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HADAMARD SPECTROMETRY FOR THERMOLUMINESCENCE INVESTIGATIONS

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A Hadamard encoded spectrometer with a special variable interference filter allows attaining high throughput and sensitivity. In our instrument the interference filter is fixed between condenser lenses. The transmitted wavelength changes continuously along the length of the filter. The multislit cyclic Hadamard mask moves step by step behind the filter to multiplex signal. Some details concerning the data recording, handling and decoding are specific for this technique of investigation of thermoluminescence spectrum.

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1. Introduction

The ability to trap some of excess carriers excited by an external source of radiation enables energy to be preserved in a metastable state. An evolution of the intensity of thermoluminescence (TL) emission is determined by the complex kinetic processes of thermal release, retrapping and radiant recombination of excess carriers. As a rule, TL is always related to the increase of temperature of investigated sample. After excitation, the increase of temperature strongly enhances the process of trap emptying, thus stimulating TL. A competition between the increasing probability of release from the trap and the depletion of filled traps and luminescence centres causes a temporary character of TL.

Each sort of trap and eventually associated recombination centre are related to their own kinetic process and to a constituent peak of a glow curve. An evolution of the spectrum of TL emission supplies infromation about the type of the active recombination centres and provides fundamental details necessary for the formation of the kinetic band model. Unfortunately, the sum of TL emission is limited and comparatively low. For example, during TL ZnSe crystal excited up to saturation in 80 K emits about 10^{13} photon/cm^3. Moreover, total light intensity and spectrum depend on time. For these reasons thermoluminescence spectrometry has specific requirements [1].

In general, two fundamental methods of spectrometry are used in TL investigations. When a monochromator is used, the entire spectrum is recorded by scanning the dispersion element. An exit slit positioned in a focus plane of spectrum selects a small portion of dispersed radiation for detection. Since only the rays of determined wavelength and bandwidth pass through the monochromator for measurements and the other are absorbed, this method, applied to the phenomenon with the limited sum of light, is extremely wasteful [2–5]. The same effect is obtained when a filter composition or continuous interference filter is used [6, 7].

In the second case, a multichannel or multidetector technique is applied. For any of several types of photodetector devices (e.g. photodiode array, vidicon, image intensifier and also photography plate) the sensitive element spreads over an area of spectrum. The spectrum corresponding to all slit positions is now monitored at once [8–11].

2. Multislit spectroscopy

A multiplexed spectrometer contains only one photodetector, but the radiation, which is allowed to impinge at the same time upon a detector, arises from many different parts of the dispersed spectrum. The manner of light mixing is controlled by an array of narrow equidistant, opened or closed slits. This multislit array forms a binary {0,1} encoding mask usually placed in the exit (or at entrance) of the focal plane of a conventional spectrometer. The beam intensity incident on detector is measured for many different configurations of mask patterns. Each mask pattern selects a group of data corresponding to the spectral density of open elements. All selected data are summed up by one detector. This way, the chosen set of spectral data goes through an encoding multiplex transformation.

The total intensity measured at the detector y_i can be written as a sum of the spectral densities x_j weighted by a binary factor a_{ij}

$$y_i = \sum_{j}^{n} a_{ij} x_j, \tag{1}$$

where $i = 1, 2, \ldots N$ are the pattern numbers and $j = 1, 2, \ldots n$ numbers of the positions of spectral elements. The coefficients a_{ij} are either 0 or 1 and correspond to attenuation or transmission.

A proper arrangement of N different masks gives for $n = N$ a desired set of linearly independent equations which allows the calculation of spectral densities x_j

$$x_j = \sum_{i}^{n} b_{ij} y_i, \tag{2}$$

where b_{ij} are coefficients of the inverse matrix.

A deep theoretical analysis performed mainly in the late 1960's was able to give solutions for several additional questions determining a possibility of wide application of the encoded multiplexing to spectrometry. The basic problems in designing this method are the following:

(a) For easy implementation, the matrix of a_{ij} coefficients is required to be cyclic. This property allows moving a mask step by step and tremendously simplifies the mask structure. Instead of n separated masks, each one with different configuration of n elements (open or close slits), the one cyclic mask contains $2n-1$ elements.

(b) The choice of the optimum mask codes a_{ij} in order to minimize the influence detector noise on the final result and maximize the signal-to-noise ratio, must be performed. The proper concept to find a solution for this question is based on the theory of digital communications and is related to mathematics of Hadamard matrices. For this reason Decker and Harwit [12] call this new field Hadamard Transform Spectrometry.

(c) Cramer's formulas are not applicable for large set of linear equations (1) therefore a simple algorithm for calculation of spectral densities x_i is required.

The details of theoretical analysis are presented in several original papers [12–15], review articles (e.g. [16]) and monographs [17–20]. As it was finally shown by Nelson and Fredman [14] in 1970, the proper answers for all these questions lie in Hadamard simplex matrices typically abbreviated as S-matrices. Especially amazing is the simplicity of the decoding algorithm. For $n = N$ the coefficients a_{ij} are transformed to b_{ij} by the following relationships:

$$\text{if} \quad a_{ij} = 0 \quad \text{then} \quad b_{ij} = -1/m,$$

$$\text{if} \quad a_{ij} = 1 \quad \text{then} \quad b_{ij} = +1/m, \tag{3}$$

where

$$m = (n+1)/2. \tag{4}$$

In the Hadamard encoding mask for each configuration m slits are open at once and the measurements are repeated n times in order to complete the set of y_i values. This leads to the high signal-to-noise ratio of the multislit method. The ratio is $\sqrt{n}/2$ times higher than for the single-slit scanning.

3. Hadamard spectrometer

The main designing assumption of the presented Hadamard spectrometer is an application for measuring spectrally resolved TL. The following preliminary terms were determined:

a) One sequence of a spectrum measurement does not take more than one minute of time. Hence for a typical heating rate of the order of 0.1 Ks^{-1} one spectrum does not cover more than 10 K of increasing temperature.

b) The spectrometer should be compatibile with our already existing arrangements and technique of measurement which was previously described [21].

c) Taking into account the conflict between spectral resolution and brightness, the rather low resolution of 5 nm is assumed in exchange for high efficiency of light gathering and system compactness.

Due to the last reason the continuous interference filter (Zeiss Jena) with an additional blocking color glass layer is applied as a dispersion element for the wavelength range of spectrum from 400 to 765 nm. This filter is a rectangular plate

of 73 × 18 mm^2 size. The transmitted wavelength changes continuously along the length of the filter with the rate of 5 nm/mm. The active part of the filter is limited by a window of size 63 × 18 mm^2. The fixed filter positions allow choosing two ranges of spectrum, 400 to 715 nm and 450 to 765 nm. For cone and tilt angles of incident light not exceeding 15 degrees the resolution power is about 5 nm. The average peak transmittance is about 0.2.

Figure 1 shows the optical configuration of the Hadamard spectrometer. A

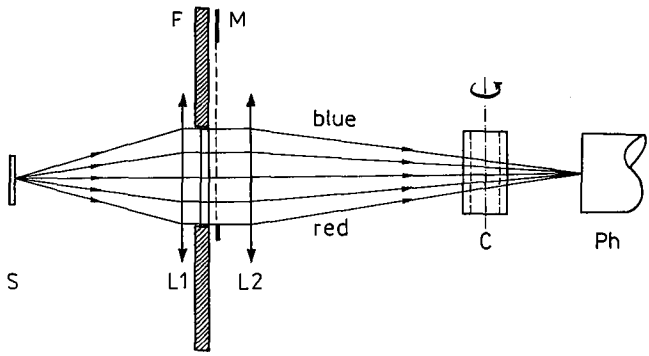

Fig. 1. A schematic diagram showing the operation of the Hadamard spectrometer with the continuous interference filter as a dispersion element and multislit encoding mask; S–sample placed at the input focus of the condenser system, L1, L2 — condenser lenses, F — window and interference filter, M — encoding mask, C — chopper and Ph — photomultiplier at the output focus of condenser. There are no input and output slits in the spectrometer presented here.

simple condenser arrangement collects light from the source placed in the input focus, collimates in the filter position and again focuses rays on the detector photocatode. Near the output focus the chopper is position to modulate beam of light for the phase sensitive detection system.

At a very small distance behind the filter the multislit mask is shifted by the precision screw feeder of 1 mm pitch. The cyclic mask consists of 125 elements, each of them in shape of opaque or transparent rectangle (1 mm wide, 18 mm high). For each 1 mm shift of the mask, a new group of 63 rectangles covers the length of the window with the continuous filter and forms a different pattern of open or close slits. For each one of the patterns 32 slits are open at once. Hence, due to the encoding cyclic mask and multiplex technique, the active area of the filter is constantly equal to 32 × 18 mm^2 = 576 mm^2 instead of 18 mm^2, relevent to the single-slit scanning.

The construction of the encoding cyclic matrix is based on primitive polynomials modulo 2. This method generates matrices having period of $n = 2^k - 1$, where k is the degree of the primitive polynomial. The first k elements of the calculated sequence may be chosen arbitrarily (except not all zero). The other $n - k$ elements of the first row of the encoding cyclic matrix are obtained by a simple algorithm [14, 17]. The following encoding pattern has been calculated for $n = 63$,

$k = 6$ and the all "seed" elements equal ones:

11111 10000 01000 01100 01010 01111 01000 11100

10010 11011 10110 01101 010.

Next, the initial 62 elements of this pattern are repeated. Hence, the pattern of the whole mask consists of 125 elements. The length of the window covers a group of 63 elements of the mask. This way, the succesive moving of the cyclic mask provides 63 patterns each containing 63 encoding elements. The initial six open fields at the beginning of the mask (seed) facilitate the precision of aligning of the mask and window edge.

4. Measurement system

The encoded light is modulated by an cylindric, two-aperture chopper. The rotation axis of the chopper is positioned along the dispersed spectrum to perform the modulation of all elements of the spectrum at once. A reference signal generated by this system controls the phase-sensitive lock-in amplifier. The chopping frequency is around 77 Hz. Filtered, encoded and modulated light is detected by the cooled photomultiplier EMI 6203.

The phototube output (1 MΩ) is equipped with an integrating filter proper to the chopping frequency (time constant is about 0.01 s). An output signal is amplified and smoothed in lock-in amplifier by the electronic band-pass (50–150 Hz) and time constant (0.1 s) filters. The analog signal from the lock-in output is transformed to TTL level by the voltage-frequency converter with the rate of 10 kHz/V.

During measurements the output signals are monitored and recorded by the multichannel analyser Tristan-1024 (Polon) connected with the small interface/driver system Izolda and a microcomputer. The analyser works as a master in multiscaler mode, switching channels with desired time rate (typically 0.5 s). One sequence of spectrum measurement uses 64 channels, where 63 channels collect data for the decoding procedure and the last 64th channel is meaningless, because it corresponds to the reverser of the mask motion.

A channel switching signal from the analyser synchronizes the Izolda, which generates TTL pulses to control the driver of stepping motor. A group of 72 pulses shifts the mask exactly 1 mm further to the next encoding configuration. The interface offers several additinal options. For example, it is possible to switch two different signals to odd and even channels for simultaneous recording a multiplexed spectrum and global TL emission or temperature. But since the TL resolving spectra are usually measured for the linear increase of temperature and this is carefully controlled by a separate set-up [21], regarding masurement efficiency, as a rule, the sample temperature is not registrated by the multichannel analyser.

In order to test, an array of commercial electroluminescence (EL) diodes (red, yellow and green) was used as a light source for the Hadamard spectrometer. This testing set-up was supplied from the low-frequency generator. Figure 2 gives an experimental example of curves registrated by the multichannel analyser; (a) shows the total EL intensity measured without a dispersion element and (b) the record of multiplexed signals for sixteen sequences. The vertical lines separate

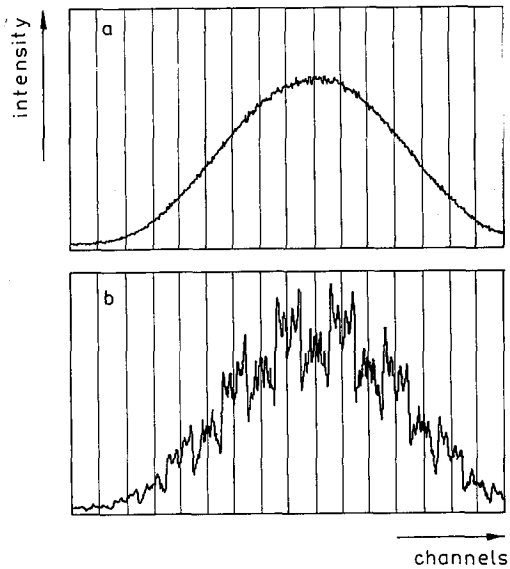

Fig. 2. Two records from the multichannel analyser showing the dependence of the light intensity on time (channels) for testing array of EL diodes supplied from a low-frequency generator; (a) the total light intensity, (b) the multiplexed signal for sixteen sequences (vertical lines).

sequences with the reverse encoding order. Data recorded by Tristan analyser are transferred via computer and stored as a disk data file. It seems to be interesting to note here that in comparison with the single-slit scanning method an amplitude of variation of the multiplexed signals is significantly lower. This effect appears to be greater for broader band spectra.

5. Data processing

The numerical procedure consists of several steps of calculations. At first, the data for reverse sequence are transposed and the file is rearranged to make the proper matrix of 63 encoded data for each sequence.

The next step of data handling is especially important for TL emission spectra. Since the light level of TL is not constant in time, the encoded 63 intensities for each sequence are corrected by the coefficients of linear approximation of light variation. The sums of matrix elements for sequences allow the calculation of averaged rates of the light evolution. Of course, the independent measurement of the total TL emission allows performing a direct normalization of encoded data.

Without the correcting treatment the decoding procedure gives the systematic error which is specific for the encoding mask and depends on the light fluctuation and spectrum. The behaviour of decoding errors is quite different from the usual spectrometric errors arising from noises, delay time or resolution power. After decoding of uncorrected signals even the negative emission densities for some broad regions of the spectrum can be obtained.

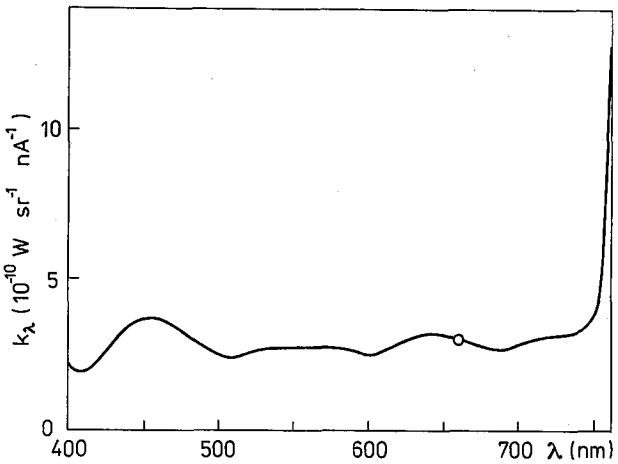

Fig. 3. The spectrum of radiant sensitivity of the whole optical and detecting system of the Hadamard spectrometer.

The corrected data, sequence by sequence, are decoded. The direct method based on formula (2) and relation (3) or any faster algorithm of calculation [14, 20] can be here applied. Next, the results must be calibrated with respect to the spectral response of the whole optical and detecting system. To determine the desired spectral factors the calibrated light source with the known spectrum (blackbody 2854 K) was used. It should be mentioned here that the spectral response shown in Fig. 3 is expressed as the absolute radiant sensitivity [W sr^{-1} nA^{-1}]. Practically, 0.1 nA can be assumed as a low limit of detected photomultiplier current (for

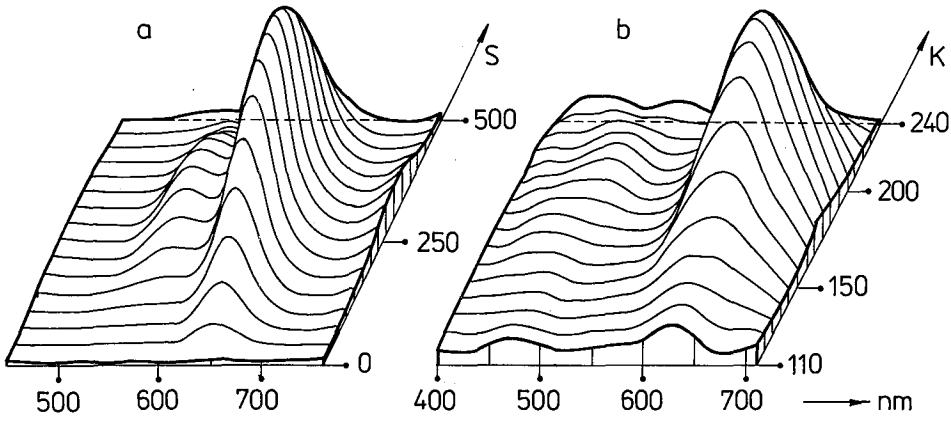

Fig. 4. Spectrally resolved luminescence; (a) the dependence of EL spectrum on time. This plot corresponds to the encoded record in Fig. 2b. (b) The curve (b) shows the temperature resolved spectra of TL for ZnSe:Ag.

0.5 s/channel). Hence, the presented curve also allows estimating the low limit of the light intensity which is sufficient to record reliable spectra. For 660 nm this limit corresponds to the intensity of about 10^8 photons sr^{-1} s^{-1}. The absolute calibration was performed for 660 nm by means of the radiometer HP 8334/8330A, photomultiplier and red EL diode.

After the calibrating treatment the matrix elements represent the desired spectral densities. Of course, the place of elements provide additional information concerning the wavelength and time of measurement. The final procedure may include several options like numerical filtering of noise, smoothing, spectral deconvolution and usually graphics program.

Figure 4 gives two examples of spectrally resolved luminescence; (a) shows the time resolved spectra of the steady-state EL emission of diode array. This plot represents the decoded record of data from Fig. 2. The temperature resolved spectra for ZnSe : Ag are shown in Fig. 4(b). The investigated crystal was excited at 80 K with the light of 365 nm and TL was measured from 110 K to 240 K for the heating rate of about 0.153 Ks^{-1}.

6. Conclusions

The presented here spectrometer has been designed for TL investigation. Hence, the main goal is to maximize the amount of light transferred from a luminescence source to the photomultiplier. The light collection efficiency of different spectrometers is well characterized by the optical extend, $G = A\ \Omega\ t$, where A is the source area, Ω the solid angle of an entrance aperture and t the transmittance of the system.

Our spectrometer accepts large area of a sample (say 2 cm^2). The investigated sample is positioned on the focal length (11 cm) from the lens collimating light onto the interference filter. Due to the multislit technique the active area of the filter is enriched to 5.76 cm^2 which leads to the solid entrance angle of about 0.048 sr. Applying $t \approx 0.2$ for transmittance of the system one can obtain the optical extend close to 0.02 sr cm^2. It is about one order more than for very bright monochromators with comparable resolution.

A certain incovenience of the encoding spectrometry is inability to reduce the investigated spectral range. The most simple remedy for it is to change the size of the mask. For this reason our next Hadamard spectrometer is equipped with three masks which can be changed easily, namely: $n = 63$, shifted by 0.3 mm, 63 by 0.1 mm and 255 by 0.1 mm. This spectrometer has a prism and is not so bright but allows reaching higher spectral resolution and is specially adjusted for steady-state photoluminescence investigation.

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References

[1] S.W.S. McKeever, *Thermoluminescence of Solids*, Cambridge University Press, Cambridge 1985.

[2] A.M. Harris, J.H. Jackson, *J. Phys. E* **3**, 374 (1970).

[3] P.L. Mattern, K. Lengweiler, P.W. Levy, *Mod. Geol.* **2**, 293 (1971).

[4] H.L. Oczkowski, *Phys. Status Solidi A* **68**, 199 (1981).

[5] P.D. Townsend, K. Ahmed, P.J. Chandler, S.W.S. McKeever, H.J. Whitlow, *Radiat. Eff.* **72**, 245 (1983).

[6] I.K. Bailiff, D.A. Morris, M.J. Aitken, *J. Phys. E* **10**, 1156 (1977).

[7] P. Brovetto, A. Delunas, V. Maxia, G. Spano, C. Cortese *Nuovo Cimento D* **12**, 331 (1990).

[8] M. Castagne, J. Gasiot, J.P. Fillard, *J. Phys. E* **11**, 345 (1978).

[9] A.J. Walton, N.C. Dobenham, *Nature* **284**, 42 (1980).

[10] D.J. Huntley, *Nuclear Tracks* **14**, 27 (1988); *J. Lumin.* **39**, 123 (1988).

[11] A.J. Walton, *PACT* **6**, 524 (1982); *Journal of the European Study Group on Physical, Chemical and Mathematical Techniques Applied to Archaeology*, Council of Europe, Strasbourg 1982.

[12] J.A. Decker, Jr., M. Harwit, *Appl. Opt.* **7**, 2205 (1968); *Appl. Opt.* **8**, 2552 (1969).

[13] N.J.A. Sloane, T. Fine, P.G. Phillips, M. Harwit, *Appl. Opt.* **8**, 2103 (1969).

[14] E.D. Nelson, M.L. Fredman, *J. Opt. Soc. Am.* **60**, 1664 (1970).

[15] J.A. Decker, *Appl. Opt.* **10**, 510 (1971).

[16] R.M. Hammaker, W.G. Fateley, D.C. Tilotta, *Spectroscopy* **3**, 14 (1988); *Spectrosc. Int.* **1**, 10 (1989).

[17] S.W. Golomb (Ed), *Digital Communications with Space Applications*, Prentice-Hall, Englewood Cliffs 1964.

[18] P.R. Griffiths (Ed), *Transform Techniques in Chemistry*, Plenum Press, New York, London 1978.

[19] A.G. Marshall, *Biophysical Chemistry*, Wiley, New York 1978.

[20] M. Harwit, N.J.A. Sloane, *Hadamard Transform Optics*, Acad. Press, New York 1979.

[21] H.L. Oczkowski, *Acta Phys. Pol.* **A76**, 649 (1989).