

## THE NUMERICAL SYNTHESIS OF THE ESR SPECTRA OF $V^{4+}$ IMPURITY IN SOME OXIDE GLASSES

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The ESR spectra of  $V^{4+}$  impurities in the oxide glasses  $Na_2O \cdot 2B_2O_3$ ,  $Na_2O \cdot P_2O_5$  and  $Na_2O \cdot 2SiO_2$  were scanned at room temperature at a 3 cm wavelength. Their models were obtained by a digital computer.

### 1. INTRODUCTION

In 1955 [1] Sands showed that ESR spectra of paramagnetic impurities in vitreous materials may also provide information about the state and structure of the impurity centres. The later literature on this problem was surveyed by Wong and Angell [2], and by Altshuler and Kozyrev [3].

In an amorphous material any orientation of an impurity centre has an equal probability. The observed spectrum is a superposition of contributions from all centres. In spite of the fact that such a spectrum shows no angular dependence, it sometimes enables us to determine the spin Hamiltonian constants of the individual anisotropic centres. The question of the relationship between the observed spectrum and the spin Hamiltonian constants has been solved mainly for spectra without a hyperfine structure [4, 5, 6]. The solution is usually based on the idea that the principal peaks arise (in the observed spectrum) approximately in such magnetic fields, in which the lines of individual centres in their angular dependence achieve extreme positions. This idea is insufficient for the interpretation of more complex spectra with a distinguishable hyperfine structure. Difficulties and uncertainties arise in the central part of spectrum due to the overlapping of spectral lines.

We suppose that better results can be obtained if we can calculate the shape of the spectrum for the given constants of the spin Hamiltonian and for the given assumptions about the shape and the width of the individual spectral line. A comparison of the synthetic spectrum obtained in the above described way with the observed spectrum is the starting point for the better estimation

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of the spectral parameters. Afterwards it may follow a new synthesis of the spectrum etc.

## II. EXPERIMENTAL

In the present work we have confined ourselves to study of vanadium ( $V^{4+}$ ) in oxide glassed  $Na_2O \cdot 2B_2O_3$ ,  $Na_2O \cdot P_2O_5$  and  $Na_2O \cdot 2SiO_2$ . Vanadium in all the samples was added in the form of  $V_2O_5$  (ca 1 mol %). A reduction of  $V^{5+}$  to paramagnetic  $V^{4+}$  was realized by the preparation of glasses in a reducing flame. We have obtained dark green optical transparent glasses. Typical ESR spectra of one sample scanned at room temperature at a frequency of 9126 MHz is shown in Fig. 1 by a solid curve. (All spectra were scanned by a ESR spectrometer with high frequency modulation, constructed by Ing. Šurka at the Institute of Experimental Physics PF UK in Bratislava.)

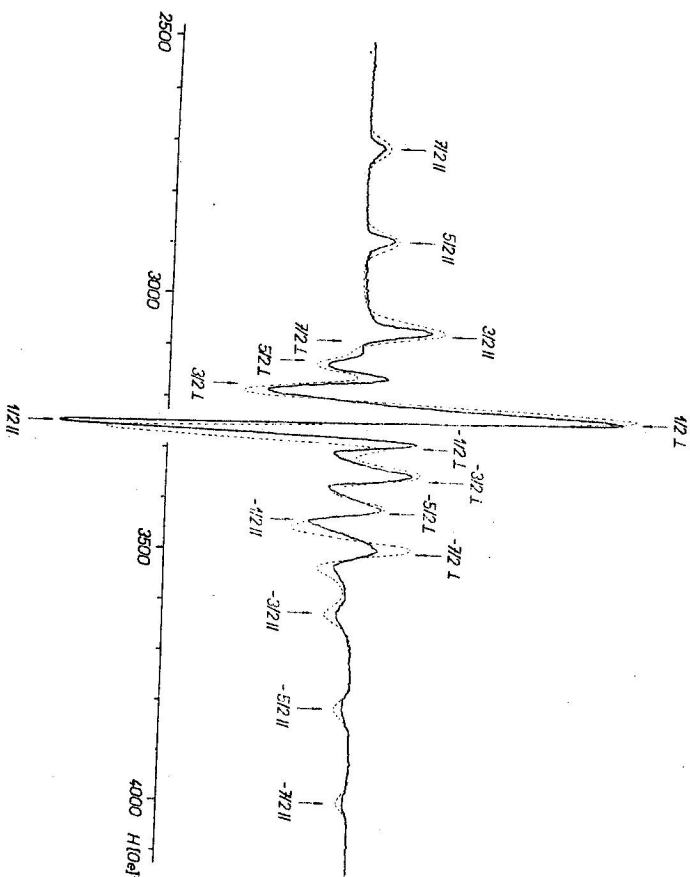


Fig. 1. The ESR spectrum of the impurity  $V^{4+}$  (2 mol %) in the glass  $Na_2O \cdot 2B_2O_3$  at a frequency of 9126 MHz and a temperature of 300 K. Solid curve — experimental spectrum, dashed curve — synthetic spectrum for  $g_{II} = 1.944$ ,  $g_{I} = 1.974$ ,  $A_{II} = 168.0 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_{I} = 55.3 \times 10^{-4} \text{ cm}^{-1}$  and  $\Delta H = 35.2 \text{ Oe}$ .

## III. CALCULATIONS

There are some papers which are devoted to similar materials [7, 8, 9]. It is generally accepted that the ESR in these glasses is caused by the molecular ion of  $VO^{2+}$ . We concentrated on the problem of the numerical synthesis of these spectra only.

We assume that a paramagnetic centre containing a  $VO^{2+}$  ion and the nearest neighbouring atoms have in the first approximation the axial spin Hamiltonian with the Zeeman and the hyperfine interaction terms only. Since the configuration of  $V^{4+}$  is  $(Ar)3d$ , the electronic spin of the centre is  $S = 1/2$ . We suppose further that the odd electron interacts only with the nucleus of  $V^{53}$ , that is  $I = 7/2$ . In the following text and formulae we use the usual notation according to [10].

If  $h\nu \gg \max(A_{II}, A_{I})$  and if  $\Delta m = 1$  (for the electronic spin) and  $\Delta M = 0$  (for the nuclear spin), then for the resonance magnetic field of the line with the nuclear quantum number  $M$  we can write

$$H_M(\Theta) = a(\Theta)M^2 + b(\Theta)M + c(\Theta), \quad (1)$$

where  $\Theta$  is the angle between the direction of the magnetic field and the centre axis. The used notations are

$$a(\Theta) = \frac{A_{II}^2}{4h\nu g\beta} \frac{A_{II}^2 + A^2}{A^2} - \frac{(A_{II}^2 - A^2)^2}{8h\nu g\beta A^2} \left( \frac{g_{II}g_{I}}{g^2} \right)^2 (\sin 2\Theta)^2 \quad (1')$$

$$b(\Theta) = -\frac{A}{g\beta}$$

$$c(\Theta) = \frac{h\nu}{g\beta} \frac{A_{II}^2}{4h\nu g\beta} \frac{A_{II}^2 + A^2}{A^2} I(I+1).$$

We shall seek the synthetic spectrum in the form

$$\chi(H) = \sum_{M=-I}^I \int_0^{\pi/2} p(\Theta) f \left\{ \frac{H_M(\Theta) - H}{\Delta H} \right\} \sin \Theta d\Theta, \quad (2)$$

where  $p(\Theta)$  is proportional to the probability of the absorption and the function  $f\{x\}$  represents a hypothetical shape of each individual line with the width parameter  $\Delta H$ .

In our numerical calculations the integration in (2) has been replaced by the summation over a sufficiently thick set of values of  $\Theta$ . The function  $f\{x\}$  was replaced by a derivative gaussian, or lorentzian one. The values of  $g_{II}$ ,  $g_{I}$ ,  $A_{II}$ ,  $A_{I}$  are determinable by the assignment of experimental spectral peaks

to the extreme positions of the spectral lines. This provides according to (1) and (1') 16 equations for 4 parameters, which can be solved by the nonlinear least square method. Difficulties arise in the central part of the spectrum, where the assignment is not unanimous. We have obtained several sets of the spectral parameters, for which we have computed the synthetic spectra. The comparison of the synthetic spectra with the experimental spectrum provided a unique choice of solution. A further synthesis for various  $\Delta H$ , for gaussian and lorentzian shapes of the individual lines enables us to conclude on the shapes and widths of the individual lines.

The calculations were performed by the little computer ODDRA (programmed in MOST). Better results were obtained for the gaussian shapes of the individual lines (see Table 1).

Table 1  
The ESR spectral parameters of  $V^{4+}$  (2 mol %) in some oxide glasses (temperature 300 K, frequency 9126 MHz)

Sample	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^4$ [cm <sup>-1</sup> ]	$A_{\perp} \times 10^4$ [cm <sup>-1</sup> ]	$\Delta H$ [Oe]
$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ : $V^{4+}$	1.944	1.974	168.0	55.3	35
$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ : $V^{4+}$	1.933	1.974	176.6	62.6	30
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ : $V^{4+}$	1.939	1.971	172.2	55.2	29

The dashed line in Fig. 1 shows the best synthetic spectrum for the glass  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ :  $V^{4+}$ .

Note: The arrows in Fig. 1 indicate the limit positions of the spectral lines calculated by (1), (1'). One can see that there are finite differences between the positions of peaks in the synthetic spectrum and the positions of these limits. The signs in the symbols  $\pm 7/2_{\parallel}$ ,  $\pm 7/2_{\perp}$ , etc. in Fig. 1 correspond to the hypothetical choice  $A > 0$ . The shape of the synthetic spectrum is independent of the sign of  $A$ .

#### IV. DISCUSSION

The syntheses of the spectra which we have calculated permit the study of some fine effects as e.g. the residual differences between the observed spectra and the synthetic ones. We mention one example only.

The ratio of the amplitudes of the border lines in the observed spectra (amplitude  $7/2_{\parallel}$ : amplitude  $-7/2_{\parallel}$ , or amplitude  $5/2_{\parallel}$ : amplitude  $-5/2_{\parallel}$ ) is ca. 4. The value of this quantity is 2 in the synthetic spectra. Similarly, the ratios of the widths of these lines are 0.5 or 1 in the observed spectra or syn-

thesized ones, respectively. This discrepancy, according to our opinion, is residual. One may explain such an effect by a dispersion of the spin Hamiltonian parameters caused by irregularities of environment of the paramagnetic centres. Some authors [11, 12] have shown that a dispersion of the parameters exhibits an influence upon the widths of the lines. If the resonance field is increasing, the width of the line is increasing, too. It may be expected that this effect is more complicated in the presence of hyperfine interactions.

#### REFERENCES

- [1] Sands R. H., Phys. Rev. 99 (1955), 1222.
- [2] Wong J., Angel C. A., Appl. Sp. Rev. 4 (1971), 155.
- [3] Altshuler S. A., Kozlyov B. M., *Elektronnyj paramagnitnyj rezonans soedinenij elementov promezhdobnych grupp*, Nauka, Moskva 1972.
- [4] Searl J. W., Smith R. C., Wyard S. J., Proc. Phys. Soc. A 78 (1961), 1174.
- [5] Kneubühl F. K., Helv. Phys. Acta 33 (1960), 1074.
- [6] Bljumenfeld L. A., Voevodskij V. V., Semenov A. G., *Primenenije EPR v obim. Novosibirsk* 1962.
- [7] Bogomolova L. D., Lazukin V. N., Petrovyeh N. V., DAN SSSR 175 (1967), 789.
- [8] Siegel I., Phys. Rev. 134 (1964), A 193.
- [9] Jafaev N. R., *Nekotorye voprosy magnitnoj radiospektroskopii*, Kazan' 1968, 23.
- [10] Abregam A., Bleaney B., *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford 1970.
- [11] Altshuler T. S., ŽETF 55 (1968), 1821.
- [12] Ibers I., Swalen I. D., Phys. Rev. 127 (1963), 1914.

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