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AN IN SITU INFRARED STUDY OF MAGNESIUM HYDROXIDE DEHYDROXYLATION UNDER ELECTRIC FIELDS

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ABSTRACT

A specially designed IR electrolysis cell is described, which allows samples to be simultaneously heated and electrolysed during the recording of their IR spectra. By means of this cell, changes in the intensity of the hydroxyl stretching band at 3670 cm^{-1} were recorded as a function of temperature both in the presence and absence of an applied electric field. The intensity of the –OH band decreases with temperature in two distinct stages, both of which are influenced by the electric field. The effect of the electric field on the regain of spectral intensity of the hydroxyl band on re-cooling the sample to room temperature was also studied, and the results discussed in terms of the delocalization of the protons from their respective molecules, possibly by a field-dependent tunnelling mechanism. The effect of the field on the shape and frequency of the –OH stretching band is also discussed.

INTRODUCTION

The dehydroxylation of $Mg(OH)_2$ is a much-studied thermal reaction, in which IR spectroscopy, particularly at elevated temperatures, has proved to be a useful technique. Freund[1] has shown that just below 300°C the hydroxyl stretching band begins to broaden, which he attributes to interactions between the OH–OH groups at the surface of the crystals. This is followed by tunnelling of the protons between adjacent hydroxyl groups, and leads to the formation of molecular water which is eliminated from the crystal lattice by diffusion[1]. In other experiments in which the samples were heated in situ, Freund[2] observed a large positive frequency shift in the OH-stretching band with temperature, which he attributed to the thermal expansion of the $Mg(OH)_2$ lattice[2].

Previous studies[3] have shown that the dehydroxylation of $Mg(OH)_2$ is markedly assisted by applied DC electric fields, which lower the onset temperature of the reaction and reduce the apparent activation energy by up to 10 kcal $mole^{-1}$. Calcula-

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tions of the effect of the electric fields on the tunnelling process[4] suggest that the dehydroxylation results cannot be explained by enhanced tunnelling alone. A possible alternative explanation in terms of the enhanced defect generation and/or anihilation[4] is based on indirect considerations, but so far, direct observations of the dehydroxylation process under the influence of electric fields have not been possible.

These considerations have led to the development of a heated IR cell in which the sample can be simultaneously electrolysed and its spectrum recorded at temperature. The direct observation of the effect of electric fields on the hydroxyl stretching band of $Mg(OH)_2$ thus obtained are presented in this paper, in which attention is also paid to the effect of thermally cycling the sample under electric fields. The effect of the field on the IR peak shape and frequency was also noted, in the hope of providing further information about the way in which electric fields interact with hydroxyl groups in solid hydroxides.

EXPERIMENTAL

Design of the IR electrolysis cell

The cell was based on a simple heated IR cell described elsewhere[5] in which the sample is sedimented on to a KBr disc which is heated by a resistance winding. Since in the present cell, electrodes have to be attached to the sample-supporting substrate, a thin spectroscopic-grade quartz plate was substituted for KBr; this is transparent in the hydroxyl-stretching region of present interest, but a sharp cut-off at about 2500 cm^{-1} severely limits the usefulness of the cell for other purposes. The experimental arrangement is shown in Fig. 1. The sample is sedimented on to the quartz substrate between the two platinum electrodes, which are fastened to the quartz plate with a refractory cement composed of kaolinite and sodium silicate. The fine Nikrokanthal windings are encased in aluminous cement to protect and insulate them and increase the thermal mass of the system. Temperature control is achieved by means of a platinum-platinum rhodium thermocouple and a digital temperature controller, accurate to 2°C.

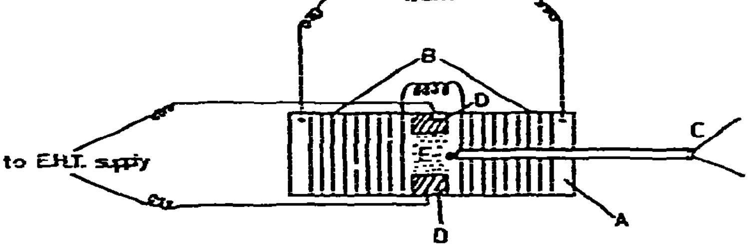


Fig. 1. Schematic diagram of IR electrolysis cell. (A) Fused quartz plate. (B) Nikrokanthal heater windings encased in high-alumina cement. (C) Pt–Pt Rh thermocouple. (D) Pt foil electrode. (E) Sample, sedimented on to plate.

Two major problems were encountered in the early experiments. One problem arose from the presence of a small amount of hydroxyl impurity in the quartz substrate plate, which interfered with the hydroxyl band of interest in the sample. This was cancelled out by placing an identical quartz plate in the reference beam. The second problem arose from the fact that the IR spectrometer used in this work (Pye Unicam SP 1100) was not of the type in which the radiation beam is chopped before impinging on the sample; radiation emitted from the heated sample is therefore in phase with the detector, and interferes with the observed spectrum. This problem was overcome quite satisfactorily in the present experiments by heating the reference cell to the same temperature as the sample cell, by winding the ends with fine Nikrokanthal wire and imbedding a thermocouple in the quartz plate in a similar position to that of the sample cell. The temperature of the reference cell was controlled by a second digital temperature controller.

The sample (Merck $Mg(OH)_2$, extra pure grade, batch No. 6182990) was sedimented on to the sample plate in a continuous strip between the electrodes. The optical density of the sample was adjusted by adjusting the concentration of the slurry. The peak height of the required hydroxyl band was then increased as far as possible by means of the expansion and baseline controls. The hydroxyl spectrum was recorded as a function of temperature, both without an applied field and with an applied field (1.3 kV, electrode gap 6 mm). Because of the difficulties experienced in setting up and carrying out this experiment, it was repeated 15 times to ensure that the results were not an artifact, and to ascertain the effect of sample particle size on the results. Further experiments were also carried out, in which the sample was heated to progressively higher temperatures and cooled to room temperature, the hydroxyl spectrum

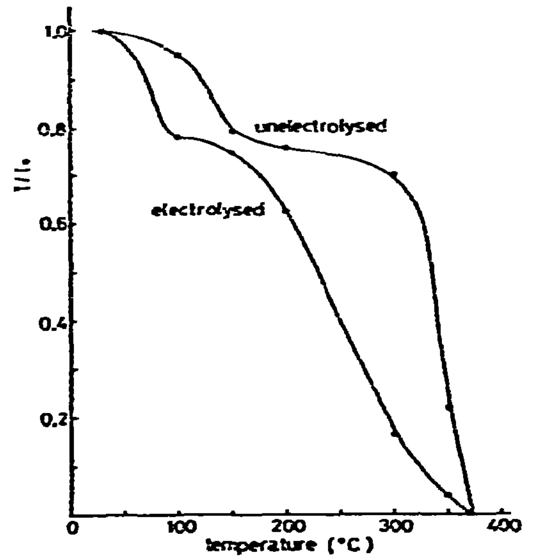


Fig. 2. Intensity change of the 3670 cm^{-1} hydroxyl band of electrolysed and unelectrolysed $Mg(OH)_2$ as a function of temperature.

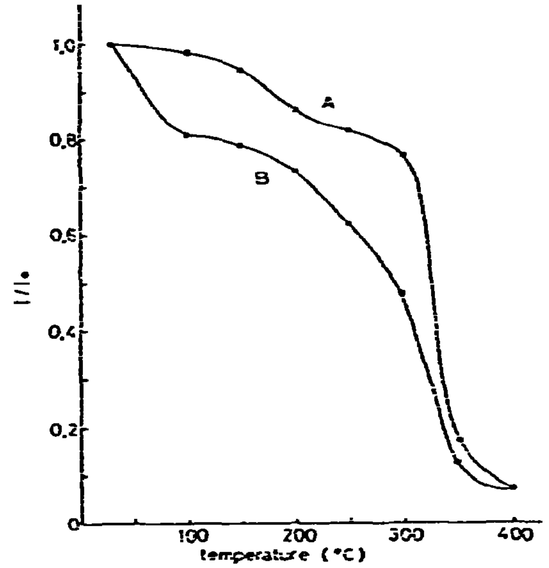
being recorded at each stage. These experiments were carried out both in the presence and absence of the electric field.

RESULTS AND DISCUSSION

The effect of fields on the intensity of the hydroxyl band

Fig. 2 shows a typical plot of the intensity of the hydroxyl band at 3697 cm^{-1} as a function of temperature, both in the presence and absence of the field. To make the results internally comparable, the intensities are presented as a ratio of the initial room-temperature intensity I_0. Fig. 2 shows that in both electrolysed and unelectrolysed samples, the hydroxyl band loses intensity in two distinct stages. This is a real effect, having been noted in all the experiments; the length of the plateau in the curve is slightly dependent on the particle size of the sample, increasing in length with increasing particle size. Fig. 2 shows that under the action of the field, the plateau is markedly shortened and shifted to lower temperatures (the two experiments shown in Fig. 2 are for samples of similar particle size). There are two possible explanations for the two-stage decrease in the intensity curves. One possibility is that hydroxyl water is physically lost in two stages, as has been observed by Martens et al.[6], who report a maximum in water evolution at about 350°C, and a second maximum at 450°C (a third maximum has been also observed in some samples around 600°C). These effects have been attributed to surface recrystallization of the trigonal hydroxide structure into cubic MgO, exposing fresh, unreacted hydroxide surfaces[6]. On the other hand, the present material is of comparatively small crystallite size, and has TG and DTG curves which show a single stage dehydroxylation weight loss starting at 284°C and reaching maximum velocity at 355°C, i.e. the initial IR intensity decrease is unaccompanied by a dehydroxylation weight loss. Again, the first weight loss reported by Martens et al.[6] at 350°C corresponds to the second IR intensity decrease, suggesting that the first IR intensity decrease is not associated with an actual hydroxyl loss. This evidence lends support for the second possible explanation, namely, that the first IR intensity decrease represents a reversible process in which the protons are "smeared out" or delocalized over the available hydroxyl groups, while the second decrease represents an irreversible intensity loss due to the elimination of hydroxyl water. Proton delocalization is well known in kaolinite, in which it is characterised by a broadening and loss in intensity of the IR hydroxyl stretching bands, which, however regain their original intensities on cooling[5, 7]. It has also been noted that the "pre-dehydroxylation state" thus described may be related to the proton tunnelling process in that tunnelling provides the mechanism by which delocalization occurs[8]. Further support for this explanation of the two-stage IR intensity decrease is provided by the heating-and-cooling experiments (see next section) in which the reversibility of the intensity decrease is investigated.

If the initial intensity decrease is indeed due to reversible proton delocalization, Fig. 2 shows that the effect of the field is to induce delocalization at temperatures at least 50°C lower than in the unelectrolysed samples. Moreover, this delocalized state



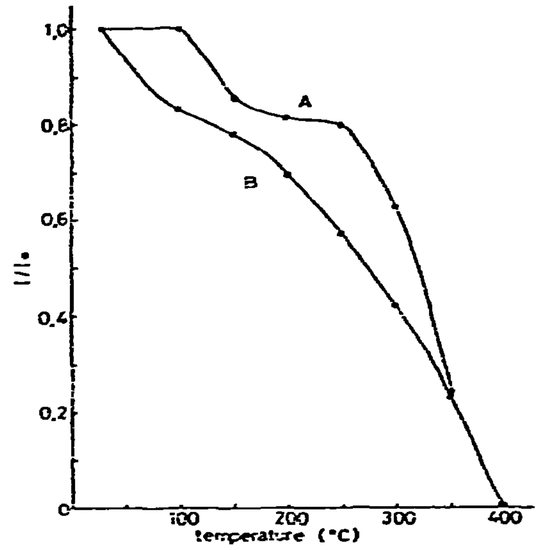


Fig. 3. Intensity changes of the 3670 cm^{-1} band of unelectrolysed $Mg(OH)_2$. (A) After heating to temperature and re-cooling to room temperature. (B) Spectral intensity measured at temperature.

Fig. 4. Intensity changes of the 3670 cm^{-1} band of electrolysed $Mg(OH)_2$. (A) After heating to temperature and re-cooling to room temperature. (B) Spectral intensity measured at temperature.

persists over a shorter temperature range under electric fields, true dehydroxylation having set in about 175°C sooner than in the unelectrolysed samples. On the other hand, the rate of dehydroxylation under the electric field is slower, and occurs over a wider temperature interval. As was noted in the earlier TG studies^3, this corresponds to a lower activation energy.

Effect of fields on the reversibility of the temperature-dependent intensity changes

In the light of the foregoing discussion, the reversibility of the intensity changes on heating and re-cooling the sample to room temperature should provide further evidence as to the nature of the processes leading to the intensity changes. In particular, processes in which hydroxyl water is not lost, but in which the IR spectrum is modified by thermal effects or polarization in the electric field, should exhibit complete reversibility when the perturbation is removed. The results of typical heating and cooling experiments are shown in Figs. 3 and 4 for unelectrolysed and electrolysed samples respectively.

Fig. 3 shows that in the absence of a field, significant differences exist between the spectral intensity of the hydroxyl band in samples at temperature and after cooling back to room temperature; superimposed upon the irreversible intensity loss (upper curve) is a reversible intensity decrease (lower curve). The intensity difference between the two curves (Δ) is a measure of the magnitude of thermally-induced reversible processes such as proton delocalization at each temperature. Fig. 4 shows that the additional effect of the electric field is to continue to induce the low-temperature intensity loss even when the thermal perturbation is removed, as in the room-

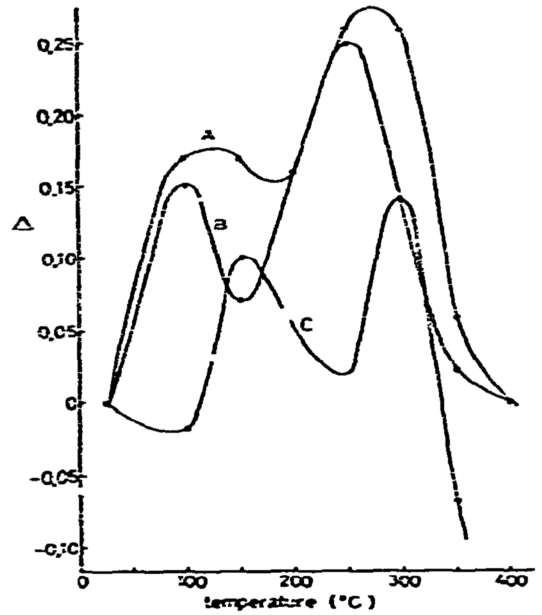


Fig. 5. Plot of reversibility function Δ (as defined in text) as a function of temperature. (A) Unelectrolysed $Mg(OH)_2$. (B) Electrolysed $Mg(OH)_2$. (C) Plot of field-only contribution Δ (E) as defined in text.

temperature spectra (upper curve). This is more obvious from a plot of Δ as a function of temperature for both electrolysed and unelectrolysed samples (Fig. 5).

Fig. 5 shows that the major difference in reversibility between the electrolysed and unelectrolysed samples occurs at about 150°C, where the reversibility factor is much smaller in the electrolysed than in the unelectrolysed samples. Reference to Fig. 4 shows that this is due to the room-temperature loss of intensity, which must result from the action of the field alone (since thermal perturbations are absent).

If we define two new parameters δ'_0(unelec) and δ'_0(elec), such that δ'_0(unelec) is the decrease in the intensity ratio of an unelectrolysed sample which has been heated to temperature t and cooled back to room temperature, and δ^0_t(elec) is the corresponding parameter for an electrolysed sample, then the decrease in room-temperature intensity due to the field alone ($\Delta(E)$) is given by

$$\Delta(E) = \delta^0_t(\text{elec}) - \delta^0_t(\text{unelec}) \tag{1}$$

It is interesting to note that if $\Delta(E)$ is plotted as a function of heating temperature (Fig. 5, curve C), the curve is of similar form to that of the plots of Δ having peaks at 150° and 300°C. Thus, the action of the field on the spectral intensity of the hydroxyl band is particularly marked at these two temperatures, the higher of which corresponds closely to the onset of weight loss in the sample. The interesting result is, however, that the present work provides evidence that the field also interacts strongly with the sample at a lower temperature. A further point is that the samples apparently need to be thermally stimulated before the action of the field becomes apparent, otherwise it would be possible to reduce the intensity of the IR peak by applying the field to unheated samples; this effect was not observed in any of the experiments.

In discussing intensity changes in the IR spectra of heated samples, a distinction must be made between intensity losses due to thermal (or electrolytic) perturbation in the sample, and losses due to actual chemical changes induced by heating or electrolysis. Since IR absorption results from a change in the dipole moment of the system due to molecular vibrations, any perturbation which increases the mean distance between the vibrating atoms will alter the dipole moment of the system, and hence the intensity of its IR absorption. Increasing temperature causes a slight decrease in the absorption intensity, the magnitude of which can be gauged from the change in the position of the baseline. This effect is fully reversible on cooling, and in the present experiments, its magnitude was found to be rather less than the intensity decrease which has been tentatively ascribed to proton delocalization due to tunnelling. It therefore seems feasible that the present intensity decrease at about 150°C could be due to a temporary departure of protons from their customary equilibrium positions; the resulting change in the dipole moment would be much larger than that resulting solely from thermal excitation of the system at this temperature. Furthermore, this temperature corresponds closely with the temperature at which the onset of proton conductivity has been reported in $Mg(OH)_2$[9]. If the mobility of the protons at those comparatively low temperatures is due to tunnelling processes, as has been suggested[9], then the effect of an applied electric field should be to enhance proton delocalization by assisting this tunnelling process, as has been discussed elsewhere[4].

Although the reversible component of the intensity loss on heating either in the presence or absence of the electric field can be explained in terms of proton delocalization, there are at least two other mechanisms which could give rise to a reversible intensity loss. These have been discussed by Fripiat et al.[10] with reference to hydroxyl-compounds such as micas and the aluminium oxyhydroxide boehmite. One possibility is that the orientation of the OH vibrational moment changes with temperature and/or electric fields. This possibility has been tested in the case of micas[11], in which the orientational relationships can be rigidly defined, and calculations of the degree of tilt of the vibrational moments on the cleavage plane which would be necessary to produce the observed change in absorbance have been made[11]. When these are used to calculate the dependence of the IR absorbance with the reflection angle, the results were at variance with the observed relationships, and it was concluded that the orientation of the hydroxide groups is not significantly influenced by heating[11]. This conclusion probably applies to other hydroxy-compounds as well[10].

A second possibility is that the electron distribution in the O–H bond could change with temperature, producing a change in the magnitude of the transition dipole[10]. If $\langle M^{0,1} \rangle$ is the matrix element of the dipole moment for the transition between the ground and first excited states of a hydrogen-bonded solid, the ratio of the IR absorption coefficients for the unperturbed stretching vibration (at room temperature) and the perturbed vibration (at higher temperatures, or under the influence of electric fields) is given by[12]

$$(\langle M^{0,1}\rangle \text{ perturbed}/\langle M^{0,1}\rangle \text{ unperturbed})^2 \tag{2}$$

where $\langle M^{G,1}\rangle$ is given by

$$\langle M^{0,1}\rangle = (b_0 - 2)^{\frac{1}{2}}/a(b_0 - 1) \tag{3}$$

For the unperturbed Morse function,

$$b_0 = 4\pi(2\mu\, De)^{\frac{1}{2}}/(ah - 1) \tag{4}$$

while for the perturbed Morse function,

$$b_0 = \{[4\pi(2\mu)^{\frac{1}{2}}\,(De - qE_p/a)]/[ah(De - qE_p/2a)^{\frac{1}{2}}]\} - 1 \tag{5}$$

where De is the dissociation energy of the O–H bond, qE_p is the electrical polarisation of the bond and a is the constant of the Morse potential energy function, defined as[12]

$$a = 0.5\,(2\,k_1/De)^{\frac{1}{2}} \tag{6}$$

where k_1 is the restoring force for the hydroxyl stretching mode. Calculations by Fripiat et al.[12] for boehmite, (AlO OH) suggest that such a polarization process would account for only about a 2.5% decrease in spectral intensity between room temperature and 350°C. This represents a decrease in the polarization term qE_p of 5.9×10^{-5} esu, as calculated from the change in frequency of the O–H stretching vibration (see next section). By a similar calculation, the polarization term for the present sample heated to 350°C is decreased by only 3.4×10^{-5} esu in the absence of a field; a still smaller decrease (1.2×10^{-5} esu) is found for the electrolysed samples, suggesting that the effect of temperature in weakening the O–H bond is being offset by the effect of the field. Although this calculation is strictly for a hydrogen-bonded system, in both the present electrolysed and unelectrolysed samples, the change in the polarization of the O–H bond is less than in boehmite[12], and cannot satisfactorily explain the 10–14% decrease in spectral intensity resulting from the application of the field alone. It is interesting to note, however, that in the case of boehmite[12], satisfactory agreement between the calculated and measured IR absorbance could be obtained by assuming an increase in the population of the vibrational levels closer to the top of the energy barrier. Such a situation is a direct consequence of a tunnelling process[12].

The present IR results also provide a clue as to why the previously reported TG dehydroxylation measurements made under the action of electric fields[3] could not satisfactorily be explained solely in terms of enhanced tunnelling[4]. Even though the field does influence tunnelling, as has been indicated by theoretical calculations[4] and by the present work, the second stage of the reaction (involving actual weight loss) is rather less influenced; as the temperature increases the IR intensity loss curves for electrolysed and unelectrolysed samples converge. Since the later stages of the reaction involve diffusional loss of neutral water molecules, the decrease in the influence of the field at higher temperatures is understandable.

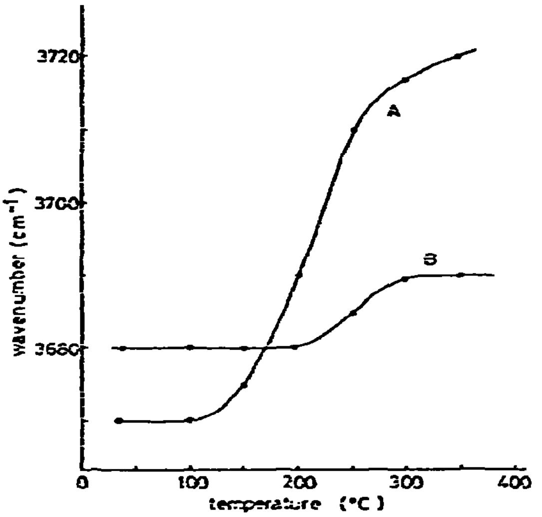


Fig. 6. Frequency shift of $Mg(OH)_2$ hydroxyl band as a function of temperature. (A) Unelectrolysed sample. (B) Electrolysed sample.

The effect of electric fields on the peak shape and frequency of the hydroxyl band

Only slight differences were recorded between the peak shapes of the electrolysed and unelectrolysed samples. The electrolysed samples exhibited relatively broader peaks than the unelectrolysed controls, particularly above 200°C. Because of the attenuated instrumental conditions under which the spectra were recorded, a certain amount of fine structure could be observed in the form of two or three shoulders at about 3600–3660 cm^{-1}. These factors are lost as the spectra broaden at higher temperatures, although below 250°C, they reappear on cooling to room temperature.

The frequency of the hydroxyl peak exhibited a significant and progressive shift to higher wavenumbers with increasing temperature, from 3670 cm^{-1} at room temperature, to 3720 cm^{-1} at 350°C. This shift was not reversible on cooling to room temperature, and must therefore be a function of an irreversible physical change taking place in the sample on heating. The variation of frequency with temperature is shown in Fig. 6.

No significant differences were noted between the peak shapes of the electrolysed and unelectrolysed samples. The broadening behaviour of the spectra of the electrolysed samples on heating and cooling was also similar to the unelectrolysed samples. Some differences were, however, noted in the frequency shift of the hydroxyl stretching peak; a shift to higher wavenumbers was again noted with increasing temperature, but the magnitude of the shift was smaller (Fig. 6). The room-temperature application of a field to a previously unheated sample was also found to cause a shift of about 10 cm^{-1} to higher wavenumbers.

The direction of the frequency shift observed in these experiments is opposite to that reported by Freund[2], and attributed by him to the anisotropic thermal expansion of the $Mg(OH)_2$ lattice, which has its largest expansion parallel to the mean OH vector. The reason for the difference between the direction of the frequency shift observed by Freund[2] and that of the present work is not obvious; most of Freund's work was however, carried out on samples pressed into KBr discs, which may have introduced "overheating" or matrix expansion effects not present in the present work.

Shifts in the frequency of the O–H stretching band in the same direction as the present work have been observed by Fripiat et al.[12] in heated boehmite, and smaller shifts in the same direction have also been reported in the IR spectra of heated kaolinite[13].

If the vibrating system is considered as a simple harmonic motion between two particles of mass m_1 and m_2, the frequency of the vibration is given by

$$\nu = [1/2\,\pi][K/m_1 m_2/m_1 + m_2)]^{\frac{1}{2}} \tag{7}$$

where K is a force constant describing the bond strength between the two atoms. In qualitative terms, K becomes larger as the bond strength increases, with a corresponding increase in the vibration frequency (or wavenumber). Thermal perturbations tend to increase the mean distance between the atoms, decreasing the bond strength and lowering the vibration frequency (a full treatment would also have to take into account the effects of vibrational anharmonicity). However, it appears that the present frequency shifts are the result of an increase in bond strength and/or a decrease in interatomic distances. One possible explanation may lie in the fact that dehydroxylation of $Mg(OH)_2$ is accompanied by a considerable volume contraction (about 50% for full dehydroxylation). If this contraction is indeed the cause of the observed frequency shift, it would follow from Fig. 6 that in the absence of the electric field, the lattice begins to collapse progressively even during the predehydroxylation stages, but the effect becomes most noticeable at the onset of dehydroxylation proper. On the other hand, this collapse is retarded by the electric field. It has been shown that during careful dehydroxylation in vacuo[14], a highly defect dehydrated intermediate can be formed, which has a hexagonal structure and lattice parameters very similar to the parent hydroxide[14]. The frequency shift in the electrolysed samples might therefore be explicable in terms of stabilization of this uncondensed defect phase by the electric field, perhaps by the electrolytic introduction of impurity cations into the vacancies of the defect structure. The possibility of electrolytic stabilization of defect phases has already been noted in the thermal reactions of kaolinite[15] and pseudoboehmite[16].

This tentative explanation does not, however, completely explain the observed results, particularly the room-temperature frequency shift induced by the field in unheated samples.

One possible explanation for this result involves the polarization of the hydroxyl bonds by the electric field. If the electric field component parallel to the direction of the O–H bond is E_p and the charge inbalance for the hydroxyl group is q, the polarization force qE_p is related to the frequency of the stretching vibration for a 0 to 1 transition in a hydrogen-bonded solid by[12]

$$qE_p/D_e a = 1 - \tfrac{1}{4}\,(\nu_s/\nu_0)^2 - (\nu_s/\nu_0)[\tfrac{1}{4} + 1/16\,(\nu_s/\nu_0)^2]^{\frac{1}{2}} \tag{8}$$

where ν_s and ν_0 are the frequencies of the perturbed and unperturbed system respectively and D_e and a are as previously defined (eqn. 6). It can be calculated from eqn. 8 that the room-temperature frequency shift observed in the present studies can be accounted for by a polarization force of 3.12×10^{-4} esu. Although this cannot be compared directly with the applied field, which is not necessarily the field acting parallel to each randomly oriented hydroxyl group, the calculation suggests that the room-temperature frequency shift might be explained in terms of a mean contraction of the O–H bond (or a mean lengthening of the Mg–O bond) by a polarization force of not unreasonable magnitude. A fuller understanding awaits a more complete theoretical treatment.

CONCLUSIONS

(1) The loss of intensity of the IR hydroxyl stretching vibration of $Mg(OH)_2$ during dehydroxylation occurs in two stages. The first stage is not accompanied by any weight loss, and may indicate a state in which the hydroxyl protons are delocalized from their respective molecules. The second stage of IR intensity loss represents dehydroxylation proper.

(2) Both stages of intensity loss are influenced by applied electric fields, which lower the onset temperature of the intensity losses, and shorten the temperature interval over which the delocalized state exists.

(3) On cooling to room temperature, a proportion of the IR intensity is regained. Maximum reversibility occurs at about 100 and 250°C, corresponding to the onset of the two stages of intensity loss. These two temperatures are also marked by maximum interaction between the sample and the electric field.

(4) The electric field does not significantly influence the IR peak shapes or their broadening characteristics at higher temperatures.

(5) A progressive shift to higher wavenumbers with increasing temperature is tentatively ascribed to the contraction of the structure on dehydroxylation. This shift is much less marked in unelectrolysed samples, possibly due to the stabilisation of a less condensed defect structure.

REFERENCES

1 F. Freund, *Angew. Chem., Int. Ed. Engl.*, 4 (1965) 445.
2 F. Freund, *Spectrochim. Acta Part A*, 26 (1970) 195.
3 K. J. D. MacKenzie, *J. Therm. Anal.*, 5 (1972) 19.
4 K. J. D. MacKenzie, *J. Therm. Anal.*, 5 (1973) 363.
5 K. J. D. MacKenzie, *J. Appl. Chem. Biotechnol.*, 23 (1973) 903.
6 R. Martens, H. Gentsch and F. Freund, *J. Catal.*, 44 (1976) 366.
7 J. J. Fripiat and F. Toussaint, *Nature, London*, 186 (1960) 627.
8 N. H. Brett, K. J. D. MacKenzie and J. H. Sharp, *Quart. Rev. Chem. Soc.*, 24 (1970) 185.
9 F. Freund and R. Hosen, *Ber. Bunsenges. Phys. Chem.*, 81 (1977) 39.
10 J. J. Fripiat, P. G. Rouxhet, H. Jacobs and A. Jelli, in R. S. Carter and J. J. Rush (Eds.), *Molecular Dynamics and the Structure of Solids*, N.B.S. Special Pub. 301 (1969) 227.
11 J. J. Fripiat, P. G. Rouxhet and H. Jacobs, *Am. Mineral.*, 50 (1965) 1937.

12 J. J. Fripiat, H. Bosmans and P. G. Rouxhet, *J. Phys. Chem.*, 71 (1967) 1097.
13 J. J. Fripiat and F. Toussaint, *J. Phys. Chem.*, 67 (1963) 30.
14 F. Freund and V. Sperling, *Mater. Res. Bull.*, 11 (1976) 621.
15 K. J. D. MacKenzie, *Trans. J. Br. Ceram. Soc.*, 72 (1973) 209.
16 K. J. D. MacKenzie, *Thermochim. Acta*, 16 (1976) 1.