

ARRAY BASIC – A POWERFUL SPECTROSCOPIC TOOL. LOTO : AN APPLICATION FOR SPECULAR REFLECTION SPECTROSCOPY

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To take full advantage of the specular reflection spectroscopy, one has to extract the information contained in the reflection spectrum. The first step is the calculation of the real (n) and imaginary (k) part of the complex refraction index. This task is usually completed employing the Kramers-Krönig approximation/transformation [1]. In the case of crystalline solids, the knowledge of the dielectric constant (ϵ') and dielectric loss (ϵ'') as well as of conductivity (σ) and resistivity (ρ) is often important. The spectral variations of the last two quantities may, at the same time, serve as a source for determination of the transversal and longitudinal optical phonon frequencies in the solid. A short computer program (*LOTO*) is presented in this contribution. The program is written in Array Basic and enables both fast and accurate calculation of all desired parameters.

Key words: specular reflection; FT-IR spectroscopy; calculation of dielectric parameters; complex refraction index; absorption index; LO-phonons; TO-phonons

INTRODUCTION

The basic principles of specular reflection spectroscopy have been known for quite a long time [1, 2]. Despite this, the use of conventional grating instruments was severally limited to favourable cases, in which the sample had enough high reflectivity, resulting in spectra with acceptable signal-to-noise ratios [3–5]. However, recording the spectrum is still the easy part of the job. In order to extract valuable information (e.g. the real – n and imaginary – k parts of the complex refraction index), the reflection spectrum has to be transformed. The Kramers-Krönig approximation is usually employed for that matter [1, 6]. This transformation has the form:

$$\theta(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{\log \sqrt{R(\omega')}}{\omega'^2 - \omega^2} d\omega' \quad (1)$$

and recalling that the reflectivity is a $R = R(\omega)$, enables the phase $\theta(\omega)$ to be calculated as a function of the angular frequency, ω . Then n and k may further be calculated:

$$n = \frac{1 - R}{1 + 2\sqrt{R} \cos \theta + R}; \quad (2)$$

$$k = \frac{-2\sqrt{R} \sin \theta}{1 + 2\sqrt{R} \cos \theta + R}$$

as well as the absorption spectrum of the sample :

$$I(z) = I(0) e^{-\alpha z} \quad (3)$$

where $\alpha = \frac{2\omega k}{c}$.

Unless the spectrometer is coupled to a computer, this is an extremely tedious (if not impossible) job, since the spectrum has to be digitized 'by hand', thus introducing large additional noise-like errors.

All features of reflection spectroscopy come true when FT interferometers are used. The principal advantage of these instruments (apart from being fully computerized) is the throughout advantage [7], resulting in excellent signal-to-noise ratios even with single scans. In addition, powerful software packages for various calculations and spectra manipulations are available.

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One of these packages is GRAMS/386 [8]. The collection of programs for this package is written in a special computer language, called Array Basic [9]. This is purpose-designed language, close to ordinary BASIC, but with extremely efficient assembly-coded routines implemented for fast manipulation with spectra (traces, as they are called) as a whole. A program for the Kramers-Krönig transformation is also available for this package and the user may enjoy seeing the effect of the Fast Fourier Transformation (FFT) applied to generate the n and k values in the whole spectral range (up to 10000 cm^{-1}) within few seconds!

In solid state spectroscopy, however, one might be principally concerned about the frequencies of transversal and longitudinal phonons (ν_{TO} and ν_{LO}), the origin of which lies in the long-range electrostatic

forces [1, 2]. Alternatively, if dealing with thin (semi-)conductor films, the knowledge of the dielectric constant (ϵ') and loss (ϵ'') becomes important. None of these quantities could be calculated with either GRAMS/386 or with other software packages available to us. The purpose of this contribution is to fill-in this gap.

Some minor comments, concerning Array Basic programming: each spectrum (*i.e.* each trace) is in one of the 30 available file slots. Slot is, in fact, a data-base that has been (or is to be) opened for use, but for simplicity one may visualise it as a box. File slots are numbered and resemble a stack, in the way they are organized. The most recently opened/loaded trace occupies slot #1, all other being pushed upwards. Traces are subject to all standard mathematical operations, much in the same way as are scalar numbers.

THE COMPUTER PROGRAM

The dielectric constant $\epsilon'(\nu)$ and loss $\epsilon''(\nu)$ are, in fact, the real and imaginary part of the complex permittivity $\epsilon^*(\nu)$:

$$\epsilon^*(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) \quad (4)$$

and may be calculated in the following way:

$$\epsilon'(\nu) = n(\nu)^2 - k(\nu)^2 \quad (5)$$

$$\epsilon''(\nu) = 2n(\nu) \cdot k(\nu) \quad (6)$$

providing $n(\nu)$ and $k(\nu)$ are known.

The ν_{TO} and ν_{LO} frequencies are equal [5] to the frequencies of the peaks in the 'spectra' of the conductivity $\sigma = \sigma(\nu)$ and resistivity $\rho = \rho(\nu)$. These last two quantities may be calculated as follows [5]:

$$\sigma(\nu) = \nu \epsilon''(\nu)/2 \quad (7)$$

$$\rho(\nu) = 2\epsilon''(\nu)/\{\nu[\epsilon'(\nu)^2 + \epsilon''(\nu)^2]\} \quad (8)$$

(The definitions are in line with the CGS rather than with the International System of units. This is, however, of no significance since the only difference in the spectra will appear in a form of a constant multiplier. The important information is contained in the *peak frequencies* and these are the same, no matter what system of units is chosen. It should be noted that other

methods for calculation of the LO and TO frequencies also exist [3]).

The first step is, obviously, to calculate $n(\nu)$ and $k(\nu)$. This is accomplished using an Array Basic program for the Kramers-Krönig transformation, within the GRAMS/386 package. As mentioned, the FFT method is surprisingly fast, but the alternative McLaurine method, although time-consuming, is more accurate and should be preferred for this task.

It is certainly possible to calculate the four unknowns, using standard programming languages (Pascal, FORTRAN, BASIC *etc.*), but it is instructive to complete the job in Array Basic. Several reasons led us to conclude that this is most probably the best possible choice. The clear advantages are:

- No need for format import/export manipulations of the spectra (the GRAMS/386 spectra files are in binary format, readable by Array Basic).
- Extra fast manipulation with traces as a whole.
- Accurate results.
- No need for use of loops.
- Fairly short and understandable program.
- Compatibility with other programs, available for GRAMS/386.

RESULTS

The results of the calculation are summarized in the spectra presented in two figures. The first figure contains the original reflection spectrum and data obtained by standard Kramers-Krönig transformation. The other one presents the calculated dielectric constant, loss, conductivity and resistivity. The quality of the results depend solely on the quality of the reflection

spectrum (hence, it is strongly recommended that a number of spectra be acquired).

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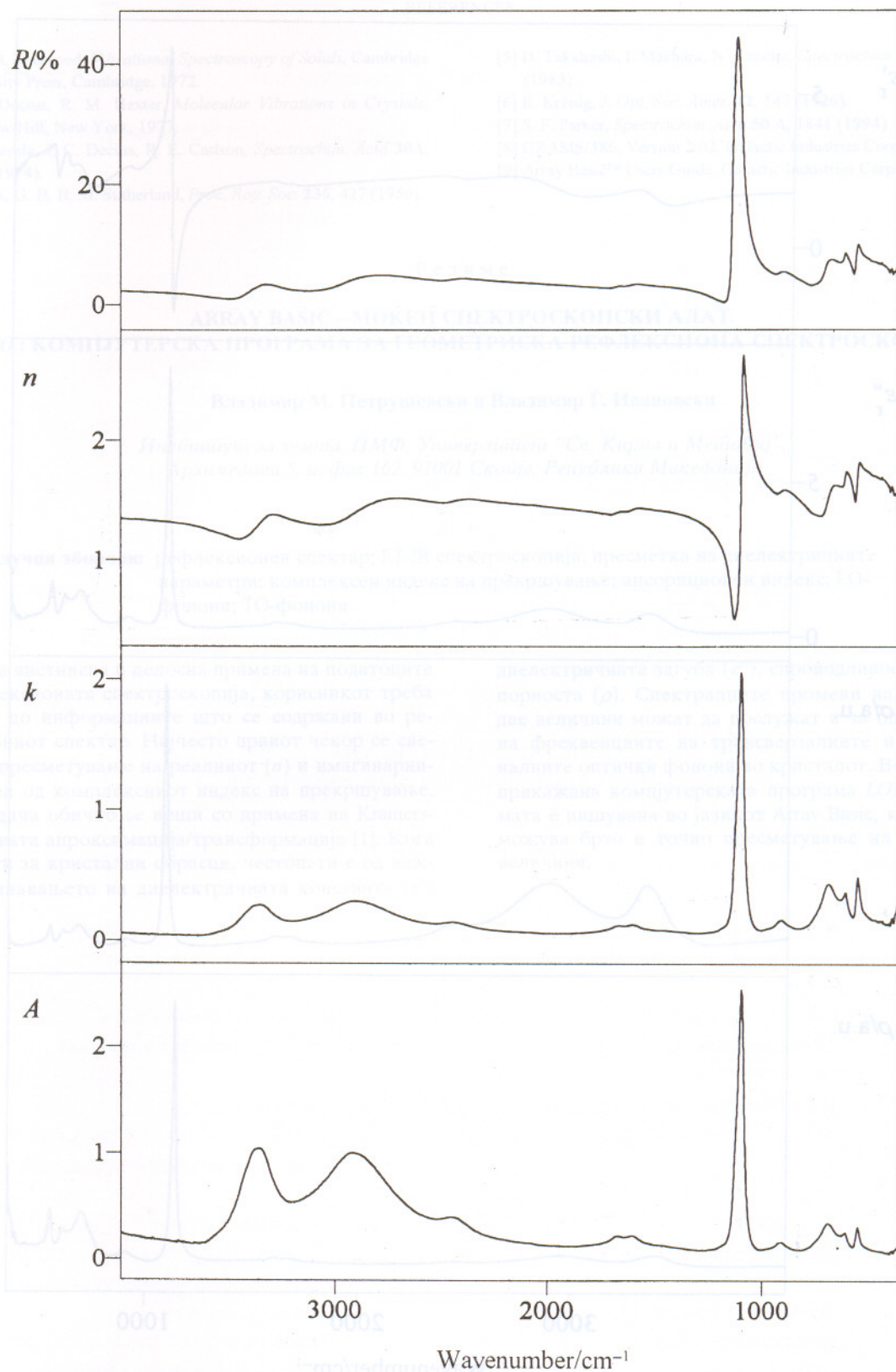


Fig. 1. Top to bottom: reflectivity (R), refraction index (n), absorption index (k) and absorbance (A) of $\text{RbCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ as a function of the radiation wavenumber. Reflectivity spectrum measured on a Perkin Elmer System 2000 FT-IR instrument, using a specular reflectance accessory; n , k , and A calculated by means of Kramers-Krönig transformation

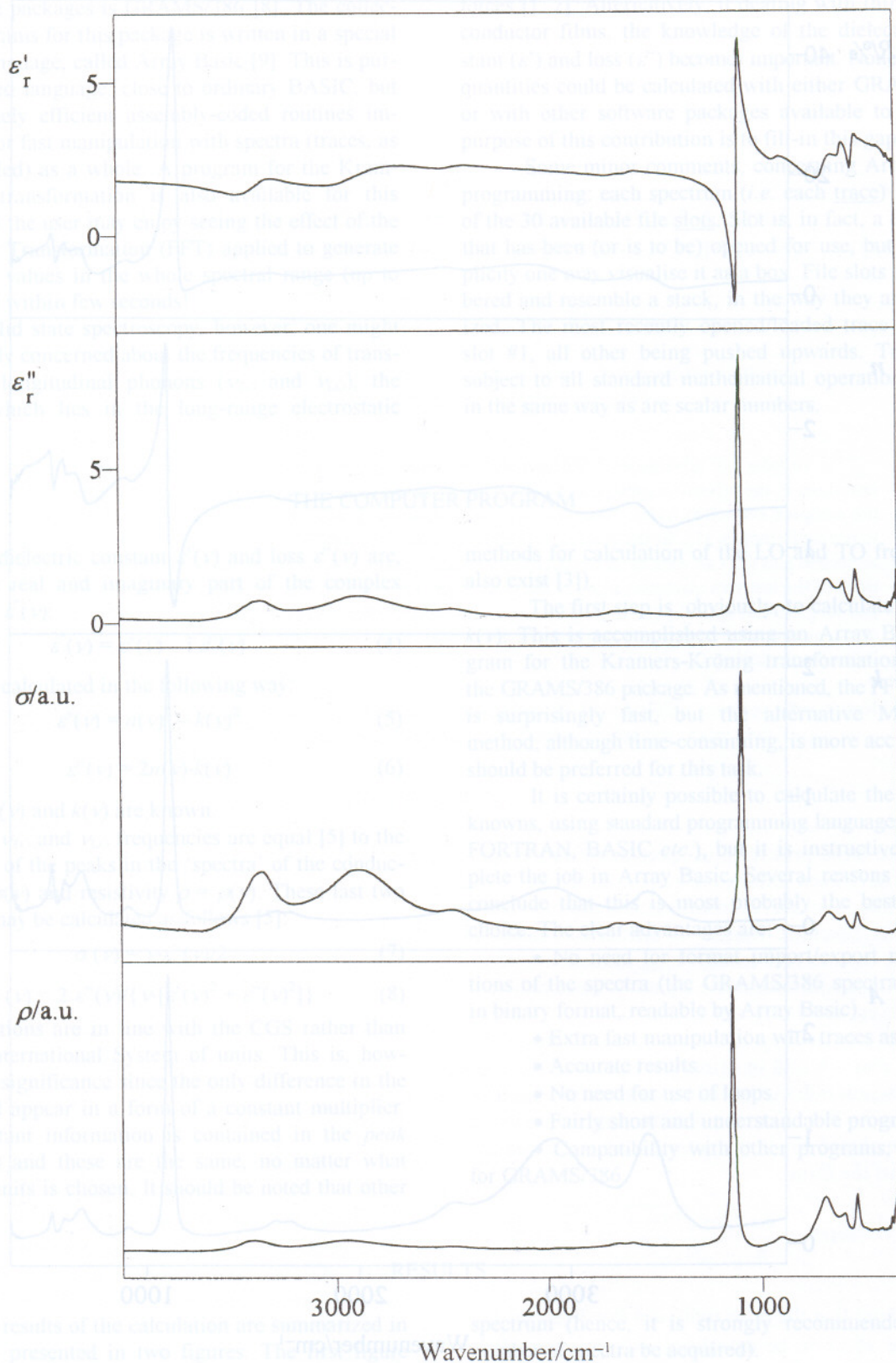


Fig. 2. Top to bottom: permittivity (ϵ_r'), dielectric loss (ϵ_r'') (relative values), conductivity (σ) and resistivity (ρ) (in arbitrary units) as a function of the radiation wavenumber. All quantities calculated by the program are presented in the paper

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Резиме

ARRAY BASIC – МОЌЕН СПЕКТРОСКОПСКИ АЛАТ.

LOTO: КОМПЈУТЕРСКА ПРОГРАМА ЗА ГЕОМЕТРИСКА РЕФЛЕКСИОНА СПЕКТРОСКОПИЈА

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Клучни зборови: рефлексивен спектар; FT-IR спектроскопија; пресметка на диелектричните параметри; комплексен индекс на прекршување; апсорпционен индекс; LO-фонони; TO-фонони

За вистинска и целосна примена на податоците од рефлексивната спектроскопија, корисникот треба да дојде до информациите што се содржани во рефлексивниот спектар. Најчесто првиот чекор се сведува на пресметување на реалниот (n) и имагинарниот (k) дел од комплексниот индекс на прекршување. Оваа задача обично се врши со примена на Kramers-Krönig-овата апроксимација/трансформација [1]. Кога се работи за кристални образци, честопати е од важност познавањето на диелектричната константа (ϵ')

диелектричната загуба (ϵ''), спроводливоста (σ) и отпорноста (ρ). Спектралните промени на последните две величини можат да послужат и за определување на фреквенциите на трансверзалните и лонгитудиналните оптички фонони во кристалот. Во работата е прикажана компјутерската програма LOTO. Програмата е пишувана во јазикот Array Basic, којшто овозможува брзо и точно пресметување на спомнатите величини.

	fillbeg ffp fillinc stp #s = fill(#s)	<ul style="list-style-type: none"> ‘ Make all y-coord. in the trace equal ‘ to the x-coord. In fact, this block ‘ generates $y = x$ function, for later use.
35	swapfile #1, #2	<ul style="list-style-type: none"> ‘ Interchange traces in file slots 1 and 2
37	menufile temp, "Select dir. and K-spectrum" onerror 70 : loadspc \$temp : onerror -1	<ul style="list-style-type: none"> ‘ Same as block 20
50	newspc epsil1.spc(np) #1 = squared(#3)-squared(#2) menufile temp, "Select name for Epsilon" savespc \$temp	<ul style="list-style-type: none"> ‘ Dielectric constant – real part, ‘ defined according to equation (5). ‘ Select a file name for the trace and ‘ save it to disk
55	newspc epsil2.spc(np) #1 = #4*#3*2 menufile temp, "Select name for Epsilon" savespc \$temp	<ul style="list-style-type: none"> ‘ Dielectric loss – imaginary part, ‘ defined according to equation (6). ‘ Same as end of previous block
60	newspc sumsquar.spc(np) #1 = squared(#3)+squared(#2) newspc sigma.spc(np) #1 = #7*#3/2 menufile temp, "Select file name for Sigma" savespc \$temp	<ul style="list-style-type: none"> ‘ Sum of squares, calculated according ‘ to equation (8), to be used later. ‘ Electr. conductivity function, ‘ defined according to equation (7). ‘ Same as end of previous block
65	newspc rho.spc(np) #1 = #4/#8/#3*2 menufile temp, "Select name for Rho" savespc \$temp	<ul style="list-style-type: none"> ‘ Electr. resistivity function, ‘ defined according to equation (8). ‘ Same as end of previous block
67	end	<ul style="list-style-type: none"> ‘ Terminate program
70	beep : dialogon "ERROR!" print "File ",\$temp;" bad or does not exist." print " " dialogoff goto 10	<ul style="list-style-type: none"> ‘ Error-trapping routine. Print ‘ some information for the user, ‘ and jump to program start