Role of Low-Frequency Modes in the Formation of Dielectric Function of β-Alanine Molecular Crystal

[1]Dovbeshko G., [2]Gridyakina A., [3]Romanyuk V.

[1]Institute of Physics of National Academy of Sciences of Ukraine, 46 Prospect Nauki, Kyiv 03039, Ukraine, galyna@ukma.kiev.ua
[2]Kiev-Mohyla Academy, 6 Skovoroda str., Kyiv 02070, Ukraine, supert@i.com.ua
[3]Institute for Physics of Semiconductors of National Academy of Sciences of Ukraine, 41 Prospect Nauki, Kyiv 03028, Ukraine, romanyuk@cir.tohoku.ac.jp

Received 11.12.2002

Abstract.

Dielectric permeability ε_0 of β-alanine (β-Ala) single crystals is studied with the IR spectroscopy technique and the appropriate calculations. We have calculated the dielectric permeability from the reflectance spectra, using the dispersive analysis and the harmonic multi-oscillator model. The calculations of ε_0 from the reflectance spectra of (010) β-Ala crystal plane in the 400-4000 cm^{-1} region have earlier shown that it is impossible to achieve the ε_0 values experimentally measured in the microwave region (ε_0^c=5.3, ε_0^a=4.0). The calculated data differ two times from those experimentally measured for one of the directions. The polarized IR reflectance spectra of β-Ala single crystal and the transmittance spectra of the corresponding powder are detected in the 100-5300 cm^{-1} region. The account for the low-frequency modes (400, 321, 218, 180 cm^{-1}) finally gives a possibility to obtain a good agreement between the calculated and experimental results. The large contribution to ε_0, which is mainly due to the oscillator at 218 cm^{-1}, is essential only for one of the alternative polarizations (E || the small axis of the (010) crystal plane). It seems to be associated with the H-bonded inter-molecular vibrations.

Key words: Dielectric function, model of non-interacting oscillators, β-alanine.

PACS: 81.10.Dn, 87.64.Rr,42.70.Jk

Introduction

Studies of the dielectric function of molecular crystals, such as amino acids, are of a great interest for both the fundamental and applied fields. Amino acids entering the bio-molecules have been under extensive studies during last 50 years. However, the most important data have been got for a gas phase or solution. It is known that amino acids manifest a neutral form in the gas phase and zwitter-ionic form in the solution or the solid state. Despite of that the amino-acid single crystals are good modeling systems, they have been given much less attention than the corresponding solutions. β-Ala single crystal is yet not included in the list of 20 conventional amino acids, which compose the proteins of a living substance. That is why the fundamental studies of the β-Ala amino acid have been rather poor. Nevertheless, β-Ala participates in a cell metabolism and enters the composition of coenzyme A. It is also worthwhile that the drugs based on β-Ala are produced for regulating the cell metabolism.

A little is still known about the optical (in particular, vibrational) and dielectric properties of β-Ala [1-5], the natural isomer of L-Ala. We have earlier studied the vibration and electronic spectra of β-Ala [6-8], calculated the potential of proton in the bifurcated H-bond of β-Ala single crystal fragment [9], and measured the

low-frequency anisotropic dielectric permeability [10]. The value of the latter has been measured at the microwave frequencies. It is equal to 5.3±0.1 and 4.0± 0.1 for the two crystallographic orientations. However, the calculations on the basis of reflectance spectra (400-4000 cm^{-1}) have shown that it is impossible to obtain the ε_0 values measured experimentally in the microwave region (ε_0=5.3, ε_0=4.0). The calculated data differ two times from the experimental ones, though the majority of experimentally detected vibrational modes are located within the spectral region under study. Therefore, in the present study we measure the polarized reflectance spectra of β-Ala single crystal and the transmittance spectra of the powder, analyze the contribution of all the vibrational modes to ε_0 in the 100-5300 cm^{-1} region and calculate the anisotropic dielectric permeability in a wider spectral range than that studied earlier [10].

Model for the calculations of dielectric permeability

Molecule of β-Ala is extended along the C-C-N skeleton, with COO^- and NH_3^+ terminal groups, and consists of 13 atoms. The β-Ala does not have any elements of symmetry, except for the identical one [11]. It crystallizes in the space group P_{bca} (D^{15}_{2h}), with 8 molecules in the unit cell. The group involves 8 symmetry elements, including an inversion center, so symmetry types distribute the total set of optical modes in the following way:

$$G = 39A_g + 39B_{1g} + 39B_{2g} + 39B_{3g} + 39A_u + \\ + 38B_{1u} + 38B_{2u} + 38B_{3u}$$

This means that different modes could be active in the Raman and IR spectra. The total number of optical vibration modes for β-Ala equals to 3nZ-3 = 3×8×13-3 = 309, where *n* denotes the number of crystal cell, Z the number of atoms in the molecule, and 3 the number of degrees of freedom for every atom. Due to the fact that the crystal cell consists of 8 molecules, a great number of vibrational modes, including the 8-folded inter-molecular and intra-molecular vibrations with close frequency positions, should be observed in both the Raman and the IR spectra of transmittance, absorption or reflectance [6]. According to the selection rule, the total number of optical vibrations that could be registered in the IR and Raman spectra is equal to 309-39=270 (39 vibrations of A_u symmetry, the so-called silence modes, are inactive in the IR spectra) [12]. From the whole set of optical vibrations, 231 ones are related to intra-molecular and 39 ($6A_g$, $6B_{1g}$, $6B_{2g}$ and $6B_{3g}$) to the crystal (or lattice) vibrations. 24 of the lattice vibrations are active in the Raman and 15 in the IR spectra ($5B_{1u}$, $5B_{2u}$ and $5B_{3u}$).

The problem of modeling the spectrum of multi-atom molecules involves some difficulties (the absence of the data about bond constants, the necessity of accounting for overlapping of electron states, etc.) [13]. Therefore, usually one cannot exactly fit the experimental and the calculated spectra. At the same time, the problem is difficult enough. The approach presented in this work does not demand the mentioned data and allows solving the problem of extraction the optical characteristics of crystal and the parameters of specific oscillators from the vibrational spectra in a simple way. Having known the precise numerical parameters of oscillators, we can estimate quantitatively the changes in the vibration parameters due to the external influences on the β-Ala crystal. For example, while exposing the crystal to microwave radiation, we can see the evident changes in the mode intensities occurring in some regions of spectrum [14].

We use the Kramers-Kronig technique or the classic dispersion analysis (CDA) (with the appropriate model for the dielectric function) for obtaining the dielectric permeability spectrum. The main requirement of the technique is the measured data for the reflectance spectrum concerning all the range, especially its low-frequency region. Besides, using of this

technique requires a large crystal thickness. In this respect, the CDA method does not have the limitations associated with the thickness or availability of several layers.

For description (parameterization) of the permittivity function of crystals, possessing dipole-active vibrations, some phenomenological models are employed. The model of non-interacting harmonic oscillators [15] (the additive model) for parameterization of dielectric function uses the value of high-frequency dielectric permeability ε_∞ and three parameters characterizing each IR-active vibration: ω_{Tj}, S_j, Γ_j, i.e., the vibration frequencies, the strength and the damping of j-th oscillator, respectively:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{\omega_{Tj}^2 S_j}{\omega_{Tj}^2 - \omega^2 - i\omega\Gamma_j} \qquad (1)$$

The four-parameter half-quantum (or factorized) model [16-18] for consideration of part of each oscillator uses the values of frequencies, their transversal and longitudinal optical vibrations ω_{Tj}, ω_{Lj}, and the corresponding dampings Γ_{Tj} and Γ_{Lj}. It takes into consideration that the lifetimes of transversal and longitudinal optical phonons can be different:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{Lj}^2 - \omega^2 - i\omega\Gamma_{Lj}}{\omega_{Tj}^2 - \omega^2 - i\omega\Gamma_{Tj}} \qquad (2)$$

This model is equivalent to the model of harmonic oscillators at $\Gamma_{Tj} = \Gamma_{Lj}$, and the relation between ω_{Tj} and ω_{Lj} can be described by the Lyddene-Sacks-Teller equation. The use of this model is expedient when the values of TO-LO splitting are larger than the Γ_{Tj}, Γ_{Lj} values, and the frequencies ω_{Tj} and ω_{Lj} can be determined experimentally (e.g., using the Raman or IR absorption/transmission spectra), that being not the case for molecular crystals.

In some cases a model can be used for describing the permittivity function of partially disordered crystals, which considers a static allocation (degradation) of some parameters of the oscillator ensemble (see, e.g., [19, 20]).

It is known [21] that the intra-molecular interactions (caused mainly by covalent bonds) in molecular crystals are much stronger than the inter-molecular interactions related to Van der Waals forces. At the same time, their separate groups and molecules are connected by a great number of hydrogen bonds, which include more than 60% of all bonds [22]. Hydrogen interactions can exceed Van der Waals forces in crystal. Hydrogen bonds are partially ionic, though their energy is less than the covalent bond energy by an order of magnitude. The vibration frequencies of the lattice are therefore much lower than the frequencies of intra-molecular vibrations. Besides, it is known from the literature (see, e.g., [18] for meta–nitro-aniline crystal) that the value of TO-LO splitting in the molecular crystals is 0.1-3 cm^{-1} for the most of vibrations, while the damping parameter is equal to 5-15 cm^{-1}. Considering optical anisotropy of the crystal, we have therefore used for description of dielectric function in β-Ala the model of non-interacting (harmonic) oscillators in the form

$$\varepsilon^\alpha(\omega) = \varepsilon_\infty^\alpha + \sum_j \frac{\omega_{Tj}^{\alpha 2} S_j^\alpha}{\omega_{Tj}^{\alpha 2} - \omega^2 - i\omega\Gamma_j^\alpha} \qquad (3)$$

where the indices α = *a, b, c* determine the vibration directions of electric field vector of the incident electromagnetic wave with respect to the crystallographic axes of anisotropic crystal, $\varepsilon_\infty^\alpha$ is the high-frequency permittivity for the corresponding directions in crystal, ω_{Tj}^α, S_j^α, Γ_j^α the frequency, force and damping parameter of the *j*-th oscillator, which is active in this polarization.

Earlier (see [7]) we have made an assignment of the vibrations observed in the Raman spectra of single crystals and the IR transmittance spectra of β-Ala powder in KBr pellet, basing on the group theory analysis and the correlation diagrams. Certain difficulties have appeared in the process of such

assignment. First, a number of modes in the absorption spectra (especially those in the 2000-5300 cm^{-1} region) could be related to the combined modes and the overtone excitation. Second, the measurements of the absorption spectrum of the crystal meet with certain technical difficulties, such as getting thin (about several microns small) single crystal plates. We usually apply in such the cases the method for pellet preparing, when a small amount (about 1%) of the material is pressed in a transparent matrix. Furthermore, precise determination of the vibration frequencies of crystal on the basis of the absorption spectra of the powder should account for the possible excitation of the surface modes (especially the Frohlich modes) in micro particles [23]. This could lead to a shift of frequency, at which the excitation is observed, from ω_T to ω_S ($\omega_T<\omega_S<\omega_L$). The condition $\varepsilon_{\beta\text{-}Ala}(\omega_S) = -2\varepsilon_{matrix}$ (with ε_{matrix} being the permittivity of the matrix material) is expected to be fulfilled for ω_S [24]. Besides, one has to consider that the molecular crystals, including β-Ala, L-Ala and L-His, are anisotropic and their optical properties are defined by a tensor of permittivity. In a mixture, of which a pellet is made, the micro-crystals are oriented chaotically. Therefore, in the absorption spectra the modes are simultaneously excited, which correspond to different possible crystal orientations. Due to the measurements of the reflection from single crystals, only the excitation of dipole-active vibrations could be observed, without any overtones and the combined modes, because only the vibrations polarized in certain plane are then detected. As a result, one can expect that the measurements of the polarized reflectance spectra on anisotropic crystal and the absorption spectra on its powder gives an additional information about the dipole-active vibrations of crystalline lattice, thus allowing to determine the dielectric function of the crystal and make the assignment of vibrations.

Sample preparation and experiment technique

The single crystals under test were grown using triple cross-crystallization from the saturated water solution of chemically pure β-Ala powder. Afterwards, they were dried in a vacuum thermostat at 340 K. For our experiments, we used single crystal samples of β-Ala with the thickness of 2-5 mm (for the investigations of reflectance spectra) and β-Ala powder in KBr or CsI matrices (for the transmittance spectra). β-Ala, KBr and CsI were milled in agate mortar and mixed according to the ratio of 0.7 mg β-Ala per 500 mg of the matrix material. Then the mixture was pressed into the ring of 20 mm-diameter.

Crystal orientation during the spectral measurement was fixed as shown in Fig. 1. The reflectance spectra were measured at the cleavage plane (010), in accordance to [11]. The polarization of the incident wave was of such a type that the direction of the electric field was parallel to the large (a) or small (c) diagonal of the (010) plane. We have obtained in the earlier experiments [6-10] that the IR spectra are the most different from each other, if the electric field (E) of the incident beam is parallel to the small or large diagonals of the [010] crystal plane, while the dielectric permeabilities have the most drastic differences for the two

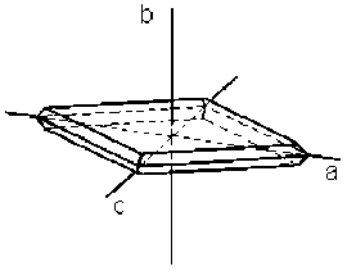

Fig. 1. Reflectance spectra are collected for the crystal layer [010]. The axial length for the corresponding axes is *a*=0.887 nm, *b*=1.381 nm and *c*=0.607 nm. The polarization of incident wave is such that the direction of electric field vibrations is parallel to large (a) or small (c) crystal diagonals.

perpendicular directions of (010). That is why we suppose that the diagonal of (010) coincides with the direction of crystal growth and one of the crystallographic axes. It is known from the crystallographic data [11] that the crystals grow as plates parallel to (100) plane and so the big diagonal would coincide with the crystallographic axis x.

We obtained the IR reflectance and transmission spectra in the 380-5300 cm^{-1} region with the Fourier-spectrometer IFS-48 (Bruker), possessing the resolution of 0.2 cm^{-1} and the wave-number accuracy of 0.01 cm^{-1}. The measurements in the 100-500 cm^{-1} region were performed with the grating spectrometer KSDI-82 (LOMO), equipped with the optical-acoustic photo-detector. We used polyethylene polarizer in our experiments. The light angle in the standard reflection device IPO-22 (LOMO) was close to the normal and was equal to 16.5°. All the measurements were made at the room temperature.

Results and discussion

The reflectance spectra of β-Ala single crystal in polarized light and the transmittance spectra of β-Ala pellet obtained in the experiments are shown in Fig.2 and Fig.3, respectively. The corresponding calculated spectra are also presented in these figures. The calculations of the reflectance and transmittance spectra were made with the matrix method [24], considering the effect of reflection from the bottom plane. The permittivity of the crystal was calculated with formula (3). While calculating the transmittance spectra of the pellet, the composite microstructure of the medium was considered following the symmetric approximation of effective medium by Bruggeman (see, e.g., [26]):

$$f_1 \frac{\varepsilon_{\beta-ala} - \varepsilon_{eff}}{\varepsilon_{\beta-ala} + 2\varepsilon_{eff}} + f_2 \frac{\varepsilon_{matrix} - \varepsilon_{eff}}{\varepsilon_{matrix} + 2\varepsilon_{eff}} = 0 \quad (4)$$

Here ε_{eff} denotes the effective permittivity of the composite medium, formed by components with the permeabilities $\varepsilon_{\beta\text{-ala}}$ and ε_{matrix} and f_1 and f_2 are their volumetric contributions ($f_1+f_2=1$).

The analysis and comparison of experimental and calculated results show that the model of the dielectric function of β-Ala single crystal used by us describes sufficiently its optical properties in the region of lattice and intra-molecular vibrations. The oscillator parameters obtained from the fitting of the reflectance spectra for the two crystal orientations and the frequency fitting of vibrations in the transmittance spectra are shown in Table 1. The obtained values of the high-frequency permittivity ε_∞^a and ε_∞^c do not differ too much and are equal to 2.52-2.53. We mean by a high frequency such frequency, which is higher than the intra-molecular and the lattice vibration ones, but lower than the frequency associated with the exciton and electron excitations located in the 20000-5000 cm^{-1} region.

As is known, KBr can be used as a matrix for measuring the transmittance spectra in the region up to 400 cm^{-1}, since it is non-transparent for lower frequencies. For deriving the transmittance spectrum of β-Ala in the region up to 100 cm^{-1}, the pellets of β-Ala in CsI matrix were made. The experimental transmittance spectra of β-Ala in these matrices are shown in Fig.2c and Fig.3c. Good fitting of the experimental transmittance spectra with the calculated ones and the values of the parameters derived from the reflectance spectra testify a correct solution of the "inverse" problem of spectroscopy, with the use of the CDA method and the equation (3) for permittivity of β-Ala molecular crystal. The halfwidth of the band in the transmittance spectrum is equal to the value of the damping parameter Γ_j^α. The transmittance spectrum is formed due to a superposition of the transmissions of chaotically oriented β-Ala micro crystals. The bands in the transmittance spectrum of β-Ala powder observed at 1611, 1431, 918, 799, 668 cm^{-1} are absent in the polarized reflectance spectra. Considering the

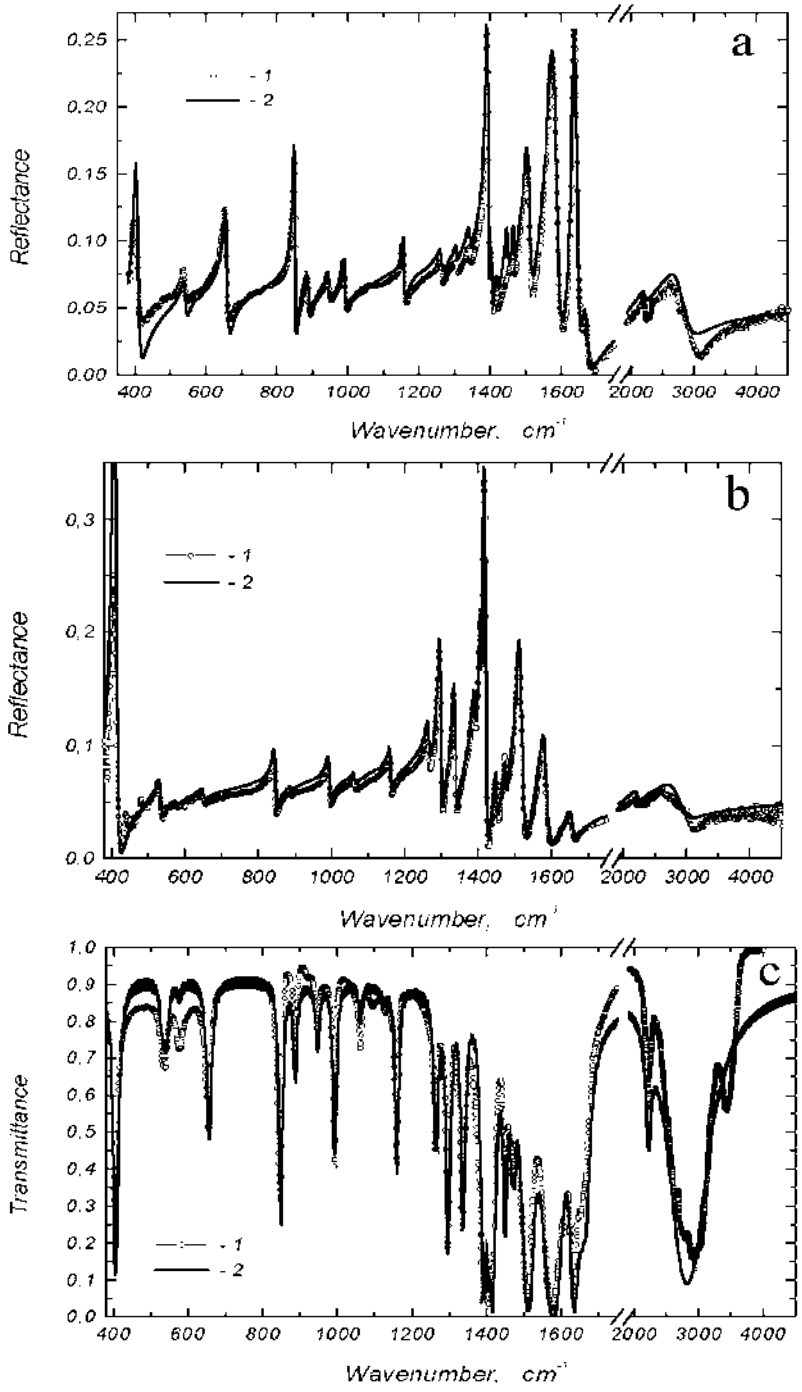

Fig.2. Reflectance spectra of β-Ala single crystal in the polarized light for the two orientations of sample: (**E** || a) - (*a*), (**E** || c) – (*b*), and unpolarized transmission spectrum of β-Ala powder in KBr matrix in the 400-5300 cm^{-1} region – (*c*). Experiment – curves1, calculations – curves2.

fact that their intensities do not differ much from the intensities of the other bands, we can presume that the overtones or the combined modes are improbable at these frequencies. We suppose these are to be dipole-active vibrations, which are active for the other polarization (**E**||*b*). We were unable to measure the reflectance spectrum for this polarization. The bands at 3441 and 2252 cm^{-1} have a high intensity, however they correspond, most probably, to the overtones or the combined modes, since they could not be assigned to any of fundamental modes.

The weak vibrations, which correspond to

Table 1. Parameters of approximation of the dielectric function for β-Ala single crystal.

Transmittance	Reflectance					
	(**E** ⎮⎮ a)			(**E** ⎮⎮ c)		
ω_j, cm^{-1}	ω_j, cm^{-1}	S_j	Γ_j, cm^{-1}	ω_j, cm^{-1}	S_j	Γ_j, cm^{-1}
	104.83	0.41473	4.37	104	0.1	7.3
	120.00	0.1	8.0	121	0.0	12.4
	137.00	0.1	8.0			
157	158.00	0.1	10.0	158.00	0.04688	4.24
175				180.95	0.49735	17.8
188	191.13	0.36112	13.68			
213	218.67	1.70023	22.28			
233				247.57	0.10851	15.3
323				321.19	0.22742	12.4
402	400.87	0.10071	13.72	400.10	0.14063	6.3
531.4, 539.8	540.65	0.01313	10.75	530.43	0.02051	13.73
575.5	574.7	0.00100	10.00	575.00	0.003	15
654.3	654.91	0.04091	12.73	649.92	0.00467	12.83
668						
799						
843, 848	847.32	0.02428	6.33	843.62	0.01378	9.54
886.8	885.68	0.00942	10.16	887.35	0.00075	5.98
918						
946.1	944.7	0.00642	10.69			
992.4	990.65	0.00843	9.05	991.59	0.00841	8.91
1061.7	1060.04	0.00036	7.28	1061.81	0.00194	8.73
1092.7						
1130.4	1125.0	0.0008	20	1125.00	0.0008	20
1159.3	1156.81	0.00682	6.72	1158.64	0.00721	9.17
1264.7	1261.58	0.00441	11.67	1263.56	0.00922	11.05
1296.2, 1306	1304.86	0.00183	7.54	1293.64	0.02284	7.93
1335, 1343	1341.1	0.00348	9.59	1333.61	0.01647	8.09
1392	1389.62	0.03217	7.97	1389.07	0.01076	9.79
1405	1402.8	0.00407	4.98	1403.40	0.01227	5.12
1416	1418.13	0.005	12.18	1412.73	0.03084	6.89
1431						
1448	1447.93	0.00612	9.04	1447.93	0.00685	9.04
1466	1466.01	0.00412	7.14	1472.90	0.00412	7.14
1510	1503.97	0.03493	18.56	1508.79	0.04074	16.96
1577	1568.82	0.08086	26.82	1575.29	0.02847	22.47
1611						
1636	1631.98	0.03251	13.16			
1655				1651.94	0.00689	18.97
1668	1664.04	0.00842	19.45			
2212	2212.00	0.010	90.0	2212.00	0.01000	90.0
2252						
2848	2758.13	0.15282	400.9	2836.54	0.10788	431.5
3441						

the modes of the second and higher orders, are located in the region from 1800 to 2500 cm^{-1}. Their absence in the reflectance spectrum proves our assumption. The principal tones and the overtones are located in the region 2500-3200 cm^{-1}. The continuous structure of the major band in this region seems to be connected with the strongly H-bonded NH_3^+ group. This

conclusion could be made on the basis of comparison of the transmittance spectra of β-Ala in crystalline and gas phases. In the latter case, the molecule of β-Ala does not form a hydrogen bond with the other molecules and so this band is absent [27]. Only H-bonding of the NH3+ group can explain high intensity of this vibration. Against the background of this band, a vibration of CH_2 group is seen only as a weak peak near 2850 cm^{-1}. This vibration makes a significant contribution to ε ($\Delta\varepsilon = S_j = 0.1$-$0.2$) and shows the important role of H-bonds in forming the structure and properties of molecular crystals, in general, and β-Ala, in particular.

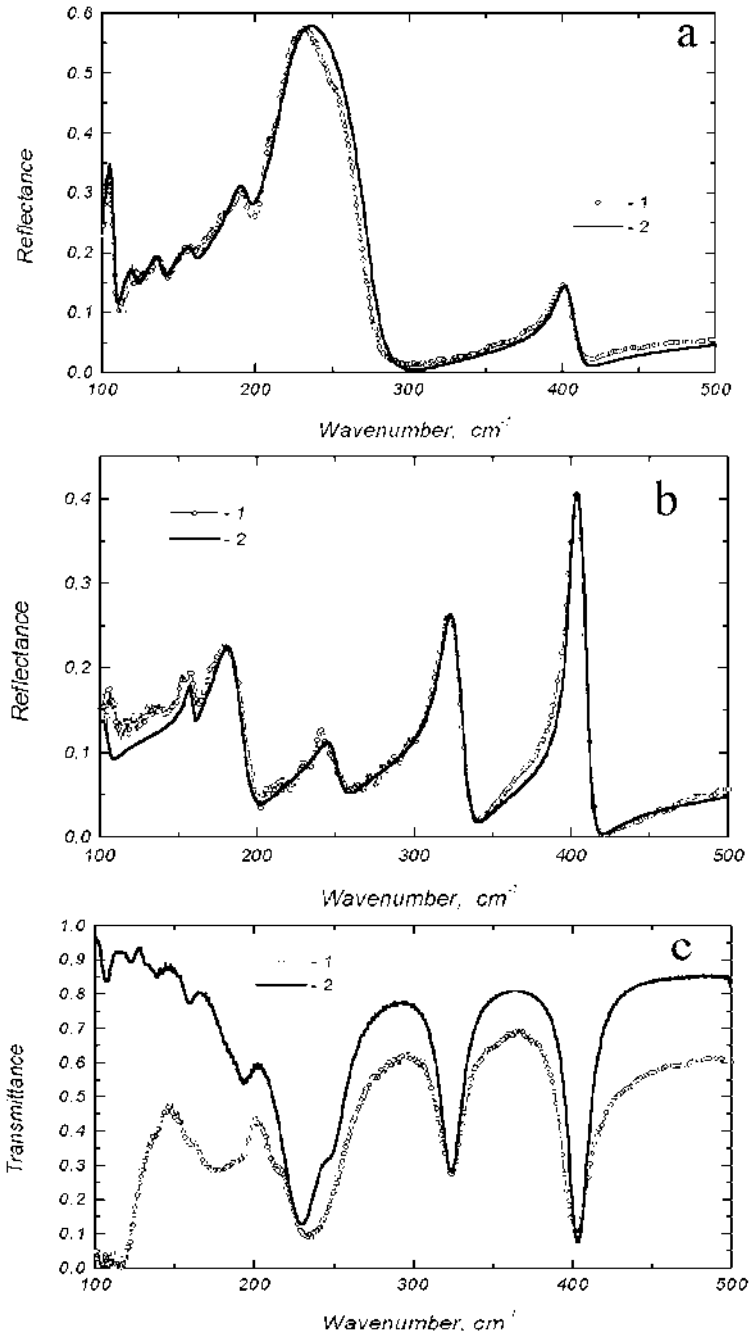

Fig.3. Reflectance spectra of β-Ala single crystal in polarized light for the two orientations of sample: (**E** || a) - (*a*), (**E** || c) – (*b*), and unpolarized transmission spectrum of β-Ala powder in CsI matrix in the 100-500 cm^{-1} region – (*c*).
Experiment – curves1, calculations – curves2.

It is known [15] that $\varepsilon_0^{\alpha} = \varepsilon_\infty^{\alpha} + \Sigma S_j^{\alpha}$. After summing the oscillator strengths for each crystal orientation, we get $\Sigma S_j^1 = 3.5$ and $\Sigma S_j^2 = 1.52$; i.e., $\varepsilon_0^a = 6.04$ and $\varepsilon_0^c = 4.04$. We could say that the main contribution to the static dielectric permeability for the (E || a) orientation originates from the low-frequency vibration at 218,6 cm^{-1} and the strength $S_j = 1,7$. This band seems to be associated with H-bonding of the adjacent molecules in a layer.

The previous measurements performed by us with the method of cavity losses gave the following parameters for β-Ala at f = 3-6 GHz: $\varepsilon' = 3.9(3.82) \pm 0.009$, and $\tan\delta = 0.07 \pm 0.005$. The measurements on β-Ala made in Kharkiv for f = 60 GHz gave the value $\varepsilon' = 5.3 \pm 0.1$ for one direction in the crystal plane and $\varepsilon' = 4.0 \pm 0.1$ for the other direction in the same plane [10]. From comparison of the experimental data obtained for the microwave frequencies and the calculations on the basis of the IR spectra with taking into account the low-frequency modes, we can get a good agreement for the ε_0 parameter. For the case of ε_0^a, the value derived from our calculations (4.01) is larger than that obtained at the microwave frequencies (3.8 – 3.9 at 3-6 GHz) and (4.0 at 60 GHz, respectively). We suppose that the reason is not correct enough IR measurements at the low frequencies (100-150 cm^{-1}) or the crystal defects. For example, a presence of micro cavities and other defects can minimize the value of ε_0 by 0.1-0.5, as we could see from the measurements in the microwave range. In case of the other direction, the ε_0 value derived from the calculations (5.2) is less than that derived from the microwave measurement (5.3). We assume the reason to lie in the fact that not all of the oscillators located in the region of 10 -100 cm^{-1} have been taken into account. We have measured four strong vibrations in the RS of β-Ala in the region lower 100 cm^{-1}. However, we could not detect them in the IR reflectance spectra, due to the instrument limitations. Therefore, these vibrations do not enter the data set used for the calculations. This causes a decrease in the permeability value obtained in the calculations.

It is known that the lifetime of electric and vibrational states can noticeably change in electromagnetic fields [28]. There are the vibrations, e.g., in the low-frequency region of the spectrum of amino acids, which are strongly polarized and make essential contributions to ε . Probably, even a slight excitation of them might cause a redistribution of the energy level population and so could affect the vibration parameters. These vibrations are linked with perturbation of strongly polar H-bonds. Therefore, the corresponding stretching and deformation vibrations would “feel” the changes in H-bonding and manifest themselves in the IR spectra, e.g., as is observed during exposing crystal with the microwave radiation [14]. The energy positions of these vibrations show that, at the room temperature (the energy corresponding to ω=200 cm^{-1}), their energy states are partly occupied [29] and so their real intensity must be higher than that in the experiment. The influence of electromagnetic field can change the parameters of these vibrations, which give almost half the contribution to the low-frequency permittivity. Therefore, even a slight microwave irradiation would be enough for changing the permittivity of crystal in this direction.

Conclusions

The data obtained from the optical studies (the Raman, reflectance and the transmission spectra) in the region of 400-5300 cm^{-1} are not enough to calculate the dielectric function of the β-Ala single crystal in the whole region of electromagnetic spectrum and to agree the static permittivity ε_0 value with the results obtained by using the method of cavity losses. It is therefore logical to expand the spectral range of optical studies towards the low-frequency region.

The polarized reflectance spectra of β-Ala single crystal have been investigated for the two

orientations of the electric vector **E**. The transmittance spectra of the powder (chaotically oriented micro crystals) in the relevant neutral matrices KBr or CsJ have been also studied in the 100-5300 cm^{-1} region. We have calculated the components of the dielectric function of β-Ala single crystal for the electric field parallel to the large and small diagonals of the (010) plane ((E||a) and (E||c)). The spectra have been calculated, using the multi-oscillator harmonic model. The corresponding parameters of the oscillators are received.

In the low-frequency region, β-Ala crystal manifests the IR-active vibrations of relatively high oscillator strengths, which could be assigned to H-bonds of the crystal lattice. For the orientation (E||a), there are the vibrations at 401, 218 and 191 cm^{-1}, while for (E||c) orientation there the frequencies are 400, 321 and 180 cm^{-1}. Taking the parameters of these vibrations and the limits of experimental accuracy into account, we get a good fit of the values of low-frequency dielectric constants ε_0 derived with the independent experimental methods and are in a position to explain a high anisotropy of this parameter.

References

1. Machida K, Kagayama A., Saito Y., Uno T. Spectr. Acta. **34A** (1978) 909-914.
2. Takeda M., Javazzo R.E.S., Garfincel D., Scheinberg I.H., Edsall J.T. J. Am. Chem. Soc **80** (1958) 3813-3818.
3. Shrader D. Raman: Infrared Atlas of Organic Compounds. Verlag Chemic. Weinheim. Germany (1989), 1226p.
4. Leifer A., Lippincott E.R. J. Am.Chem.Soc. **79** (1957) 5098-5101.
5. Pearson J.F., Slifkin M.A. Spectrochim. Acta. **28A** (1972) 2403-2413.
6. Berezhinsky L.I., Dovbeshko G.I., Lisitsa M.P., Litvinov G.S. Spectrochimica Acta **54A** (1998) 349-358.
7. Dovbeshko G.I., Berezhinsky L.I. J. Mol. Structure **450** (1998) 121-128.
8. Berezhinsky L.I., Dovbeshko G.I., Talik E., Woznjak K., Zawada K., Bukowska I. Functional Materials **7** (2000) 722-725.
9. Dovbeshko G., Berezhinsky L., Pashchuk O., Sekirin I. Ukr. Fiz. Zhurn. **46** (2001) 541-545. (in Ukrainian).
10. Makeev Yu.G., Motornenko A.P., Ermak G.P., Dovbeshko G.I. Biophysical Bulletin **2** (2001) 83-85.
11. Jose P., Pant L.M. Acta Crystallogr. **18** (1965) 806-810.
12. Dovbeshko G., Berezhinsky L., Lisitsa M.P., Litvinov G.S., Mashovets V.P. Quantum Electronics **46** (1994) 96-104. (in Russian).
13. Gribov L.A. Theory of infrared spectra of polymers. Moscow, Nauka (1977), 240p. (in Russian).
14. Litvinov G.S., Berezhinsky L.I., Lisitsa M.P. Molecular Mat. **87** (1993) 215-219.
15. Born M. Wolf E. Principles of optics: electromagnetic theory of propagation, interference and diffraction of light. 6-th ed.Oxford. New York. Pergamon Press (1980), 794p.
16. Gervais F., Piriou B. J. Phys. C: Solid St. Phys. **7** (1974) 2374-2386.
17. Merten L., Borstel G. Z.Naturforsch. **27A** (1972) 1792.
18. Szostak M.M., Le Calve N., Romain F., Pasquier B. Chem. Phys. **187** (1994) 373-380.
19. Lynch D.K. Astrophys. J. **467** (1996) 894-898.
20. Kopylevich Yu.I., Makarova E.G. Opt. Spectr. **63** (1987) 147-153.
21. Turrell G. Infrared and Raman spectra of crystals. Academic Press. London and New York (1972), 384p.
22. Zaenger W. Hydrogen bonding in biological molecules. Springer-Verlag (1991), 563p.
23. Bryksin V.V, Gerbstein Yu.M., Mirlin D.M. Phys. Sol. St. **13** (1971) 1603-1610.
24. Genzel L., Martin T.P. Phys. Stat. Sol. **51** (1972) 91-106.
25. El-Gohary A.R., Parker T.J., Raj N., Tilley D.R., Dobson P.J., Hilton D., Foxon C.T.R.

Semicond. Sci. Techn. **4** (1989) 388-392.

26. Venger E.F., Goncharenko A.V., Dmitruk M.L. Optic of small particles and dispersed matter. K.: "Naukova Dumka" (1999), 347p. (in Ukrainian).
27. Ivanov O.Yu. Molecular structure and thermodinamic parameters of isomer transitions of doped bioorganic molecules, condensed in low-temperature matrices of inert gas. Ph.D thesis. Kharkiv (1999), 20p. (in Russian).
28. Amelkin S.V., Oraevsky A.N. Multiphoton excitation of molecular vibrations in electric field. Proceedings FIAN (1988) 178-201. (in Russian).
29. Elyashevich M.A. Atomic and molecular spectroscopy, State Publ. Phys.-Math. Lit. Moscow (1962), 892p. (in Russian).