

THE INFLUENCE OF THE CHRISTIANSEN EFFECT ON I.R. SPECTRA OF POWDERS

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Abstract—The Christiansen effect appears in the i.r. spectrum of powders embedded in a solid, liquid or air matrix as an apparently anomalous transmittance (Christiansen peak) of the incident electromagnetic radiations. The peak appears at wavelengths for which the refractive index of the sample and the refractive index of the matrix are equal (Christiansen wavelength: λ_{chr}).

On account of the great variation of the sample refractive index in the immediate neighborhood of the absorption bands (anomalous dispersion curve), one often observes the occurrence of a transmittance peak or of a band deformation in this spectral range. A change in the position of this transmission peak with the value of the matrix refractive index is indicative of the Christiansen effect.

The equality of the refractive indices of the sample and of the matrix for λ_{chr} has been used to determine some points of the anomalous dispersion curve in the neighborhood of the hydroxyl stretching band (3678 cm^{-1}).

Spectral distortions caused by the Christiansen effect can be reduced by preparing the sample in such a manner that the width at half-maximum ($\Delta\nu_{1/2}$) of the Christiansen peak is several times greater than this of the absorption band itself. Clarke's theoretical formula, which gives an estimation of $\Delta\nu_{1/2}$, has been qualitatively verified and thus gives an appropriate guide in the choice of the parameters which one can optimize during the sample preparation. One can reduce the Christiansen effect spectral modifications, without running the risk of modifying the sample itself, particularly by overly severe grinding.

INTRODUCTION

I.R. SPECTROSCOPY of powders is possible by several techniques (Lecomte, 1958; Farmer *et al.*, 1968). The preferred technique depends not only on the size and shape of particles and the extinction coefficient of the sample, but also on the characteristic to be measured (for example, the dichroic character of the bands). These various procedures can be grouped as follows: deposition on a disc transparent to electromagnetic radiation; self supporting films; and embedding the powder in a solid or liquid transparent to radiation. To decrease loss of light for reasons other than absorption, the particle size should be reduced to a value smaller than the wavelength of the radiation. Also, the embedding medium should have a refractive index near that of the sample in the desired spectral range.

When oriented deposits are used to study the dichroic character of the i.r. bands, the second condition cannot always be satisfied. In this case, the matrix is air with a refractive index of one. Because of anomalous dispersion (i.e. the change of the refractive index of the sample near the absorption bands, see Fig. 1) the sample and matrix refractive indices are equal only for certain values of the wavelength (λ). Between these values of λ , varia-

tion of the refractive index can induce great variations in optical properties of the sample, which result in an increase of light lost other than by absorption. Some aspects of the variability of powder transmittance with λ have been studied previously (Henry, 1948). In particular, the Christiansen effect is the increase of the crystalline powder transmittance at those wavelengths where the sample and matrix refractive indices are equal.

The purpose of this paper is to study the changes, with respect to λ , in transmittance of powders embedded in various matrices, absorption being neglected. The essential features of the Christiansen effect will be reviewed and its existence demonstrated in the case of powdered talc. The influence of the Christiansen effect on the profile, intensity and position of the i.r. absorption bands will then be discussed. The paper will conclude with precautions to be taken in sample preparation and the quantitative and qualitative interpretation of spectra.

MATERIALS AND METHODS

Two size fractions of talc were used. The first, $<50\ \mu\text{m}$, was obtained by sieving; the second, $<2\ \mu\text{m}$, by sedimentation. The spectra of talc were

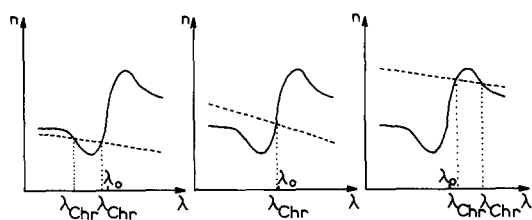


Fig. 1. Schematic representation of the relative variations of the anomalous dispersion curve of sample in the neighborhood of an absorption band (solid line) and of the dispersion curve of the matrix (dotted line). The three figures correspond to matrices with different dispersion curves.

obtained by the pellet technique with KBr, CsBr, and CsI in a 1:50 weight ratio. A thin oriented deposit on a CaF₂ window, prepared by evaporation of a talc suspension in CCl₄, was used to obtain the talc spectrum in an air matrix. The transmission peak (Christiansen peak) increases in intensity with the angle between the normal to the window and the i.r. beam direction. Change of this angle permits observation of the dichroic character of the absorption band due to talc hydroxyl groups. The spectrum marked "air" in Fig. 2 corresponds to an angle of 45°. Spectra of talc suspended in different solvents were obtained in a liquid cell of variable

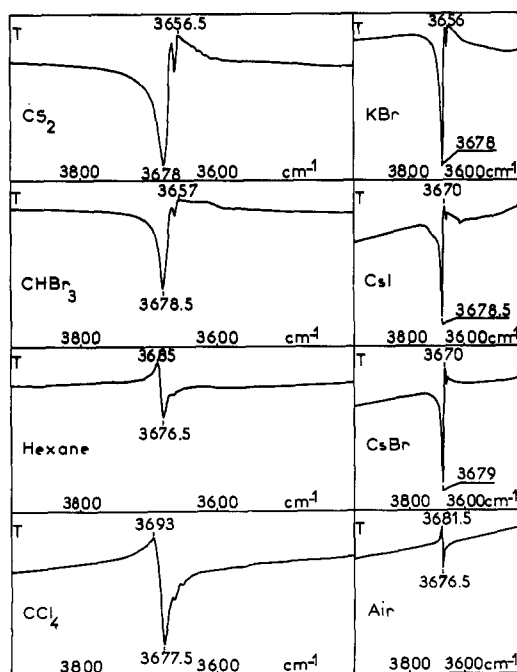


Fig. 2. I.R. spectra of talc powder (grain size $<50\mu\text{m}$) in different matrices.

thickness maintained at 20°C. The cell thickness was minimum, and an identical cell filled with solvent was put in the reference beam.

Recordings were made with a Beckman I.R. 12 spectrophotometer.

THEORY

A Christiansen filter is made of powder embedded in a matrix, which can be another solid, a liquid or air. At certain values of λ , termed the Christiansen wavelengths (λ_{Chr} , see Fig. 1), the dispersion curve of the solid intersects that of the matrix, the system becomes optically homogeneous, and thus has a greater ability to transmit electromagnetic radiation. The transmittance increase at λ_{Chr} is called the Christiansen peak. The characteristics of this peak follow.

(a) *Position.* According to the relative changes of the matrix and sample dispersion curves, there are one or two values of λ (λ_{Chr}) for which the refractive indices of sample and matrix are equal. In the three cases shown in Fig. 1, one value is near the maximum absorption wavelength (λ_0). This situation makes the observation of a transmittance increase very difficult. On the other hand, the Christiansen peak can be observed easily at other λ_{Chr} on either side of the absorption maximum.

(b) *Width at half-maximum* ($\Delta\nu_{1/2}$, where ν designates cm^{-1}). Experimental observations show that $\Delta\nu_{1/2}$ becomes greater as the following properties become smaller: the angle between the tangents of the dispersion curves of sample and matrix at λ_{Chr} , particle size, concentration of particles, and the filter thickness.

Clarke (1968) suggests the following formula for the fractional bandwidth between the half power points (in decibels) of the Christiansen peak:

$$\frac{[\Delta\lambda]}{\lambda_c} 3\text{dB} = \left[\frac{2.77}{K}\right]^{1/2} \cdot \left[\frac{1}{CL\alpha}\right]^{1/2} \cdot \frac{1}{\Delta n'} \quad (1)$$

where:

C = volume concentration
 L = length of Christiansen cell
 α = average particle radius

$$\Delta n' = \frac{d}{d\lambda} (n_{\text{liquid}} - n_{\text{particles}})$$

rate of change with wavelength of the differential refractive index.

λ_c = Christiansen wavelength
 $\Delta\lambda$ = shift in wavelength from λ_c
 K = constant

(c) *Intensity.* Accurate information on the Christiansen peak intensity is not available; however, Barnes and Bonner (1936) found that the intensity depends on the quantity of light lost by reflection, refraction or diffusion.

In summary, the transmittance is modified, particularly at λ_{Chr} , by the change of the solid refractive index in the neighborhood of the absorption band. Under these conditions it may not be valid to assume that the base line of absorption bands are always straight lines, which poses a problem in quantitative use of spectra. Therefore, it is necessary to recognize this effect and, if it exists, to choose experimental conditions for which the effect does not disturb the interpretation of spectra.

DEMONSTRATION OF THE OCCURRENCE OF CHRISTIANSEN EFFECT. APPROXIMATION OF THE ANOMALOUS DISPERSION CURVE OF TALC NEAR THE STRETCHING OF LATTICE HYDROXYL GROUPS

The most reliable means of verifying the occurrence of a Christiansen peak is to use matrices of distinct refractive index since λ_{Chr} must change. We have used this technique in the case of talc.

Figure 2 shows the hydroxyl stretching band of talc particles, with a diameter less than $50 \mu\text{m}$, mixed with matrices of different refractive indices. The spectrum consists of two bands located near 3662 cm^{-1} and 3678 cm^{-1} . Assignment of these bands was made by Vedder (1964) on the basis of random distribution of Fe^{2+} ions in octahedral sites. The 3678 cm^{-1} band corresponds to hydroxyl groups bound to three Mg^{2+} ions (Mg^{2+} , Mg^{2+} , Mg^{2+}) and the 3662 cm^{-1} band to hydroxyl groups bound to two Mg^{2+} ions and one Fe^{2+} ion (Mg^{2+} , Mg^{2+} , Fe^{2+}). Because the talc contains little iron, bands corresponding the other possible configurations (Mg^{2+} , Fe^{2+} , Fe^{2+} and Fe^{2+} , Fe^{2+} , Fe^{2+}) are not visible.

On each spectrum in Fig. 2 a transmission peak is located at the base of the absorption band. Also, the transmission maximum shifts from one to the other side of the absorption band, according to the refractive index of the matrix. This shift indicates the occurrence of the Christiansen effect. Thus, when a transmission peak alters the profile of an absorption band the occurrence of the Christiansen effect can be verified by use of several matrices with different refractive indices.

We have utilized the index equality property of the Christiansen peak in order to determine some points of the anomalous dispersion curve of talc near 3680 cm^{-1} . It is sufficient to know the matrix refractive index at λ_{Chr} in order to deduce immediately the refractive index of the sample at the

same wavelength. We have assumed that the apparent maximum of the Christiansen peak corresponds to the λ_{Chr} which is the most distant from λ_0 (Fig. 1). For spectra of talc embedded in a matrix, the refractive index of which is lower than that of talc outside of the absorption band, the Christiansen peak is located on the high frequency side; there is thus no ambiguity for the λ_{Chr} determination. On the other hand, for a matrix of refractive index greater than talc, the determination of λ_{Chr} is more difficult because of the existence of the 3662 cm^{-1} band. In all cases we have assumed that λ_{Chr} falls within the position of the transmission maximum. The values of λ_{Chr} have been assembled in Table 1.

Table 1.

Nature of the matrix M	λ_{Chr} (cm^{-1})	Refractive index of M at 20°C and for λ_{Chr}
CsI	3670	1.744
CsBr	3670	1.686
KBr	3656	1.537
CHBr_3	3657	1.563
CS_2	3656.5	1.580
CCl_4	3693	1.444
CH_2Cl_2	3688	1.402
Hexane	3685	1.354
Air	3681.5	1

The refractive indices of the matrices have been taken from the literature. From these results we can then determine some points of the anomalous dispersion curve of talc (Fig. 3). Although not very accurate, (as pointed out by Lecomte, 1962) this technique is the only one which can be used in the case of powders.

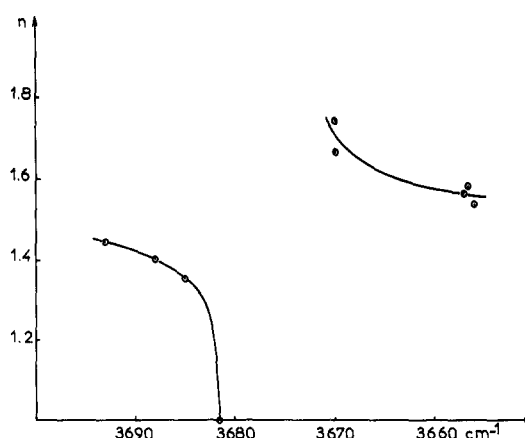


Fig. 3. Anomalous dispersion curve of talc in the neighborhood of the hydroxyl groups stretching of the mineral (3678 cm^{-1}).

PRACTICAL CONSEQUENCES OF THE CHRISTIANSEN EFFECT

The most visible manifestations of the Christiansen effect are the change of the absorption band profile and a significant shift of its maximum frequency. In the talc case, the shift is small because the band is narrow. The question of band profile comes up only if we try to resolve the components of more complex absorption features. In fact, it is the base line rather than the absorption band which is altered. The base line is formed by transmission peaks which appear at each value of λ equal to λ_{chr} . Thus, when the matrix dispersion curve intersects the anomalous dispersion curve of the sample at two different frequencies there are two Christiansen peaks. The characteristics of these peaks are significant, but due to the difficulty of exact determination we can only indicate the direction of change of each. One principally discusses the width at half-maximum on the basis of the Clarke's (1968) formula.

The spectra of Fig. 2 show that the Christiansen peak becomes narrower as λ_{chr} approaches the absorption maximum. Comparison of the spectra of talc in KBr and talc deposited on a CaF_2 window illustrates this point. It is a consequence of the $\Delta n'$ variation which is much greater when the matrix is air than when it is KBr. This fact has been pointed out previously by several authors (Denmark and Cady, 1935; Barnes and Bonner, 1936; Jeramec, 1958).

Another parameter previously considered by other workers is the size of the particles (α). Such a consideration is essential for the realization of good Christiansen filters (Denmark and Cady, 1935). Jeramec (1958) obtained a good Christiansen filter with particles which had a size equal to ten times λ_{chr} . Nevertheless, theory predicts that the Christiansen effect exists even when the relationship between particle size and λ_{chr} is not fulfilled, and, in particular, even when the particle size becomes smaller than λ_{chr} . In order to confirm this prediction we prepared pellets of talc powder with particles $< 2 \mu\text{m}$, in KBr, CsBr and CsI. Figure 4 gives absorbance spectra.

A distinct dissymmetry of the absorption band is observed in every case. Nevertheless, λ_{chr} is difficult to locate because of the increase of $\Delta\nu_{1/2}$ of the Christiansen peak. This change of $\Delta\nu_{1/2}$ with particle size is not new. Denmark and Cady (1935) have studied the effect in a systematic way and show a significant increase of $\Delta\nu_{1/2}$ with a decrease of particle size. However, these authors used larger particles ($170 \mu\text{m}$) than those examined in this study.

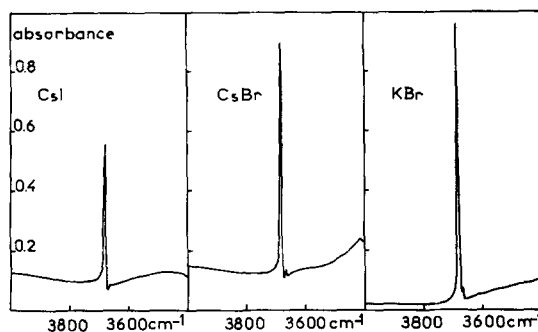


Fig. 4. I.R. spectra of talc powder (grain size $< 2 \mu\text{m}$) in different matrices.

Nevertheless, $\Delta\nu_{1/2}$ increases rapidly as particle size decreases. Welber (1967), using MgO particles with an average diameter of $1 \mu\text{m}$, obtained spectra with a width at half maximum of several hundred wavenumbers (cm^{-1}). These conditions are encountered in the study of clays by i.r. spectroscopy.

Thus, the Christiansen effect does not disappear when the particle size becomes lower than λ_{chr} , but $\Delta\nu_{1/2}$ of the Christiansen peak increases, which reduces the dissymmetry of the absorption band. Thus, if $\Delta\nu_{1/2}$ is several times greater for the Christiansen peak than for the absorption band, there would be only a small deformation of the base line.

If we consider Clarke's (1968) formula for $\Delta\nu_{1/2}$ we see that the thickness of the Christiansen filter (L) has the same influence as the particle size (α). From a practical standpoint this observation is important, because it is not always possible to diminish the particle size sufficiently. To investigate this point, we have examined talc deposits, of different thickness, in the 1265 cm^{-1} spectral range, where the dispersion curve of talc intersects the dispersion curve of air. Fig. 5 presents spectra obtained from deposits of talc particles of 50 and $2 \mu\text{m}$ dia. on 35 mm dia. CaF_2 windows.

The weight of the deposit is given for each spectrum. It is apparent that, for a given particle size, it is not possible to study i.r. bands in the $2000\text{--}4000 \text{ cm}^{-1}$ range if the deposit is too thick. This lack of transmission is due to scattering. For this reason one must use a very thin deposit to obtain spectra of hydroxyl groups in air.

Thus, we can check at least qualitatively all the parameters in Clarke's (1968) formula. In the preparation of powder samples for spectroscopy, it is important from a practical point of view to choose parameters so that $\Delta\nu_{1/2}$ is as large as possible without significant alteration of the sample, since Farmer (1957) has pointed out that grinding may result in difficulty.

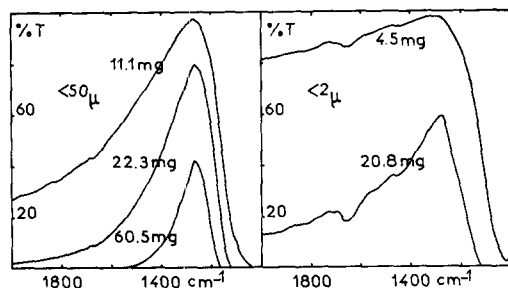


Fig. 5. I.R. spectra of talc powder deposits of increasing thickness (L) on CaF_2 window (dia. 35 mm). Total deposit weight is noted on each curve. The experiment was made with particles of two different sizes:

a — $< 50 \mu\text{m}$
 b — $< 2 \mu\text{m}$

Recordings of Figs. a and b were made without changing the adjustment of the apparatus.

CONCLUSION

The Christiansen effect plays an important part in i.r. spectroscopy of powders. It is essential in the interpretation of spectra to know if this effect is present. We suggest the simple method of taking spectra of the sample embedded in different matrices of distinct refractive indices. If the effect exists, change in the position of the transmission maximum or alteration of the profile of the absorption band will be observed. These points have been illustrated by the spectrum for talc.

Also, the Christiansen effect can be used to determine the refractive index of the sample near an i.r. absorption band. This method was used to determine some points of the anomalous dispersion curve of talc near the stretching band of the structural hydroxyl groups.

The Christiansen effect can be a source of error in quantitative analysis of spectra. Thus, band dissymmetry and shifts of the absorption maximum interfere with the measurement of integrated intensity, since the transmission becomes a function of the matrix and of all parameters which modify the Christiansen peak. Thus, precautions are necessary in the determination of extinction coefficients of i.r. absorption bands of powders.

Moreover, the alteration of band shape results in most cases from superposition on the absorption band of two Christiansen peaks with different parameters due to the change of $\Delta n'$ with λ . Thus, in order to decrease the consequences which result from the occurrence of these two Christiansen peaks, the sample characteristics can be modified to increase the width at half-maximum of Christiansen peaks. Clarke's theoretical formula, which gives an estimation of $\Delta \nu_{1/2}$, is an appropriate guide in the

choice of the parameters which can be optimized during the sample preparation. Since $\Delta n'$ is always important for the Christiansen peak near λ_0 , it is not appropriate to change this parameter.

The choice of a matrix with a refractive index near that of the sample outside of the absorption band changes the width at half-maximum of that Christiansen peak which is on the side of the band only, and also decreases scattering losses on both sides of the band.

Since the alteration of the profile of the absorption bands is important only on one side of the band, we can choose a matrix which transfers the Christiansen effect to the other side. The determination of the exact position of the low frequency band of talc would be a case in point.

Because of the little change in the position of the band with the matrix used in taking i.r. spectra, it is important to specify its nature.

Finally, in order to diminish scattering, it is possible in some particular cases to choose characteristics of the Christiansen filter, made of the solid embedded in a matrix, in such a way to have a Christiansen peak with a large width at half-maximum in the studied spectral range.

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Résumé—L'effet Christiansen se manifeste sur le spectre d'absorption infrarouge des poudres mélangées à une matrice qui peut être un solide, un liquide ou l'air, par une transmission plus importante (pic de Christiansen) des radiations électromagnétiques incidentes. Cet effet apparaît aux longueurs d'onde pour lesquelles l'indice de l'échantillon et l'indice de la matrice sont égaux (longueur d'onde de Christiansen: λ_{chr}).

A cause de la très grande variation de l'indice de réfraction de l'échantillon au voisinage immédiat des bandes d'absorption (courbe de dispersion anormale) on note fréquemment la présence, dans cette région du spectre, d'un pic de transmission ou d'une déformation de la bande. Si la position de ce pic de transmission change avec la valeur de l'indice de réfraction de la matrice il s'agit alors d'effet Christiansen.

L'égalité des indices de réfraction de l'échantillon et de la matrice pour λ_{chr} a été utilisée pour déterminer quelques points de la courbe de dispersion anormale du talc au voisinage de la bande de vibration de valence des hydroxyles (3678 cm^{-1}).

On analyse ensuite les perturbations apportées par l'effet Christiansen sur le profil, la position et l'intensité des bandes d'absorption. Un moyen de réduire ces inconvénients consiste à préparer l'échantillon de telle sorte que la largeur à mi-hauteur ($\Delta\nu_{\frac{1}{2}}$) du pic de Christiansen soit plusieurs fois supérieure à celle de la bande d'absorption elle-même. La formule théorique de Clarke qui donne une estimation de $\Delta\nu_{\frac{1}{2}}$, et dont on ne propose qu'une vérification qualitative, constitue un guide approprié dans le choix des grandeurs sur lesquelles nous pouvons agir lors de la préparation des échantillons. On peut ainsi réduire les inconvénients inhérents à l'existence de l'effet Christiansen, sans courir le risque d'altérer l'échantillon lui-même, en particulier par un broyage trop poussé.

Kurzreferat—Der Christianseneffekt tritt in Infrarotspektren von Pulvern, die in fester, flüssiger oder gasförmiger Matrix eingebettet sind, als eine offensichtlich anomale Durchlässigkeit (Christiansenpeak) der einfallenden elektromagnetischen Strahlung in Erscheinung. Der Peak tritt bei Wellenlängen auf, für welche die Brechungsindizes der Probe und der Matrix gleich sind (Christiansen-Wellenlänge: λ_{chr}).

Infolge der großen Veränderung des Brechungsindex der Probe in unmittelbarer Nachbarschaft der Absorptionsbande (anomale Dispersionskurve) beobachtet man oft das Auftreten eines Durchlässigkeitsmaximums oder einer Bandendeformation in diesem Spektralbereich. Ein Wechsel in der Lage dieses Durchlässigkeitsmaximums mit der Größe des Brechungsindex der Matrix ist ein Anzeichen für den Christianseneffekt.

Die Gleichheit der Brechungsindizes von Probe und Matrix für λ_{chr} ist benutzt worden, um einige Punkte der anomalen Dispersionskurve in der Nachbarschaft der Hydroxylvalenzschwingungsbande (3678 cm^{-1}) zu bestimmen.

Durch den Christianseneffekt hervorgerufene Verzerrungen des Spektrums können vermindert werden, wenn die Probe so präpariert wird, daß die Breite des Christiansen-peaks in halber Höhe des Maximums ($\Delta\nu_{1/2}$) um das Mehrfache größer ist als die der Absorptionsbande selbst. Clarke's theoretische Formel, die einen Schätzwert für $\Delta\nu_{1/2}$ ergibt, wurde qualitativ bestätigt und stellt somit ein geeignetes Hilfsmittel für die Wahl der Parameter dar, die bei der Probenherstellung optimiert werden können. Die Veränderungen des Spektrums durch den Christianseneffekt können vermindert werden, ohne daß die Gefahr einer Veränderung der Probe selbstinsbesondere durch übermäßig scharfes Mahlen besteht.

Резюме—Эффект Кристиансена проявляется на инфракрасном спектре порошков внедренных в землю, жидкости или матрице воздуха очевидно в виде аномального пропускания (пик Кристиансена) падающей электромагнитной радиации. Пик появляется на длине волны для которой показатель преломления образца и показатель преломления матрицы равны (Длина волны Кристиансена: λ_{chr}).

В виду большой вариации в показателе преломления образца вблизи полосы поглощения (аномальная кривая дисперсии), часто замечается появление пика коэффициента пропускания или деформации полосы в этой области спектра. Изменение положения этого пика передачи вместе с величиной показателя преломления матрицы являются показателями эффекта Кристиансена.

Равенство показателей преломления образца и матрицы λ_{chr} применялось для определения некоторых точек аномальной кривой дисперсии по соседству с полосой распространения гидроксила (3678 см^{-1}).

Спектральное искажение вызванное эффектом Кристиансена можно уменьшить подготовкой образца таким образом, чтобы ширина полу максимума ($\Delta\nu_{\frac{1}{2}}$) пика Кристиансена была бы на несколько раз больше, чем полоса поглощения. Теоретическая формула Кларка дающая оценку в $\Delta\nu_{\frac{1}{2}}$ была качественно проверена и таким образом был найден подходящий критерий в выборе параметров, которые можно довести до оптимума при подготовке образца. Посредством жесткого помола можно уменьшить эффект Кристиансена на спектральные изменения без риска изменения самого образца.