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Anisotropy of the Absorption of Gypsum Crystals in the Infrared Region

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A microscopic adapter and a polarizer were built for the infrared spectrometer, and the anisotropy of absorption and reflection of the gypsum crystals in the region 2-11μ investigated. For a series of spectrum bands corresponding to the vibrations of the molecules of water and $SO_4^=$ groups, pleochroism and splitting into variously polarized components were observed. The origins of some bands were determined and conclusions were drawn about the character of coupling of vibrations in the lattice.

1. THE infrared spectra of gypsum crystals have been investigated several times since the end of the last century. The old investigations were reviewed by Shefer and Matossi[1]. Recently Ellis[2] and Louisfert[3] investigated the absorption spectra of gypsum crystals in the wavelength region 0.9-2μ. Miller and Wilkins[4] investigated, together with other inorganic substances, the emulsion of crystalline gypsum powder in an organic oil. Matsumura[5] studied the spectra of a single crystal of gypsum in the region around 3μ.

Also, the Raman spectra of gypsum crystals have been thoroughly investigated. A most thorough investigation of these spectra was made by Krishnan[6]. Investigations in polarized light were carried out by Cabannes and Aynard[7]. They also analyzed the results for vibrations in the 3000 cm^{-1} region.

Gross and Valkov[8] investigated the Raman scattering of gypsum in the region up to 200 cm^{-1}, and they ascribed the detected vibration frequencies to the hydrogen bond.

Stekhanov[9], studying the Raman spectra of gypsum in the region of 3000 cm^{-1}, detected in the neighborhood of the fundamental lines 3486 and 3408 cm^{-1} a number of associated lines at the distance up to 200 cm^{-1}. These lines are ascribed to the intermolecular vibrations.

The purpose of our work was to investigate systematically the anisotropy of the infrared absorption of gypsum crystals in the region of fundamental frequencies.

2. A spectrometer with an auto-collimator provided with a NaCl 70° prism was used in the investigation. The focal distance of the mirrors was 600 mm, the prism height was 70 mm, and the height of the slits up to 30 mm. The radiation detector consisted of a thermo-couple with an electro-optical amplifier.[10] The polarizer was composed of three laminae of selenium, each about 3μ thick. The maximum obtainable polarization exceeds 90%. The polarization planes of the monochromator and the polarizer were parallel to each other. The rotation of the polarization plane with respect to the specimen was realized by the rotation of the latter.

The absorption spectra were obtained by using thin (10-60 μ) sheets of the crystal with a well-defined orientation. The measurements were made by using a microscopic adapter with the spectrometer. The adapter consists of two identical mirror objectives with an aperture of 0.45. The first objective projects a nine-time reduced image of Nernst's rod on the object. The object with the reduced image of Nernst's rod is then magnified nine times and projected by the second objective through the polarizer on the entrance slit of the spectrometer (Nernst's rod appears in its natural size).

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[1] K. Shefer and F. Matossi, *Infrared spectra*, ONTI, 1935.

[2] J. W. Ellis, Phys. Rev. **38**, 693 (1931).

[3] J. Louisfert, J. Phys. Radium **8**, 22 (1947).

[4] F. A. Miller and H. Wilkins, Anal. Chem. **24**, 1253 (1952).

[5] On Matsumura, Mem. Faculty Sci., Kyusyu Univ, **1B**, 1-3 (1951); Chem. Abst. 4365 i (1952).

[6] R. S. Krishnan, Proc. Ind. Acad. Sci. **A22**, 274 (1945).

[7] J. Cabannes and R. Aynard, J. Phys. Radium **3**, 137 (1942).

[8] E. F. Gross and V. I. Valkov, Dokl. Akad. Nauk SSSR **68**, 473 (1949).

[9] Stekhanov, Dokl. Akad. Nauk SSSR **92**, 281 (1953).

[10] B. P. Kozyrev, Uspehki Fiz. Nauk **44**, 173 (1951).

The use of the micro-adapter was necessary because of the difficulties in preparation of thin sheets of gypsum crystals with various orientations having sufficiently large dimensions. For our measurements specimens of dimensions of 0.2 × 1.5 mm were sufficient.

It is easy to show that, for a given sensitivity threshold of the radiation receiver (which determines the resolving power of the spectrometer), the minimum area of the specimen depends on the aperture of the micro-adapter. The aperture found in micro-objectives for infrared spectrometers is not greater than 0.8, even in objectives of lower image quality. Attempts to use specimens with smaller areas than that determined by the aperture of the micro-adapter and thus not filling completely the monochroator, resulted actually in a sharp reduction of the resolving power of the spectrometer.[11] It should be noticed that, because of its relatively large aperture, the use of the micro-adapter introduces some uncertainty in the results of the experiments. This fact, and also the difficulties in preparation of thin sheets of gypsum crystals having an orientation perpendicular to the principal cleavage plane (010), obliged us to perform a series of measurements by the method of reflection. The source of radiations – Nernst's rod – was projected on the polished surface of the specimen by means of a spherical mirror. By means of a second spherical mirror the image of the source and the surface of the specimen is projected through the polarizer on the entrance slit of the spectrometer. The aperture of the beam is not greater than 0.1; the angle of incidence is 4 °. Under these conditions there is practically no influence of the oblique incidence on the results of the measurements. The polished surfaces had been obtained on a well-developed single gypsum crystal.

3. The gypsum crystal $CaSO_4 \cdot 2H_2O$ belongs to the monoclinic system. The crystal has a laminated structure and the principal cleavage planes separate the layers of water molecules between which the double layers of Ca^{++} ions and of complex ions SO_4^{--} are enclosed..

The structure of an elementary cell of gypsum (Fig. 1) was established by Wooster.[12]

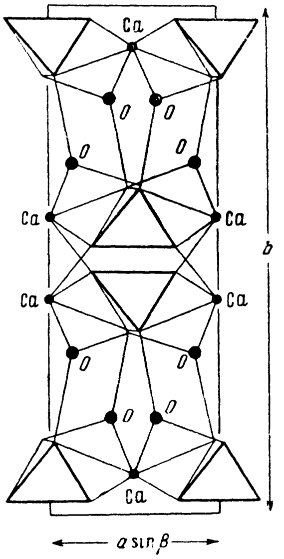

FIG. 1. The unit cell of gypsum according to Wooster. The tetrahedrons represent the SO_4^{--} groups. The positions of the hydrogen atoms of the water molecules are not shown.

Figure 2 (curve *I*) shows the absorption spectrum of a fine gypsum powder $CaSO_4 \cdot 2H_2O$ as compared with the spectrum of $CaSO_4 \cdot 0.5H_2O$ powder (curve *II*) and with the spectrum of anhydrous $CaSO_4$ (curve *III*). It is known that the intense lines in the region 1100-1200 cm^{-1} are related to the vibration of the SO_4^{--} ions. The 1615 cm^{-1} line is obviously caused by deformational vibrations (ν_2) of the crystallization water molecules (in liquid water $\nu_2 = 1640$ cm^{-1}). A weaker line, 1675 cm^{-1}, could be observed in the spectra obtained by several investigators, beginning with Koblentz, but no suggestion was made to explain its origin. The 2220 cm^{-1} line belongs to the crystallization water (Raman frequency); the 2130 cm^{-1} line is due to the SO_4^{--} group (second harmonic of the 1100-1200 cm^{-1} line). In the spectrum band 3300-3600 cm^{-1} very strong absorption is observed. Certainly, here must appear the symmetrical ν_3, and the anti-symmetrical ν_2, vibrations of water molecules (in liquid water $\nu_1 = 3450$ cm^{-1}; $\nu_3 = 3580$ cm^{-1}). In the same region also should be situated the harmonics of the 1675, 1615, and 1100-1200 cm^{-1} lines. It is also possible that the 3300-3600 cm^{-1} band is broadened by the presence of hydrogen bonds in the crystal.

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[11] D. L. Wood, Rev. Sci. Instr. **21**, 764 (1950).

[12] W. A. Wooster, Z. Kristall. **94**, 375 (1936).

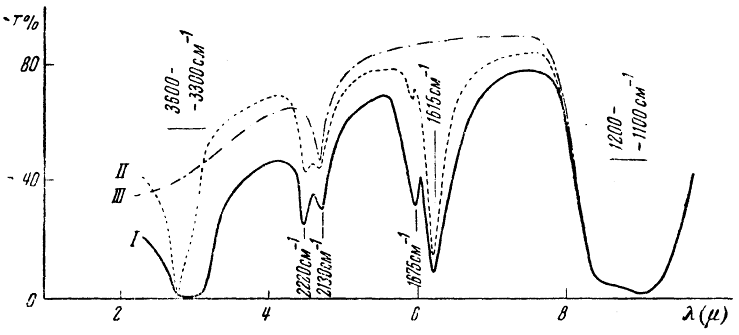

FIG. 2. The absorption spectra of gypsum powders $CaSO_4 \cdot 2H_2O$ (curve *I*), $CaSO_4 \cdot 0.5\ H_2O$ (curve *II*) and $CaSO_4$ obtained by heating to 600° C (curve *III*). *T* is the transmission coefficient of the specimens.

The absorption spectra of a lamina of gypsum 50μ thick, cut parallel to its principal cleavage plane, are represented in Fig. 3. The direction of the light beam coincides in this case with the *b* axis of the crystal. The electric vector was oriented either parallel to the direction of the fibrous cleavage of the crystal (curve II) or perpendicular to it (curve *I*). Curve *III* was obtained for a crystal cut parallel to the *b* axis and to the direction of the fibrous cleavage. The electric vector is in this case perpendicular to the *b* axis. The data obtained indicate a strong anisotropy of absorption of gypsum crystals. It was impossible to obtain a full picture of the directions of maximum absorption for all lines; the attempts to resolve the 3300-3600 cm^{-1}band by using larger dispersion (LiF prism) and smaller thickness of the specimen (up to 2μ) were unsuccessful. It was impossible also to resolve the band around 1100-1200 cm^{-1}. Therefore, an investigation was made of reflection spectra in polarized light. This enabled us to detect many important details. The results of these investigations are represented in Fig. 4. This figure shows also the directions of the incident radiation and of the vibrations of the electric vector.

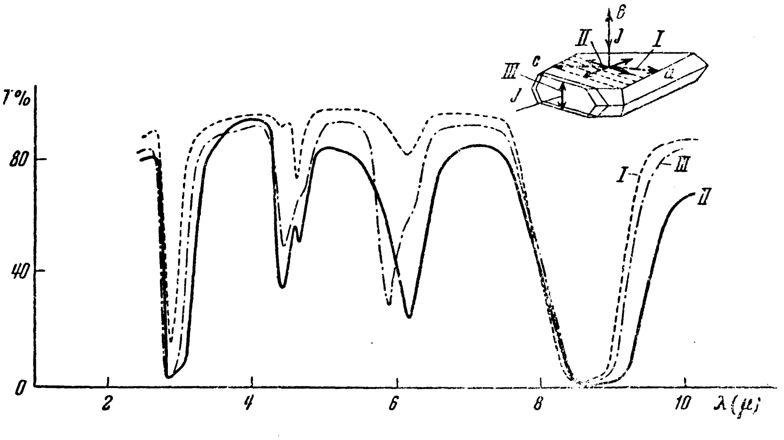

FIG. 3. The absorption spectra of gypsum crystal sheets in polarized light. The orientation of the cuts and the direction of the light polarization are shown in the figure. *T* is the transmission coefficient of the specimens.

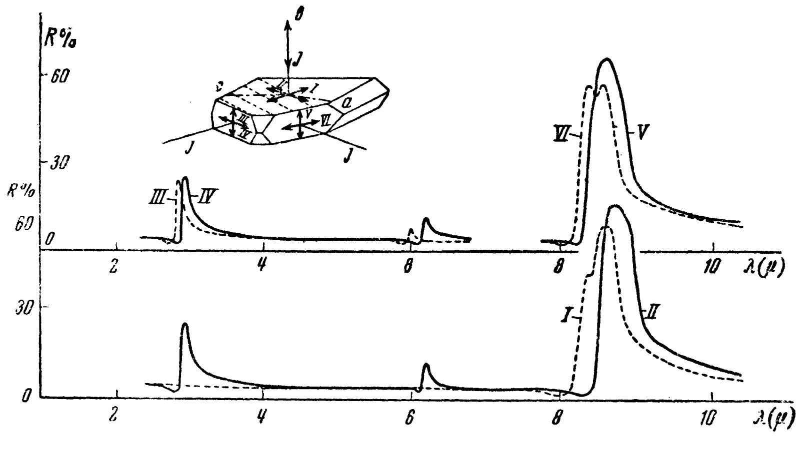

FIG. 4. The reflection spectra of gypsum crystals. The orientation of the polished surfaces and the direction of the polarization are shown in the figure. *R* is the reflection coefficient of the specimen.

The spectrum band 1100-1200cm^{-1} shows a clear anisotropy in the reflection. On curves *I* and *VI* (Fig. 4) two components of this band are resolved. They are situated at about 1180 and 1150 cm^{-1}. A third component appears on graphs *II* and *V*, but it was not possible to resolve it, even when a slit was used with a spectral width of 3 cm $^{-1}$and the crystal cooled to the temperature of the liquid air. The maximum of this component is, according to our estimation, situated at about 1120 cm^{-1}. It should be pointed out that dependence of the maximum on the orientation of the polarization plane is observed also in the second harmonic of the considered vibrations around 2130 cm^{-1} (Fig. 3), but the influence of the neighboring 2220 cm^{-1} line, associated with the crystallization water, makes the study difficult in this case.

The reflection spectra in the region 1615-1675 cm^{-1} shown in Fig. 4 were obtained by taking into account the absorption due to the atmospheric humidity. Here also the dichroism clearly appears. The position of the observed lines, whose maxima are shifted by 5 cm^{-1} in the direction of low frequencies with respect to the lines obtained by absorption, does not depend on the directions of observation and polarization. This is also true for the maxima of reflection in the region of valence vibrations of the water molecules which are situated around 3400 and 3510 cm^{-1}. The second of these maxima is a little deformed because of the superposition of absorption lines of the atmospheric moisture. It is not clear, however, why the broad band of absorption in the region 3000-3600 cm^{-1} appears in the reflection spectrum only in the form of two narrow maxima and, moreover, why the line of absorption observed on curve *I* (Fig. 3)around 3485 cm^{-1} does not appear in the reflection spectrum with corresponding orientation of the electric vector of the incidence radiation. These questions merit further study.

The results discussed above were obtained with an arbitrarily chosen orientation of the electric vector of the incidence radiation. In order to determine the direction of the maximum absorption, the polar diagrams of reflection were measured by rotating the investigated specimen around an axis perpendicular to the reflecting plane without changing the polarization plane. Analogous diagrams were also obtained by absorption. In this case, the spectrometer separated the narrow interval of wavelengths near the maximum of the investigated absorption band. The investigations were made on those specimens which had been used for the measurement of spectra. The obtained curves have a characteristic form of the figure eight. The direction of the greatest absorption coincides clearly with the long of the axis eight.

4. The directions of the absorption maxima were determined for the frequencies 1120, 1150,1180cm^{-1} associated with the vibrations of atoms of the SO$_4^{--}$ ion, and also for frequencies 1615, 1675, 3400 and 3510 cm^{-1} associated with the vibrations of the molecules of crystallization water. The polar diagrams for the frequencies 1120 and 1180 cm^{-1}, and particularly for the frequency 1150 cm^{-1}, are a little deformed,probably as a consequence of superposition of lines. Nevertheless, the asymmetry of the curves is very great, and the direction of the maximum absorption is defined without ambiguity.

The Table and Fig. 4 show the orientations of the dipoles for fundamental frequencies of vibrations, expressed by means of the angle of elevation ρ and the azimuth φ measured with respect to the axes b and a of the elementary cell of the crystal. The experimental values agree with the values computed on the basis of Wooster's model, according to which eight molecules of water present in the elementary cell of gypsum can be reduced, as a result of the crystal symmetry, to four identical orientations in space. If the dipoles responsible for the infrared absorption of water molecules in the crystal are orientated, as in free molecules, along the diagonal of the triangle H-O-H (ν_1 and ν_2) and along the normal to its plane (ν_3), then for each frequency the four dipoles would be grouped two by two in the directions shown on Fig. 5 and denoted by ν_3 and ν_1, ν_2.

The Directions of the Maximum Absorptions

Vibration Frequency in cm^{-1}	Values calculated on the basis of Wooster's model		Experimental Results	
	ρ_0	φ_0	ρ	φ
3510	40 140	33	0	—
3400	53 127	9	90	3
1675	—	—	0	—
1615	53 127	9	90	3
1180	90	100	90	103
1150	0	—	0	—
1120	90	10	90	25

The directions of the maximum absorption of the lines 1615 and 1675 cm^{-1} coincide with the bisectrices of the angles between the vectors ν_1 and ν_2 Fig. (5).

Both these frequencies should be ascribed to the deformational vibrations of water molecules ν_2; the corresponding line, according to the theory of Davydov,[13] is separated into two mutually perpendicular components. The ratio of intensities of these components is in qualitative agreement with the predictions of the theory. This interpretation agrees with the results obtained by comparison of the spectra of gypsum $CaSo_4 \cdot 2H_2O$ with the spectra of $CaSO_4 \cdot 0.5H_2O$ (Fig. 2). In this last case the line 1675 cm^{-1} is not visible. The observed split of the line 1615-1675 cm^{-1} indicates that deformational vibrations of individual water molecules in the gypsum crystal are not independent of each other and that the absorption and radiation in this special region is linked with the propagation of the excitation wave through the crystal.

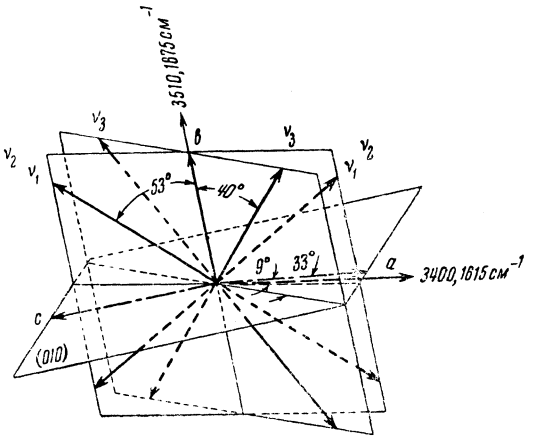

FIG. 5. The directions of the dipoles, corresponding to different vibrations of the water molecules, according to the model of the crystal, Fig. 1. The heavy arrows show the observed direction of the maximum absorption.

One would expect an analogous split of lines related to the valence vibrations of water molecules. In the corresponding region of the spectrum we found, however, the vibrations of two frequencies only: 3510 cm^{-1} oriented (as 1675 cm^{-1}) along the b axis and 3400 cm^{-1} oriented (as 1615 cm^{-1}) in the direction normal to the first one. The first of the frequencies should be related with the asymmetrical (ν_3) and the second with the symmetrical (ν_1), valence vibrations of the water molecules. We did not succeed, however, in detecting second components of these lines. One would conclude therefore from these results that the valence vibrations of individual water molecules in gypsum crystal are independent of each other, and that the excitation by light absorption has a localized character. It still re-

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[13] A. S. Davydov, *Theory of Light Absorption in Molecular Crystals*, Trudy. Inst. Phys., Acad. Sci. USSR 1, 1951.

mains unexplained, however, why there is observed for each frequency a single, sharply defined direction of maximum absorption, coinciding with the bisectrix of the smaller angle between the corresponding dipoles (Fig. 5). Inasmuch as the angle between these dipoles is near 90°, with the direction of the incidence light normal to the planes ν_1 and ν_3, the corresponding lines should exhibit only slight anisotropy. It has to be kept in mind that the data considered were obtained only by the reflection method and we see no reason to consider them as complete. It should be noted that Cabannes and Aynard[7], studying the Raman spectrum of gypsum in polarized light, observed also in the same region only two components instead of the expected four. On the other hand, Matsumura[5], whose paper we know only from a digest, discovered in the region of 3μ four components in the absorption spectrum of gypsum crystals. It is thus seen that the spectrum of valence vibrations of crystallization water in gypsum deserves further study.

Let us consider the spectrum of the group SO_4^{--}. As known, the vibrations 1100-1200 cm^{-1} have a triple degeneracy. The field of the crystal splits them into three components, which in the slightly perturbed tetrahedron SO_4^{--} should be mutually perpendicular[14]. The orientations of the corresponding dipoles are the same for all SO_4^{--} groups; therefore, it cannot be expected that each of the components would be split.

The orientation of the component 1120 cm^{-1} is not normal to the orientations of two other components (see Table). This deviation exceeds the limits of experimental error and is obviously caused by the asymmetry of the field of the crystal acting on the tetrahedron SO_4^{--}

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[14] G. Herzberg, *Vibrational and Rotational Spectra of Polyatomic Molecules.*

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