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Analysis of the Raman spectra of an ammonium chloride crystal in the order-disorder phase transition region

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The Raman spectra on external vibrations of the crystal lattice in an ammonium chloride crystal in the temperature range close to the temperature of the order-disorder phase transition are measured. The temperature dependence of the parameters of the Raman spectral lines on TO- and LO-phonons is analyzed. It is shown that in the temperature range close to the temperature of the phase transition, the ordered and disordered phases coexist simultaneously. It is proposed that near the temperature of the phase transition, the ordered phase exists in the form of clusters of nanometer size. Using phonon confinement model, an estimate of the cluster size was made. In the region of phase transition temperature, the cluster size is units of nanometers, and the temperature dependence of the cluster size is close to linear. Measuring the degree of polarization Raman scattering of light made it possible to isolate the proportion of radiation of the ordered phase in the total intensity recorded in the experiment and correct the results of calculating the size of clusters.

Keywords: order-disorder phase transition, Raman scattering of light, ammonium chloride, phonon confinement model.

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1. Introduction

Crystals of ammonium chloride (NH_4Cl) undergo an order-disorder phase transition at a temperature of 242 K (T_0). An orientationally disordered phase is realized in a CsCl type crystal lattice at above T_0. The lattice disorder is attributable to the random distribution of tetrahedral (asymmetric) ammonium ions in the lattice nodes between two energetically equivalent orientations in space. One direction of the ammonium ion becomes more energetically favorable below the temperature of T_0 and all ammonium ions have an ordered orientation. The point symmetry group of the crystal lattice in the ordered phase does not contain an inversion transformation because of the asymmetry of the ammonium ion and decreases to T_d [1,2].

Raman scattering spectroscopy (RSS) is an effective method for studying the microscopic structure of substances. Measurement of the temperature dependences of the intensity, position and width of the RSS spectral lines allows studying the phonon-phonon and electron-phonon interactions in a crystal [3–5], identifying the presence of a phase transition and determining its most important parameters. The oscillation representation of the NH_4Cl lattice in the ordered phase has the following form [2]:

$$T_k = (F_1 + F_2) + (A_1 + E + F_2 + F_2).$$

The expression in the first bracket here describes the external oscillations of the crystal lattice. The symmetry type F_1 corresponds to the libration oscillation of the ammonium group inactive in the RSS spectrum $(NH_4)^+$, dipole-active type F_2 — translational oscillation of the ammonium group relative to chlorine atoms. F_2 is observed in the RSS spectra in the form of spectral lines of light scattering on transverse (TO) and longitudinal (LO) optical phonons. The expression in the second bracket describes the internal oscillations of the ammonium group. The oscillations of the types A_1 and E as well as F_2 are active in the RSS spectrum [2,6].

Measurement of the temperature dependence of the intensity of the RSS in samples of NH_4Cl [7,8] demonstrates that the intensity of the RSS decreases monotonously in the region of the phase transition when the crystal is heated. Measurements of the neutron scattering intensity also demonstrate that the number of ammonium ions with an ordered orientation decreases in the phase transition region, when the crystal is heated. Neutron scattering occurs in individual scattering acts on the nuclei of ammonium ion hydrogen atoms and allows determining the relative number of ammonium ions with an ordered orientation (order parameter) [9]. Unlike neutron scattering, the RSS scattering on external oscillations of the crystal lattice is a scattering on collective excitations of the volume of the ordered phase of the crystal. A decrease of the intensity of the RSS when approaching T_0 may suggest both a change of the oscillation properties of the ordered phase and a reduction of the volume of the ordered phase.

The relationship of the oscillation properties of the ordered phase of the NH_4Cl crystal with the order parameter was studied in [8,10,11]. A change of the dynamic properties of the crystal lattice, depending on the order parameter, results in a change of the oscillation frequency, the probability of phonon decay, and changes the magnitude of the derivative of the polarizability of the crystal along the normal coordinate, which explains the change of the RSS intensity.

On the other hand, there is an experimental confirmation of the co-existence of an ordered and disordered phase of NH_4Cl near the phase transition temperature [12]. Measurements of the electro-optical effect and numerical calculations in NH_4Cl [12–14] demonstrated that the phase transition to an ordered phase in case of cooling results in the formation of a domain structure. The reverse transition can occur independently in each domain, which results in the presence of a region of coexistence of two phases near T_0. Therefore, the order parameter demonstrate the relative number of oriented ions averaged over two phases near T_0 and does not indicate whether they are evenly distributed in the crystal volume or grouped into clusters.

If a decrease of the RSS intensity when approaching T_0 can be associated with a reduction of the volume of the ordered phase, then it is possible to assume that near T_0 the volume of the ordered phase exists in the form of separate clusters of the ordered phase in their disordered phase environment. The fact that the recorded RSS spectrum is similar to the RSS spectrum of the ordered phase suggests that clusters have a certain minimum volume in which the light scattering selection rules hold, and the spectrum of collective excitations (phonons) of the cluster is close to the spectrum of phonons in a large crystal.

RSS spectra in nanometer-sized clusters are known to differ from the RSS spectra in large crystals; a shift of the frequency of the maximum spectral line towards lower frequencies and an increase of its width is observed in the experiment. The phonon localization model in nanocrystals [15,16] establishes a relationship between the size of the nanocrystalline cluster and the frequency shift of the peak of the RSS spectral line. The phonon localization model and its improved variants for special cases [17,18] are currently broadly used for estimation of the size of nanocrystals in many materials [19]. In particular, this method was used for estimating the size of silicon nanocrystals in an amorphous silicon matrix at various annealing temperatures [18,20,21]. The annealing temperature in this case characterized a parameter that affects the spatial ordering of the atom in the lattice and the formation of a crystal cluster.

The temperature is also a parameter that affects the orientation ordering of the ammonium ion in the lattice and the formation of an ordered phase cluster in the case of the NH_4Cl crystal. Similarly to positional ordering, it is possible to assume the possibility of an orientation ordering mechanism in clusters. The number of clusters formed may increase with a decrease of the temperature and completely fill the entire volume, some average cluster size may increase or both processes may take place simultaneously.

The purpose of this paper is to study the properties of clusters of the ordered phase of NH_4Cl using the RSS method to estimate the size of clusters using a phonon localization model.

2. Experiment. Measurement procedure

The RSS spectra was measured using upgraded spectrometer DFS-52 with a PMT H6240-01. An Ar^+ ion laser LaserPhysics 150t with a wavelength of 488 nm and a power of 18 mW was used to excite the RSS.

The studied sample was an ammonium chloride crystal with a size of $5 \times 2 \times 5$ mm that was polished and oriented along the crystallographic directions $x \parallel [100]$, $y \parallel [010]$, $z \parallel [001]$ of the ordered phase. The laser beam was directed along the axis y, the scattered radiation was collected in the direction x. The lattice oscillation F_2 is permitted in such a configuration by the selection rules in the RSS spectrum. The TO and LO components of the spectrum were measured without a polarizer analyzer in the configuration $y(z, y+z)x$, the width of the entrance slit of the spectrometer was 0.4 mm. The width of the entrance slit of the spectrometer was 0.2 mm in case of measurement only of the current component. The scattered radiation was emitted through a polarizer analyzer for measuring the polarized components of the RSS intensity on phonons and was recorded in the configurations of $y(zy)x$ and $y(zz)x$, the width of the entrance slit of the spectrometer was 0.2 mm.

The recorded spectra were analyzed using the Origin 8 program for determining the parameters of spectral lines. Each spectral line was approximated using a Gaussian contour, the position of the peak ν_m and width Γ were determined for the contour. The spectral line intensity was defined as the area under the spectral contour.

The sample was put in a pumped cryostat cooled with liquid nitrogen. The temperature was measured and maintained using a system with regulator TRM -01 and a chromel-alumel thermocouple. The RSS spectra were measured in the temperature range from -70 to -20°C. The sample was cooled to a temperature of -70°C and then gradually heated, the heating step in the phase transition region is 1°C.

3. Measurement and calculation results

3.1. Spectral line intensity and Faust–Henry coefficient

Figure 1 shows the RSS spectra of the sample for three temperature values. The RSS intensity on LO-phonons is about 40 times lower than on TO-phonons, an enlarged fragment of the spectra is shown in the insert in the region 270 cm^{-1} (right scale). The spectra changed with the increase of the temperature and approaching the phase transition temperature, the intensity of the spectral lines decreased, the peak shifted towards low frequencies, and the line width increased. The measurement results are in

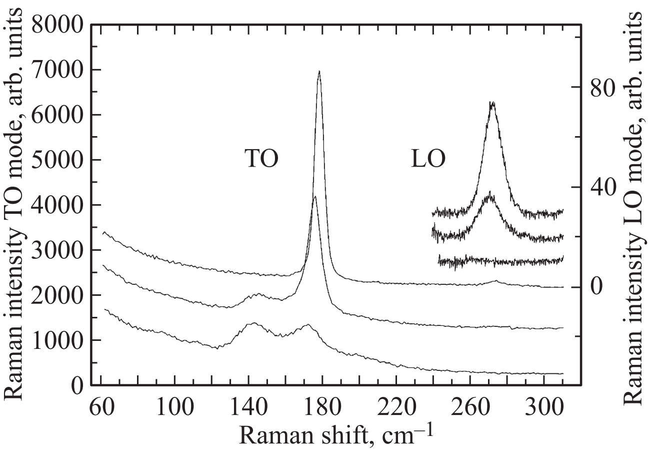

Figure 1. RSS spectra of the sample of NH_4Cl, configuration $y(z,z+y)x$, temperature −60, −34, −24°C (from top to bottom). An enlarged fragment of the spectrum in the LO-phonon region in shown in the inset (right scale).

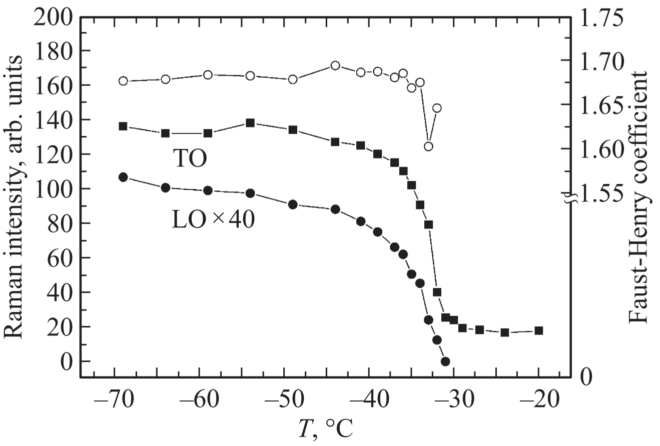

Figure 2. Temperature dependence of the RSS intensity on TO- and LO-phonons. Temperature dependence of the Faust–Henry coefficient (right axis).

good agreement with the literature data [7,8]. The RSS spectrum at $T \ll T_0$ (−60°C, upper curve) corresponds to an ordered phase. The RSS spectrum at $T \gg T_0$ (−24°C, lower curve) corresponds to a disordered phase. The appearance of the spectrum in the vicinity of the phase transition temperature (−34°C, middle curve) is consistent with the assumption of the simultaneous coexistence of two phases. The temperature dependence of the intensity of the RSS on TO- and LO-phonons is shown in Figure 2.

The RSS intensity for the stokes component measured in the experiment is equal to [6]:

$$I=\frac{\omega_s^4 V I_0}{(4\pi)^2 c^4}\,|\mathbf{e}_s\mathbf{R}\,\mathbf{e}_i|^2(n+1)\,\frac{\hbar}{2\Omega}, \tag{1}$$

where ω_s — the frequency of scattered light; I_0 — the intensity of exciting radiation; Ω — the optical phonon frequency; $n=1/\left(\exp(\frac{\hbar\Omega}{kT})-1\right)$; V — the phase volume; $\mathbf{e}_i$ and $\mathbf{e}_s$ — single polarization vectors of exciting and scattered light; $\mathbf{R}$ — the RSS tensor. The tensor $\mathbf{R}$ has a single independent component d for the F_2 oscillation of symmetry T_d, the value of which is determined by the derivative of the polarizability of the crystal along the normal coordinate [6]:

$$R(x)=\begin{pmatrix}0&0&0\\0&0&d\\0&d&0\end{pmatrix},\quad R(y)=\begin{pmatrix}0&0&d\\0&0&0\\d&0&0\end{pmatrix},$$

$$R(z)=\begin{pmatrix}0&d&0\\d&0&0\\0&0&0\end{pmatrix}.$$

Theoretical consideration of the RSS in a crystal without an inversion center (ordered phase of NH_4Cl) shows that the RSS intensity on the phonons of the crystal lattice is determined by both the deformation potential and the electrical and optical interaction. The ratio of the mechanical binding force (deformation potential) to the electrical binding force in the case of electron-phonon interaction in case of light scattering is expressed by the dimensionless Faust–Henry coefficient. The ratio of the components of the RSS tensor for LO- and TO-scattering has the following form given that the electro-optical effect affects light scattering only on LO-phonons [6]:

$$\frac{d_{\mathrm{LO}}}{d_{\mathrm{TO}}}=\left(1-\frac{\Omega_{\mathrm{LO}}^2-\Omega_{\mathrm{TO}}^2}{C\Omega_{\mathrm{TO}}^2}\right), \tag{2}$$

C —the Faust–Henry coefficient, Ω_{LO}, Ω_{TO} — the optical phonon frequencies. For the selected scattering pattern on 90° with certain directions of the polarization vectors $\mathbf{e}_i$ and $\mathbf{e}_s$, in the configuration $y(z,y+z)x$ from (1) and using the tensor $\mathbf{R}$ can be obtained for scattering on LO- and TO-phonons

$$\frac{I_{\mathrm{LO}}}{I_{\mathrm{TO}}}=\left(\frac{\omega_s^{\mathrm{LO}}}{\omega_s^{\mathrm{TO}}}\right)^4\left(\frac{d_{\mathrm{LO}}}{d_{\mathrm{TO}}}\right)^2\frac{(n_{\mathrm{LO}}+1)}{(n_{\mathrm{TO}}+1)}\,\frac{\Omega_{\mathrm{TO}}}{\Omega_{\mathrm{LO}}}. \tag{3}$$

A formula for calculating the Faust–Henry coefficient using the intensities I_{LO} and I_{TO} measured in the experiment is obtained by substituting (2) in (3) and explicitly expressing C. The results of calculation in the studied temperature range are shown in Figure 2, right scale.

The obtained dependence $C(T)$ demonstrates that in the region of the phase transition, when both phases coexist in the sample volume and the ordered phase is concentrated in clusters the value C remains the same as in the case when the entire sample volume contains only one ordered phase. Only two points closest to the temperature T_0 ($T=-32$ and -33°C) demonstrated a significant difference.

On the assumption that the ordered phase is concentrated in clusters in the region of the phase transition based on the constancy of the coefficient C, it is possible to make a conclusion that these clusters retain the oscillational properties of a large crystal, and the perfection of the crystal lattice in clusters of the ordered phase remains the same as in a crystal of the ordered phase at temperature away from the phase transition temperature. An interspersed orientationally disordered ammonium ion (or group of ions) will act as a defect(s) for lattice oscillations for the ordered phase of NH_4Cl. If the lattice imperfection does not increase, and the RSS intensity of the ordered phase decreases, then this is reason to assume that the reduction of the volume of the ordered phase makes the main contribution to reduction of the RSS intensity (in case of heating). (factor $(n+1)$ in the studied temperature range varies by less than 2%).

Strictly speaking, the found constancy of the Faust–Henry coefficient indicates only that the ratio of mechanical and electronic contributions to the electron-phonon interaction remains constant, but not the values of the parameters of this interaction themselves. Nevertheless, the experience shows that the value of the Faust–Henry coefficient changes when the imperfection of the crystal lattice changes. The impact of the electro-optical effect on the ratio of LO- and TO-scattering intensities in the equation (2) is determined without taking into account the anharmonic interaction, and the theoretical quantum mechanical calculation of the value of C often turns out to be significantly different from the experimentally measured values [6]. In practice, the measurement of the Faust–Henry coefficient can be used for evaluation of the perfection of the crystal structure. In particular, such a relation is discussed for GaAs crystals [22]. The impact of phonon attenuation on the value of the Faust–Henry coefficient in GaP crystals was experimentally studied in Ref. [3]. The experiment in Ref. [23], demonstrates the relationship between the defect of the InP crystal and the magnitude of TO- and LO-splitting in the spectrum, the intensity ratio $I_{\mathrm{LO}}/I_{\mathrm{TO}}$ and the value of the Faust–Henry coefficient. The defects in the InP crystal were created by implantation with high energy heavy ions.

3.2. Frequency shift of the spectral line and estimation of cluster size

Figure 3 shows the dependence of the frequency of the maximum LO and TO spectral lines on temperature. The temperature dependence away from the phase transition correlates with the thermal expansion of the crystal and may be approximated by a linear function. The frequency of the spectral line near the phase transition monotonously deviates from the linear function, when the phase transition temperature is reached, the frequency changes again according to a law close to a linear one.

Suppose that the decreasing volume of the ordered phase concentrates in separate clusters as it approaches the temperature T_0. Then an additional significant decrease of the frequency of the spectral line peak may be associated with a decrease of the cluster size when approaching the temperature T_0. The RSS spectrum of a cluster of size L and the dispersion of optical phonons $\Omega(q)$ is represented as follows according to the phonon localization model [18]:

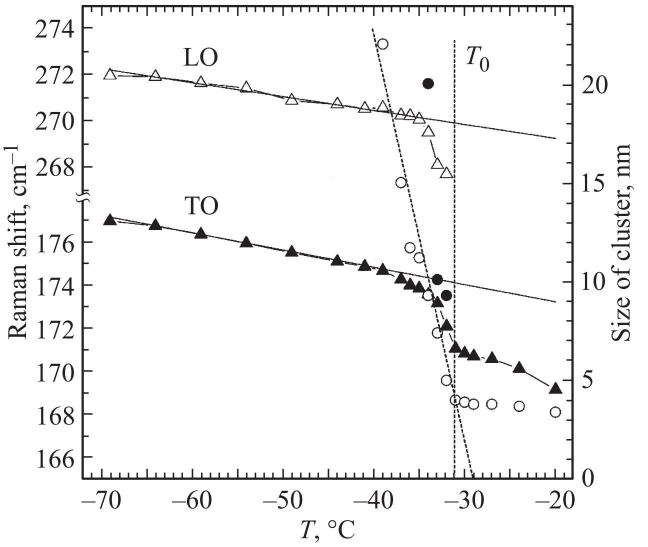

Figure 3. Dependences of the peak frequency of the LO and TO spectral lines on temperature. A linear approximation of the temperature dependence is shown by a solid line. Calculation of the cluster size of the ordered phase based on the data of TO (hollow circles) and LO (solid circles) RSS (right axis). The vertical dotted line shows the phase transition temperature T_0. Oblique dotted line shows a linear approximation of the temperature dependence of the cluster size (right axis).

$$I(\nu) = \int_0^1 \frac{\exp[-\frac{q^2L^2}{8}]q^2dq}{(\nu - \Omega(q))^2 + (\frac{\Gamma}{2})^2}. \qquad (4)$$

Integration is performed according to the model, spherical Brillouin zone. The spectrum of phonons in ammonium chloride was studied by experiment and calculations [24]. It was found that the value of the dispersion of the TO-phonon from the point Γ to the point X is 38.6 cm^{-1} in the crystallographic direction [100] and there is no TO-phonon dispersion in the direction [111] to the point R. It is necessary to take into account for averaging that a cubic crystal has 6 directions of type [100] and 8 of type [111]. The resulting dependency for $T = -50$°C can be represented as

$$\Omega(q) = \frac{8}{14}176.4 + \frac{6}{14}\big(157.1 + 19.3\cos(\pi q)\big). \qquad (5)$$

The model RSS spectrum was calculated using the formula (4) 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 the frequency in a large crystal were determined for each spectrum. The dependence $\Delta\nu(L)$ was determined as a result of the calculation. The value of the lattice constant $a = 0.39$ nm was used in the calculations [25].

The frequency shift of the peak of the TO-phonon $\Delta\nu$ was determined in experiment as the difference between the linear function and the frequency of the peak of the RSS line (Figure 3). The sizes of the ordered phase model cluster L were calculated based on the dependence $\Delta\nu(L)$ for each value $\Delta\nu$. The calculation results are presented in Figure 3. The resulting dependence $L(T)$ is close to linear dependence at $T < T_0$. The cluster size exceeds 100 lattice constants at temperatures below −40°C, the RSS spectrum of clusters of this size is indistinguishable from the RSS spectrum of a large crystal.

The calculation of the cluster size based on the frequency shift of the peak of the LO-phonon spectral line is also shown in Figure 3. The frequency of the peak of the LO-phonon spectral line deviates less from the linear approximation (only 3 points deviated). The value of the dispersion of the LO-phonon from the point Γ to the point X is $36.8\,\mathrm{cm}^{-1}$ in the crystallographic direction [100] according to the data of [24], and it is equal to $84.2\,\mathrm{cm}^{-1}$ in the direction [111] to the point R. Similarly, the cluster size is estimated by creating (5) averaged dependence $\Omega(q)$ for LO-phonons and calculating the integral (4) for this dependence. The obtained values differ from the calculations based on the data of the spectral line of the TO-scattering. The main error seems to be related to the complexity of determination of the approximation line for calculating the frequency shift of the peak of $\Delta\nu$ LO-phonon.

3.3. Spectral line width. Anharmonicity and phonon localization

Figure 4 shows the results of measurement of the width of the RSS spectral lines in the studied temperature range. An increase of the width of the RSS spectral line with an increase of temperature may be associated with an increase of the anharmonicity of oscillations of the crystal lattice.

Theoretical studies [26] demonstrate that an increase of the width of the spectral line of light scattering on an optical phonon with a frequency of Ω due to anharmonicity can be described by an increase of the probability of its decay by 2 phonons with frequencies of Ω/2 according to the formula

$$\Gamma(T) = A(1 + 2n_2), \tag{6}$$

where A — the coefficient,

$$n_2 = 1/\left(\exp\left(\frac{\hbar\Omega}{2kT}\right) - 1\right).$$

The calculation using the formula (6) is shown in Figure 4 in the form of solid lines. The values $\Omega_{\mathrm{TO}} = 176\,\mathrm{cm}^{-1}$; $\Omega_{\mathrm{LO}} = 271\,\mathrm{cm}^{-1}$ were used in the calculations, coefficients A were selected by fitting $A_{\mathrm{TO}} = 2.77\,\mathrm{cm}^{-1}$; $A_{\mathrm{LO}} = 5.2\,\mathrm{cm}^{-1}$. The slope of the calculated dependence is in good agreement with the slope of the dependence obtained in the experiment, which indicates the acceptability of the proposed mechanism for describing anharmonicity in the ordered phase of the crystal. There is a significant deviation from the calculated dependence near the phase transition.

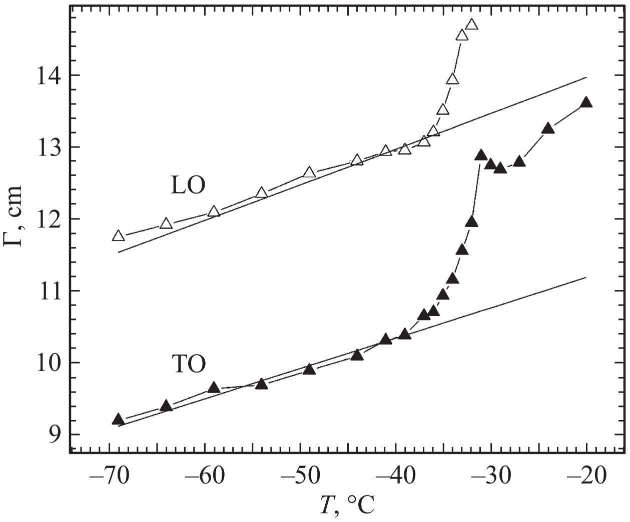

Figure 4. Dependences of the width of the RSS spectral lines on LO- and TO-phonons. The solid line shows the calculation according to the formula (6).

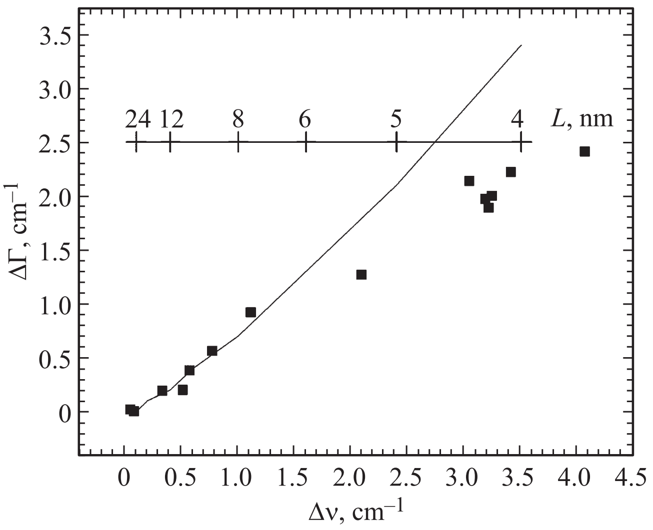

Figure 5. The relationship between the peak frequency shift and the increase of the width of the RSS spectral line on TO-phonon. The calculated dependence of the increase of the width of the model spectrum (4) on the magnitude of the peak frequency shift for clusters of sizes 4–24 nm (solid line).

We determine the value of the deviation ΔΓ of the experimental value from the calculated value for the RSS on the TO-phonon and compare it with the value of the peak frequency shift $\Delta\nu$, for each temperature. The result is shown in Figure 5. The data show that the values are in direct proportion. This relationship can be explained and described by the phonon localization model. A solid line in Figure 5 shows the calculated dependence of the increase of the width ΔΓ of the model spectrum (4) on the magnitude of the peak frequency shift $\Delta\nu$ for clusters of sizes 4–24 nm.

The calculated dependence is in good agreement with the experiment in the range of frequency shifts up to 1.2 cm^{-1} (cluster sizes from 24 to 7 nm). The experimental points for large shifts are less consistent with the calculation. Clusters of less than 5 nm in size correspond to these points. These points correspond to a temperature range equal to and above the phase transition temperature according to Figure 3. For comparison, the experimental values of the peak shift and the increase of the spectral line width in silicon are in good agreement for nanocrystals of size 2–8 nm [27] and 2–15 nm [28].

3.4. The degree of polarization of the RSS and the RSS intensity of the ordered phase near the phase transition temperature

Let's consider scattering by 90° in the configurations $y(zy)x$ and $y(zz)x$, which differ in the rotation of the polarizer-analyzer in case of scattered radiation recording. The selection rules for the scattering configurations selected in the experiment can be determined by the calculation of the convolution of the tensor $\mathbf{R}$ and the unit polarization vectors $\mathbf{e}_i$ and $\mathbf{e}_s$ of the selected configuration (1). The calculation demonstrates that the configuration $y(zy)x$ for TO- and LO-oscillation is permitted, and $y(zz)x$ is prohibited.

Figure 6 shows the RSS spectra of the sample in the TO-scattering region at $T = -40$ and -20°C in two configurations. The spectrum shows a non-zero intensity value in the prohibited configuration. Such a violation of the selection rules in NH_4Cl was previously described in Ref. [29] and, apparently, it is associated with the strongly pronounced nonlinear properties of the crystal [2], its domain structure and the error of crystal orientation in crystallographic directions.

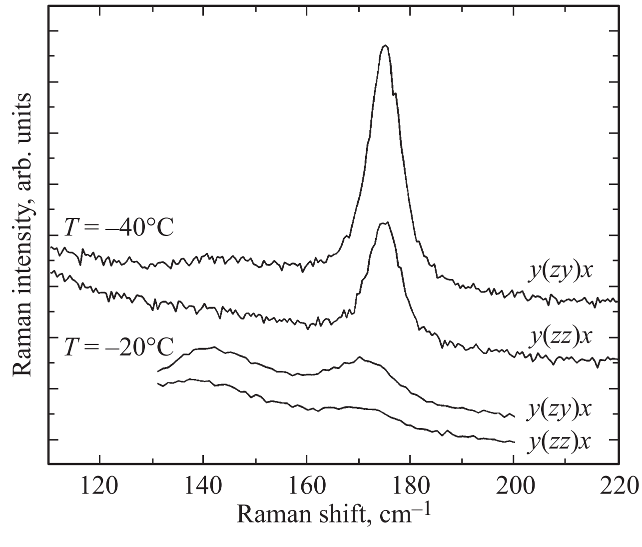

Figure 6. The RSS spectrum in the TO-scattering region for configurations $y(zy)x$ and $y(zz)x$ at $T = -40$ and -20°C.

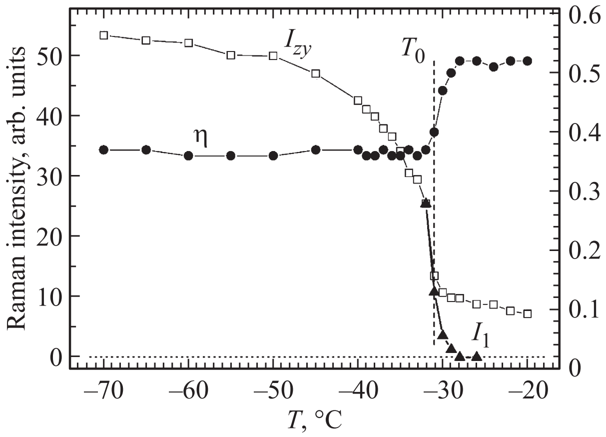

Figure 7. Temperature dependence of the degree of polarization of the RSS (right axis). Temperature dependence of the intensity of the component I_{zy} (left axis). The vertical dashed line shows the phase transition temperature T_0. The calculated dependence of the intensity of the RS of the ordered phase I_1 (equation (10)).

The spectra for the two temperatures presented are significantly different in intensity, and the degree of polarization of the RSS radiation is significantly different. Let's calculate the degree of polarization using the formula

$$\eta = \frac{I_{zy} - I_{zz}}{I_{zy} + I_{zz}}.$$

at $T = -20$°C. The value of $\eta = 0.52$, at $T = -40$°C the value $\eta = 0.37$.

RSS spectra were measured in this experiment in 2 configurations in the range from -70 to -20°C and the temperature dependence $\eta(T)$ was calculated. The dependence graph is shown in Figure 7 (right axis). The temperature dependence of the intensity of the permitted component I_{zy} is shown on the graph for comparison (left axis). It follows from the measurements that the degree of polarization of the recorded radiation of the ordered phase ($T < T_0$) and the disordered phase ($T > T_0$) are markedly different and constant. A monotonous change is observed in the region of the phase transition $\eta(T)$. The intensity of the RSS phases significantly differs (by about 8 times), so the presence of a disordered phase in the region ($T < T_0$) does not affect the value in this region. Even the minor presence of an ordered phase in the region ($T > T_0$) results in a difference in magnitude from the value characteristic of the disordered phase. This is observed in a narrow temperature range of about 4°C near T_0.

Let's represent the intensity of the total radiation and the polarization of the total radiation of the two phases in the form

$$I = I_1 + I_2; \quad \eta = \eta_1 \frac{I_1}{I} + \eta_2 \frac{I_2}{I},$$

where the symbols 1 and 2 refer to the ordered and disordered phases. We obtain by solving the system of equations with respect to the intensity of the ordered phase that

$$I_1 = I\,\frac{\eta_2 - \eta}{\eta_2 - \eta_1}. \tag{10}$$

The calculation of the value I_1 is shown in Figure 7. The value η remains constant in the temperature range below T_0 and is equal to η_1, the dependence $I_1(T)$ coincides with $I(T)$, the value of I_1 sharply decreases to zero in the temperature range above T_0.

4. Analysis of measurement and calculation results

The RSS of the first order is prohibited by the selection rules in a CsCl type lattice (disordered phase). The RSS is permitted for LO and TO phonons in the ordered phase, cubic lattice with symmetry T_d, at the point Γ of the Brillouin zone. The group-theoretic analysis [30] demonstrates that the observed RSS at temperatures above T_0 in the frequency range $176\,\mathrm{cm}^{-1}$ occurs on phonons at points R and M of the Brillouin zone (local maxima of the density of states). Conservation laws prohibit the manifestation of first-order scattering on phonons in the RSS spectra in regular lattices at other points in the Brillouin zone except the point Γ. The disruption of the regularity of the lattice because of the orientation disorder of the ammonium ion at T greater than T_0 results in the observation of this scattering in the spectrum [1]. We observe two different degrees of polarization of the RSS in two phases with regard to the results of polarization measurement because these are two different oscillations with similar frequencies.

Cluster size calculations using the formula (4) are based on a change of the phonon frequency in the vicinity of the point Γ of the lattice with symmetry T_d and are related only to the ordered phase. Figure 7 shows that the adjusted intensity of the RSS I_1 of the ordered phase above T_0 sharply decreases and disappears. The calculation of the cluster size (Figure 3) demonstrates that the cluster size stops to decrease and remains equal to 4 nm when the sample is heated and the temperature T_0 is reached. The obtained calculation needs to be adjusted, since the calculation of the cluster size for temperatures above the temperature $-28^\circ\mathrm{C}$ is not justified, because there is no ordered phase.

The RSS intensity on the phonons of the disordered phase at a temperature of T_0 and above up to -28° is comparable and higher than the RSS intensity on the phonons of the ordered phase because of the small volume of the ordered phase in this temperature range. In this situation, the frequency of the phonon of the ordered phase cannot be determined, which means that it is impossible to calculate the cluster size. It is possible to assume based on the linear dependence of the cluster size on temperature that the cluster size continues to decrease with the increase of the temperature. If the linear dependence of the cluster size is extended (oblique dotted line in Figure 3), then the line will cross the zero value at a temperature of $-29^\circ\mathrm{C}$, i. e. at a minimum temperature when the ordered phase still exists (Figure 7).

Points that deviate from the calculated line in Figure 5 for $\Delta\nu > 3\,\mathrm{cm}^{-1}$, were measured for temperatures T_0 and higher, when a significant part of the radiation in the measured spectrum is radiation from scattering on phonons at points M and R of the Brillouin zone, and these measurements should be excluded from consideration. The coincidence of the experiment and calculations is complete for points with $\Delta\nu < 2\,\mathrm{cm}^{-1}$, which indicates a good agreement of the model spectrum (4) with experimental data and on the adequacy of the application of the phonon localization model for estimation of the size of clusters.

The impact of the RSS on phonons at the points M and R of the Brillouin zone of the disordered phase near the temperature T_0 may have distorted the intensity of TO-scattering (overestimated values) for calculating the Faust–Henry coefficient (strong downward deviation of two points in Figure 2) According to (2) overestimated TO-scattering values result in a reduction of the Faust–Henry coefficient. Therefore, these data are not justified for calculations, the remaining calculation results indicate the permanent imperfection of the crystal lattice of clusters.

It is characteristic that when the crystal is heated from -70 to $-40^\circ\mathrm{C}$ the intensity of the TO and LO modes has already markedly decreased (about 20%), and the change of the phonon frequency remains within the linear approximation of thermal expansion (Figure 3). Similarly to the phonon frequencies, the change of the widths of the phonon spectral lines also remains within the linear approximation up to $-40^\circ\mathrm{C}$. The linear approximation in this case confirms that the decrease of the RSS intensity is not associated with additional changes of the oscillational properties of the ordered phase. This agrees well with the assumption that the reduction of the volume of the ordered phase has the main contribution to the reduction of the RSS intensity. Calculations using the phonon localization model for the TO-mode (Figure 3) demonstrate that the cluster size of the ordered phase at $T = -40^\circ\mathrm{C}$ is 22 nm. Supposing that the clusters are isolated from other clusters with a minimum thickness of the disordered phase equal to 3 lattice constants (1.2nm), then the volume of the ordered phase will be 85% of the crystal volume, i.e. it corresponds to a decrease of the RSS intensity due to reduction of the phase volume by about 15%. The change of the TO-mode intensity of the ordered phase I_1 in Figure 7 (in this temperature range I_1 coincides with I_{zy}) is 18% and is in good agreement with the estimations.

5. Conclusion

The analysis of the RSS spectra in the region of the order-disorder phase transition in ammonium chloride demonstrated that there is a certain temperature range when both phases coexist in the crystal. An assumption was made that the volume of the ordered phase in this temperature range exists in the form of separate clusters of the ordered phase in the disordered phase environment surrounding them.

The cluster size was calculated using the well-known phonon localization model in limited clusters. The cluster size equals to the units of nanometers, and the temperature dependence of the cluster size is close to linear for temperatures in the phase transition region.

It was concluded based on the analysis of the temperature dependence of the Faust–Henry coefficient in the phase transition region that the crystal lattice of clusters does not show an increase of imperfection compared with a large crystal.

The measurement of the degree of polarization of the RSS made it possible to correct the temperature dependence of the RSS intensity of the ordered phase near the phase transition temperature and to correct the results of calculation of the cluster size.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] T. Geisel, J. Keller. Phys. Chem. Solids **39**, 1 (1978).
[2] V.S. Gorelik. V sb.: Sovremennye problemy spektroskopii kombinacionnogo rasseyaniya sveta. Nauka. M. (1978). 298 p. (in Russian).
[3] B.H. Bayramov, Y.E. Kitaev, V.K. Negoduiko, Z.M. Khashozhev. FTT **16**, 2036 (1974). (in Russian).
[4] B.H. Bairamov, V.K. Negoduyko, Z.M. Khashkhozev. Light Scattering Study of Anharmonicity of Lattice Vibrations in GaP. The Physics of Semiconductors. 12th. Int. Conf. on Physics of Semiconductors / Ed. M.H. Pilkhun. Teubner GD, Stuttgart (1974). P. 445–452.
[5] G. Irmer, V.V. Toporov, B.H. Bairamov, J. Monecke. Phys. Status Solidi B **119**, 595 (1983).
[6] Rasseyanie sveta v tverdykh telakh / Ed. by M. Kardon, G. Gunterodt. Vyp. 2. Mir, M. (1984). 328 s. (in Russian).
[7] C.H. Wang, R.B. Wright. J. Chem. Phys. **58**, 1411 (1973).
[8] H. Yurtseven, T.U. Tuzer. Spectrochim. Acta A **71**, 862 (2008).
[9] J. Topler, D.R. Richter, T. Springer. J. Chem. Phys. **69**, 3170 (1978).
[10] H. Yurtseven, W.F. Sherman. J. Mol. Struct. **80**, 217 (1982).
[11] H. Yurtseven, M.H. Tumkaya. Spectrochim. Acta A **62**, 926 (2005).
[12] J.P. Pique, G. Dolino, M. Vallade. J. Phys. France **39**, 1003 (1978).
[13] J.P. Pique, G. Dolino et M. Vallade. J. Phys. France **38**, 1527 (1977).
[14] B. Winkler, M. Chall, C. Pickard, V. Milman. J. Phys.: Condens. Matter **12**, 2093 (2000).
[15] H. Richter, Z.P. Wang, L. Ley. Solid State Commun. **39**, 626 (1981).
[16] I.H. Campbell, P.M. Fauchet. Solid State Commun. **58**, 739 (1986).
[17] G. Faraci, S. Gibelisco, P. Russo, A.R. Pennisi, S. La Rosa. Phys. Rev. B **73**, 033307 (2006).
[18] V.A. Volodin, V.A. Sachkov. ZhETF **143**, 100 (2013). (in Russian).
[19] A.K. Arora, M. Rajalakshmi, T.R. Ravindran, V. Sivasubramanian. J. Raman Spectrosc. **38**, 604 (2007).
[20] D.V. Shuleiko, F.V. Kashaev, F.V. Potemkin, S.V. Zabotnov, A.V. Zoteev, D.E. Presnov, I.N. Parkhomenko, I.A. Romanov. Optika i spektroskopiya **124**, 770 (2018). (in Russian).
[21] A.V. Igo. Optika i spektroskopiya **128**, 1115 (2020). (in Russian).
[22] J. Biellmann, B. Prevot, C. Schwab. J. Phys. C **16**, 1135 (1983).
[23] P. Hu, J. Zeng, S. Zhang, P. Zhai, L. Xu, W. Ai, K. Maaz, H. Xue, Z. Li, Y. Sun, J. Liu, Y. He. J. Raman Spectrosc. **52**, 971 (2021).
[24] C.H. Kim, H.A. Rafizadeh, S. Yip. J. Chem. Phys. **57**, 2291 (1972).
[25] V. Anselmo, N. Smith. J. Phys. Chem. **63**, 1344 (1959).
[26] M. Balkanski, R. Fallis, E. Haro. Phys. Rev. B **28**, 1928 (1983).
[27] I.I. Reshina, E.G. Guk. FTP, **27**, 728 (1993). (in Russian).
[28] P. Mishra, K.P. Jain. Phys. Rev. B **62**, 14792 (2000).
[29] L.R. Fredrickson, J.C. Decius. J. Chem. Phys. **66**, 2297 (1977).
[30] M. Couzi, J.B. Sokoloff, C.H. Perry. J. Chem. Phys. **58**, 2965 (1973).

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