acetate results in changes in intensity and frequency of the hydroxyl bands in the stretching and deformation regions. When kaolinite is intercalated with potassium acetate at 1 bar and 25 °C, a new band is observed at 3605 cm^{-1} with a concomitant loss of intensity

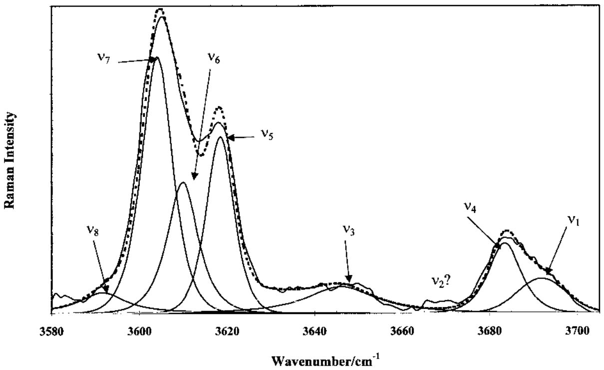

FIGURE 2. Band component analysis of the Raman spectrum of the hydroxyl stretching region of potassium acetate intercalated kaolinite pressure formed at 20 bars and 220 °C.

in the ν_1 to ν_4 modes. It could be expected that water would also intercalate at the same time as the potassium acetate. The H_2O molecules serve to hydrate the cation and fill the interlayer spaces. However to intercalate with water only requires deintercalation using washing or thermal treatment of certain types of kaolinites intercalated with potassium acetate or urea (Kristof et al. 1997). Thus, when the Raman or IR spectrum of the kaolinite intercalated with potassium acetate is obtained, the spectrum consists of the spectrum of the modified kaolinite, the inserting molecule, and water. Each molecule has its own characteristic spectral region. In this paper only the spectra of the modified hydroxyl kaolinite surfaces are reported.

Upon intercalation under 20 bar pressure and at 220 °C of the low defect kaolinite, additional Raman bands (ν_6, ν_7, and ν_8) are observed at 3590, 3604, and 3609 cm^{-1}. The band component analysis of the Raman spectrum of the hydroxyl stretching region is illustrated in Figure 2. The intensity of these bands as determined by the band areas are 1.5, 30, and 17.5% of the total normalized band profile of the hydroxyl-stretching region. When the kaolinite is fully intercalated, the intensity of the ν_1, ν_4, ν_2, and ν_3 modes assigned to the inner surface hydroxyl groups will approach zero. Significant intensity in the 3684 and 3693 cm^{-1} bands being 5.5 and 2.5% remains after intercalation. Such values indicate the kaolinite is only partially intercalated. Such results were unexpected, as it was originally thought that the effect of pressure would cause an increase in the intercalation of the kaolinite. The exact opposite was found. Instead of observing one new additional Raman band at ~3605 cm^{-1} upon intercalation, three additional Raman bands were obtained. Further, the ability to obtain high quality Raman spectra diminished with the pressure formed intercalate, such an observation is associated with a decrease in crystallinity that is observed when an increase in the defect structures of the kaolinite occurs. As a consequence, accurately analyzing the bands in terms of various components is more difficult for the Raman hydroxyl region, nevertheless estimates of the spectroscopic parameters of these hydroxyl-stretching bands can be made. Table 1 reports the spectroscopic parameters for hydroxyl stretching region of the ordered kaolinite, the potassium acetate intercalated kaolinite, and the pressure formed potassium acetate intercalated kaolinite. The bandwidth of the inner hydroxyl stretching Raman mode for the untreated kaolinite is 5.7 cm^{-1}, but in both the 1 bar (1 atm) and 20 bar formed intercalate, the bandwidths are 12.4 and 9.7 cm^{-1}, respectively. The band (ν_5) for the inner hydroxyl is broadened considerably upon intercalation. The bandwidth may depend on the fitting of the adjacent ν_6 and ν_7 bands. Nevertheless, the band is broadened upon intercalation. The inserting molecule consists of both the anion bonded to the inner surface hydroxyls and the potassium cation. The reason for such broadening of the ν_5 band lies with the presence of the cation from the inserting acetate salt in that the cation sits in the ditrigonal space of the siloxane layer and consequently influences the position of the inner hydroxyl group. Within the precision of the spectroscopic experiment, the band position of the Raman band of the inner hydroxyl shifts to lower frequencies upon intercalation. The band is at 3620 cm^{-1} for the untreated kaolinite and is at 3619 cm^{-1} for the pressure formed intercalate.

The ratio of ν_4/ν_1 bands in the untreated, low defect kaolinite is 3.89. This ratio is indicative of a highly ordered kaolinite. In the room temperature potassium acetate intercalated kaolinite, the ratio is 1.52, although the intensities of these bands represent the small amount of kaolinite that was not intercalated. For the potassium acetate intercalated kaolinite pressure formed at 20 bars and 220 °C, the intensity of the ν_1 and ν_4 bands is considerable and the ν_4/ν_1 ratio is 1.40. This value is indicative of a kaolinite with greater defect structures. The bandwidths of the three bands at 3590, 3603, and 3609 cm^{-1} are 16.5, 12.0, and 13.9 cm^{-1}, respectively. The bandwidth of the 3605 cm^{-1} band for the room temperature potassium acetate intercalated kaolinite was 11.5 cm^{-1}. The increased band widths of the additional Raman bands formed upon intercalation show the kaolinite has become more disordered. It is concluded that the intercalation of the kaolinite under a pressure of 20 bars caused the kaolinite to become disordered.

The ability to obtain quality IR spectra is not as effected by the order-disorder of the kaolinite and quality DRIFT spectra are easily obtained. The DRIFT spectra of the pressure formed intercalated kaolinite also showed additional bands at 3595 and 3605 cm^{-1}, which correspond well with two of the Raman bands (Figure 3). Previous studies of the potassium acetate intercalated kaolinite formed at 1 bar and 25 °C showed only one additional IR band at 3605 cm^{-1} (Kristof et al. 1997). Table 2 reports the spectroscopic data for the DRIFT spectra of the hydroxyl stretching region of the 220 °C pressure formed potassium acetate intercalated kaolinite and also for the 120 °C pressure formed potassium acetate intercalated kaolinite. For the first intercalate, additional bands were ob-

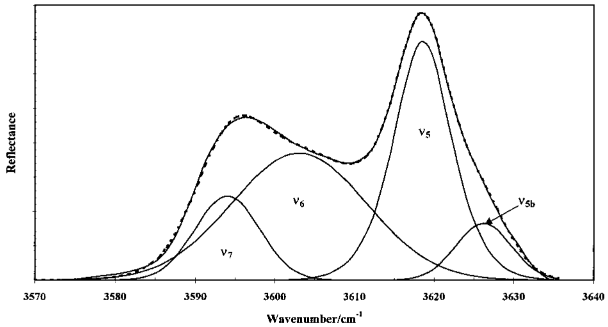

FIGURE 3. Band component analysis of the DRIFT spectrum of the hydroxyl stretching region of potassium acetate intercalated kaolinite pressure formed at 20 bars and 220 °C.

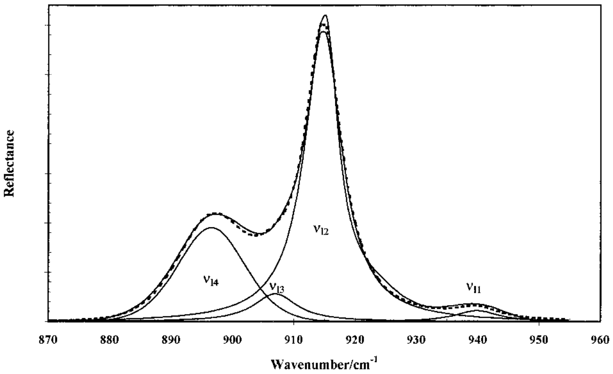

FIGURE 4. Band component analysis of the DRIFT spectrum of the hydroxyl deformation region of potassium acetate intercalated kaolinite pressure formed at 20 bars and 220 °C.

served at 3595 and 3605 cm^{-1} and for the second intercalate, additional bands were observed at 3592, 3600, and 3606 cm^{-1}. These additional IR bands also indicate increased disorder in the kaolinite. Such disorder is observed in potassium acetate intercalated halloysite, where two additional infrared reflectance hydroxyl bands were also observed (Frost and Kristof 1997). Potassium acetate also has a Raman active, infrared inactive band at 928 cm^{-1}. This band is assigned to the CH rocking mode (ρ_{CH}) and it does not interfere with the band component analysis of the DRIFT hydroxyl deformation modes. Further, upon intercalation, both additional Raman and IR bands were observed in the hydroxyl deformation region. Additional bands were observed at 897 and 907 cm^{-1}, together with bands at 915, 923, and 939 cm^{-1} (Figure 4). These additional bands were attributed to hydroxyl groups, which were hydrogen bonded to the acetate ion. The two IR bands at 897 and 910 cm^{-1} had relative band areas of 27 and 7% of the total normalized band areas with bandwidths, as full widths at half height of 13 and 8.5 cm^{-1}. The width of the 897 cm^{-1} band shows that this deformation vibration is not well defined compared with the 915 cm^{-1} band where the bandwidth is 7.4 cm^{-1}. This is also indicative of hydroxyl librations (Frost 1998) that are free to move in many directions. Such motion occurs when the hydroxyl group is not hydrogen bonded. The libration of the hydroxyl groups is illustrated by the circular arrows in Figure 1.

For potassium acetate intercalated kaolinite, formed at 2 bars and at 120 °C as opposed to 20 bars and 220 °C, additional IR bands were observed at 3592, 3600, and 3606 cm^{-1} (Fig. 5). These IR bands correspond well with the three observed Raman bands. These bands made up 8.8, 10.2, and 9.9% of the total normalized band areas with the bandwidths determined as 8, 10.3, and 11.4 cm^{-1}, respectively. These bands are attributed to the inner surface hydroxyl groups that are hydrogen bonded to the intercalating acetate ion. The thermal treatment of this kaolinite under 2 bars pressure was milder than the previous case when under a pressure of 20 bars the temperature reached 220 °C. The effect of lower temperature and lower pressure upon the intercalation of the kaolinite caused the appearance of three additional IR bands. It is considered that as the pressure is applied to the kaolinite, the inserting molecule causes the hydrogen bonds between the adjacent kaolinite layers to be broken allowing for the creation of space for the intercalating molecule. A direct result will be the increase in the defect structures in the kaolinite, i.e., the kaolinite will become more disordered. This is evidenced by the additional three IR and Raman bands in the 3590 to 3605 cm^{-1} region. The question arises as to why three additional bands are found. In the unit cell there are three inner surface hydroxyl groups (Fig. 1) that point in different directions (Giese 1982, 1988; Hess and Saunders 1992; Frost and Van der Gaast 1997). It is proposed that in the intercalation of kaolinite under pressure of 2 bars and 120 °C, the three inner surface hydroxyl groups were intercalated such that the directions of the hydroxyl groups were maintained during the intercalation process. In this intercalation, the three inner surface hydroxyl groups maintain their orientations as depicted in Figure 1. These hydroxyl groups are then hydrogen bonded to the acetate ions. When the kaolinite is intercalated at the higher pressures and at 220 °C, the intercalation process caused the directions of the hydroxyl

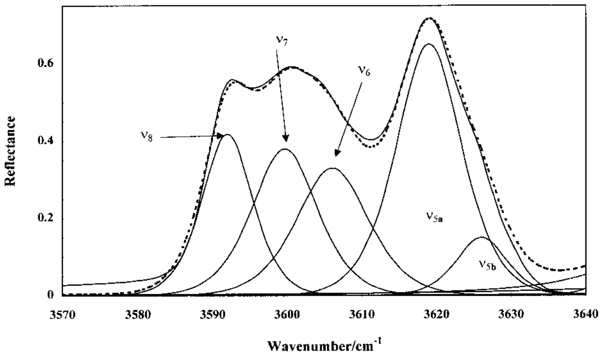

FIGURE 5. Band component analysis of the DRIFT spectrum of the hydroxyl stretching region of potassium acetate intercalated kaolinite pressure formed at 2 bars and 120 °C.

TABLE 1. Raman data for the hydroxyl stretching region of kaolinite

Sample	Band	Band center (cm⁻¹)	FWHH (cm⁻¹)	Area (%)
K	ν_5	3620	5.7	20.8
	ν_3	3651	11.5	14.5
	ν_2	3670	15.4	15.4
	ν_4	3684	9.5	30.0
	ν_1	3693	15.2	17.7
KA1	ν_6	3605	11.5	62.5
	ν_5	3620	12.4	22.0
	ν_3	3645	19.1	3.4
	ν_2	3670	17.5	2.2
	ν_4	3685	11.5	6.4
	ν_1	3695	19.1	4.2
KA2	ν_8	3590	16.5	1.5
	ν_7	3603	12.0	30.0
	ν_6	3609	13.9	17.5
	ν_{5a}	3619	9.7	23.2
	ν_{5b}	3626	11.4	4.4
	ν_3	3649	19.0	12.0
	ν_2	3668	10.3	0.3
	ν_4	3684	12.0	5.5
	ν_1	3693	16.5	2.5

Note: K symbolizes the untreated kaolinite; KA1 = kaolinite intercalated with potassium acetate at 1 bar and 25 °C; KA2 = kaolinite intercalated with potassium acetate under a pressure of 20 bars and 220 °C; KA3 = the kaolinite intercalated with potassium acetate under 2 bars pressure and 120 °C.

TABLE 2. DRIFT data of the hydroxyl stretching region of kaolinite

Sample	Band	Band center (cm⁻¹)	FWHH (cm⁻¹)	Area (%)
KA2	ν_7	3595	14.5	13.6
	ν_6	3605	14.2	8.5
	ν_{5a}	3619	10.0	15.1
	ν_{5b}	3628	11.9	5.0
	ν_3	3650	19.0	13.6
	ν_2	3668	11.6	7.9
	ν_4	3682	14.0	3.0
	ν_1	3693	18.0	25.6
KA3	ν_8	3592	8	8.8
	ν_7	3600	10.3	10.2
	ν_6	3606	11.4	9.9
	ν_{5a}	3619	10.3	17.5
	ν_{5b}	3626	8.0	3.1
	ν_3	3650	16.6	7.9
	ν_2	3670	16.6	3.6
	ν_4	3684	—	0.0
	ν_1	3693	17.0	38.9
	H_2O	3556	broad	

Note: K symbolizes the untreated kaolinite; KA1 = kaolinite intercalated with potassium acetate at 1 bar and 25 °C; KA2 = kaolinite intercalated with potassium acetate under a pressure of 20 bars and 220 °C; KA3 = the kaolinite intercalated with potassium acetate under 2 bars pressure and 120 °C.

groups to become similar. Thus, three additional inner surface hydroxyl bands (ν_6, ν_7, and ν_8) were obtained in the case of the milder thermally treated kaolinite and two additional inner surface hydroxyl bands in the intercalate formed under harsher conditions.

To fit the spectral profile an additional component was needed at 3626 cm⁻¹. This is shown as ν_{5b} in Tables 1 and 2 and Figures 3 and 5. This band is attributed to the inner hydroxyl of the kaolinite that has been effected by the intercalation process. Such bands for kaolin polytypes were observed previously for halloysites (Frost and Shurvell 1997). It is possible, as has been previously suggested, that the presence of the potassium cation keys into the ditrigonal cavity of the siloxane surface of the kaolinite and this polarizes the inner surface hydroxyl group resulting in the formation of a new band at 3626 cm⁻¹ (Frost et al. 1997b). This band at 3626 cm⁻¹ is normally observed in disordered kaolinites. The band profile of the infrared spectrum of the hydroxyl deformation region for the lower pressure/lower temperature formed potassium acetate intercalated kaolinite now shows increased complexity. However, better resolution in the band profile is obtained (Fig. 6) and hydroxyl deformation modes are observed at 897, 909, 915, 922, and 939 cm⁻¹. The areas of these bands were 42, 13.5, 18.3, 15.5, and 8.6%, respectively, with band widths of 15.2, 12.2, 5.4, 11.9, and 16.3 cm⁻¹. The band at 897 cm⁻¹ is attributed to the hydroxyl deformation mode of the ''free'' or non-hydrogen bonded hydroxyl group. This band now makes up more than 40% of the total normalized band area and is indicative of a high degree of disorder. The band at 909 cm⁻¹ may be associated with the second inner hydroxyl stretching vibration at 3626 cm⁻¹. As the frequency of the stretching vibration of the inner hydroxyl group decreases, it would be expected that the frequency of the deformation mode would also decrease. Again, the appearance of a second band in this part of the hydroxyl-stretching region is a sign of increased disorder.

The effect of intercalation of an ordered kaolinite under pressure caused an increase in the defect structures of the kaolinite. This is evidenced by additional new bands at 3596, 3600, and 3605 cm⁻¹ in both the Raman and infrared hydroxyl stretching region spectra. It is suggested that these three bands are attributable to the three inner surface hydroxyl groups and that the formation of the intercalated kaolinite under pressure resulted in the differentiation of the inner surface hydroxyl groups. Additional bands were also observed in the hydroxyl deformation

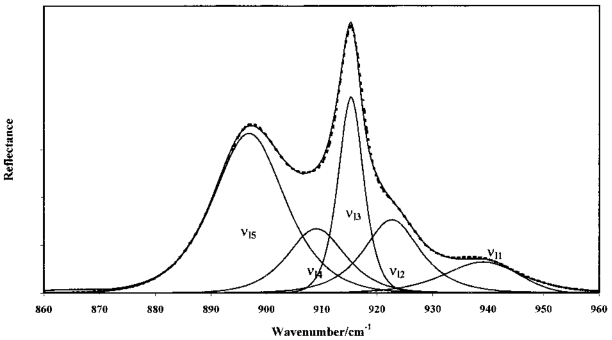

FIGURE 6. Band component analysis of the DRIFT spectrum of the hydroxyl deformation region of potassium acetate intercalated kaolinite pressure formed at 2 bars and 120 °C.

region at 895 and 906 cm^{-1}. These bands were attributed to hydroxyl groups hydrogen bonded to the acetate. It is proposed that the intercalation of the ordered kaolinite under pressure caused the kaolinite to become disordered with a consequential increase in the defect structures of the kaolinite.

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