Infrared polarization reflectance spectra of the single crystal of natural natrolite

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Infrared polarization reflectance spectra of a single crystal of natural natrolite were measured in a normal and parallel orientation to its crystallographic *c*-axis. The spectra were monitored in the wavenumber range 20—$2500 \, cm^{-1}$ under the normal *p*, *T* conditions.

From the corrected spectra, dispersion curves of the absorbance index, of both components of the dielectric permittivity, index of refraction, and molar absorption coefficient were calculated with the help of Kramers—Kronig theorem.

In various orientations of the crystal the reflectance spectra in the polarized radiation (R_pII) do not differ significantly. This can be attributed to the poor anisotropy of the crystal and to the superposition of the LO and TO modes of vibrational bands. The dispersion curves respond in their character to the theoretical prediction.

Поляризационные инфракрасные спектры отражения монокристалла природного натролита были измерены нормально и параллельно его кристаллографической оси *c*. Спектры снимались в диапазоне волновых чисел 20—$2500 \, cm^{-1}$ при нормальных давлении и температуре.

Исходя из откорректированных спектров были с помощью теоремы Крамерса—Кронига рассчитаны дисперсионные кривые индекса поглощения, обеих составляющих диэлектрической проницаемости, показателя преломления и молярного коэффициента поглощения.

При различных ориентациях кристалла спектры отражения при поляризованном облучении (R_pII) не отличались значительным образом. Это может быть объяснено слабой анизотропией кристалла и суперпозицией колебательных полос типов LO и TO. Дисперсионные кривые по своему характеру соответствуют теоретическому предсказанию.

During the spectroscopic studies of crystals and inorganic glasses, the main attention is paid to the determination of optical parameters of these substances. Only the calculation of optical constants, both the real (*n*) and imaginary (*k*) parts of the complex index of refraction N ($N = \sqrt{\varepsilon}$; ε is the complex dielectric permittivity) enables further theoretical investigation of vibrational spectra.

There exist several methods for determination of the optical constants of absorbing media. Their application depends on the character of the studied substance and on the radiation wavelength. One of the most extended methods is the infrared spectroscopy (both absorption and reflectance). For substances, which absorb heavily within the wavelength range of infrared radiation (for example inorganic glasses and crystalline oxides), the reflection method of infrared radiation is most suitable. Its theoretical fundaments are described in many publications by *e.g. König* [1], *Kronig* [2], *Poulet* and *Mathieu* [3], among others. For exact determination of $N(\lambda)$ and $K(\lambda)$, which characterize truthfully the optical properties of material at a known wavelength, the following reflection methods may be used:

1. Coefficient of reflectance R at two different incidence angles of the radiation;
2. coefficient of reflectance R_p of polarized radiation, the electric vector of which vibrates within the radiation plane of incidence;
3. coefficient of reflectance R_s of polarized radiation, the electric vector of which vibrates normally to the radiation plane of incidence;
4. R_s and R_p at two incidence angles;
5. the ratio R_s/R_p at two incidence angles.

Recently the method of the disturbed full internal reflection (DFIR) has been used for computing the optical constants. Theoretical basis for this method is discussed by *Mathieu* [3]. Actually, methods connected with the calculation of Kramers—Kronig relations [4] are in broader use.

Basing on the solution of the Kramers—Kronig theorem, the corrected reflectance spectrum and dispersion curves of both components of the dielectric permittivity, index of refraction and the absorbance index are obtained. The present paper reveals the reflectance spectra of the natrolite single crystal, measured in polarized infrared radiation R_p in a normal and parallel orientation to the crystallographic axis c of natrolite. The Kramers—Kronig theorem was used for computing the optical constants.

Experimental

Reflectance spectra of the natural natrolite (Kola, USSR) were measured on optically polished plates 10 mm × 10 mm × 3 mm, cut out from mineral single crystals. One plate was oriented parallelly and the other one normally to its crystallographic axis c. Measurements were made on the interferometer Bruker AM GmbH IFS 113 V (Dr. Petzelt, Institute of Physics, Czechoslovak Academy of Sciences) within the wavenumber range of 20—2500 cm^{-1} using polarized (R_pII) radiation and mirror technique. Computing of optical constants was effected by the program KKK 1 (Petzelt, Kroupa — Institute of Physics, Czechoslovak Academy of Sciences) modified by O. Navrátil (Institute of

Geology and Geotechnics, Czechoslovak Academy of Sciences) for computer Tesla JPR 12 R. The computed values were graphically plotted on computer-controlled X-Y plotter.

The corrected experimental reflectance spectra for 100 % reflectance on an Al mirror (R/% reflectance, solid line), dispersion curves of the absorbance index (A — dotted line), molar absorption coefficient (K — dotted line), index of refraction (N — solid line), real part of the dielectric permittivity (E_1 — solid line), and imaginary part of the dielectric permittivity (E_2 — dotted line) are illustrated in Figs. 1—6. The evaluation of the oriented reflectance spectra in the polarized infrared radiation is shown in Table 1.
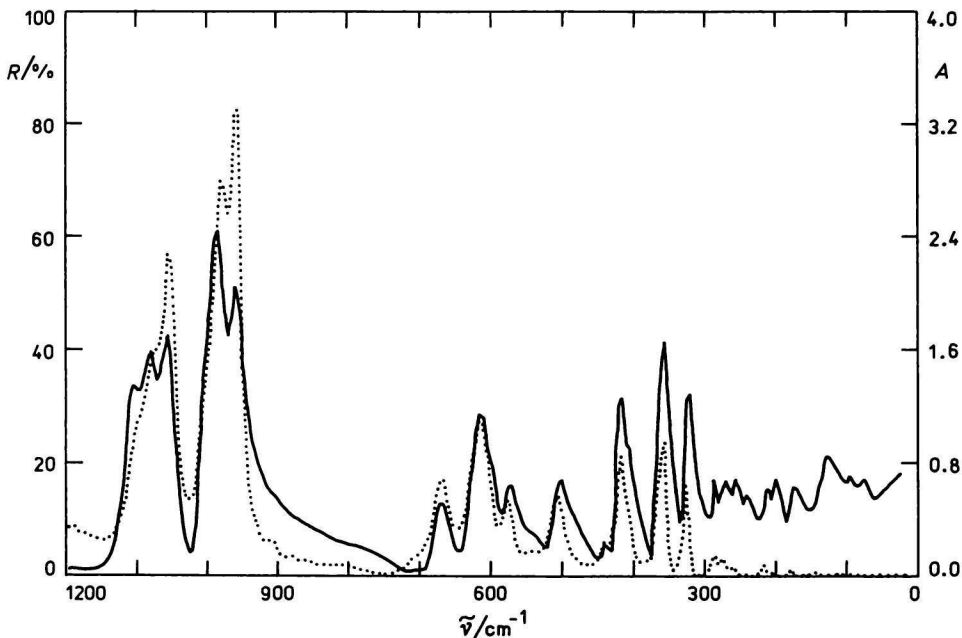
Fig. 1. Polarization reflectance spectra of the single crystal of natrolite. The direction of the infrared radiation (R_pII) normal to the *c*-axis (full line). Wavenumber range 20—2500 cm^{-1}. The dispersion curve of the absorbance index (A) calculated by means of the KKK-1 program from the reflectance spectrum (dotted line).

Discussion

Reflectance spectra of the natrolite single crystal (Figs. 1 and 4) in the polarized infrared radiation do not exhibit, in both orientations (beam direction normal and parallel to the crystallographic axis *c*), any significant differences
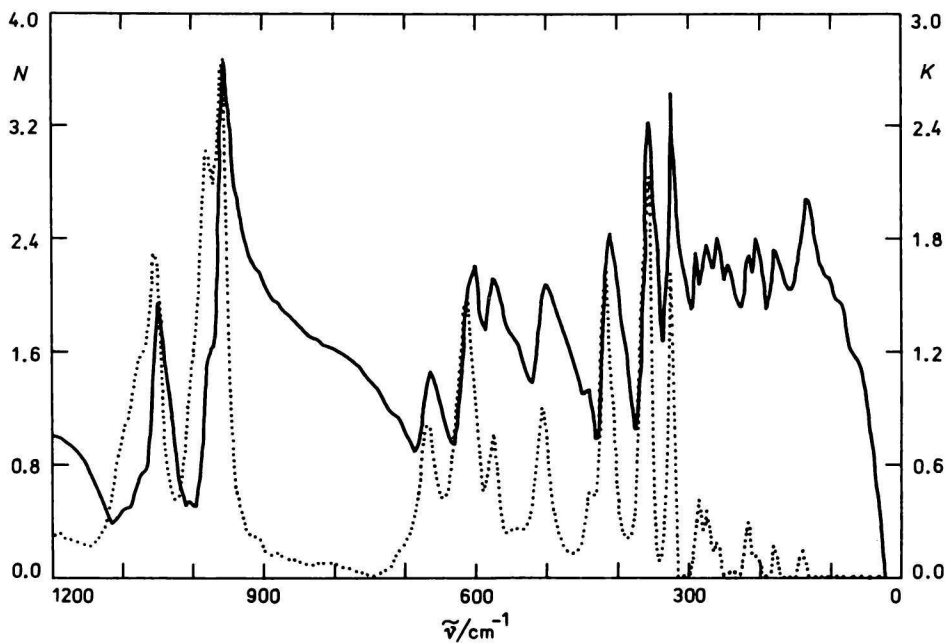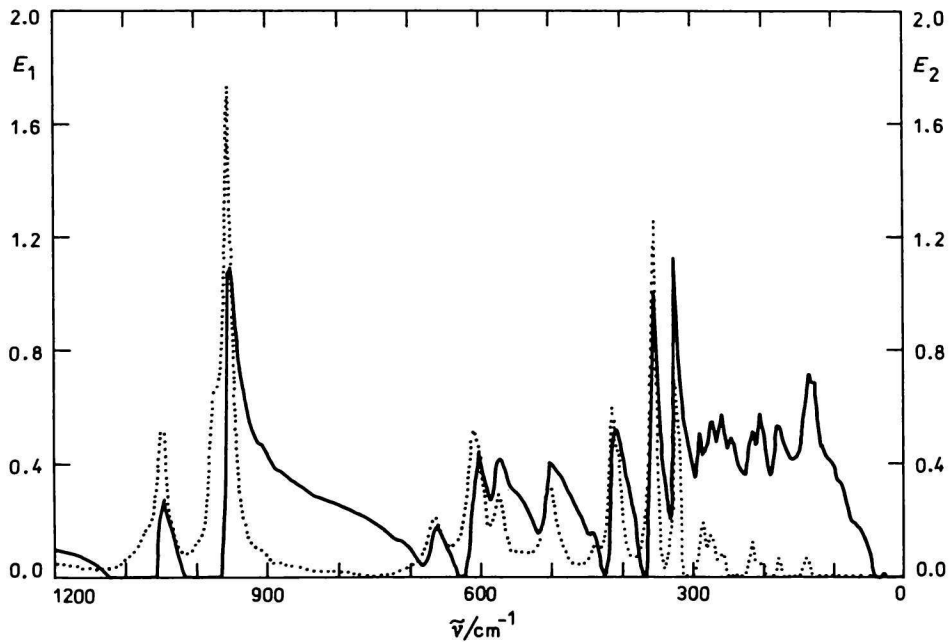
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either in wavenumber or in band intensities of individual vibrations. The proximity of vibrations at various orientations, to the crystallographic axis c, is connected with the weak anisotropy of small-diameter forces, and depends only on the Coulombian-type forces. They approach, by their character, the optically
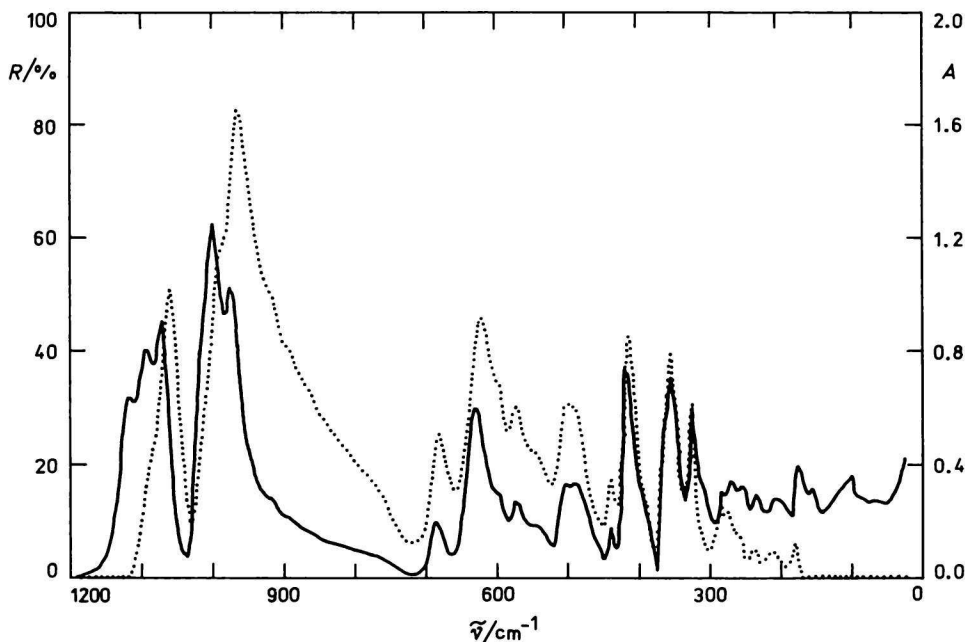

Fig. 4. Polarization reflectance spectra of the single crystal of natrolite. The direction of the infrared radiation (R_pII) parallel to the c-axis (full line). Wavenumber range 20—2500 cm^{-1}. The dispersion curve of the absorbance index (A) calculated by means of the KKK-1 program from the reflectance spectrum (dotted line).

uniaxial crystals. The peaks of TO and LO modes of vibration are in close position to each other and their recognition is impossible.

This concerns spectra ranges from wavenumbers 20—300 cm^{-1} and 1100—2500 cm^{-1}. The range of spectra between $\tilde{v} = 300$ cm^{-1} and 1100 cm^{-1},
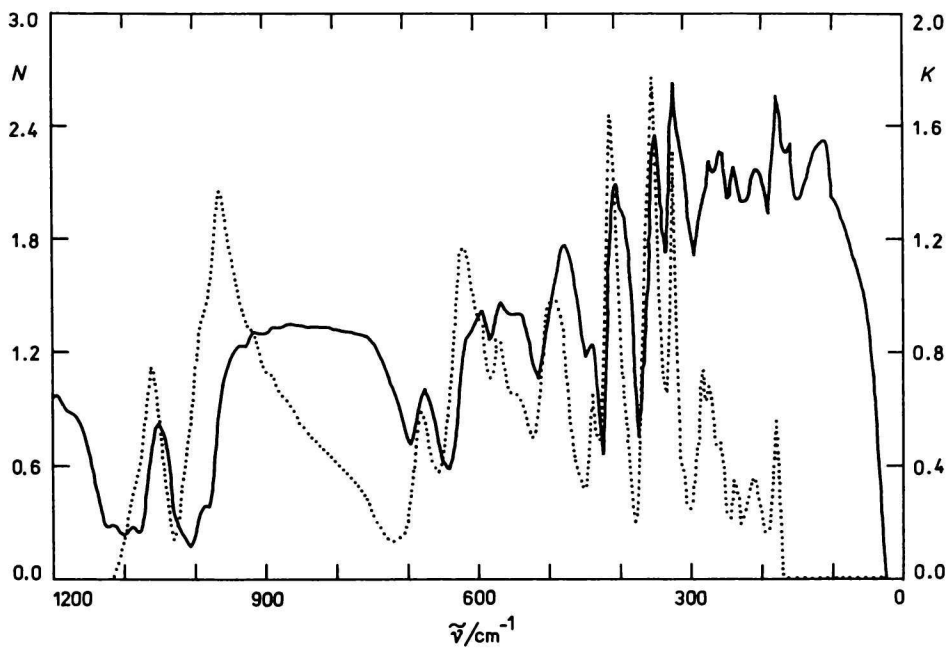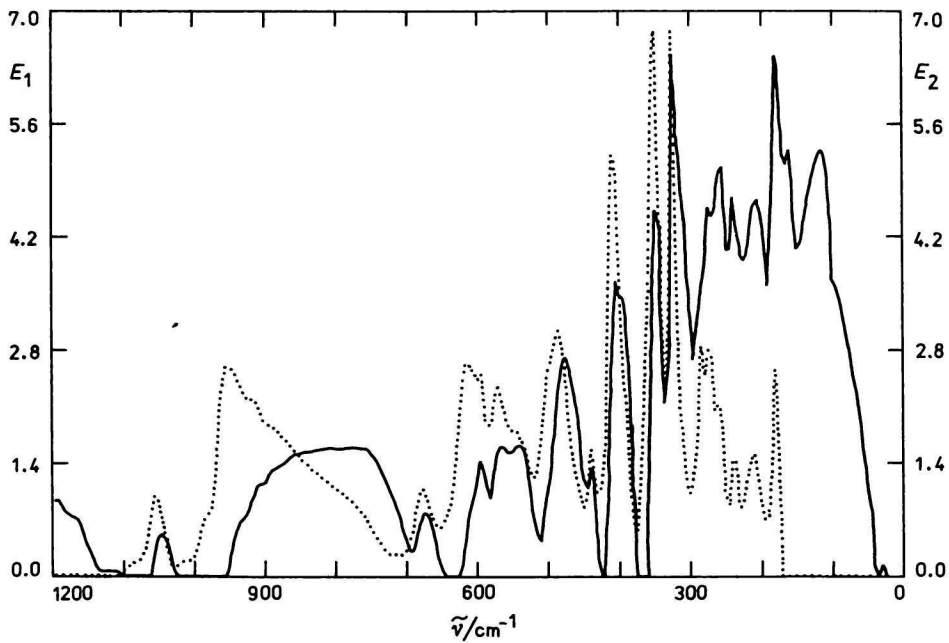
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Fig. 5. Dispersion curves of the dielectric permittivity calculated from the reflectance spectrum in Fig. 4. E_1 (full line) — the real part, E_2 (dotted line) — the imaginary part.

Table 1

Evaluation of the infrared polarization reflectance spectra of the single crystal of natural natrolite

Orientation normal to the c-axis of crystal		Orientation parallel to the c-axis of crystal	
$\tilde{\nu}/cm^{-1}$	$R/\%$	$\tilde{\nu}/cm^{-1}$	$R/\%$
1110	35	1110	31
1080	40	1095	41
1065	43	1060	45
995	60	990	62
960	53	965	52
675	15	675	27
625	32	620	18
575	18	575	17
575	19	505	18
—	—	480	18
440	6	440	8
415	35	420	40
405	23	395	infl
—	—	365	27
355	42	350	36
325	36	325	30
290	17	—	—
275	17	275	17
260	18	260	16
240	16	240	10
220	17	—	—
205	15	205	8
180	20	185	18
135	23	135	20

where vibrations of the bonds T—O, O—T—O, and T—O—T (T = Si, Al) are situated, gives sharp and relatively narrow peaks of bending vibrations O—T—O and T—O—T around $\tilde{\nu} = 400 \, cm^{-1}$ and those of the asymmetric stretching vibrations of T—O bonds within the wavenumber range of 900—1100 cm^{-1} are very intense (Table 1). The latter vibrations give a doublet

Fig. 6. Dispersion curves of the index of refraction (N — full line) and of the molar absorption coefficient (K — dotted line) calculated from the spectrum in Fig. 4 by means of the KKK-1 program.

(995 cm^{-1} (60 %) and 960 cm^{-1} (53 %)) and a triplet (1110 cm^{-1} (35 %), 1080 cm^{-1} (40 %), and 1065 cm^{-1} (43 %)) with a slight shifting of wavenumbers in both orientations of the crystal. Here the separation of the TO—LO modes of these vibrations could take place. At the same time, the LO modes could be expected in the direction towards the high-frequency edge of bands [4].

Within the low-frequency spectral range, where bands of the T—O—T torsional vibrations and lattice modes can be found at $\tilde{v} = 20$—300 cm^{-1}, there occur relatively broad and rounded bands with low intensity; starting from $\tilde{v} = 100$ cm^{-1}, only a broad diffuse background is perceptible. Beyond $\tilde{v} = 1100$ cm^{-1}, only a single broad diffuse band with low intensity and a flat peak around $\tilde{v} = 1500$ cm^{-1} can be found. It seems to belong to the combination band of the T—O—T torsional vibration with the stretching vibration of the T—O bonds. The dispersion curves of the absorbance index (A) have their maxima shifted towards frequencies, compared with the reflectance maxima. They have a smaller half-width and double intensity. This is in agreement with the theory [4].

The dispersion curves of the real part of the dielectric permittivity (E_1) lie within the zone of maximum transmissivity and minimum reflectance, which corresponds to the relation $E_1 = N^2 - A^2$. Dispersion curves of the imaginary part of the dielectric permittivity (E_2) follow the profile of reflectance spectra and have a higher intensity. They correspond, by their character, to curves A (Figs. 2 and 4). This is in agreement with the relation $E_2 = 2NA$ for the computation of the imaginary part of dielectric permittivity [4]. The course of dispersion curves (Figs. 3 and 6) of both parts of the refraction index, N and K, corresponds to curves of the dielectric permittivity (E_1, E_2). All results suggest that natrolite has a very low anisotropy of the optical properties and main refraction indices. Those which are identical with 2-fold axes of the crystal are very similar to each other. Maximum of the absorbance index corresponds to the maximum of transversal vibration modes and the maximum of dielectric conductivity coincides with the region of maximum transmissivity of the crystal in both orientations.

Conclusion

Measurement of the polarized infrared spectra of a natrolite single crystal is a suitable method for exact determination of dispersion curves of constants within the studied wavenumber range. This is especially useful for further study of vibration spectra and further measurements for the determination of physical parameters of crystals for their eventual practical utilization.

References

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