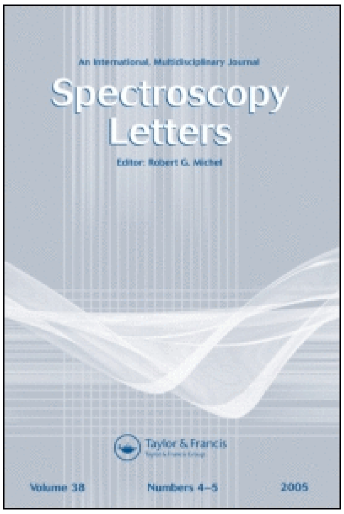

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Fundamental Concepts of Electron Spin Resonance Technique in the Determination of the Crystal Field Structure of O^-_2 Ions in TiO_2

I. O. B. Ewa[a]
[a] Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

To cite this Article Ewa, I. O. B.(1994) 'Fundamental Concepts of Electron Spin Resonance Technique in the Determination of the Crystal Field Structure of O^-_2 Ions in TiO_2', Spectroscopy Letters, 27: 5, 701 — 708
To link to this Article: DOI: 10.1080/00387019408000864
URL: http://dx.doi.org/10.1080/00387019408000864

SPECTROSCOPY LETTERS, 27(5), 701-708 (1994)

FUNDAMENTAL CONCEPTS OF ELECTRON SPIN RESONANCE TECHNIQUE IN THE DETERMINATION OF THE CRYSTAL FIELD STRUCTURE OF O_2^- IONS IN TiO_2

KEY WORDS: Electron spin resonance, paramagnetism, g-factors, crystal symmetry

Ewa, I. O. B.
Centre for Energy Research and Training,
Ahmadu Bello University, Zaria, Nigeria.

ABSTRACT

The basic principles of Electron Spin Resonance (ESR) as applicable in crystal field characterization of paramagnetic species has been outlined. Fundamental concepts of the precessional motion of electrons and their magnetic moments at resonance were developed. The theory of ESR based on the response of unpaired electron(s) as they undergo spin-spin or spin-lattice relaxation when subjected to strong external magnetic fields was examined. Ions of the O_2^- group adsorbed on TiO_2 were studied using a Varian Spectrometer. The resulting spectral diagrams obtained were used in calculating the g-factors which gave results for orthorhombic crystal symmetry for O_2^- ions in TiO_2.

INTRODUCTION

Electron Spin Resonance (ESR) is one of the analytical methods used in the characterization of paramagnetic species. Che and Taarit [1] considered the relaxation process of a spining electron in a magnetic field as a two stage phenomenon of spin-spin and spin-lattice events. This is in good agreement with an earlier proposed 'two-stage theory' of paramagnetic relaxation as suggested by Casimir and du Pre [2].

The interaction of an ion in a crystal field in paramagnetic studies is a fruitful application of ESR in field characterization of transition elements, since these group of elements preserve their unfilled electron shells during crystal formation. Excellent work on crystal field theory as related to the transition metal ions could be referred to in Griffiths [3] and Watanabe [4]. This paper is restricted to the relaxation phenomenon associated with paramagnetic species of the $3d^n$ transition group with a focus on localized O_2^- species within a TiO_2 crystal field when subjected to an irradiation with an appropriate resonance frequency.

THEORY OF ESR.

Paramagnetic species are usually associated with the presence of one or more 'free electrons'. The interaction between such a 'free electron(s)' in a magnetic field is given by an expression for μ_e which defines the magnetic dipole moment.

This magnetic moment ($\vec{\mu}_e$), associated with the spin of an electron is a vector, collinear and anti-parallel with the angular momentum vector. This moment is given by

$$\vec{\mu}_e = \gamma \vec{S} \qquad 1$$

Where

γ = the magnetogyric ratio ($e\hbar / mc$)

The symbol e represents the electronic charge, h the Planck's constant, m the mass of an electron while c is the velocity of light in vacumm

$\vec{S} = \hbar S$, defining the spin angular momentum in units of h

For a magnetic moment associated with the spin of a free electron equation (1) could be written in terms of the Bohr Magneton ($\beta = e\,h / 2mc$)

$$\mu_e = -2\beta\vec{S} \qquad 2$$

However, a thorough (quantum electrodynamic) theoretical treatment shows that the numerical factor is not exactly 2. The value determined by Atherton [5] theoretically is 2.0023 and this factor is usually called the free electron g-factor (g_e). Thus one can write equation (2) as

$$\vec{\mu}_e = -g_e\beta\vec{S} \qquad 3$$

The interaction energy (E) available for a free electron in a magnetic field H could be defined in terms of the magnetic moment μ_e as follows:

$$E = -\vec{\mu}_e \bullet \vec{H} \qquad 4$$

Defining the quantum mechanical Hamiltonian $\mathcal{H}$ and re-writing equation (4) by the appropriate operator.

$$\mathcal{H} = g_e\beta\vec{S}\bullet\vec{H} \qquad 5$$

If the field is defined in the z-direction, then $H_x = H_y = 0$, whence the scalar product yields

$$\mathcal{H} = g_e\beta S_z H_z \qquad 6$$

Where S_z denotes the spin component along the z-axis with only two possible M_s values ($\pm 1/2$) assumed for S_z. The Eigen values are therefore

$$E = (\pm 1/2)\, g_e\beta H_z \qquad 7$$

with the lowest state (negative sign) corresponding to the magnetic moment aligned parallel to the field. The energy difference between the two states is given by ΔE and equals a quantum of radiation ($h\nu$) defined by the Planck-Einstein formula thus:

$$\Delta E = g_e\beta H_z = h\nu \qquad 8$$

By irradiating the species under investigation with a frequency (ν) that statisfies the condition in equation (8), transitions between the two states will be induced with the populations given by the Maxwell-Boltzman law.

$$n_1/n_2 = e^{-\Delta E/kT} = 1 - \Delta E/kT \qquad 9$$

where

k is the Boltzman constant and

T is the absolute temperature to which the species is subjected to and

n_1, n_2 are the spin populations which are characterized by the M_s values of $\pm 1/2$ as shown in figure 1.

The frequency of the oscillating field that induces transition, leading to resonance is given in the relation

$$h\nu = g_e\beta H \qquad 10$$

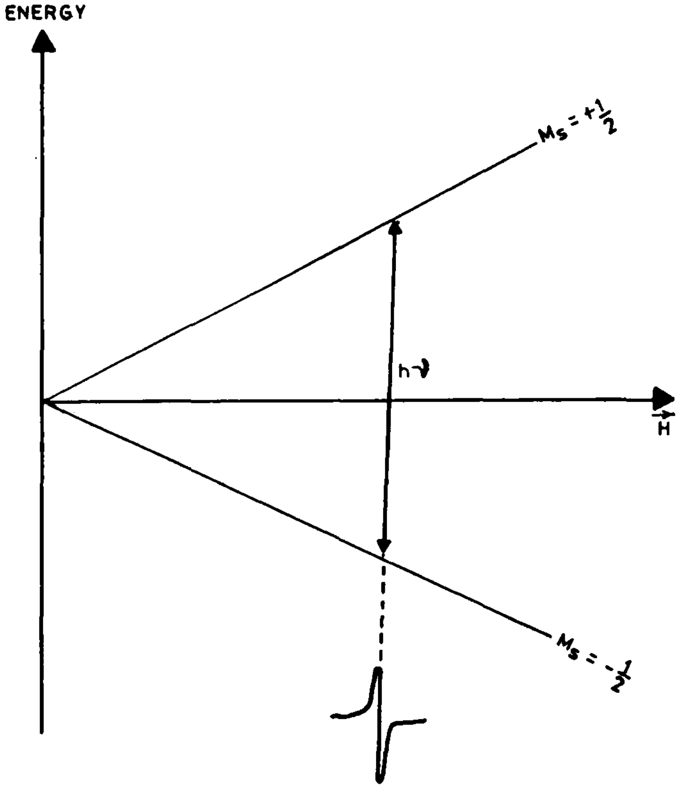

Fig.1 Energy level splitting of spin states when subjected to a variable magnetic field.

The frequency ν of equation (10) is that of the oscillation, field that induces transition as is governed by the resonance condition in equation (8). The energy therefore at resonance promotes electrons from the lower to upper energy states. As energy is absorbed in the process, n_1 and n_2 tends to equalize while the odd electrons from the upper level give up the hν quantum to return to the lower level, satisfying the Maxwell-Boltzman law. Che and Taarit [1] reported that this energy dissipated within the lattice in vibrational, rotational and translational states, occur as 'spin-lattice' relaxation while any energy exchange between spins without transfer of energy to the lattice could be refered to as the "spin-spin" relaxation. These transitions between the electron spin states in a magnetic field is the basis of crystal field characterization by ESR and is reported below.

EXPERIMENTAL

A Varian ESR spectrometer having a homogenous magnetic field strength within the range of 0 - 20,000 Gauss was used for the irradiation of O_2^- ions adsorbed on titanium oxide (O_2^- / TiO_2).

The samples (O_2^-/TiO_2) were placed in an evacuated quartz tube and inserted in the ESR cavity as shown in figure 2. The experiment was carried out for samples at room temperatures (25 °C) as well as Liquid Nitrogen temperature (-196 °C). The microwave energy was supplied by a Klystron and propagated along a wave-guide. The frequency of radiation being 3cm (9.39 GHz). The absorption cell or the ESR cavity is where the sample was inserted. The cell is located between the powerful magnets where the microwave power is concentrated. A detector diode measures the energy absorbed by the sample at resonance while a convenient amplifier system and recorder translates the crystal field reponse into a derivative ESR spectrum.

The ESR experiment consist of sweeping the magnetic field at constant microwave frequency until the resonance condition of equation 10 is achieved. This was performed for both sample (TiO_2) and standard (Di-phenyl-picryl-hydrazyl or DPPH). Having known the g_{ref} value for the standard (DPPH) given by Lunsford [6] to be 2.0036 the g_{samp} was therefore calculated using the relation.

$$g_{samp} = [g_{ref} \times H_{ref}] [H_{samp}]^{-1} \qquad 11$$

Both the magnetic yield strength of standard (H_{ref})and sample (H_{samp}) were obtained after an appropriate calibration of the system, and using also the derived ESR spectra from the DPPH and that of the sample(figure 3).

RESULTS AND DISCUSSION

The definitive response of the one or more unpaired electrons characterizing paramagnetic species in its precessional motion defines the non-zero electron magnetic moment to which is incorporated the g-factor used as 'finger prints' in crystal field characterization. Figure 3 shows triplet states of g-tensors from O_2^- ions adsorped on TiO_2. The ESR cavity was maintained at liquid nitrogen temperature (-196 °C) and room temperatures (25 °C) for different sample runs. Spectral diagrams of the standard (DPPH) were used to obtain g-values for the sample as stated in equation (11). Table 1 gives the data of the resulting crystal field as the O_2^- radical is adsorped on TiO_2. The g-tensors were obtained for both temperaturers stated.

The magnitudes of the g-tensors obtained from the triplet states give useful information on the symmetry of the crystal field [5] . For axial symmetry the tensors show that $g_{zz} = g_{//}$ (parallel) and $g_{zz} = g_{yy} = g\perp$ (perpendicular) while for orthorhombic symmetries $g_{xx} \neq g_{yy} \neq g_{zz}$. In cases of high symmetries the g-tensors are isotropic with $g_{xx} = g_{yy} = g_{zz} = g_{iso}$. This occurs for perfect octahedral. tetrahedral and spherical symmetries[1]. Usually in such cases a single ESR line is obtained.

The components of the g-tensors obtained from the ESR spectum could at times yield unexpected results in most cases where there is poor resolution of the ESR spectrum, crystal field response due to the environment or temperature differences, high concentration of the paramagnetic species and anisotropy due to mobility effects where paramagnetic species are undergoing rapid orientation. Olivier and co-workers [7] suggest an averaging process since the g-components must be reversible. Information about rotation and oscillation motion was investigated by subjecting the sample to two differerent temperature states. A slight variation of one of the g tensors was observed (Table 1). Such a slight variation could be as a result of trapping defects prevailing at a particular orientation of the crystal structure at a high temperature. In most cases the environment of the adsorbed O_2^- determines the magnitudes of the g-tensors as reported by various authors(Table 2).

The results of the g-tensors obtained in this work show that the crystal filed is orthorhombic. Such symmetries have been reported for ion pairs in TiO_2 by Meriaudeen [8]. The spectral diagrams (fig. 3) and the results obtained (Table 1) show that the triplet states were relatively stable at both room and liquid nitrogen temperatures except for the slight variation of the g_{zz} tensor when the ESR spectrum was determined at liquid nitrogen temperature.

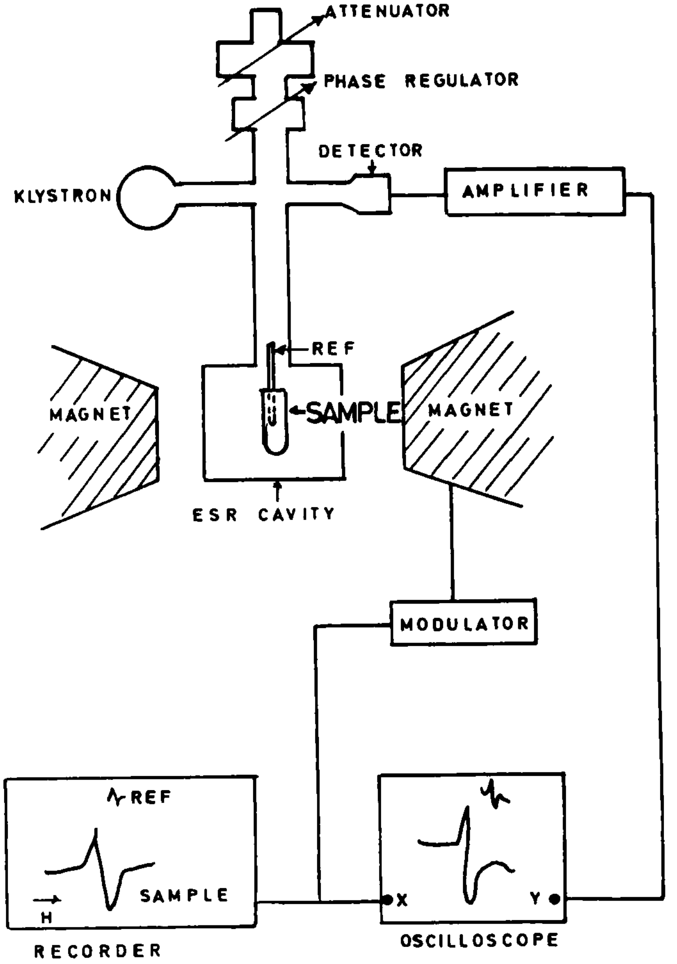

Fig-2: Schematic representation of an ESR spectrometer.

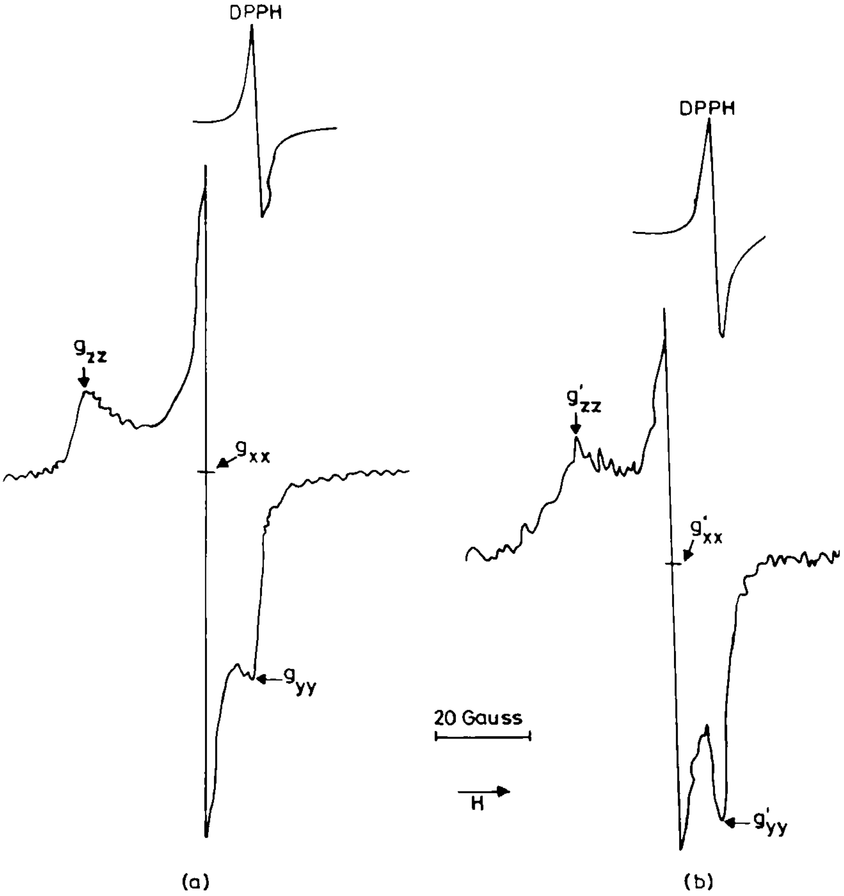

Fig. 3 : Triplet states of g-tensors from O_2^- ions

(a) Liquid Nitrogen (-196° C)

(b) Room Temperature (25°C)

Table 1. The g-tensors determined for O_2 ions adsorbed on TiO_2.

Radical	Sample Temperature	g_{zz}	g_{yy}	g_{xx}
O_2^-/TiO_2	-196 °C	2.0050	2.0042	2.0035
O_2^-/TiO_2	25 °C	2.0052	2.0042	2.0035

Table 2. The g-tensors for ions adsorbed on various crystal field structures

Radical	g_{zz}	g_{yy}	g_{xx}	Reference
SO_2^-/MgO	2.0047	2.0052	2.0028	[9]
SO_2^-/TiO_2	2.0103	2.0055	2.0018	[10]
CO_2/MgO	2.0029	2.0017	1.9974	[11]

CONCLUSION

The fundamental concepts of ESR has been outlined. It's theory and use in the study of the crystal field of paramagnetic species has been developed. The O_2^- radical was investigated through adsorption on TiO_2. The ESR spectra obtained was used in calculating the g-tensors which is the basis of crystal field analysis. While the ESR technique is regarded as a rapid, non-destructive and extremely sensitive method for crystal field studies, it should be noted that the investigation of the adsorbed species within a crystal field could yeild complicated line intensities and structures beyond the scope discussed so far. Another severe limitation of the ESR technique is that the method is mainly applicable to paramagnetic substances.

ACKNOWLEDGEMENT

The use of the Varian spectrometer and other associated facilities of the Institut de Recherche Sur La Catalyse, CNRS, France is hereby acknowledged. Useful discussion with Prof. Y.B. Taarit over this work and his stimualtion of my enthusiasm for ESR studies require my personnal gratitude.

REFERENCES

1. Che. M. and Taarit, Y.B. The Paramagnetic Resonance: Principles and Fundamental Parameters in Powder Spectra; Advances in Colloid and Interface Science,1985, Vol. **23**; 179-213.

2. Casimir, H.B.G and F.K. du Pre. Physica **5**, 1938 ; 507.

3. Griffiths, J.S. *The Theory of Transition Metal Ions,* Cambridge Univ. Press. 1961.

4. Watanabe, H. *Operator Methods in Ligand Field Theory*, Englewood Cliff, New Jersey, Prentice-Hall, Inc., 1966.

5. Atherton, N.M. *Electron Spin Resonance*, New York, John Wiley ; 5 -19; 1973

6. Lunsford, J.H., J. Phys. Chem., 1967, No. **46**: 4343.

7. Olivier, D., Marachi C. and Che. M. J. Phys. Chem., 1979, No. **71**. : 4688.

8. Meriaudeau, P., Clergaud, B and Che, M. , J. Phys. Chem., 1983, No. **87** : 3872.

9. Schoonheydt, R.A and Lunsford., J. Phys. Chem., 1972, No. **76** : 323.

10. Atkins, P.W., Horsfield, A. and Symons, M.C.R., J. Chem. Soc., 1964 : 5220.

11. Lunsford, J. H. and Jayne, J. P., J. Phys. Chem., 1965, No. **69** : 2182.

Date Received: January 6, 1994
Date Accepted: March 2, 1994