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FOREWORD

On behalf of the Asia Research Centre, Yangon University, I am much delighted to extend my warmest congratulations on the publication of the first issue of the Journal of the Asia Research Centre, Yangon University.

In this 21st century, all nations in the world are making all-out efforts to meet the challenges of the globalization process. In the education sectors many nations are now collaborating and cooperating at the national level as well as the institutional levels for the promotion of education standards and the development of highly qualified human resources. With the aim of building Myanmar as a peaceful, developed and modern nation through education the higher education institutions are implementing the 30-year long-term education promotion plan. Under this plan the research programmes are now under implementation at the higher education institutions in Myanmar with the objectives: to conduct research at international level, to establish research laboratories fully equipped with modern instruments, to achieve research outcomes which are directly beneficial to the development of the nation, to enhance skills, creativity and capabilities in the performance of research, and to create new generation of outstanding researchers. In order to fulfill these objectives, various research activities are being conducted extensively at the higher education institutions.

Since its establishment on the 19th August 2002, the Asia Research Centre, Yangon University has been making the financial support to the researchers from Yangon University and other institutions to conduct a good number of outstanding research projects. The principal financier of the Asia Research Centre is the Korea Foundation for Advanced Studies(KFAS).

This journal consists of 19 research papers resulted from the outstanding research projects conducted by the academic departments of Yangon University. I would like to express my appreciation and congratulations for the concerted effort of the researchers who have made a great deal of contributions to this issue.

I also would like to express my heartfelt thanks to Prof. Dr Kim Jae Youl, Secretary General of the Korea Foundation for Advanced Studies for his continued support to the Asia Research Centre, Yangon University.



Rector Dr Soe Yin
Chairman of Board of Trustees
Asia Research Centre, Yangon University

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CONGRATULATORY MESSAGE

Dear Colleagues,

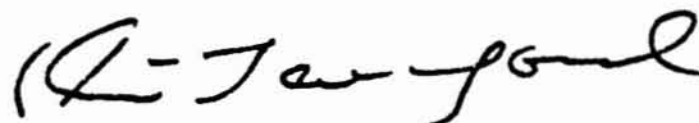
On behalf of the Korea Foundation for Advanced Studies, I would like to extend to you my warmest congratulations on the publication of the inaugural issue of the *Journal of Asia Research Centre, Yangon University*.

Since the foundation of the Asia Research Center at Yangon University in August 2002, the Center has endeavored to carry out its objectives of contributing to the development and improvement of scientific research in Myanmar. I highly appreciate the initial success achieved by the Asia Research Centre, which includes the completion of 19 research projects of various fields of interests in the academic year 2003-2004, and hope that its activities will continue to encourage the hardworking Myanmar scholars. As one of the thirteen Asia Research Centers established at various countries across Asia, the one at Yangon University has proved to be fully competent in facilitating scientific research and academic growth.

Without a doubt, the *Journal of Asia Research Centre, Yangon University* will serve to be a vital forum for researchers and scholars to promote cooperation and academic exchange both on a national and international level. It will circulate important information regarding the Center's activities and prove to be a good source of opportunity for enhancing mutual understanding between the Myanmar scholars and scholars elsewhere in the Asian region.

On this special occasion, I wish to express my great appreciation for the efforts made by the Asia Research Centre at Yangon University in publishing the journal, as well as its **support** and enthusiasm for the activities and programs initiated by the Korea **Foundation** for Advanced Studies. I wish the publication much success.

Sincerely,



Jae-youl Kim, Ph.D.
Secretary General

Ferroelastic-Superprotonic Phase Transition of $[K_3]_x[(NH_4)_3]_{1-x}H(SO_4)_2$ Single Crystal Studied by Raman Scattering

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Abstract

Vibrational modes of the sulphate ion in mixed crystals, $[K_3]_x[(NH_4)_3]_{1-x}H(SO_4)_2$ of Tripotassium Hydrogen Disulphate, $K_3H(SO_4)_2$ and Triammonium Hydrogen Disulphate, $(NH_4)_3H(SO_4)_2$ were studied by Raman Scattering Spectroscopy. The ν_1 - mode frequency of the sulphate ion at room temperature is found to be shifted downwards with different crystalline environments contributed by the increase of counter-cation K_3^+ content. The temperature dependence of frequencies and that of linewidths of the ν_1 mode show anomalous changes near the ferroelastic-superprotonic phase transition temperature. Critical slowing-down of the $H...SO_4$ defect motion is observed.

Key Words: Mixed Crystals of Tripotassium Hydrogen Disulphate and Triammonium Hydrogen Disulphate, Vibrational Modes of the Sulphate Ion, Raman Scattering, Ferroelastic-Superprotonic Phase, Transition, Critical Slow-down.

1. Introduction

The crystals of $M_3H(XO_4)_2$ type (where $M = K, NH_4, Rb$ and $X = S, Se$) belong to the well-known family of superprotonic conductors^(1, 2). All the crystals are monoclinic at room temperature. The crystals are isomorphic at room temperature and consist of dimmers formed by two XO_4 tetrahedra linked with a short hydrogen bond. Vibration modes of sulphate ions are investigated under the influence of K-NH₄ substitution in $[K_3]_x[(NH_4)_3]_{1-x}H(SO_4)_2$ mixed crystal by Raman scattering. The results are compared to those of Tripotassium Hydrogen Disulphate, $K_3H(SO_4)_2$ and Triammonium Hydrogen Disulphate, $(NH_4)_3H(SO_4)_2$ pure crystals. $(NH_4)_3H(SO_4)_2$ at room temperature is monoclinic with the space group "A 2/a" and has a unit cell parameters: $a_m = 10.153 \text{ \AA}$, $b_m = 5.854 \text{ \AA}$, $c_m = 15.410 \text{ \AA}$, $\beta_m = 101.76^\circ$. The lattice constant a_m , b_m and c_m are measured as function of temperature. The β_m value drops suddenly to just above T_C and the crystal becomes rhombohedral with space group $R\bar{3}m$. The lattice parameters obtained at 413 K are given as $a_t = 8.29 \text{ \AA}$ and $\alpha_t = 41.7^\circ$ ^(3, 4).

The crystal structure of $K_3H(SO_4)_2$ has the "A 2/a" space group at room temperature. Monoclinic cell parameters were obtained as $a_m = 9.777 \text{ \AA}$, $b_m = 5.67 \text{ \AA}$, $c_m = 14.667 \text{ \AA}$ and $\beta_m = 102.97^\circ$. A preliminary microscopic examination suggests that the $K_3H(SO_4)_2$ crystal may transform to higher symmetry at about 200 °C although no X-ray diffraction pictures have yet been taken to confirm this.

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The description of the transformation of the isomorphous ammonium salt and rubidium salt also give this suggestion. Following this line of thought, an attempt was made to propose a structure above $T_C = 200\text{ }^\circ\text{C}$ for the smaller hypothetical unit cell of dimensions $a_r = a_1 = a_2 = a_3 = 7.85\text{ \AA}$, $\alpha = 42.2^\circ$. This cell contains one formula unit $\text{K}_3\text{H}(\text{SO}_4)_2$. It was assumed on the basis of the observed twinning pattern that the space group of this hypothetical unit cell would be $R\bar{3}m^{(3)}$.

When destruction and reconstruction of hydrogen bonds occur in the high temperature phase, some of the O atoms may change into the OH-states or vice versa, and the bonding faces of the S-O pair may also change. This change would produce certain effect on the temperature dependent Raman spectra. We particularly expected to see the effects of HSO_4 rotation and the formation of dynamic O-H-O network.

2. Experimental

The mixed crystals of $[\text{K}_3]_x[(\text{NH}_4)_3]_{1-x}\text{H}(\text{SO}_4)_2$ were grown by slow evaporation method from the aqueous solution containing the mixture of $[\text{K}_2\text{SO}_4]_x$ and $[(\text{NH}_4)_2\text{SO}_4]_{1-x}$ (wt 40%) and H_2SO_4 (wt 24%) at the room temperature. The solution was set at the temperature higher than room temperature. The supersaturated solution was filtered into the beaker and warmed about 2°C higher than the previous temperature. The beaker was then covered and set aside at the room temperature for a few days. Single crystals were polished with wet filter papers.

Raman spectra of mixed crystal were recorded on RSI 2001S Raman Spectrometer. The excitation light source was the solid-state diode laser (red laser) with the constant output 500mW at 785 nm. The temperature of the samples were controlled within the resolution of 1°C .

3. Results and Discussion

3.1 Raman Scattering Study of $[\text{K}_3]_x[(\text{NH}_4)_3]_{1-x}\text{H}(\text{SO}_4)_2$ at Room Temperature

Raman Spectra for the sulphate-ion internal modes of the mixed crystals with the various contents (x) of countercation K_3^+ are given in Figure 3.1. As indicated by the guide line in the figure, the noticeable spectral changes are observed in the ν_1 mode of sulphate ion. This ν_1 mode frequency varies with the content (x) of K_3^+ in the mixed crystal as shown in Figure 3.2. The ν_1 mode frequency of pure $\text{K}_3\text{H}(\text{SO}_4)_2$ is 936 cm^{-1} and that of pure $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ is 972 cm^{-1} .

It is observed that the frequency becomes nearer to that of pure $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ as the content (x) of K_3^+ is decreased. There are many vibrational modes of sulphate ion namely symmetric stretching, antisymmetric stretching and deformation ⁽⁴⁾. The ν_1 mode vibration represents a symmetric stretching of hydrogen-linked sulphate ion, H-SO_4^- . Among other vibrational modes, symmetric stretching mode ν_1 is more sensitive to the crystalline environment in which the substitution of K_3^+ takes place in the NH_4^+ position around the isolated hydrogen bond.

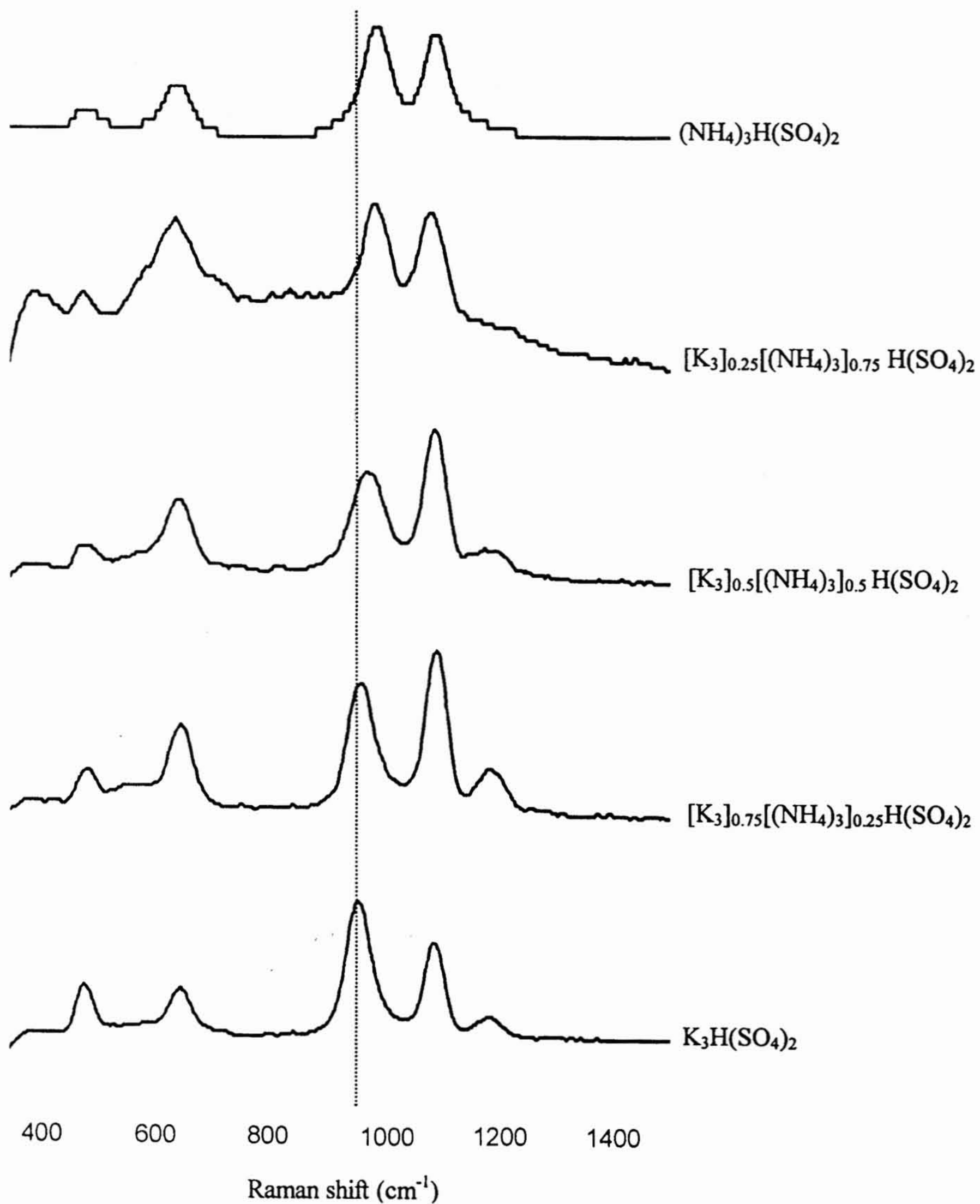


Fig 3.1 Raman spectra of $[\text{K}_3]_x[(\text{NH}_4)_3]_{1-x}\text{H}(\text{SO}_4)_2$ where $x = 0, 0.25, 0.50, 0.75$ and 1.00 in the geometry $c^*(x\ x)c^*$ at $20\text{ }^\circ\text{C}(293\text{K})$.

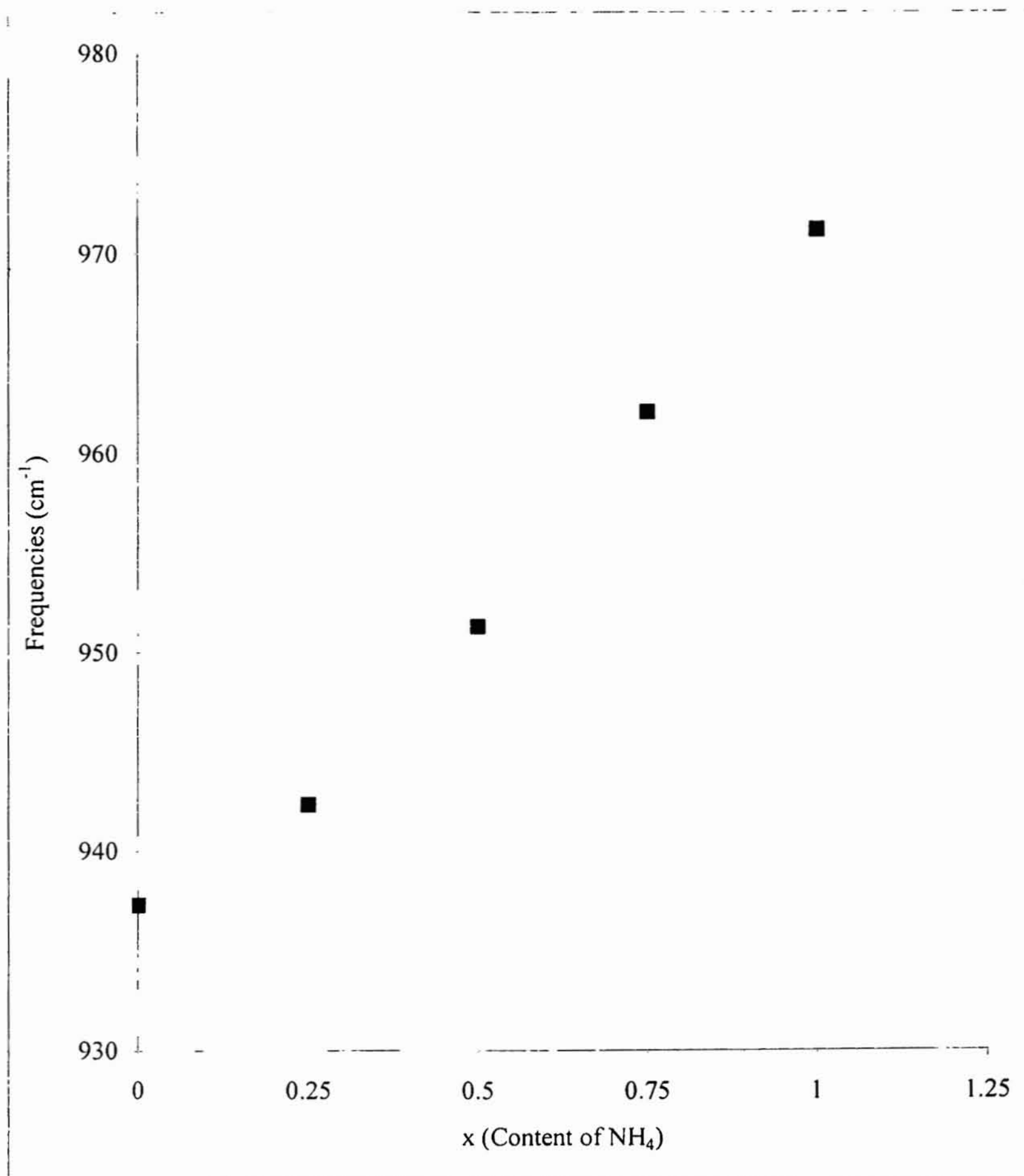


Fig 3.2 Variation of the frequency of ν_1 mode with the content x of NH_4^+ .

It is clear that the variations of the central element (X) and the counter cation (M) in $M_3H(XO_4)_2$ give rise to materials which have subtly different solid state properties. The ν_1 mode is the characteristic one and becomes one of the probes to detect the high temperature superprotonic phase transition of $M_3H(XO_4)_2$ family and its mixed crystals.

3.2 Raman Scattering Study on the Ferroelastic-Superprotonic Phase Transition of $[K_3]_x[(NH_4)_3]_{1-x}H(SO_4)_2$

Raman spectra of $K_3H(SO_4)_2$, $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ in back scattering geometry observed from the temperature of 20 °C to 260 °C are shown in Fig 3.3, Fig 3.4 and Fig 3.5 respectively. Fig 3.6, Fig 3.7 and Fig 3.8 show the temperature dependences of the frequencies and linewidths of their ν_1 mode that represents the totally symmetric stretching vibration of HSO_4^- .

The fact that the peak frequency shifts to an upper value as the temperature is increased is consistent with the fact that the presence of K_3^+ ion or NH_4^+ ion is changed from a tilted position to a position collinear with an S-O bond of HSO_4^- in the z direction⁽⁶⁾. According to the X-ray structure analysis, at room temperature, the tilted angle between K^+ ion and the S-O bond of HSO_4^- is greater than that of NH_4^+ ion. Therefore, the upward frequency shift of ν_1 mode for $(NH_4)_3H(SO_4)_2$ is smaller than that for $K_3H(SO_4)_2$ when the temperature changes from a room temperature to a temperature greater than T_C . Reasonably, the frequency shift of ν_1 mode for $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ with increasing temperature follows the middle path between that for $(NH_4)_3H(SO_4)_2$ and that for $K_3H(SO_4)_2$. The critical temperatures T_C of $K_3H(SO_4)_2$, $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ are about 200°C, 170 °C and 140 °C respectively.

The phase transition model⁽⁷⁾ involves a change from H-bonded SO_4^- dimmers below T_C to a dynamic two-dimensional O-H...O bonded network formed by reorienting HSO_4^- groups above T_C . This is indeed expected for the case of fast reorientations of the HSO_4^- groups around the c-axis while forming a two-dimensional dynamic O-H...O bond network parallel to the a-b plane.

Rapid three-fold reorientation of HSO_4^- about the z-axis can modulate the Raman polarizability tensor and hence contribute to the spectral linewidth associated with the HSO_4^- vibration. The spectral linewidth of HSO_4^- stretching vibration shows an anomaly near the phase transition temperature, and can be interpreted as fluctuation in the ν_1 mode coupling due to the random motion of HSO_4^- defects. According to the Stochastic Theory of line shape, the line shape for fast modulation where $\tau_c \Delta \ll 1$ is expressed as

$$I(\omega) \propto \frac{1}{\pi} \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$

where the linewidth = $\gamma = \Delta^2 \cdot \tau_c$,

$\Delta^2 = \langle \omega_1^2 \rangle$ = a measure of the magnitude of the random frequency modulation and

τ_c = the correlation time or the rate of modulation.

Fig 3.9, Fig 3.10, and Fig 3.11 show the temperature dependence of the linewidths of ν_1 mode that represent the totally symmetric stretching vibration of HSO_4^- of $\text{K}_3\text{H}(\text{SO}_4)_2$, $[\text{K}_3]_{0.5}[(\text{NH}_4)_3]_{0.5}\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. In addition to the usual temperature dependence of the linewidth of ν_1 mode, the anomalous line broadening ∇ associated with the phase transition is found near T_C . Here ∇ is defined to be the difference between the observed temperature dependence and the extrapolated one from high temperature region to T_C under the assumption that temperature dependence without the phase transition is assumed to be linear for simplicity.

The inverse of the linewidth depends linearly on temperature near T_C as shown in Fig 3.12, Fig 3.13 and Fig 3.14. The inverse of anomalous linewidth decreases with decreasing temperature down to T_C . The anomalous broadening of the linewidth indicates that the random motion slows down near T_C .

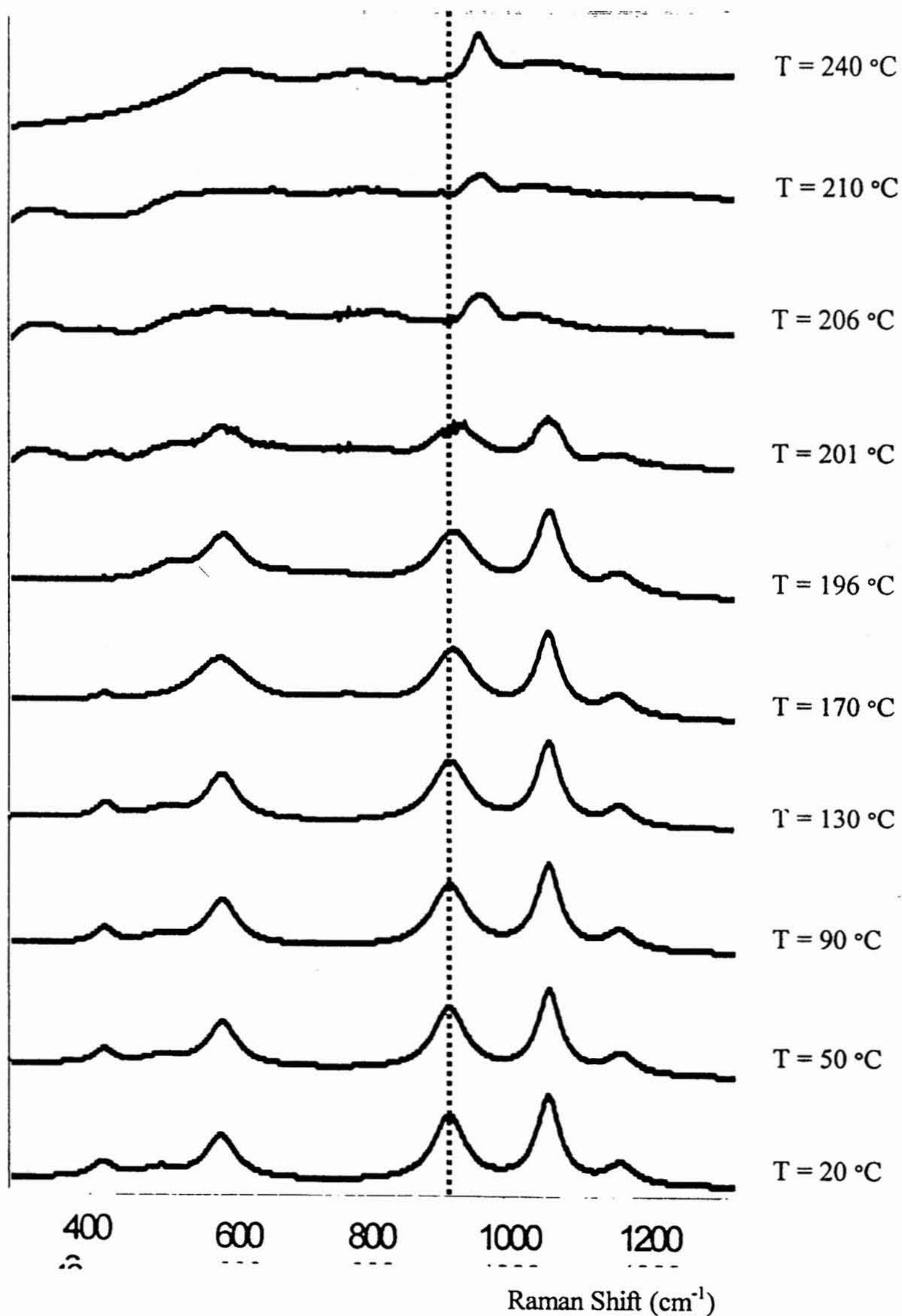


Fig 3.3 Raman Spectra of $K_3H(SO_4)_2$ observed in $c^*(x\ x)c^*$ geometry at several temperatures above the room temperature

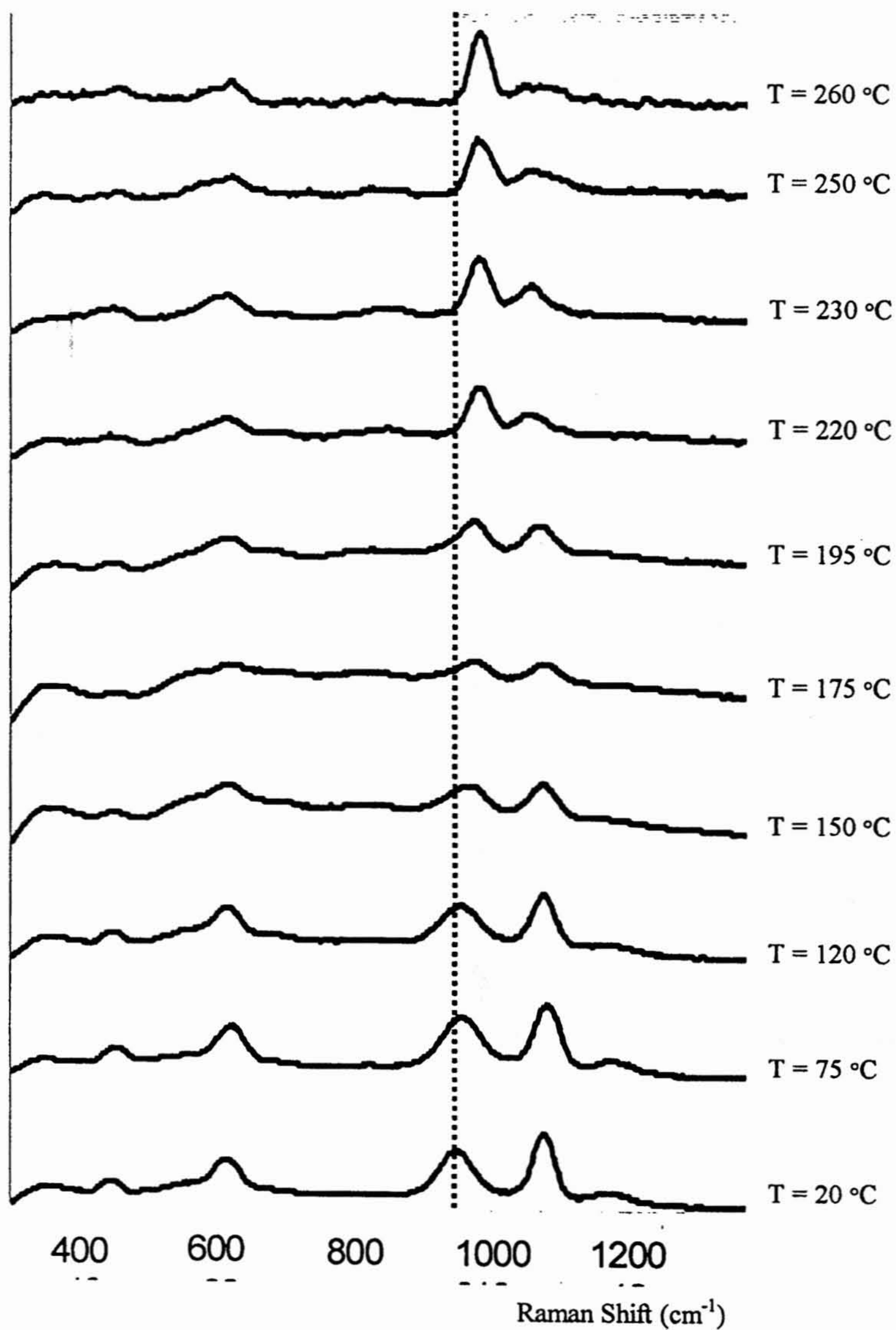


Fig 3.4 Raman Spectra of $[K_3]_{0.50}[(NH_4)_3]_{0.50}H(SO_4)_2$ observed in $c^*(x \times)c^*$ geometry at several temperatures above the room temperature

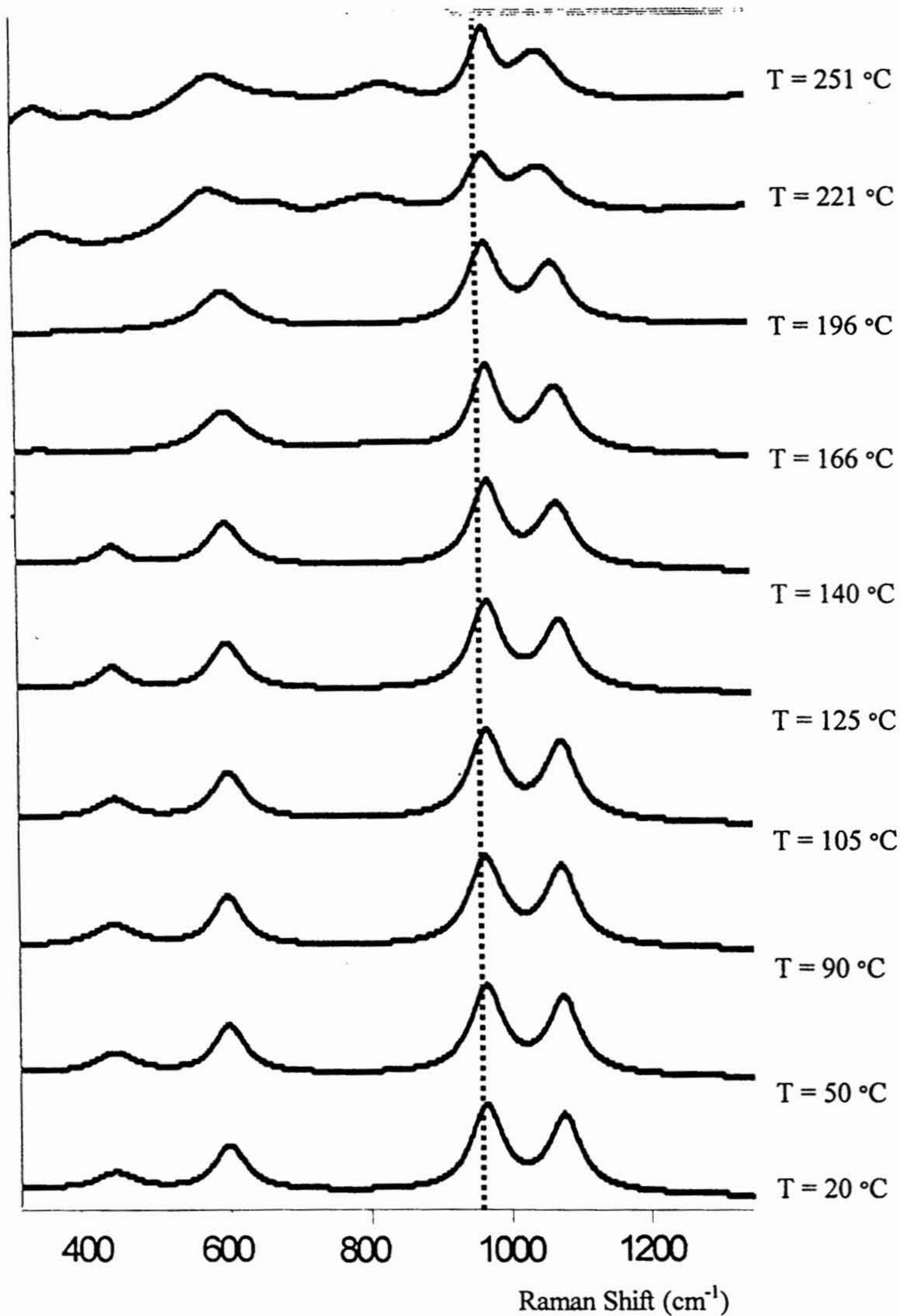


Fig 3.5 Raman Spectra of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ observed in $c^*(x\ x)c^*$ geometry at several temperatures above the room temperature

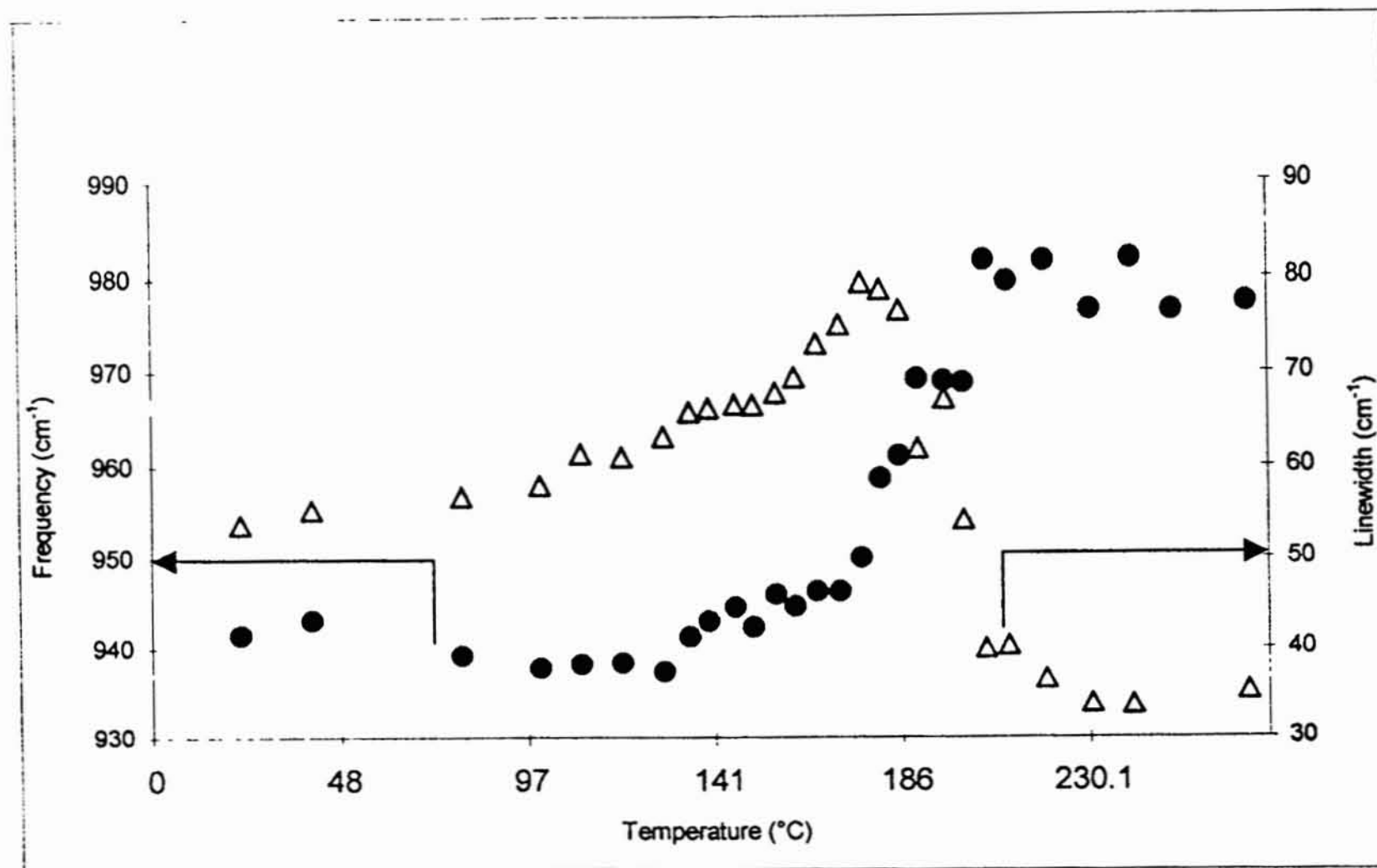


Fig 3.6 Temperature dependence of frequency and linewidth of ν_1 mode of $K_3H(SO_4)_2$ crystal

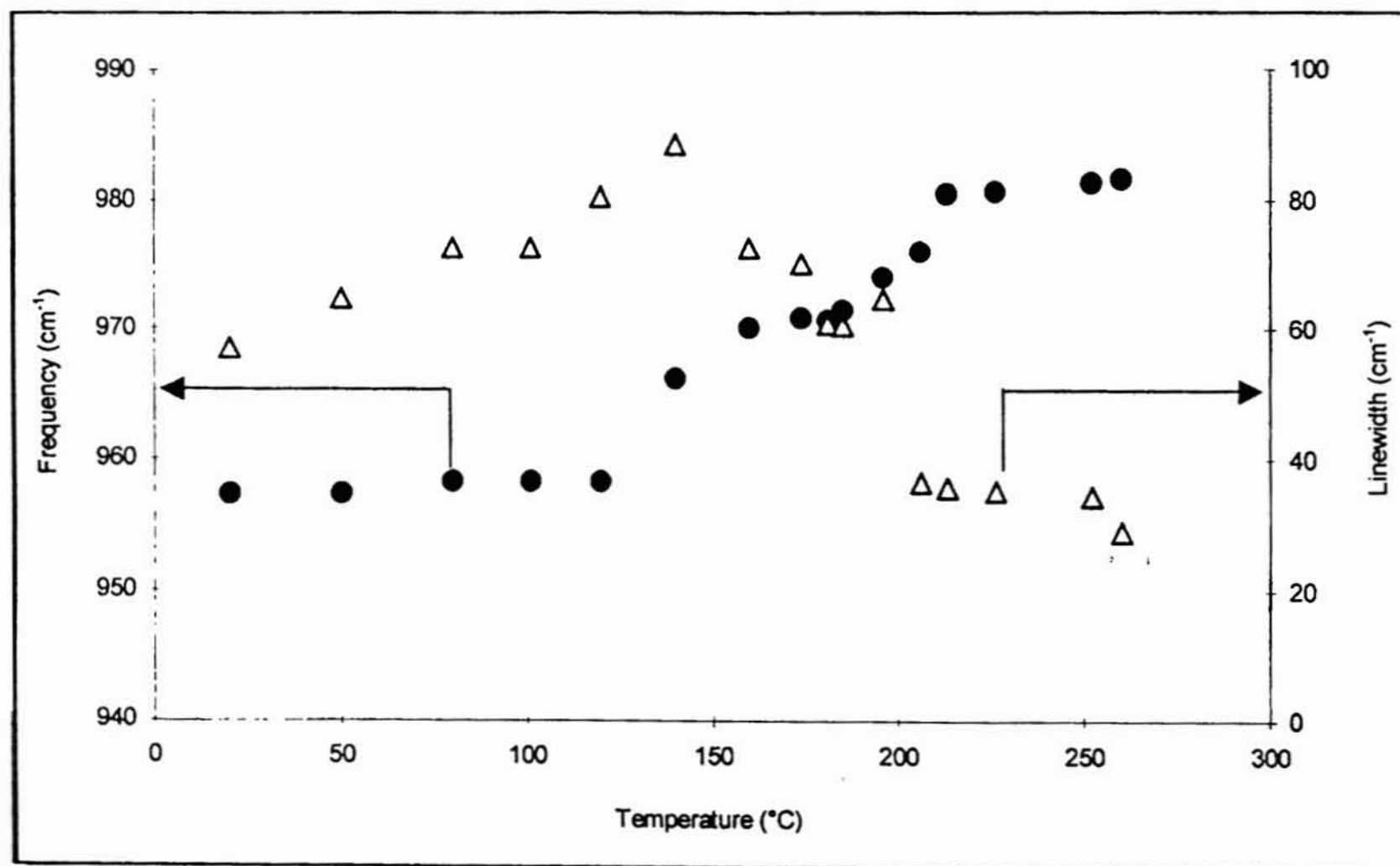


Fig 3.7 Temperature dependence of frequency and linewidth of ν_1 mode of $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ crystal

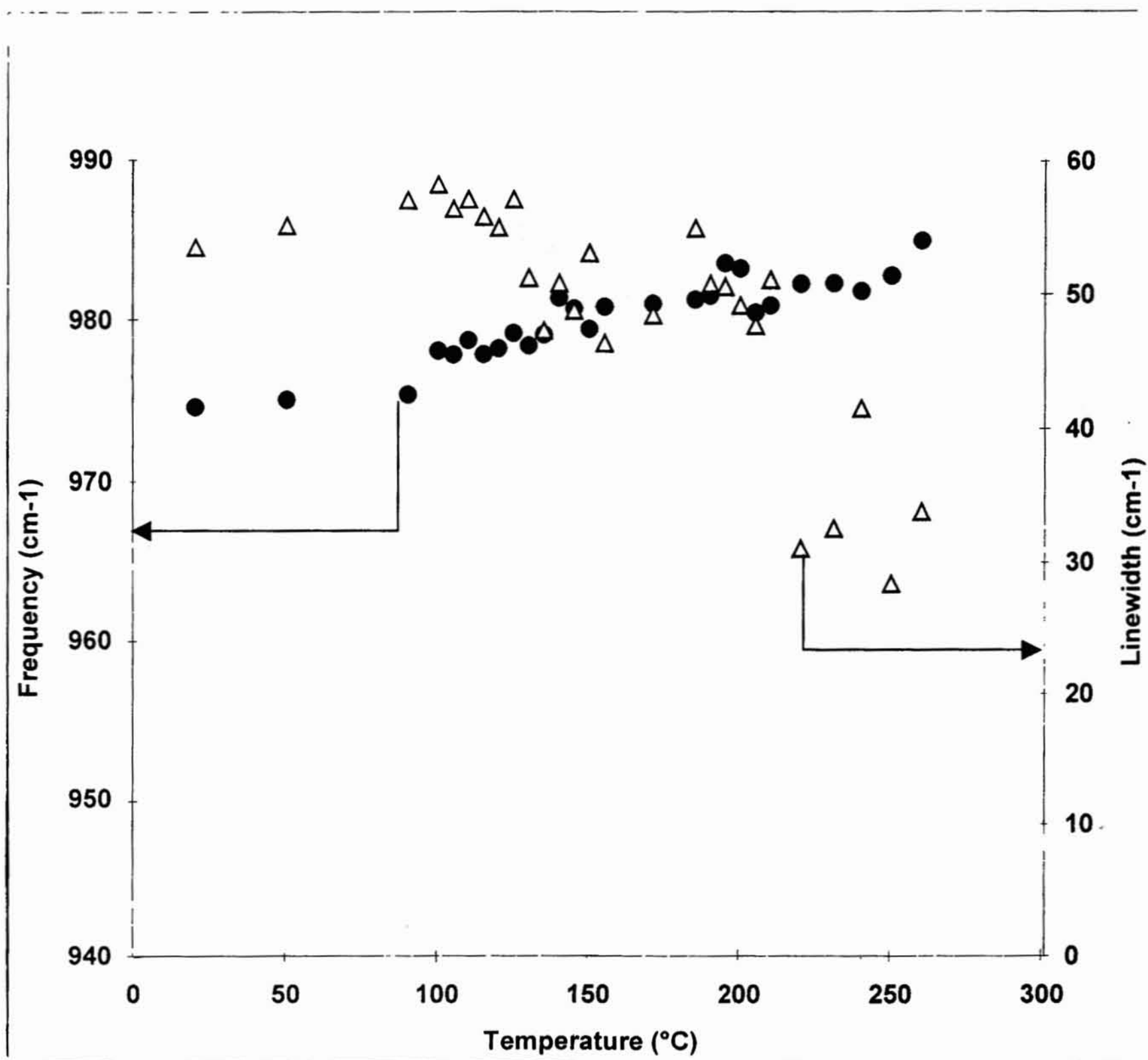


Fig 3.8 Temperature dependence of frequency and linewidth of ν_1 mode of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ crystal

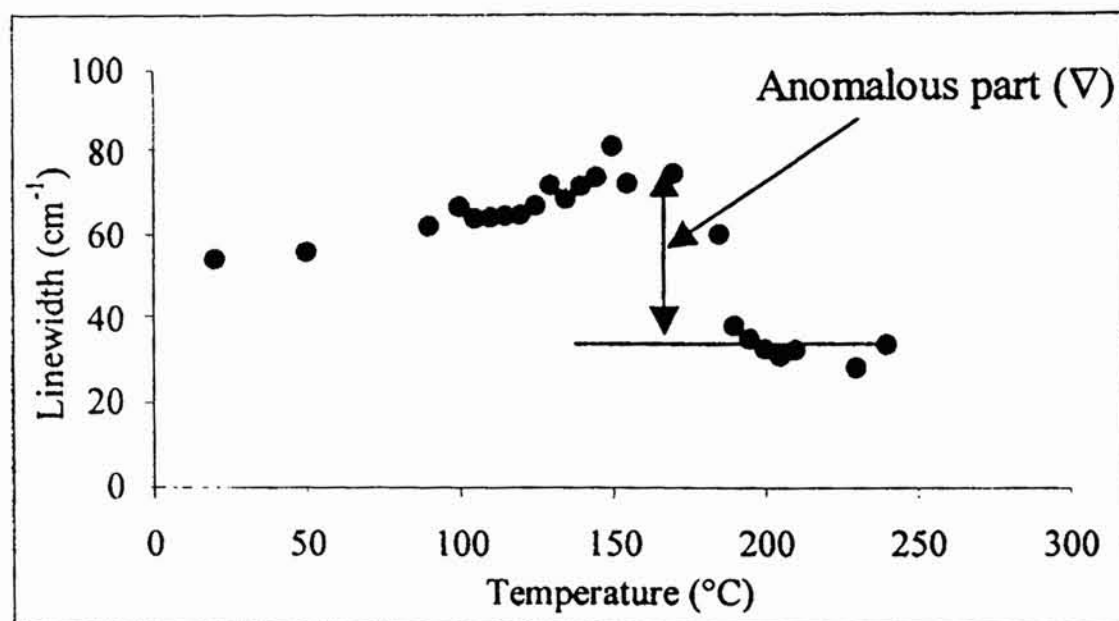


Fig 3.9 Temperature dependence of linewidth of ν_1 mode of $\text{K}_3\text{H}(\text{SO}_4)_2$

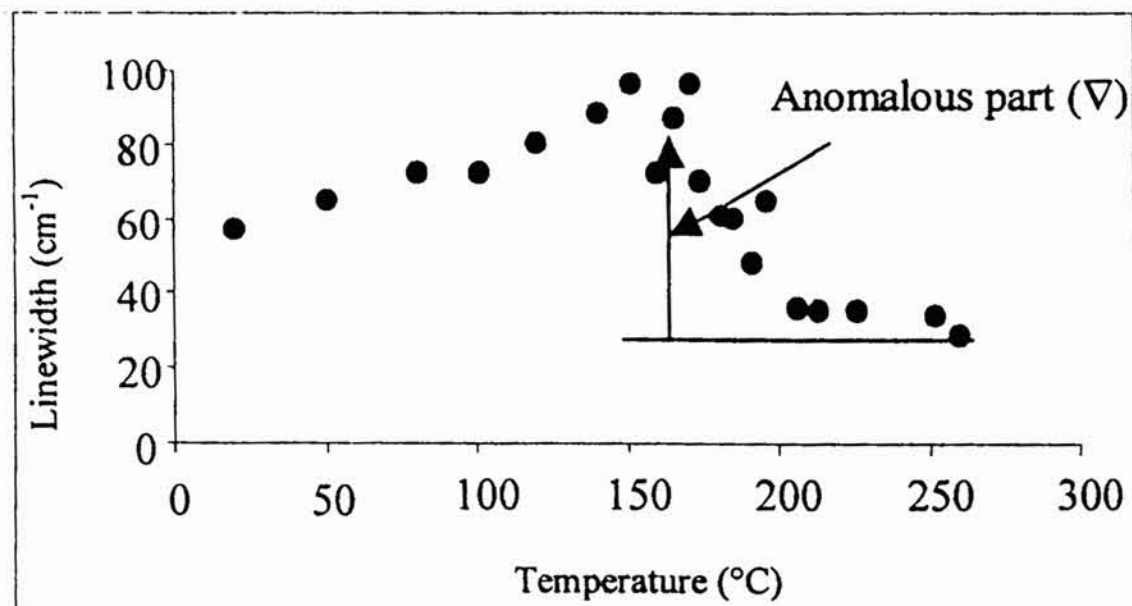


Fig 3.10 Temperature dependence of linewidth of ν_1 mode of $[\text{K}_3]_{0.5}[(\text{NH}_4)_3]_{0.5}\text{H}(\text{SO}_4)_2$

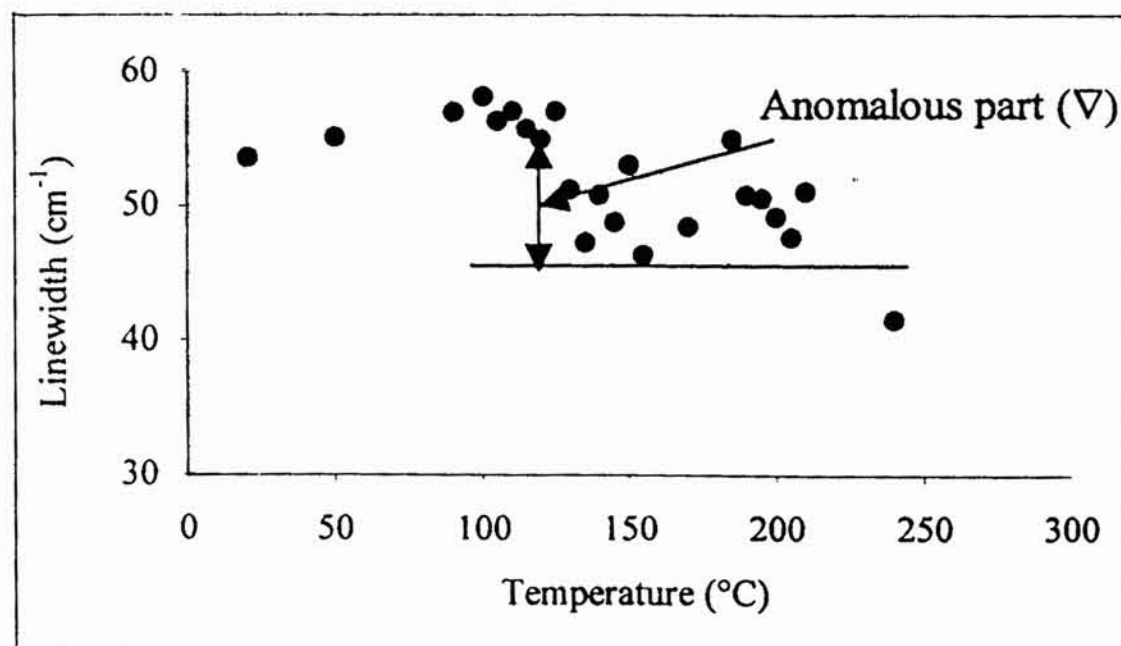


Fig 3.11 Temperature dependence of linewidth of ν_1 mode of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$

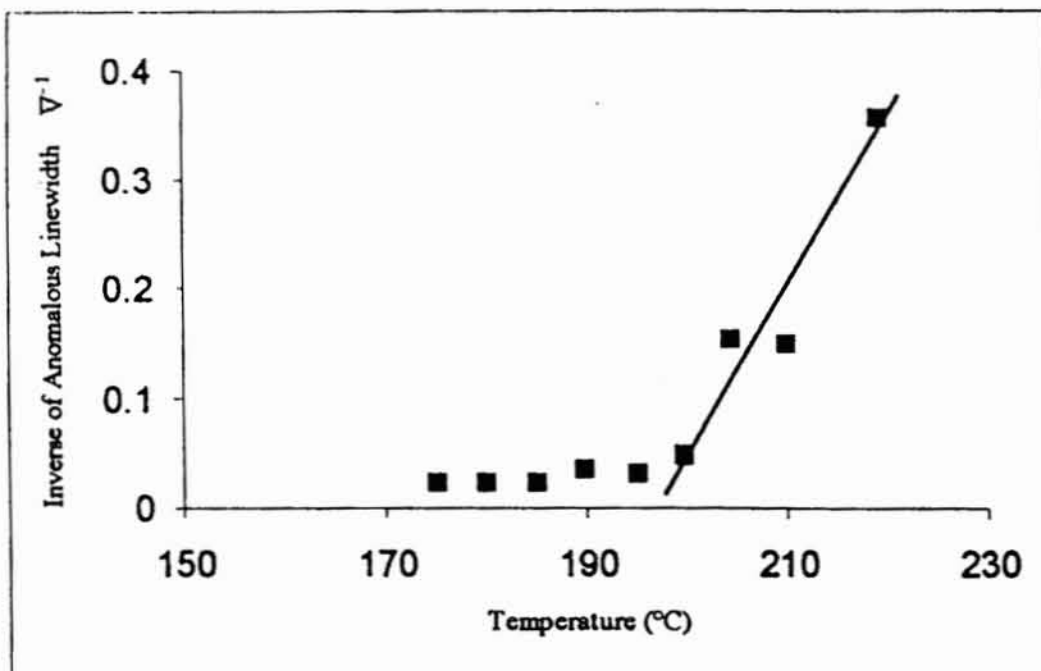


Fig 3.12 Temperature dependence of inverse of linewidth of ν_1 mode for $K_3H(SO_4)_2$

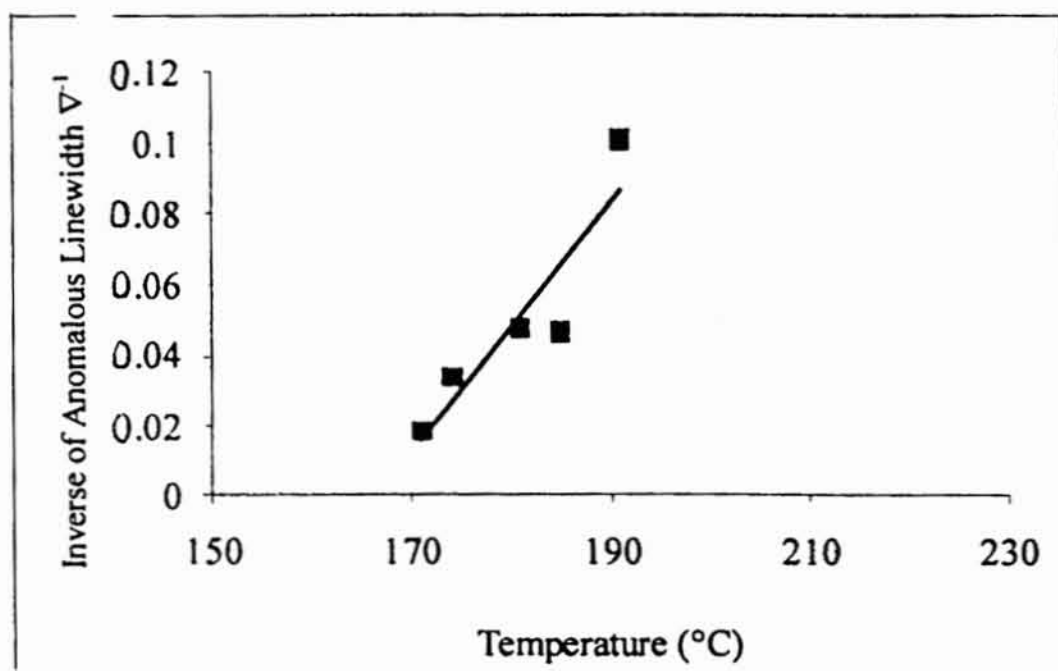


Fig 3.13 Temperature dependence of inverse of linewidth of ν_1 mode for $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$

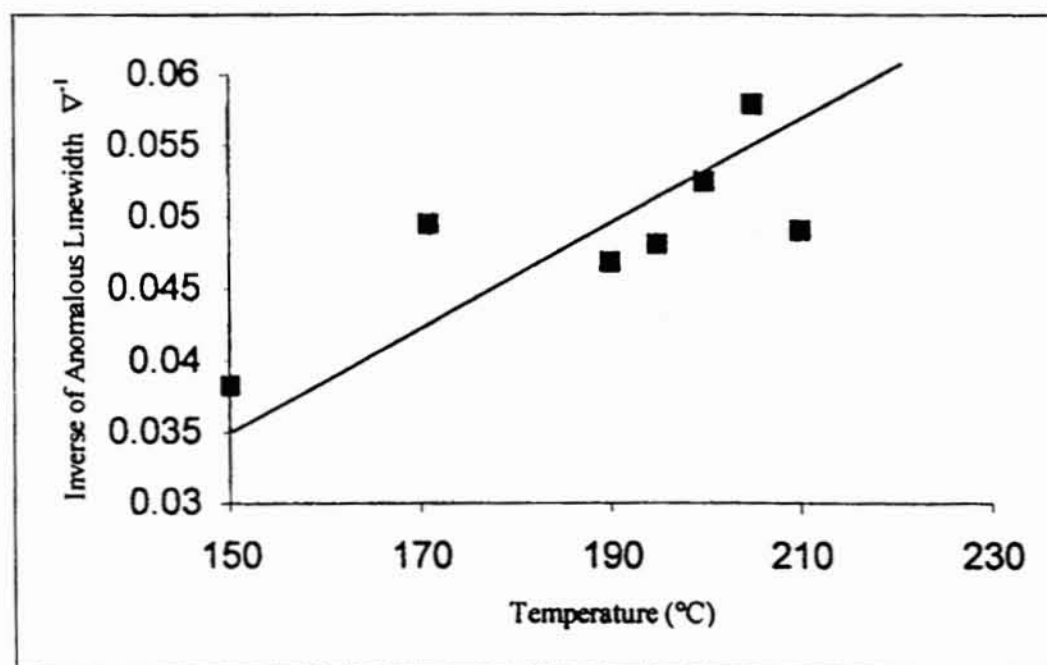


Fig 3.14 Temperature dependence of inverse of linewidth of ν_1 mode for $(NH_4)_3H(SO_4)_2$

4. Conclusion

Raman spectra of $K_3H(SO_4)_2$, $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ in back scattering geometry have been observed from the temperature of 293 K to 573 K. The inverse of anomalous linewidths of ν_1 mode of $K_3H(SO_4)_2$, $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ decrease with decreasing temperature down to T_C . Since the H-----SO₄ reorientations are accompanied by proton transfer between neighbouring H bonds, the inverse of the linewidths represent at the same time also the motion of H interbond exchange. This motion slows down near the critical temperature. The phase transition temperatures are found to be 200 °C, 170 °C, and 140 °C for $K_3H(SO_4)_2$, $[K_3]_{0.5}[(NH_4)_3]_{0.5}H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ respectively.

Acknowledgement

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