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Raman spectra of $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ crystals in the proton glass state

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Abstract. Polarized Raman spectra of $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ (PCHS) single crystals were measured in the frequency range 0–4000 cm^{-1} at 20–300 K, i.e. both below and above the glass transition temperature (T_g). The evolution of the spectra with decreasing temperature indicates that the orientational disorder of SO_4^{2-} ions and H_2O molecules changes at T_g from the dynamical to a static one. A scenario for the glass transition and a model of the resulting glass state is suggested, in which the water molecules (H bonds) play the role of binding constituents of the isolated sulphate complexes $\text{H}_3(\text{SO}_4)_4^{5-}$.

1. Introduction

Pentacaesium trihydrogen tetrasulphate monohydrate crystals $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ (PCHS) belong to the family of hydrosulphates and hydroselenates of alkali metals, which exhibit a high proton conductivity at high temperatures (Baranov *et al* 1992, 1993). In comparison with other members of this family, PCHS exhibits a behaviour which is exceptional: even at room temperature, its hexagonal phase with a dynamically disordered network of hydrogen bonds is isostructural with that of $\text{Cs}_5\text{H}_3(\text{SeO}_4)_4 \cdot \text{H}_2\text{O}$ (PCHSe) (Merinov *et al* 1994a, b), which exists above 346 K. A phase transition occurs in PCHS at $T_{si} = 414$ K; the high-temperature crystalline phase exhibits a much higher conductivity (up to $10^{-1} \Omega^{-1} \text{cm}^{-1}$) (Kabanov 1993). Recently (Yuzyuk *et al* 1994, 1995a), Raman spectra of PCHS at high temperatures (300–500 K) were studied. Low-frequency Raman spectra of this substance are characteristic of crystals with a high ionic conductivity.

Below 240 K (earlier work by Baranov *et al* (1992) determined this temperature as 260 K), an anomalous low-frequency dielectric relaxation has been observed (Baranov *et al* 1993), which is typical for transitions to the state of orientational (or proton) glass and stems from a ‘freezing’ of the orientational and/or positional disorder in some sublattice(s)—in this case, in the network of hydrogen bonds. The glass transition temperature, T_g , as determined from differential scanning calorimetry (DSC), shows a remarkable hysteresis: 248 K on cooling and 261 K on heating (Yuzyuk *et al* 1995b). It is worth mentioning that earlier studies of proton glasses encompassed only mixed crystals (e.g., $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ and $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$; Höchli *et al* (1990)), where a competition of statistical interactions leads to a disordered distribution of dipole moments over a wide region of concentrations, $0.25 \leq x \leq 0.75$. Dielectric behaviour of ‘monocomponent’ (i.e., unmixed) PCHS,

recognized as a characteristic of dipolar glass, allowed Baranov *et al* (1993) to classify PCHS as constituting a new class of proton glasses.

The aim of this work is to collect data on the lattice dynamics of PCHS at low temperatures and to use them in determining the structural distortions that take place in the glassy state of PCHS.

2. Experimental details

Raman spectra of PCHS have been measured using samples in the form of oriented and optically polished rectangular parallelepipeds measuring $2 \times 3 \times 4 \text{ mm}^3$, with faces normal to $z \parallel c_h$, $y \parallel a_h$ and $x \perp (y, z)$, where $a_h = 6.245 \text{ \AA}$ and $c_h = 29.69 \text{ \AA}$. A continuous-flow liquid He optical cryostat was used; the sample was mounted on a copper block, placed in He exchange gas. The 488 nm and 476.5 nm lines of an Ar^+ laser were chosen for excitation; the scattered light was analysed in the right-angle scattering geometry, using a PC-controlled SPEX-14018 double spectrometer equipped with a standard photon-counting detector. The spectral width of slits amounted to about 2 cm^{-1} . Some measurements concerning Rayleigh scattering have been repeated with a DFS-24 double monochromator.

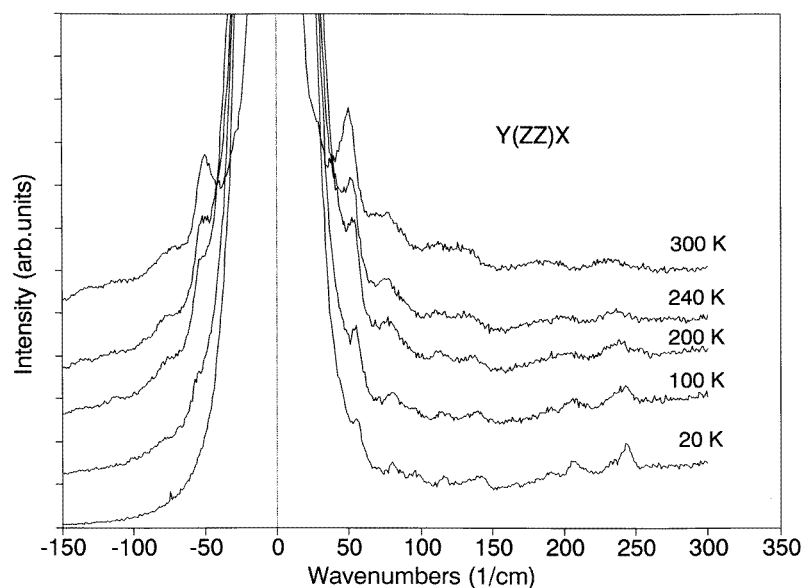


Figure 1. Temperature evolution of the low-frequency Raman spectra of PCHS.

3. Results and discussion

3.1. Peculiarities of the crystal structure and the Raman spectra

At room temperature, the unit cell of PCHS contains two formula units and the crystal assumes the symmetry $P6_3/mmc$ (Merinov *et al* 1994b). Caesium atoms occupy all of the sites 2(b), with a local symmetry $G_{ss} = D_{3h}$ and two 4(f) sites with a symmetry C_{3v} . Sulphur atoms are located in 4(e) and 4(f) sites with the same local symmetry C_{3v} , but the

corresponding tetrahedra $SO_4(1)$ and $SO_4(2)$ are in different states: oxygen atoms belonging to $SO_4(2)$ occupy two 12(k) and one 24(l) positions, with the probability 1/2, 1/3, and 1/4, respectively. Because of that, $SO_4(2)$ tetrahedra differ from $SO_4(1)$ ones by an orientational disorder, characterized by the angle of reorientation about the axis perpendicular to (001); this angle has been determined by Merinov *et al* (1994b) to be about 40° .

The room-temperature Raman spectra of PCHS have been studied in detail by Yuzyuk *et al* (1994, 1995a); it was supposed that—owing to hopping movements of oxygen atoms of the $SO_4^{2-}(2)$ tetrahedron over (k) and (l) sites— $SO_4^{2-}(2)$ tetrahedra occupy the positions of reduced symmetry and thus of higher multiplicity, preserving $G_{ss} = C_{3v}$ only as the average over the crystal lattice. Such a reduction of the true symmetry of these complexes manifests itself in an increased number of Raman-active vibrations.

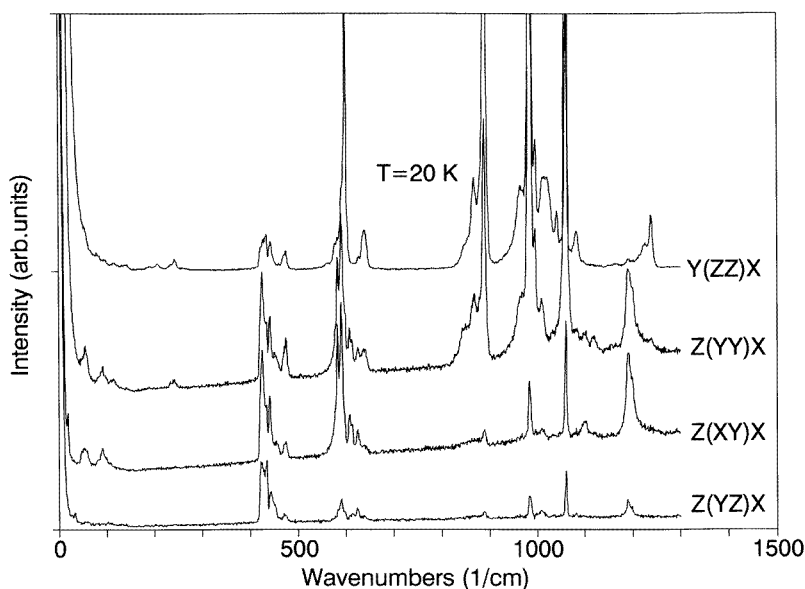


Figure 2. An overall view of the Raman spectra at 20 K.

X-ray determination of the positions water molecules occupy in the PCHS structure presented serious difficulties (Merinov *et al* 1994b). In the case of PCHSe, the positions of H_2O molecules were determined as 12-fold (k) with the occupancy coefficient 1/6 (Merinov *et al* 1994a). Later, Merinov *et al* (1994b) suggested that H_2O molecules in PCHS occupy 2(c) positions with the occupancy coefficient 1/2. Water molecules in the PCHSe structure perhaps possess a greater orientational mobility in comparison with those in PCHS. This assumption is in accord with the difference in temperatures at which the hexagonal structure appears: in PCHSe, it is by higher 60 K than in PCHS, a difference substantial for such a quasilinear molecule like H_2O . Moreover, a dehydration of the sample used by Merinov *et al* (1994b), only 0.2 mm in diameter, could in principle take place. The samples used in this work for Raman scattering experiments—with linear dimensions greater by one order of magnitude—always yielded good lines of water vibrations.

Three types of hydrogen bond have been found in PCHS with lengths 2.68, 3.03 and 2.89 Å; the corresponding crystallographic positions of their centres are: 6(h), 12(k) and 24(l), with occupancy coefficients 1/3, 1/6 and 1/12, respectively. It is well known that the

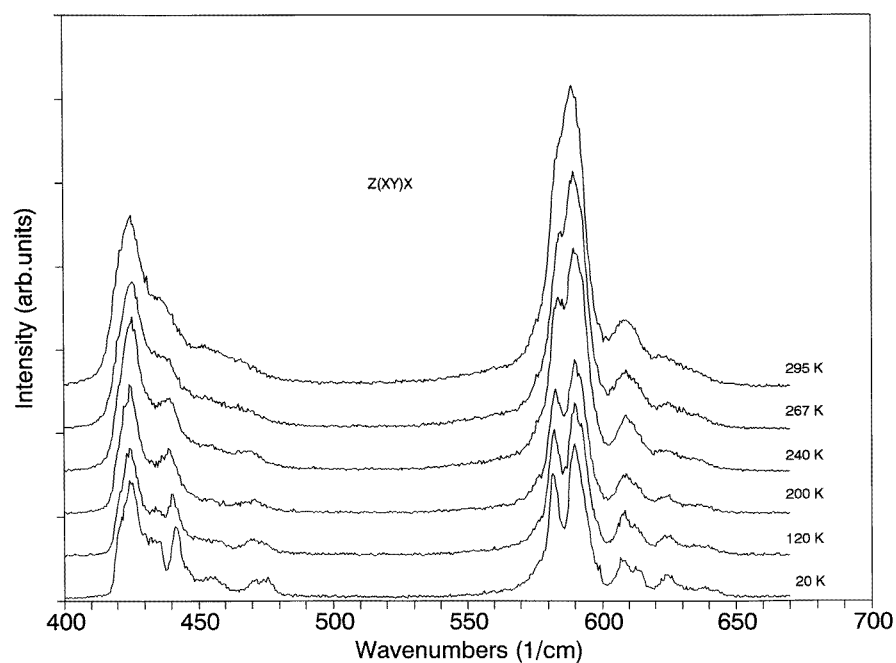


Figure 3. Temperature evolution of the Raman spectra of PCHS in the region of the SO_4^{2-} bending modes ν_2^s and ν_4^2 .

proton is in a double-minimum potential well at such lengths of the H bonds; protons are thus disordered in double-minimum potentials along each of the three hydrogen bonds and, moreover, an interbond disordering of protons takes place. This situation favours both the proton transport in PCHS structure at high temperatures and the ‘freezing’ into a glass state at low temperatures. A low local symmetry of the proton positions causes proton vibrations to be Raman active in all of the scattering geometries. The fact that the maximum intensity of H-bond stretching vibrations occurs in the $y(zz)x$ orientation points to a predominant orientation of H bonds along the z axis. In a comparison with other hydrogen-containing crystals, attention should be drawn to higher intensities of the deformational vibrations of H bonds in the region of $840\text{--}990\text{ cm}^{-1}$. Apparently, this feature is due to a larger amplitude of this motion in PCHS than, e.g., in CsH_2PO_4 or RbH_2PO_4 . This quantitative difference also correlates with the interbond disorder of protons suggested above.

3.2. Changes of the Raman spectra with temperature

The transition to the glass state at T_g is not accompanied by any noticeable changes in the spectra below 300 cm^{-1} , with the exception of Rayleigh scattering which will be dealt with below. Local imperfections in the crystal lattice evolve gradually on cooling and their manifestation becomes really distinguishable at temperatures $T \leq T_g - 100\text{ K}$, though initial symptoms of imperfections can be traced even above T_g . The macroscopic symmetry of PCHS (D_{6h}^4) is preserved down to low temperatures, but the observed changes in Raman spectra are associated with a reduction of the true symmetry of sulphate ions with the gradual freezing-in of their orientational movements. This gradual process is reflected in

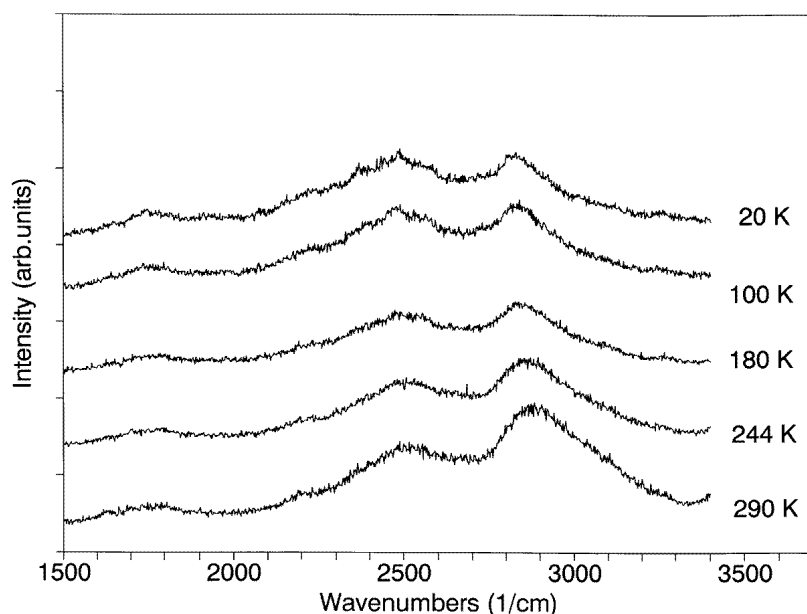


Figure 4. Raman spectra of PCHS in the region of H-bond stretching vibrations on cooling.

a gradual splitting of spectral lines. For example, in the region of lattice vibrations in the $y(zz)x$ orientation, the broad lines at 78 and 191 cm^{-1} split below 200 K to doublets at 81, 99 cm^{-1} and 188, 207 cm^{-1} (see figure 1). On further cooling, the band at 240 cm^{-1} splits at 20 K to lines at 237 and 244 cm^{-1} . At 20 K, in this orientation corresponding to A_{1g} modes, we thus have nine lines in total, which is undoubtedly due to a reduction of the local symmetry of SO_4^{2-} anions in comparison with the situation at room temperature.

The spectrum of internal modes of SO_4^{2-} ions changes monotonically on cooling: the half-widths of lines decrease, there are no sudden changes in their peak positions, and the asymmetric wings of lines that we see at 300 K become fine structured at low temperatures, so the total number of observed lines is increased, but only by the splitting of broad lines which are characteristic of the room-temperature phase. For the lowest temperature set (20 K), the line frequencies are given in table 1. An overall view of the spectra is given in figure 2. The increase in the number of components of internal vibrations ν_i^s is also connected with a reduction of local symmetry of SO_4^{2-} tetrahedra in the glass phase. The number of components that we see at 20 K (corresponding to the fundamental modes of SO_4^{2-}) allows us to state unambiguously that the true local (not averaged) symmetry of both kinds of SO_4^{2-} ion is C_1 , since only in this case is the number of lines observed in Raman spectra in agreement with the factor-group analysis:

$$\begin{array}{ll} \nu_1^s: & 3(A_{1g} + E_{1g} + E_{2g}) \\ \nu_2^s: & 6(A_{1g} + E_{1g} + E_{2g}) \\ \nu_3^s \text{ and } \nu_4^s: & 9(A_{1g} + E_{1g} + E_{2g}). \end{array}$$

This situation is illustrated in figure 3, which shows the splitting of the deformation modes ν_2^s and ν_4^s in the region 300–700 cm^{-1} . Moreover, if the local symmetry of SO_4^{2-} is C_1 , ν_1^s should occur in all orientations (due to the correlation relations $T_d-C_{3v}-C_1-D_{6h}$). A considerable increase in the intensity of the ν_1^s -mode actually occurs in the $z(yz)x$ and

Table 1. Frequencies (in cm^{-1}) of observed Raman lines in PCHS.

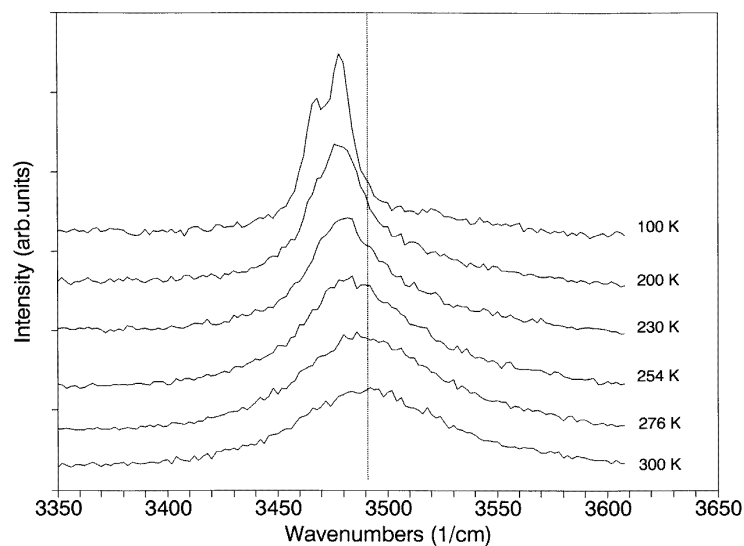
A_{1g} 300 K	$X(ZZ)Y$ 20 K	$A_{1g} + E_{2g}$ 300 K	$Z(YZ)X$ 20 K	E_{2g} 300 K	$Z(YX)Y$ 20 K	E_{1g} 300 K	$Z(YZ)Y$ 20 K	Line assignments
		20		21	19			
31						32	33	
52	56	54	56	52	53	52	56	
						70		Cs ⁺ translations
76	80		86		83			
		91	92	91	91		93	
	96		96			102		Translations and
113	116	110	112					librations
131	143							
185	192							of SO ₄ ²⁻
	208							
232	237		236					
	244		242					
	422		422		422		423	
	426	429	425	431	425	429	427	
435	433	439	433		433		434	ν_2^s
	443		442	440	441	440	443	
		466	452	460	454	461	450	
470	473		474		473		472	
	584		582		583		583	
sh	591	593	591	594	591	593	590	
603	599		598				599	
			607		608			ν_4^s
		614	612	614	613		614	
	626	632	625	630	624	624	624	
			636				636	
640	638		640		640		641	
	851	861	850	860				
sh	867		868				869	
887	888	887	889	888	888		889	H-bond
972	965	973	967					
	983		984		984		984	bending
990	996	990	996	992			996	
	1012		1010		1010		1010	
1029	1021							
1045	1041							
1063	1060	1063	1061	1061	1061		1061	ν_1^s

$z(xy)x$ geometries below 100 K (Yuzyuk *et al* 1995b).

Figure 4 shows the temperature evolution of PCHS spectra in the region of stretching vibrations of H bonds. An important difference in behaviour of H-bond bands in PCHS spectra in comparison with those in the spectra of such ordered crystals as, say, CsH₂PO₄ lies in the fact that the H-bond bands in PCHS do not narrow even at considerably reduced temperatures (down to 20 K). On cooling, the maxima of all bands of the H-bond stretching vibrations shift towards lower frequencies by 20–70 cm^{-1} , which speaks for a shortening of H bonds in the glass state. Since overall symmetry remains unchanged, we must infer that the SO₄²⁻ tetrahedra freeze in randomly distributed (they assume all of the equivalent orientational states at random), so the H-bond lengths in question decrease and this process

Table 1. (Continued)

A_{1g} 300 K	$X(ZZ)Y$ 20 K	$A_{1g} + E_{2g}$ 300 K	$Z(YX)X$ 20 K	E_{2g} 300 K	$Z(YX)Y$ 20 K	E_{1g} 300 K	$Z(YZ)Y$ 20 K	Line assignments
	1081		1082				1083	
		1119	1102 1120	1102	1101			
	1165		1190		1190		1163 1189	ν_3^s
	1193	1196	1198	1196	1198	1195	1194	
1227	1225	1230						
1236	1237		1237					
1800		1800 2230	1760					$\nu_2^w?$
2483		2532	2488	2534		2494		H-bond
2624								stretching
2860		2892	2820	2906		2875		
3000		3064						
3500		3496	3463 3478	3500				ν_1^w, ν_3^w
			3520 3540					Overtones?

**Figure 5.** Temperature evolution of the ν_1^w - and ν_3^w -modes of water in PCHS.

is accompanied with a tilting of tetrahedra; that is, the triad axis of the tetrahedra deviates from the cell hexad. Such a behaviour, together with the sulphate-ion dynamics, points to a freezing-in of protons in a disordered hydrogen-bond network.

The temperature dependence of stretching vibrations of water molecules is shown

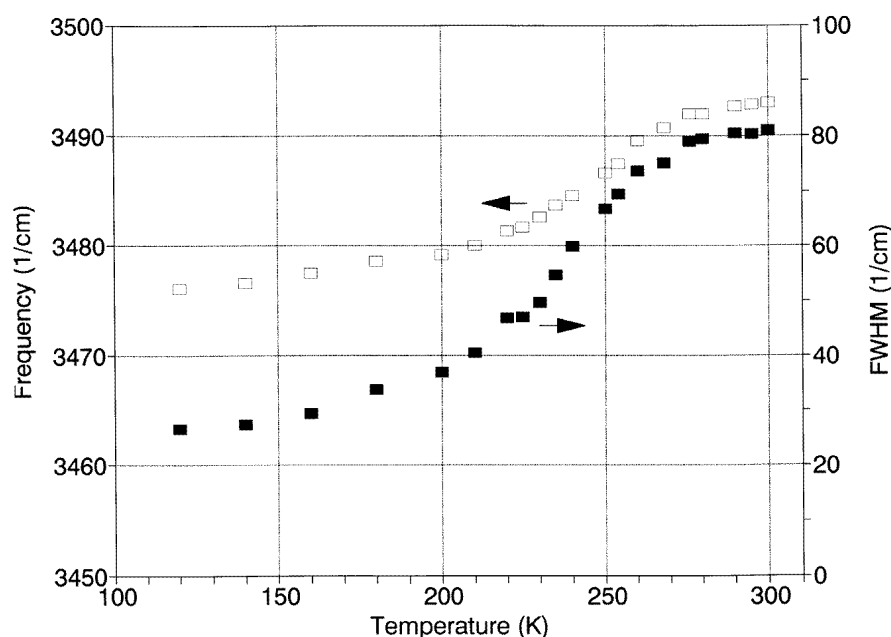


Figure 6. Temperature dependences of the frequency and FWHM (full width at half-maximum) of the 3490 cm^{-1} band on cooling.

in figure 5. At room temperature, the lines of symmetric and nonsymmetric stretching vibrations of H_2O (ν_1^w and ν_3^w) form one broad band with a maximum at $\sim 3500\text{ cm}^{-1}$. In the glass transition range (between 260 and 210 K), a considerable narrowing of this band (~ 2 times) occurs and the maximum of this band shifts by nearly 15 cm^{-1} (figure 6). Let us stress that this is the most pronounced change in the whole Raman spectrum of PCHS near T_g , which speaks for the freezing-in of water molecules. On further cooling, the half-widths of ν_1^w and ν_3^w narrow further, so below 100 K the two maxima become clearly distinguishable at 3463 and 3478 cm^{-1} .

The observed spectra of internal vibrations of crystal water allow one to draw conclusions about the character of the interconnection of water with the surrounding lattice constituents. Firstly, frequency values of ν_1^w and ν_3^w lying above 3400 cm^{-1} point to a weak interaction of H_2O with neighbouring cations—in other words, the additional H bonds between H_2O and oxygen from the SO_4^{2-} group (which plays the role of a proton acceptor) are sufficiently weak. Secondly, a low value of ν_1^w – ν_3^w splitting ($\Delta\nu \approx 20\text{ cm}^{-1}$) is a result of nonsymmetrical interaction of H_2O with nearest sulphate anions either because only one additional H bond forms or due to a nonequivalence of structure fragments, with which two weak additional H bonds form.

3.3. Quasielastic scattering in the glass phase

On cooling below 255 K, a strong Rayleigh light scattering was observed for PCHS. Above this temperature, the path of the laser beam through our colourless crystal is practically invisible, which means that the optical inhomogeneity due to inclusions, admixtures, cracks, dislocations, etc is low. The width of the Rayleigh line does not exceed 10 cm^{-1} at 290 K

and is nearly the same in all scattering geometries. Below 255 K, the path of the laser beam through the crystal volume is clearly seen even with the naked eye. The intensity of scattered light is maximal for the wave vector of the scattered light perpendicular to the z axis (i.e., the sixfold axis). The scattered light is nearly totally polarized: the polarization direction is perpendicular to the plane of scattering (given by the direction of the incident beam and the direction of observation) which is characteristic of molecular scattering due to fluctuations of optical permittivity, which in turn are due to the density fluctuations and orientational fluctuations of molecular groups. It is known (see, e.g., Fabelinskii 1965) that the linear dimensions of volumes causing molecular scattering are small in comparison with the wavelength of the exciting light ($10^{-7} \text{ cm} < V^{1/3} < 10^{-5} \text{ cm}$).

When studying the scattered light intensity as a function of the analyser position, it was found that a nearly total polarization of scattered light occurs in the 90° scattering geometry which corresponds to a scattering on the isotropic fluctuations of $\Delta\epsilon$ at the excitation of polarized light ($I \sim I_0 \sin^2 \Theta$).

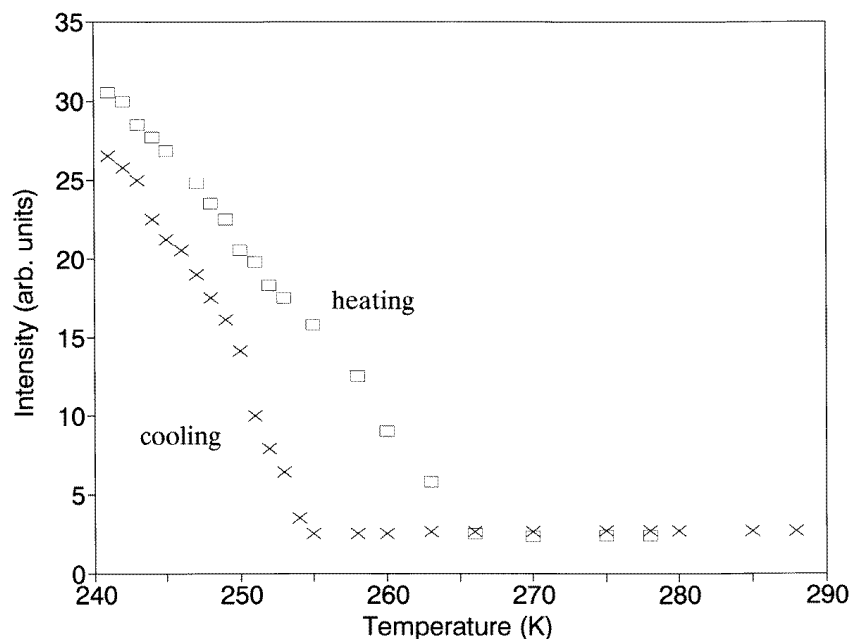


Figure 7. The temperature dependence of the isochromatic ($\sim 20 \text{ cm}^{-1}$) intensity of scattered light in $y(zz)x$ scattering geometry.

The temperature dependence of the isochromatic intensity of scattered light (taken at the slope of the Rayleigh line at $\sim 20 \text{ cm}^{-1}$) is presented in figure 7 for the $y(zz)x$ geometry. At a cooling rate of $\sim -10 \text{ K h}^{-1}$, the scattered light intensity rises more than 20 times, between 255 K and 240 K. There, at a fixed temperature, the intensity rises further gradually with time, and an intensity saturation which would indicate that an equilibrium state is established is not reached even for observations lasting several hours. This indicates that long-lasting relaxational processes take place in the crystal structure. On heating the sample from 240 K to 290 K, the intensity of scattered light drops and the anomalous scattering vanishes above 265 K; the span of the temperature hysteresis revealed in this experiment is thus close in

magnitude to that found by DSC calorimetry (Yuzyuk *et al* 1995a, b). After the cooling–heating cycle, above 265 K, the width of the Rayleigh line returns to its original magnitude and the Raman spectrum fully copies the original one. This means that no static (permanent) microinhomogeneities (dislocations, cracks, etc) which could enhance the elastic Rayleigh scattering arise during the cooling/heating cycle. To eliminate ‘chancy’ effects of external factors, the observations and measurements were repeated with identical samples at two different spectrometers, at various cooling–heating rates and at various laser lines. The results turned out to be independent of all of these factors.

4. Conclusions

Our results of Raman scattering experiments at low temperatures combined with the above-mentioned x-ray study of PCHS structure at room temperature (Merinov *et al* 1994b) allow us to outline, in greater detail, the features of the glass state which forms in PCHS below T_g . The temperature evolution of parameters of lines of both the external lattice vibrations and the internal vibrations of sulphate ions and water molecules indicates that the dynamical orientational disorder of sulphate ions and water molecules starts to change at T_g to a static one, which leads to a localization of H bonds (this means that the intercell diffusion of protons ceases), and to their ordering. In this process, the hexagonal symmetry of the disordered phase remains preserved on average. Just these hydrogen bonds called ‘principals’ (Merinov *et al* 1994a) bind together sulphate groups to isolated complexes $\text{H}_3(\text{SO}_4)_4^{5-}$ of a ‘propeller-like’ form, which—as allowed by a general disordering in this crystal structure—assume several orientations in the PCHS structure. Even at low temperatures, all of the allowed orientations of this complex are equally probable; this means that their reorientations (however, substantially less frequent than for $T > T_g$) are possible. Each reorientation of the $\text{H}_3(\text{SO}_4)_4^{5-}$ complex causes a reconstruction of the system of principal hydrogen bonds; we suggest that it is realized by over-barrier processes and not by tunnelling. The relaxational character of this process thus clearly follows from this picture. Weak hydrogen bonds of water molecules connect these complexes to more voluminous aggregates; their presence in the glass state manifests itself by an intense Rayleigh scattering. Since the $\text{H}_3(\text{SO}_4)_4^{5-}$ complexes are oriented at random, the water molecules which connect them together by weak hydrogen bonds are in the majority of cases nonsymmetrically strained. This picture corresponds well to the character of vibrational spectra of water molecules as discussed in section 3.2. The amount of crystal water in the PCHS structure thus determines the mean dimension of dipolar relaxing ‘clusters’ and it seems probable that there exists a critical concentration of crystal water below which the average dimension of the aggregates will be no longer be sufficient to allow formation of the glass state.

Experiments with crystals with checked composition (water content) and known history, for controlled humidity and other relevant conditions, would be of interest.

Acknowledgments

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