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# COORDINATE SYSTEMS FOR DETERMINING THE ELECTRON SPIN RESONANCE (ESR) LINESHAPE

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**The investigation of interactions between paramagnetic centres can be carried out by analysis of the shape and the width of the resonance curve, normally having the form of the first derivative of absorption. In the case of solids, when dipolar and exchange interactions are present, the ESR profile is known to consist of a Lorentzian central part with wings of Gaussian form. We developed a method of linear anamorphosis, in which the integral or the derivative of the resonance curve will be utilized. In special coordinate systems we have presented the ESR lineshape of ultramarine blue. This presentation proves that the central part of resonance curve of ultramarine blue is Lorentzian in shape and the outer wings are Gaussian.**

## INTRODUCTION

The method of linear anamorphosis of single symmetric ESR lines proposed by Tikhomirova and Voevodskii (Tikhomirova & Voevodskii, 1959) can be used for analysis of the shape of an ESR line narrowed by exchange interaction. This method gives better results than the method of moments (Van Vleck, 1948) or the cut-off method (Anderson, 1951; Kittel & Abrahams, 1953). Using this method it was found by Więckowski (Więckowski, 1970) that the paramagnetic polysulphide radical-anions $S_3^-$, responsible for the blue colour and paramagnetism of ultramarine blue, form a face-centred cubic lattice with an elementary cell of linear dimensions twice larger than the lattice constant d = 0.906 nm.

## EXPERIMENTAL DETAILS

The ESR measurements of ultramarine blue sample were performed using an X-band spectrometer BRUKER EMX-10 with microwave frequency 9.35 GHz. The amplitude of second magnetic field modulation with frequency 100 kHz was 0.05 mT. Time constant was 82 ms. The ESR spectra were recorded at the temperature of liquid nitrogen (77 K) for sample placed in a quartz tube. The resolution of magnetic field axis was 1024 points. The ESR spectrum obtained in the form of the derivative of absorption was integrated with the BRUKER WIN-EPR Simphonia program, version 3.03. The ESR spectrum of ultramarine blue is shown in Figure 1. The investigated sample of ultramarine blue with approximate formula $[Si_3Al_3O_{12}]Na_4S_2$ of the primary elementary cell, was manufactured by the factory Polifarb, Kalisz, Poland.

## RESULTS AND DISCUSSION

*Line shape functions*

According to the theories of Anderson and Weiss (Anderson & Weiss, 1953) and Kubo and Tomita (Kubo & Tomita, 1954; Kubo, 1954) the function of the line shape function $f(x)$ of a single ESR line is the Fourier transform of the characteristic function $\varphi(t)$. In simplified form the line shape function $f(x)$ can be given by the following formula (Więckowski, 1997):

$$f(x) = (2\pi)^{-1} \int \varphi(t) \exp(-itx) dt \tag{1}$$

$$\varphi(t) = \exp[-(\sigma^2/\omega_e^2)[(\pi/2)^{1/2}\omega_e t \Phi(\omega_e t) + \exp(-\omega_e^2 t^2/2) - 1]] \tag{2}$$

$$\Phi(\omega_e t) = (2/\pi)^{1/2} \int_0^{\omega_e t} \exp(-\tau^2/2) d\tau \tag{3}$$

where: $\Phi(\omega_e t)$ – Gauss probability integral, $x$ – frequency (or magnetic field) measured from the centre of the line, $\sigma$ – linewidth of the Gaussian curve caused by dipole interactions, $\omega_e$ – exchange frequency (or exchange field).

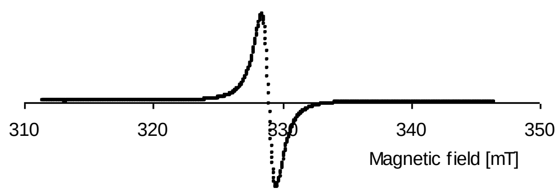


Fig. 1. The ESR spectrum of ultramarine blue.

It can be shown that the formula describing the wings of the resonance line has the form of the Gaussian function:

$$f(x) = (2\pi)^{-1/2}(1/\sigma)\exp[(-1/2)x^2/\sigma^2] \tag{4}$$

and the formula describing the central part of the resonance line has the form of the Lorentzian function:

$$f(x) = (1/\pi)\{\exp[(2/\pi)^{1/2}\Delta\omega/\omega_e]\}\Delta\omega/[(\Delta\omega)^2 + x^2] \tag{5}$$

$$\Delta\omega = (\pi/2)^{1/2}\sigma^2/\omega_e \tag{6}$$

where $\Delta\omega$ – linewidth of the Lorentzian curve.

Knowing the linewidths $\Delta\omega$ and $\sigma$ we can calculate the exchange frequency (exchange field) $\omega_e$. The most often used approximations of the single ESR lines are limited to the Lorentzian function, the Gaussian function, and the Voigt function which is a convolution of the Lorentzian and the Gaussian function. Also rational fractions (Padé approximations) (Maltempo, 1986; Sartorelli, Ochi & Sano, 1986) and Tsallis functions (Howarth, Weil & Zimpel, 2003) were used for approximation of the resonance curve.

*Linear anamorphosis of the ESR line*

To apply numerical methods for fixed-frequency ESR lineshape analysis, we will use shape functions in the following simplified forms of the Gaussian and Lorentzian function respectively:

$$y = a_G \exp[-x^2/(2b_G^2)] \tag{7}$$

$$y = a_L/(1 + x^2/b_L^2) \tag{8}$$

where: $y$ – absorption ordinate, $x$ – magnetic field abscissa measured as the distance from the centre of the line (resonance field), $a_G$, $a_L$ – amplitude of absorption, $b_G$ – slope-width (half-width between points of maximum slope of absorption line), $b_L$ – half-width (half-width at half height of the amplitude $a_L$).
Differentiation of these lineshape functions yields:

$$y' = -(a_G/b_G^2)x\exp[-x^2/(2b_G^2)] = -(1/b_G^2)xy$$

Gaussian function (9)

$$y' = -2(a_L/b_L^2)x/(1 + x^2/b_L^2)^2 = -2/(a_L b_L^2)xy^2$$

Lorentzian function (10)

where: $y'$ – first derivative of absorption ordinate.
It follows immediately that with the variables:

$$Y = y'/y^2, \qquad X = x/y \tag{11}$$

$$Y = y'/y, \qquad X = x \tag{12}$$

$$Y = y', \qquad X = xy \tag{13}$$

the Gaussian function gives a straight line described by the equation

$$Y = -(1/b_G^2)X \tag{14}$$

and the Lorentzian function gives a curve.
In these special coordinate systems we have analysed the ESR lineshape of ultramarine blue. In Figure 2 we present the results in these coordinate systems, in which the Gaussian part of ESR line gives a straight line. For better observation of the results, in some cases we show only one quadrant of coordinate system.

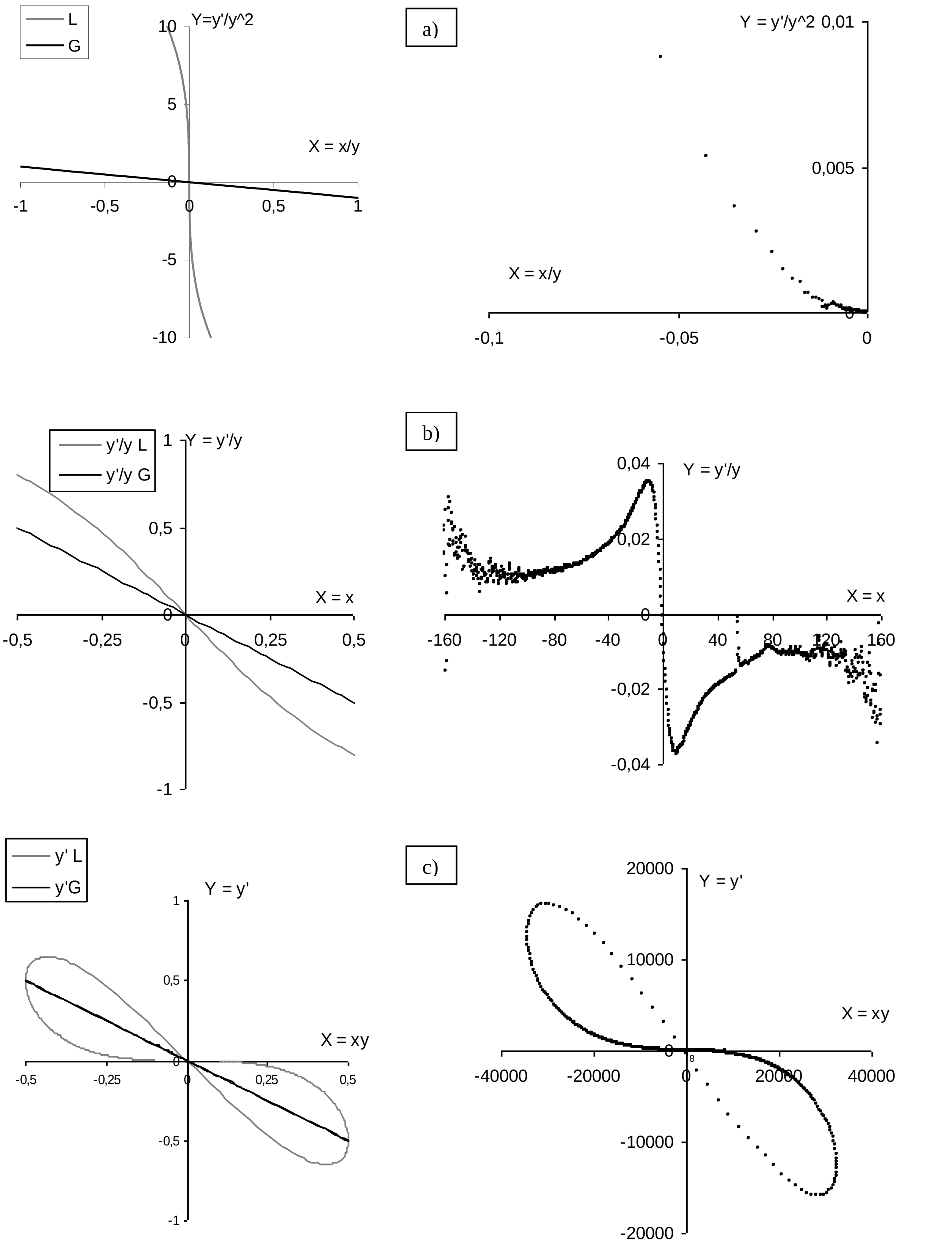


Fig. 2. The ESR lineshape of ultramarine blue in coordinate systems, in which the Gaussian part of ESR line gives straight and Lorentzian part gives a curve line: a)$Y = y'/y$^2 and $X = x/y$, b) $Y = y/y$ and $X = x$, c)$Y = y'$ and $X = xy$. Theoretical diagrams are presented on left and experimental data on right.

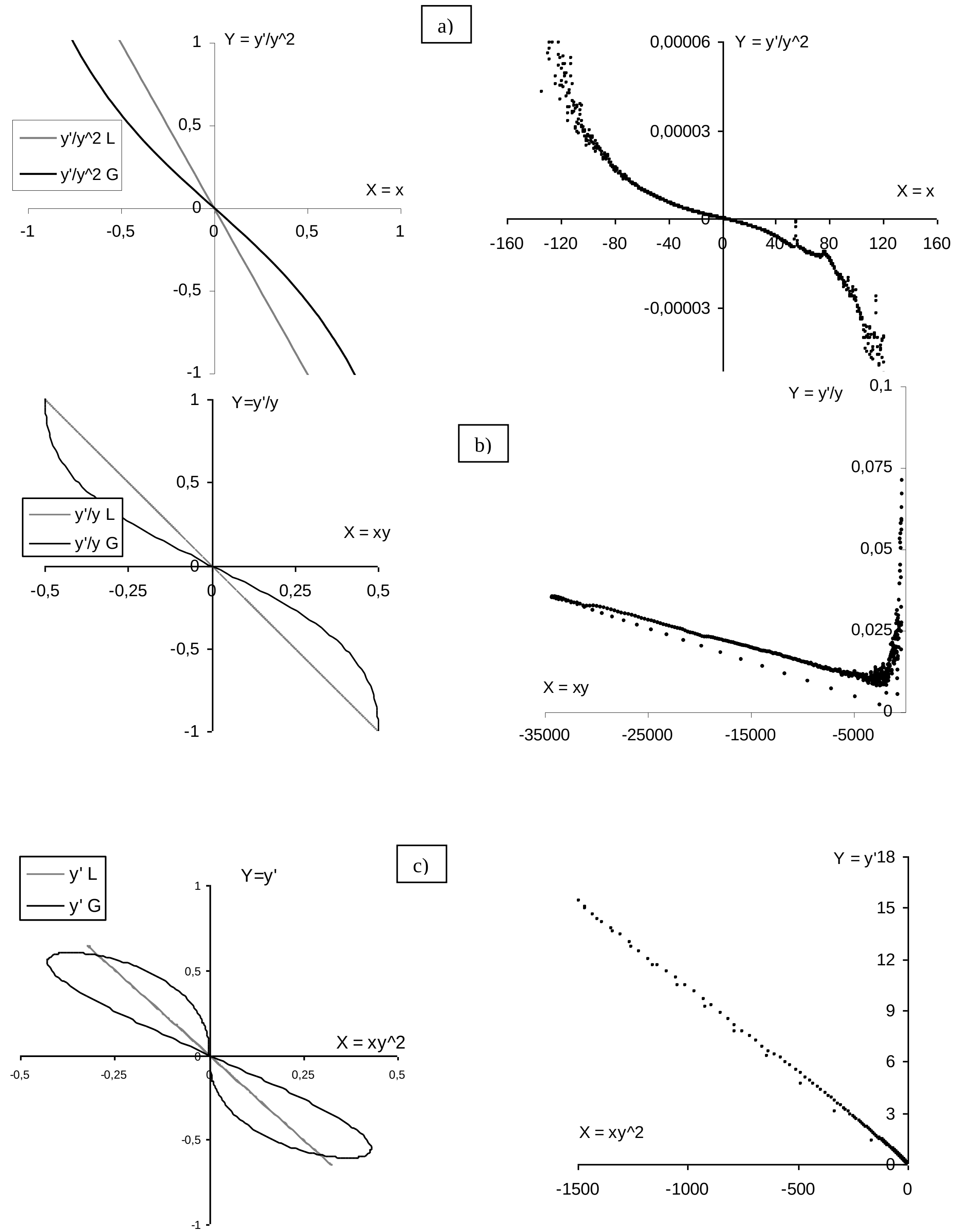


Fig. 3. The ESR lineshape of ultramarine blue in coordinate systems, in which the Lorentzian part of ESR line gives straight and Gaussian part gives a curve line: a)*Y = y'/y*^2 and *X = x*, b) *Y = y'/y* and *X = xy*, c)*Y = y'* and *X = xy*^2. Theoretical diagrams are presented on left and experimental data on right.

Similarly, with the variables:

$$Y = y^{'} / y^{2}, \qquad X = x \tag{15}$$

$$Y = y^{'} / y, \qquad X = xy \tag{16}$$

$$Y = y^{'}, \qquad X = xy^{2} \tag{17}$$

the Lorentzian function gives a straight line described by the equation

$$Y = -2/(a_L b_L^2)X \tag{18}$$

and the Gaussian function gives a curve.

In Figure 3 we show coordinate systems in which the Lorentzian part of single ESR line gives a straight line. For better observation of the results, in some cases we show only one quadrant of coordinate system.

## CONCLUSION

This presentation proves that the central part of the resonance curve of ultramarine blue is Lorentzian in shape and the outer wings are Gaussian. These methods visualize the differences in lineshape of the central part of single ESR spectra and their wings.

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