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Manifestation of Phonon Mode Dispersion in Potassium Dihydrogen Phosphate Crystals in Raman Spectra in the Phase Transition Region

© A.V. Igo

Ulyanovsk State University,
Ulyanovsk, Russia
E-mail: igoalexander@mail.ru

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Raman spectra of potassium dihydrogen phosphate crystals near the order-disorder phase transition temperature are measured. During the analysis, the temperature dependences of the spectral line parameters are compared with the known calculation data on the dispersion of optical phonons, on which Raman scattering occurs. As a result of the analysis, an assumption is made that in the region of the phase transition temperature there is a temperature region when both phases coexist in the crystal. The ferroelectric phase, when cooled below the phase transition temperature, appears in the form of nanometer-sized clusters and, upon further cooling of the sample, fills the entire space due to an increase in the cluster size. The estimates made on the basis of the known phonon confinment model show that in the range of about 10°C from the phase transition temperature, the size of the model cluster increases from zero to about 20 nm.

Keywords: order-disorder phase transition, Raman scattering, potassium dihydrogen phosphate, phonon confinement model.

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1. Introduction

A crystal of potassium dihydrogen phosphate (KH_2PO_4) undergoes an order-disorder phase transition at a temperature of $T_0 = -150^\circ C$ [1]. The symmetry of the crystal at temperatures above T_0 belongs to the group D_{2d}. The symmetry group of the crystal decreases to C_{2v} at temperatures below T_0, and the crystal lattice is polarized along the C_2 axis of the lattice, this phase is called ferroelectric (FE), and the high-temperature phase is called paraelectric (PE).

The source of polarization and decreased symmetry of the lattice is the displacement of K^+ and $(PO_4)^{3-}$ ions in opposite directions. The displacement becomes possible and energetically advantageous at temperatures below T_0, due to the redistribution of the electron density in the plane perpendicular to the axis of displacement. Studies have shown that the main role in this redistribution is played by the spatial redistribution (ordering) of the arrangement of hydrogen bonds between ions in the FE phase, therefore this phase transition is classified as an order-disorder type.

Such a significant structural change in the crystal lattice is experimentally manifested in the RS spectra of optical phonons. Each of the phases has a phonon spectrum determined by the symmetry of the crystal lattice. The phonon spectra of these phases significantly differ and have been theoretically calculated [2,3].

In experiments on the detailed study of the RS spectrum in the temperature range near the phase transition, it was found that some spectral lines show a smooth change in frequency and intensity, and some spectral lines appear (disappear) rather abruptly [4–6]. This temperature range, when a significant restructuring of the phonon spectrum occurs, is on the order of units of degrees and is of interest for studies. The change and rearrangement of the phonon spectrum of a crystal clearly correlates with the occurrence and magnitude of the resulting polarization of matter. Moreover, phonon modes are the key to understanding the stability of various phases and the origin of phase transitions [7].

In the case where, in a macroscopically significant volume, some of the hydrogen bonds are ordered and some are not, it can be assumed that both phases coexist in this temperature range. After all, it must be borne in mind that each of the phases occupies its own volume at the microscopic level, in which its phonon spectrum is realized in accordance with its symmetry, i. e. phonons are vibrational excitations of a specific volume of the phase.

KH_2PO_4 lattice in the PE phase belongs to tetragonal symmetry (D_{2d}) and has the following oscillatory representation [2]:

$$T_P = 4A_1 + 5A_2 + 6B_1 + 7B_2 + 13E.$$

The lattice symmetry group decreases to orthorhombic in the FE phase (C_{2v}) and has the following oscillatory representation:

$$T_F = 11A_1 + 11A_2 + 13B_1 + 13B_2.$$

Group theory shows that doubly degenerate modes E are divided into symmetry modes B_1 and B_2 during the transition from tetragonal symmetry to orthorhombic. The disturbance of symmetry caused by the displacement of the proton center leads to the replacement of representations A_1 and B_2 by A_1, and A_2 and B_1 — by A_2 [2]. The symmetry and frequency of the phonon branches change in the region of the phase transition, and there is a smooth change in the frequency and intensity of the RS spectral line on these phonons in the RS spectra. A smooth change of the magnitude of the polarization, intensity, and frequency of the spectral line may be associated with a smooth change in the volume of the FE phase.

Phonon modes can be divided into external, lattice (translational and librational) modes and internal vibrational modes of a complex ion according to the accepted division. This paper studies lattice modes, their frequencies lie in the range of less than $250\,\mathrm{cm}^{-1}$ [2].

Comparison of calculated data of the dispersion of phonon branches [2] and known experimental results [4–6] shows that modes with significant dispersion show a significant frequency change in the RS spectra, and modes with low dispersion show a small frequency change in the RS spectra in the temperature range near the phase transition. Frequencies other than the phonon frequency at the point Γ can be manifested in the RS spectra, due to the dispersion of the phonon branch if, the FE phase nucleates in the PE phase in case of crystal cooling in the form of nanocrystalline clusters. Such an ordering mechanism (phase transition) was considered earlier for ammonium chloride [8]. It is known [9] that the selection rules for Raman scattering are relaxed in nanoscale clusters, and scattering is allowed not only at the point Γ, but also in some of its vicinity. If the dispersion of the phonon mode is significant, then the RS spectrum of a sample consisting of nanocrystalline clusters exhibits a shift of the peak frequency of the spectral line. The quantitative relationship between cluster size and frequency shift is described by the well-known phonon localization (PL) model [10, 11].

The purpose of this study is to experimentally study the RS spectra of KH_2PO_4crystals in the temperature range close to the phase transition temperature and compare these data with the results of calculation of the dispersion of phonon modes for the stable FE phase. Using the PL model, we estimate the size of the clusters of the FE phase, using the calculated data of the dispersion of the phonon branches and the experimentally observed values of the RS frequency shift.

2. Experiment. Measurement procedure

The RS spectra were measured using upgraded DFS-52 spectrometer with PMT H6240-01. The spectrometer's entrance slit width was 0.2 mm. A laser with a wavelength of 532 nm and a power of 20 mW was used for RS excitation. The scattered radiation was passed through a polarizer analyzer and recorded at an angle of 90° in the configurations $y(xy)x$ and $y(xz)x$.

The studied sample with the size of $4 \times 2 \times 4$ mm was cut from a crystal of potassium dihydrogen phosphate. The crystal was grown from a supersaturated aqueous solution of KH_2PO_4. The sample was polished and oriented along the edges of the original tetrahedral crystal, the axis of the highest symmetry was directed along the axis z of the laboratory coordinate system. The sample was put in a pumped cryostat cooled with liquid nitrogen. The temperature was measured and maintained by a system with TPM −01 regulator and a chromel−alumel thermocouple. The RS spectra were measured in the temperature range from −170 to −146°C. The sample was cooled to a temperature of −170°C and then smoothly heated with a heating step of 2°C.

3. Measurement and calculation results

Figure 1 shows the RS spectra measured in the configuration $x(xz)y$. Doubly degenerate symmetry fluctuations E can occur in the spectra according to the form of the RS tensor for the symmetry group D_{2d} [12,13] (PE phase) in this configuration. These lattice vibrations correspond to spectral lines *1*−*4* of the spectrum at $T = -150$°C in Figure1 (spectrum *4*). As the sample temperature decreases below the phase transition temperature, the lattice symmetry decreases to C_{2V}, and only phonons of symmetry B_1 can appear in the configuration $x(xz)y$ according to the form of the RS tensor for this group [12]. (Spectra *1*−*3*) correspond to this situation in Figure 1. Degenerate spectral lines *1*−*4* are split into a and b components.

The frequencies of the components are listed in Table 1. The frequencies for the FE phase are given for the temperature of −170°C. The frequencies for the PE phase are given for the temperature of −150°C. The calculated frequency values are given in accordance with the operation [2]. The values obtained in the experiment are in good agreement with the known values [4–6].

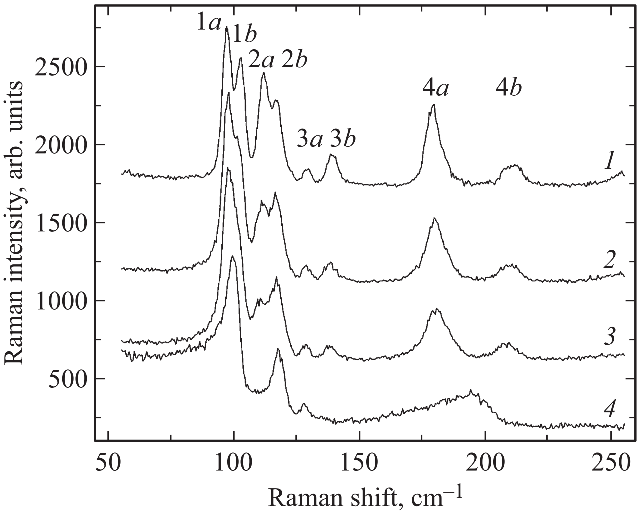

Figure 1. RS spectra of the sample in the configuration $x(xz)y$ at $T = -164$°C (*1*), −154°C (*2*), −152°C (*3*), −150°C (*4*).

Table 1. Component frequencies

Number on Figure 1	PE phase, $x(xz)y$, phonon E (D_{2d})		FE phase, $x(xz)y$, phonon B_1 (C_{2v})		
	Calculation [2], cm^{-1}	Experiment., cm^{-1}	Experiment., cm^{-1}	Calculation [2], cm^{-1}	Calculation of [2] dispersion, cm^{-1}
1	71	100	97 102	104 106	< 0.5
2	131	117	112 117	138	< 0.5
3	133	128	129 138	145 157	< 0.5
4	205	195	178 211	189 213	< 0.5

Table 2. Component frequencies

Number on Figure 1	PE phase, $x(xy)y$, phonon B$_2$ (D$_{2d}$)		FE phase, $x(xy)y$, phonon A$_2$ (C$_{2v}$)		
	Calculation [2], cm^{-1}	Experiment., cm^{-1}	Experiment., cm^{-1}	Calculation [2], cm^{-1}	Calculation of [2] dispersion, cm^{-1}
1	–	–	139	179	13
2	189	187	208	221	32

The spectrum of the sample changed as the temperature changed in the FE phase, as can be seen in Figure 1 (spectra *1–3*). The intensities of the components a and b changed for spectral lines *1, 2, 3*, at the same time, the frequencies of all components of the spectral lines did not change and were within the measurement error limit of 0.5 cm^{-1} over the entire temperature range. Spectral line *4* does not exhibit any temperature dependence of the intensity of the components in the studied temperature range.

The dependences of the relative intensity of components S for spectral lines are shown in Figure 2. The relative intensity of the split components remains constant for temperatures far from T_0 for the FE phase. The value of S decreases to zero starting from the temperature of -158°C, as it approaches T_0 , which corresponds to a situation where there is no phase in the sample, the components of which are split, i. e. FE phase. It can be assumed that both phases coexist in the intermediate temperature range, and the relative volume of these phases can be estimated by the value of S. For example, the ratio changed from 2.2 to 1.3 for a spectral line *3* at a temperature of -154°C, then we obtain 0.6 volume fraction of the FE phase making up the proportion. A similar calculation yields similar values for spectral lines *2* and *1*.

Figure 3 shows the RS spectra measured in the configuration $x(xy)y$. Fluctuations of symmetry B_2 are allowed in the spectra in this configuration according to the form of the RS tensor for the symmetry group D_{2d} [12] (PE phase) The spectral line corresponds to this lattice vibration *2* at $T = -150$°C in Figure 3 (spectrum *4*). The lattice symmetry decreases to C_{2V} as the sample temperature decreases below the phase transition temperature, and only phonons of symmetry A_2 can appear in the configuration $x(xy)y$ according to the form of the RS tensor for this group [12]. The spectra *1–3* correspond to this situation, the spectral lines *1* and *2* correspond to the symmetry phonons A_2 in Figure 3. The values obtained in the experiment are in good agreement with the known values measured in this configuration [4–6]. The experiment is compared with the calculated frequency values and

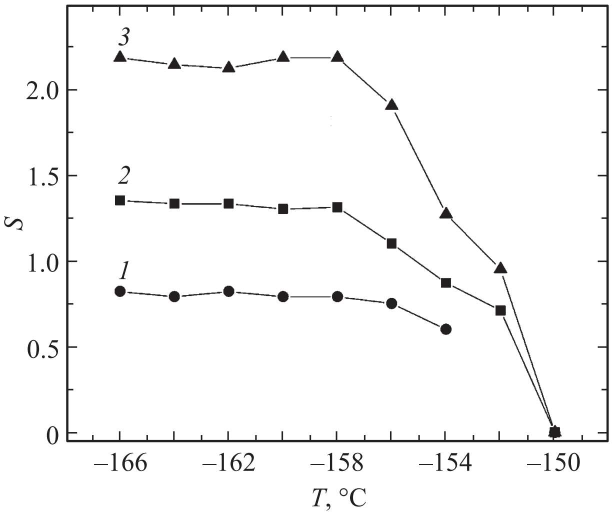

Figure 2. Dependence of the relative intensity of the spectral line components S on temperature.

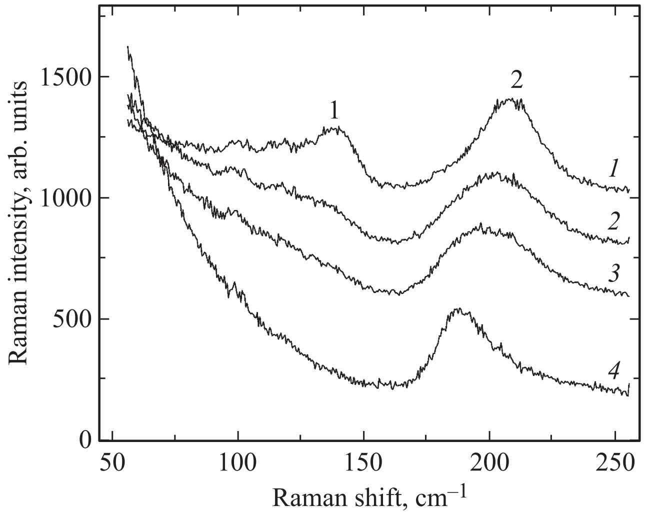

Figure 3. RS spectra of the sample in the configuration $x(xy)y$ at $T = -164^\circ$C (*1*), -154°C (*2*), -152°C (*3*), -150°C (*4*).

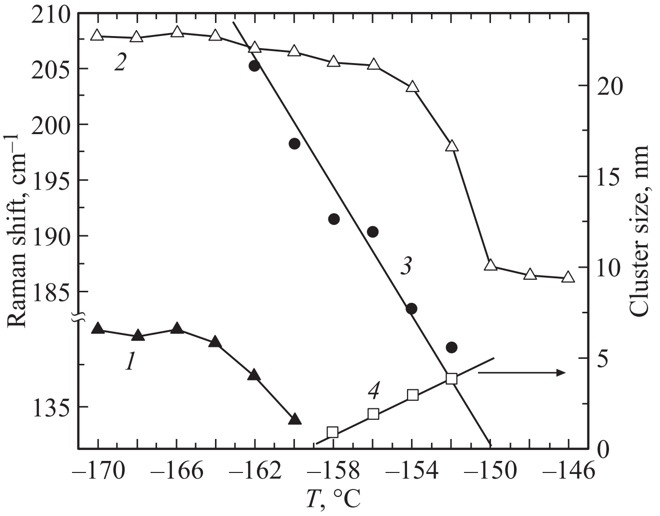

Figure 4. Temperature dependence: positions of spectral line peak *1* and *2* (left axis), calculation of the size of FE phase model cluster (*3*), calculation of the size of the gap between clusters (*4*) (right axis).

dispersion values in Table 2. Spectral lines *1* and *2* show a significant dependence of the peak position on temperature in the region of the phase transition temperature (Figure 4).

The frequencies of maxima of RS spectral lines on phonons B_1, observed in the $x(xz)y$ configuration in the experiment, exhibit no change as the phase transition temperature approaches (Figure 1). This is consistent with the absence of dispersion of these phonons in the vicinity of the point Γ of the Brillouin zone in all directions of the wave vector q. The calculation results presented in Ref. [2] show the dispersion of these phonons to be less than $0.5\,\mathrm{cm}^{-1}$.

The frequencies of the maxima of the RS spectral lines on phonons A_2, observed in $x(xy)y$ configuration in the experiment, show a significant change as they approach the phase transition temperature (Figure 4). The calculation results presented in Ref. [2] show a significant amount of dispersion of these phonons. These values differ in different directions of the Brillouin zone, the largest dispersion value in the direction of the point Z of the Brillouin zone is shown in Table 2.

Spectral lines undergo additional broadening in the RS spectrum in a cluster of limited size due to the size of the cluster L. The small cluster size creates uncertainty in the magnitude of the vector q of the order of $2\pi/L$. This uncertainty is transferred to the uncertainty in frequency through the variance dependence $\Omega(q)$ [9]. The peak frequency shift will be also observed in addition to the increase of the width of the spectral line if the dispersion of the optical phonon is significant. For example, the size of cluster it7 of lattice constants (of the order of 5 nm) leads to the uncertainty of the wave vector of the order of $\Delta q \approx 1.3\,\mathrm{nm}^{-1}$, which corresponds to the order of 0.15 of magnitude of the phonon wave vector at the boundary of the Brillouin zone. This uncertainty Δq gives a fraction of the dispersion of the order of $5\mathrm{cm}^{-1}$ with a total phonon dispersion of $32\,\mathrm{cm}^{-1}$, which can manifest itself in an increase of the width of the spectral line and a shift of the peak intensity.

It can be assumed that in the region of the phase transition temperature, two phases can coexist simultaneously, and the volume of the FE phase decreases when approaching the phase transition temperature (during heating) and concentrates in nanometer-sized clusters surrounded by the PE phase. The appearance of the spectra (Figure 1) and the temperature dependences of the relative intensity of the spectral line components (Figure 2) are consistent with this assumption. The qualitative estimates made are also consistent with the assumption of the simultaneous coexistence of the two phases. Thus, neither a shift of the peak frequency nor a significant increase of the width of the spectral line is observed in the RS spectrum on optical phonons, which have no dispersion in the vicinity of the point Γ. Spectral lines of RS on optical phonons with dispersion in the vicinity of the point Γ exhibit a shift of the peak frequency and an increase of the width in the region of the phase transition temperature.

The PL model is used to estimate the size of nanocrystals and clusters of various materials [13]. The RS spectrum of a cluster with size L and optical phonon dispersion $\Omega(q)$ is represented as [8,11,13]:

$$I(\omega) = \int\limits_0^1 \frac{\exp\left[-\frac{q^2L^2}{8}\right] q^2 dq}{\left(\omega - \Omega(q)\right)^2 + \left(\frac{\Gamma}{2}\right)^2} \qquad (1)$$

Integration is performed according to the model, spherical Brillouin zone. We use the calculated dispersion value in the direction of the point Z of the Brillouin zone of the optical phonon 2 (Table 2) and the experimental value $\Omega(0) = 208\,\mathrm{cm}^{-1}$ and $\Gamma = 27.6\,\mathrm{cm}^{-1}$ for temperature of -170°C. We obtain the dispersion curve in the form:

$$\Omega(q) = 192 + 16\cos(\pi q).$$

The model RS spectrum was calculated using the formula (1) for cluster sizes L in the range from 3 to 40 nm. The frequency of the peak intensity and its shift $\Delta\nu$ relative to $\Omega(0) = 208\,\mathrm{cm}^{-1}$ were determined for each spectrum. The dependence $\Delta\nu(L)$ was determined as a result of the calculation and it was compared with the observed frequency shifts in the experiment for the spectral line *2* (Figure 4). The results of cluster sizing are shown in Figure 4. (line *3*, right axis). The size of the FE phase cluster increases from zero to a size of about 20 nm in the temperature range of the order of 10°C from the temperature of the phase transition.

The analysis of the temperature dependence of the parameter$S$ (Figure 2) and modeling of the RS spectrum (*1*) determined that the volume of the FE phase decreases and it concentrates in clusters approaching the phase transition temperature. Individual clusters of the FE phase have a model size that linearly depends on temperature according to the law: $L = k_1(T - T_0)$; value $k_1 = 1.8\,\mathrm{nm}/^\circ\mathrm{C}$. Clusters of the FE phase are surrounded by the PE phase. A cluster with size L occupies volume L^3. Let us suppose that the clusters are evenly distributed over the sample volume, then there is a certain volume of PE phase between the clusters, which surrounds the cluster on all sides with a uniform layer with thickness x. Then the volume ratio of the two phases will be:

$$\frac{V_1}{V_2} = \frac{L^3}{3L^2x} = \frac{k_1(T - T_0)}{3x}.$$

Measuring the temperature dependence of the parameter S (Figure 2) for all *3* lines equally shows that in the region of approximately 10°C, the volume of the FE phase increases from 0 to complete filling of the sample almost linearly, with a coefficient $k_2 = 0.1^\circ\mathrm{C}^{-1}$, then the following equation can be written for this temperature range:

$$\frac{S}{S_{\max}} = \frac{V_1}{V_1 + V_2} = k_2(T - T_0).$$

Excluding the volume ratio from the system of equations, we obtain that the thickness of the PE phase between the model clusters is on the order of 5 nm at the moment of cluster nucleation and decreases linearly to zero at temperature when the clusters size increases and they fill the entire space. The calculation is shown in Figure 4 (line *4*).

4. Conclusion

The RS spectra of KH_2PO_4crystal were measured in 2 configurations in this paper and the changes of the RS spectra from temperature near the phase transition temperature were analyzed. The temperature dependences of the spectral line parameters are compared during the analysis with the ab initio calculation data [2] of dispersions of optical phonons on which Raman scattering occurs. The comparison took into account that the lattice (external) phonons are elementary excitations of a certain volume of the phase and the intensity of the RS spectral line is proportional to the volume of the phase. A decrease of the volume of the phase and its localization in a cluster of the nanometer range leads to the fact that the RS spectral lines undergo a certain broadening and a shift of the peak frequency. The quantitative relationship between the cluster size and the shift of the spectral line peak frequency is determined by the amount of optical phonon dispersion.

The completed analysis showed that the RS spectral lines on phonons with zero dispersion in the experiment exhibit neither an increase of the width of the spectral line nor a shift of the peak frequency. RS spectral lines on phonons with significant dispersion in the experiment show a significant increase of the width of the spectral line and a shift of the peak frequency.

It was assumed that there is a temperature range in the phase transition temperature range, where both phases coexist in the crystal. The low-temperature FE phase, when cooled below the phase transition temperature, appears in the form of clusters in the nanometer range and fills the entire space with the further cooling of the sample due to the increase of the size of the clusters. The estimates based on the PL model show that the size of the model cluster increases from zero to a value of the order of 20 nm in the range of the order of 10°C.

Conflict of interest

The authors declare that they have no conflict of interest.

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