A Raman Study of The Phase Transition in Iron Perchlorate Hexahydrate

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ABSTRACT

Raman spectra of crystalline iron perchlorate hexahydrate ($Fe(ClO_4)_2 \cdot 6H_2O$) in region of lattice and anion internal modes are obtained over the temperature range 80 to 385 K. The temperature dependent Raman results are consistent with those from previous works showing that two phase transitions occur around 336 and 245 K, respectively. The transition at 336 K may be considered as an order-disorder transformation while the one at 245K is associated with the configurational disorder of the perchlorate tetrahedron ions.

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Introduction

Iron perchlorate hexahydrate, $Fe(ClO_4)_2 \cdot 6H_2O$(FePH), crystallizes into a triply twined hexagonal form[1] which rarely occurs in crystal physics. Measurements by ERP[2], specific heat[3], susceptibility[4,5] and proton magnetic relaxation[6] works all indicated that there exists a phase transition at~240K. The Raman spectra of FePH have been recorded previously[7] but only at room temperature. The crystal structure of FePH at room temperature was determined by West[1] and was focused to be isostructural with other metal perchlorates. The lattice is orthorhombic pseudo-hexagonal with a=7.79 $\mathring{A}$, b=13.48 $\mathring{A}$, and c=5.24 $\mathring{A}$, belonging to space group Pmn21(C_{2v}^7).

In this report we present studies of the high resolution laser-Raman spectra of polycrystalline FePH at various temperatures from 80 to 385 K of the entire spectral region including lattice and intramolecular vibrations and try to gain some information about the phase transitions in this material. Besides, in this work we have also performed differential scanning measurements on FePH in order to confirm the structural phase transitions exhibited in this crystal.

Experimental

Polycystalline FePH powder was obtained from ICN Pharmacentials Inc., and dried at 320 K for 30 minutes. The solid powder were then loaded into the quartz cell and placed in an Oxford Instruments DN 1714 variable temperature liquid nitrogen cryostat. The temperature sensor is a standard 100 ohm platinum resistor mounted on the heat exchanger. The heat exchanger is also fitted with a heater for temperature varying operation in conjunction with a DTC-2 temperature controller and the temperature resolution is nearly 0.1 K.

The FePH sample was excited using a Coherent Innova 90-4 Argon ion laser, operated at 0.2~0.4 W in the 5145 $\mathring{A}$ and 4880 $\mathring{A}$ lines. The light was

scattered trough 90° and analyzed with a J.Y. Ramanor U100 double monochromator equipped with a chilled phtotmultiplier tube (RCA C31034A-02) and Spex DPC-2 digital photometer. The spectral slit widths were set to maintain a resolution of about 1 cm^{-1}.

Results and Discussion

Orthorthombic $Fe(ClO_4)_2 \cdot 6H_2O$ contains two formula units in the primitive unit cell. Our discussion of the observed Raman spectra may be analysed in terms of the Iron aqua-complex cation $[Fe(OH_2)_6]^{2+}$ and the perchlorate anions ClO_4^-. The ClO_4^- ion is a regular tetrahedron having T_d molecular symmetry and the stretching modes (ν_1 , ν_2 , ν_3 , ν_4) belong to the species $A_1^{(R)}$, $E^{(R)}$ and $2F_2^{(R.IR)}$ respectively. The $[Fe(OH_2)_6]^{2+}$ octahedron is distorted with the T_h point group symmetry. Vibrational modes belong to the species $3Ag^{(R)}$, $3Eg^{(R)}$, $5Fg^{(R)}$, $Au^{(ia)}$, $Eu^{(ia)}$ and $8Fu^{(IR)}$. The two possible site symmetries for the C_{2v} space group are $C_s(2)$ and $C_1(4)$ where 2 and 4 are the occupation numbers. Hence, two $[Fe(OH_2)_6]^{2+}$ and four ClO_4^- groups in the unit cell naturally occupy the sites $C_s(2)$ and $C_1(4)$, respectively. Correlation diagrams between the point group and the space group through the site symmetries are described in previous paper[8].

The observed Raman spectra will follow the natural separation of modes into stretching and lattice vibrational modes. Figs. 1 and 2 show the Raman spectra of the lattice and stretching modes of $Fe(ClO_4) \cdot 6H_2O$ in different phases at various temperatures over the range 80~385 K. Fig. 3 shows the temperature dependence of the two lattice modes (V_{Tr}^{P} , V_{Tr}^{W}) of $Fe(ClO_4)_2 \cdot 6H_2O$. Figs. 4 and 5 indicate the temperature dependence of the peak intensity and half-widths of the internal stretching modes of perchlorate ions.

As shown in Fing. 1, there are many lattice vibrational peaks as expected in the correlation table. The proposed assignments of these lattice peaks are

discussed as follow. According to previous works on $NaClO_4$[8], the low frequency lattice transitional (V_{Tr}^{P}) and librational (P_{L}^{P}) modes of perchlorate ions are usually below 200 cm^{-1}, such that the peaks at 35, 41, 64, 74, 84, 89, and 172 cm^{-1} and be assigned as V_{Tr}^{P} and P_{L}^{P}. The six nearest neighbours of the metal ions (Fe) and all water molecules forming an octahedron so that. in addition to the three fundamental stretching modes of the free water molecules, coordinate water is expected to show other modes. Nakagawa and Shimanonchi[9] carried out normal coordinate analyses on the $[M(H_2O)_6]$ ions and suggested that 435 cm^{-1} peak is the metal-oxygen stretching mode (V_{M-O}^{MO}). The other peaks at (182, 192, 209), (~274, ~291, ~336) and (374, 392, 413) bands may be assigned as the deformation wagging and rocking modes (V_{OMO}^{MO} , V_{W}^{MO} , V_{R}^{MO}). Hence, the remaining peaks at 127 and 644 cm^{-1} are assigned as lattice vibrational modes of those coordinate water (V_{Tr}^{W} and V_{L}^{W}), respectively.

As shown in Figure 1, in the temperature range between 80 K and 248 K, significant "softening " of the two lattice modes, 127 cm^{-1} of V_{Tr}^{W} and 35cm^{-1} of V_{Tr}^{P}, is observed when the T_{C1} is approached form below. When the temperature is raised form 80 K, the bands and 127 and 35 cm^{-1} gradually softens to 102 and 29.5 cm^{-1}, respectively, and then completely disappear when T_{C1} is approached. The results are summarized in Figure 3. Beyond T_{C1}, the bands do not reappear and that these "soft phonon modes " show that the limit of stability of the crystalline phase is approached as the frequency of a certain lattice vibration approaches zero. It is believed that a change in the degree of configurational disorder is associated with the perchlorate tetrahedron ions during this phase transition (T_{C1}). It is also noted that in temperature range 248 and 350 K the remaining lattice bands show "softening " when T_{C2} is approached from below. Above 336 K the lattice bands merge to become the shoulder of the broadened Rayleigh wing. Since the sample melts above 385 K, the transition at 336 K may

be considered as an order-disorder transition. In this work, we also perform the DSC experiment and the result (not shown here) shows an anomaly occuring around 336 K which is consistent with the Raman spectra studies.

Since the stretching, bending and librational modes of water molecules appear as weak broad and diffuse bands in Raman spectra, so that the internal modes of the ClO_4^- ion can be unambiguously assigned. Figure 2 shows the temperature dependent Raman spectra of the V_1^P, V_2^P, V_3^P, V_4^P, V_{Lib}^P and V_{O-H}^W modes. The V_1^P (933 cm^{-1}) modes is a totally symmetric stretching mode with on temperature dependence being observed as the temperature was varied and only one sharp peak was exhibited even at 80 K. V_4^P (630cm^{-1}) is the triply degenerate mode which also contains only one single peak as the temperature was varied instead of the predicted three components. However, the doubly degenerate V_2^P (462 and 470 cm^{-1}) exhibits two well resolved peaks at 80 K and gradually merge into one peak as the temperature pass through T_{C1}. The mode associated with the triply degenerate stretching V_3^P mode appears as a set of resolved features (1049, 1085, 1105, 1120, 1134 and 1146 cm^{-1}) at 80 K. Above T_{C2}, the V_3^P mode contains only one band. Then, it gradually becomes asymmetrical as the temperature is lowered below the T_{C2} phase transition point and two components are observed. Further lowering the temperature below T_{C1}, the two resolved peaks finally split into six components when temperature lowers to 80 K. The above discussed variation in the peak structure may indicate that the compound has two phase transitions near 336 and 245 K as detected by the EPR and DSC techniques. These splittings may arise due to the correlation field.

Curves of the peak height (intensity) and halfwidth of internal stretching modes of perchlorate ions are shown in Figures 4 and 5 for all of the modes, the resultant intensity decreases smoothly and regularly except in some small range

of temperature around T_{C1} and T_{C2} where some discontinuity happened.

It is clear from the above discussion that the temperature-dependent Raman results of $Fe(ClO_4)_2 \cdot 6H_2O$ are consistent with the EPR and DSC experiments, in which two phase transitions occur at~336 and ~245 K. The phase transition occurs at ~336 K may be considered as an order-disorder transition while a change in the degree of configurational disorder is associated with the perchlorate tetrahedron ions during the phase transition at 245 K.

Reference

(1) C.D West, Z. Kristall., 91A, 480 (1935)

(2) R. Dayal, D. Ramachandra Rao and P. Venkateswarlu, J. Magn, Reson., 36, 99 (1979)

(3) A. K. Jain and G.C. Upreti, Phys. Status Solidi, A58, 155 (1980)

(4) M. Rachwalska and T. Stanele, Phys. Status Solidid, A48, 297 (1975)

(5) B. K. Chaudhuri and D. Ghosh, Phys. Status Solidi, A23, 649 (1974)

(6) I. Svare and B. O. Fimland, J. Chen. Phys., 24, 5977 (1981)

(7) M. B. Patel, A. Agarwal and H. B. Bist, J. Raman Spectro., 14, 406 (1983)

(8) K. F. Pai, Y. C. Chen, J. S. Hwang, W. S. Tse and C. S. Fang, Chin. J. Phys., 26, No. 1, 26 (1988)

(9) H. D. Lutz, R. A. Becker, B. G. Kruska and H. J. Berthold, Spectrochim. Acta., part A, 35, 797 (1979)

(10) I. Nakagawa and T. Shimanonchi, Spectrochim. Acta., 20, 429 (1964)

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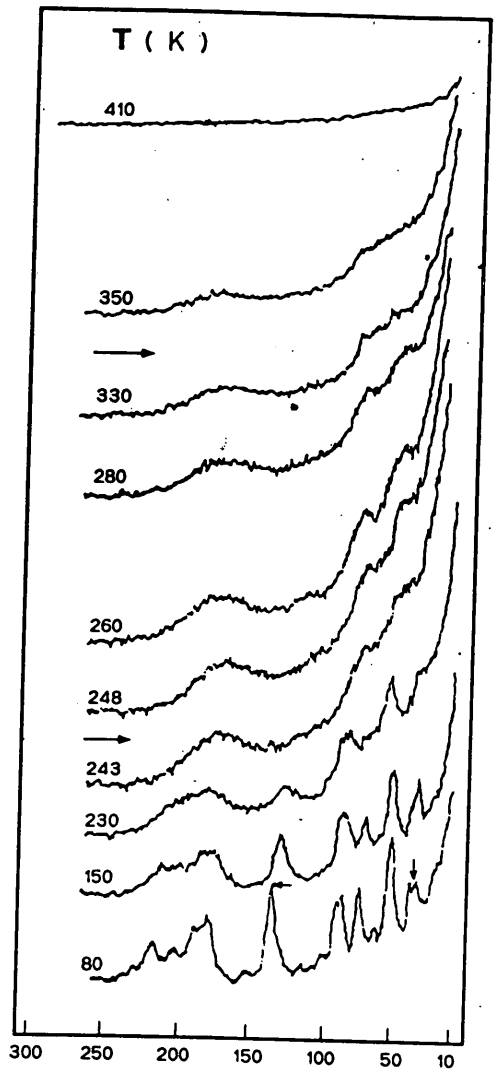

Figure 1 : Lattice modes of Fe $(ClO_4)_2 \cdot 6H_2O$ at different temperatures

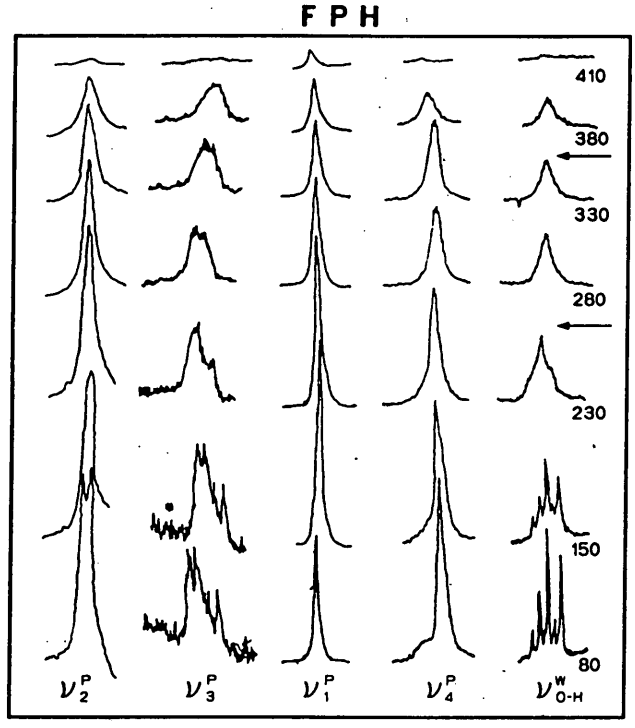

Figure 2 : Temperature dependence of the internal modes (ν_1^P, ν_2^P, ν_3^P, ν_4^P, ν_{O-H}^W) of Fe $(ClO_4)_2 \cdot 6H_2O$

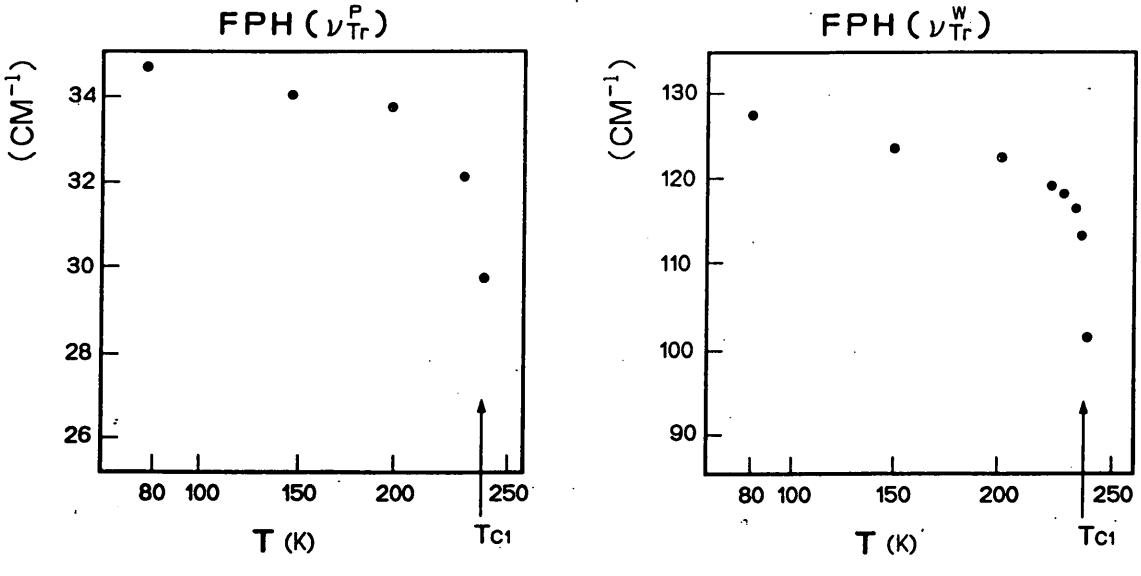

Figure 3 : Temperature dependence of the two lattice modes (ν_{Tr}^P, ν_{Tr}^W) of Fe $(ClO_4)_2 \cdot 6H_2O$

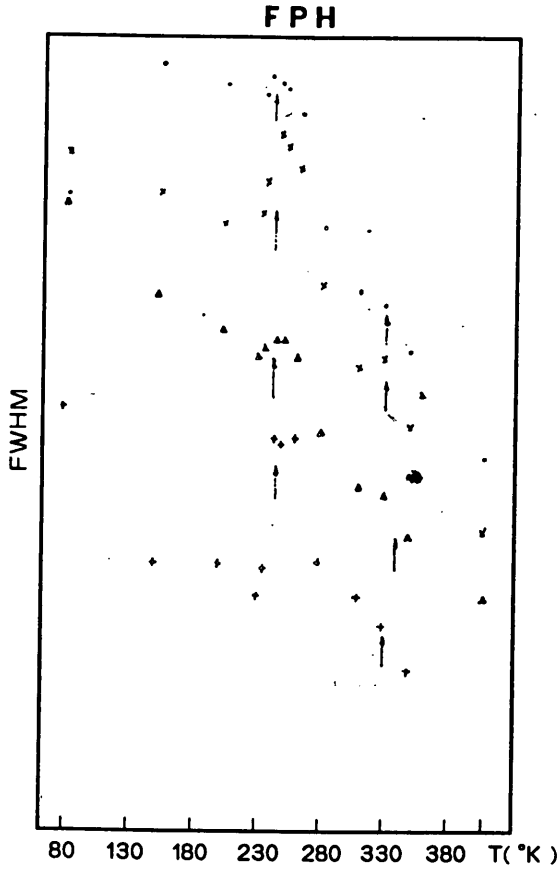

Figure 4 : Temperature dependence of the peak intensity of the internal stretching modes of perchlorate ions

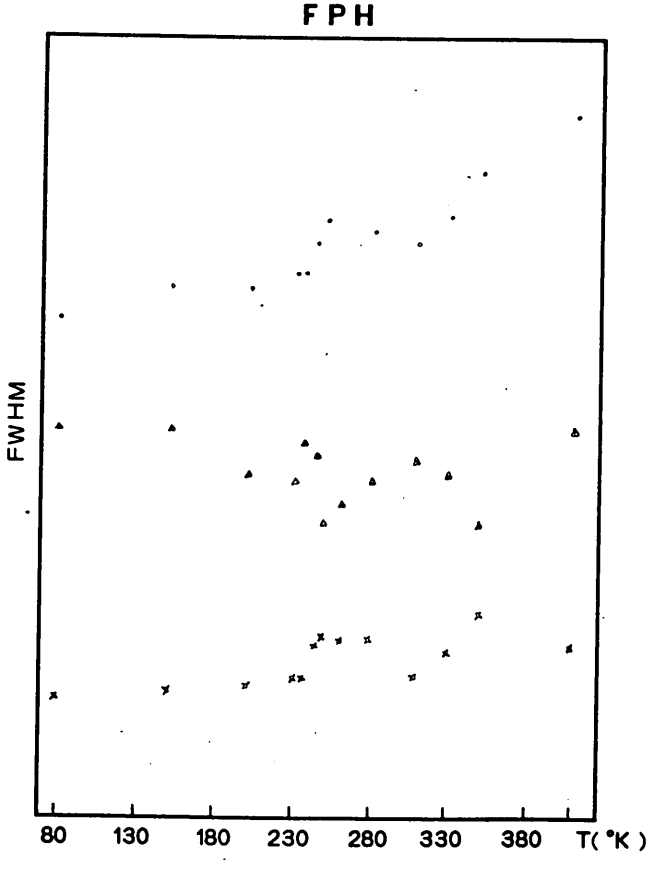

Figure 5 : Temperature dependence of the half-widths of the internal stretching modes of perchlorate ions

六水過氯酸鐵之拉曼光譜相變研究

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摘 要

利用拉曼光譜法得到結晶六水過氯酸鐵之溫度改變拉曼光譜，包括晶格振動模式及伸縮振動模式兩種。溫度範圍爲 80K 至 385K，由獲得之溫度變化光譜圖形可看出該晶體有二個相變化溫度，分別爲 336K 及 245K，這結果與先前由別種方法所測得之相變化溫度一致。其中 336K 之相轉變可能爲有序一無序之相變化機制，而 245K 則可能爲過氯酸四面體離子之方向無序所導致之變化。

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