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THE NUMERICAL OPTIMALIZATION OF THE ESR SPECTRA OF V^{4+} IN SOME GLASSES

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The approximately estimated experimental values of the spin-Hamiltonian constants of the V_2O_5 impurity in glassy $Na_2O.2B_2O_3$, $Na_2O.P_2O_5$ and $Na_2O.2SiO_2$ were optimalized by a digital computer. An outline of the computing method and the optimalization results are presented.

ЧИСЛОВОЕ ОПРЕДЕЛЕНИЕ ОПТИМАЛЬНЫХ ХАРАКТЕРИСТИК СПЕКТРА ЭЛЕКТРОННОГО СПИНОВОГО РЕЗОНАНСА ИОНОВ V^{4+} В НЕКОТОРЫХ СТЁКЛАХ

В работе с помощью цифровой вычислительной машины проведена оптимизация приближённо вычисленных экспериментальных значений констант спинового гамильтониана для примесей V_2O_5 в стекловидных соединениях $Na_2.2B_2O_3$, $Na_2O.P_2O_5$ и $Na_2O.2SiO_2$. Приводятся также схема метода вычисления и результаты оптимизации.

I. INTRODUCTION

The approximate parameters of the spin-Hamiltonian of ESR spectra of V_2O_5 impurity in the glasses $Na_2O.2B_2O_3$, $Na_2O.P_2O_5$ and $Na_2O.2SiO_2$ were reported in paper [1]. An algorithm for the evaluation of the above spectra for the given values of the spin-Hamiltonian parameters and for the given microwave frequency, the width and the type of the individual spectral line was described in the same paper. Even though there was a good agreement between experimental and computed spectra, the existence of a better approximation of the spectral parameters could not be excluded, i.e. possibilities which offered the applied theoretical model could not be completely utilized. An attempt to find a better set of spectral parameters than reported in [1], without a computer, has failed. A computer optimalization of the spectral parameters using an iterative algorithm to solve a nonlinear least square problem is discussed in the present paper.

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II. FORMULATION OF THE PROBLEM

An experimental spectrum is defined by a set of the points (x_i, y_i, w_i), $i=1, 2, \ldots, M$, where M is the total number of the points and x_i is a magnitude of the magnetic field, y_i is a corresponding value of the derivative of the absorption spectrum measured from an arbitrary zero level in arbitrary units and w_i is a statistical weight, all at the i-th point.

A theoretical model is represented by a function

$$y=\alpha f(x, P)+\beta, \tag{1}$$

where $P=(p_1, p_2, \ldots, p_N)$ is a row matrix of N spectral parameters. In our case $P=(g_{\parallel}, g_{\perp}, A_{\parallel}, A_{\perp}, \Delta H)$. The meaning of the present notation of spectral parameters and the algorithm for the evaluation of $f(x, P)$ has been reported in [1]. The parameters α and β are used to enable us to choose arbitrarily both the zero level and units of y when the spectrum is processed.

The aim of our calculations is to find the optimal values of α^{ex}, β^{ex} and P^{ex}, which minimalize the function

$$\chi^2(\alpha, \beta, P)=\sum_{i=1}^{M} w_i\{y_i-[\alpha f(x_i, P)+\beta]\}^2. \tag{2}$$

The parameters α, β are separated from the others, because of the linear dependence of y on the former. Their optimal values are calculated as the coefficients of a linear regression in each of the iteration steps before the calculation of the P-correction is started, i.e. during each step of iteration the function (1) is replaced by the function

$$y=F(x, P)=\alpha^{ex}f(x, P)+\beta^{ex}. \tag{3}$$

III. METHOD OF CALCULATION

If $R(P)$ is a residual matrix defined as

$$R_i(P)=y_i-F(x_i, P); \qquad i=1, 2, \ldots, M$$

and W is a weighting matrix defined as

$$W_{ij}=\delta_{ij}w_i; \qquad i, j=1, 2, \ldots, M,$$

then (2) with respect to (3) can be written as

$$\chi^2(P)=R(P)\, WR^T(P).$$

The optimal value of P^{ex} can be found in solving the set of normal equations

$$[\mathrm{grad}_P \chi^2(P)]_{P=P_{ex}}=0,$$

or

$$R(P^{ex})\, WD(P^{ex})=0, \tag{4}$$

where $D(P)$ is a matrix defined as

$$D_{ij}(P)=\frac{\partial F(x_i, P)}{\partial p_j}, \qquad i=1, 2, \ldots, M \quad j=1, 2, \ldots, N.$$

In general, the set of equations (4) is nonlinear and it can be solved by an iterative process supposing that

$$R(P^{ex})=R(P_k+Q_k)\simeq R(P_k)-Q_k D^T(P_k), \tag{5}$$

where P_k is the k-th approximation of P^{ex} and Q_k is its correction

$$Q_k=[D^T(P_k)\, WD(P_k)]^{-1}R(P_k)\, WD(P_k)= \tag{6'}$$

$$=-\frac{1}{2}[D^T(P_k)\, WD(P_k)]^{-1}\,\mathrm{grad}_P \chi^2(P_k)$$

and

$$P_{k+1}=P_k+Q_k. \tag{6''}$$

The convergence of the iterative solution process (6) depends on properties of the function $\chi^2(P)$ and on the choice of the initial approximation P_0 as well. This process has a number of modifications which extend its use [3—6]. In each iterative step in our algorithm the program is sent to the "little cycle" until the convergence test

$$\chi^2(P_{k+1})<\chi^2(P_k), \tag{7}$$

is obeyed. Each element of the matrix Q_k is reduced by the factor 1/2 in the "little cycle" and a new convergence test is done. Only 4 repetitions of the "little cycle" in one iterative step are allowed, else the computing is interrupted. The computing is finished either when a given value of an error (8) or a given number of iterative steps have been reached.

The result of the optimalization is supplemented with an average square error of a single measurement [2]

$$\sigma y_i=\left[\frac{\chi^2(P)}{w_i(M-N)}\right]^{1/2} \tag{8}$$

and with average square errors of the optimalized parameters [2]

$$\sigma p_i=\{[D^T(P)\, WD(P)]^{-1}\}_{ii}\left[\frac{\chi^2(P)}{M-N}\right]^{1/2}, \tag{9}$$

where the first factor is the j-th diagonal element of a matrix inverse to $D^T(P)\, WD(P)$.

IV. RESULTS

The program was written in FORTRAN according to an algorithm which was described in a previous chapter and the calculations were performed by the digital computer SIEMENS 4004/150 at the ÚVT VŠ in Bratislava. Information on the preparation of samples, the taking of spectra, the obtaining of initial approximations and on the function which produces the shape of the spectra has been published in [1]. Information on the optimalizations for 3 different kinds of glasses is presented in Tab. 1., where all the optimalized parameters were supplemented with their average square errors computed by (9) and in column $\sigma y/y_{max}$ the average square error of a single measurement (8) divided by the maximal value of the spectrum is shown. It could be seen that a fast decrease of the $\sigma y/y_{max}$ during the first 5—8 steps was followed by its stabilization, its residual value being about 5 %.

The optimalizations were performed for gaussian and lorentzian shapes of the individual lines but better results were obtained for the first. It can be concluded that the parameters of the spin-Hamiltonian in [1] were determined with a satisfactory accuracy but the values of ΔH had to be corrected considerably. The great deal of the residual errors may be explained, probably, by means of the effect of random deformations and irreqularities of the nearest environment on a paramagnetic centre in the glass.

Table 1

The course of the optimalization of the ESR spectral parameters of V^{4+} (cca 2 mol %) in various glasses. The spectra were scanned at 300 K and frequency of 9126 MHz. The individual line was supposed to be gaussian.

Glass	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ 10^4 [cm^{-1}]	$A_{\perp}$ 10^4 [cm^{-1}]	ΔH [Oe]	$\frac{\sigma y}{y_{max}}$	Note
$Na_2O.2B_2O_3$	1.944	1.974	168.0	55.3	35.2	7 %	Initial parameters [1]
	1.9455 ±0.0003	1.9746 ±0.0002	167.1 ±0.5	54.8 ±0.1	22.3 ±0.2	2.7 %	Fitted parameters after 12 cycles
$Na_2O.P_2O_5$	1.933	1.974	176.6	62.6	30.0	11 %	Initial parameters [1]
	1.9336 ±0.0003	1.9745 ±0.0002	178.6 ±0.5	63.8 ±0.1	18.1 ±0.3	7.2 %	Fitted parameters after 11 cycles
$Na_2O.2SiO_2$	1.939	1.971	172.2	55.2	29.2	8 %	Initial parameters [1]
	1.9392 ±0.0002	1.9729 ±0.0002	171.8 ±0.5	57.9 ±0.1	20.0 ±0.3	3.7 %	Fitted parameters after 11 cycles

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