

Random glass structure and electron localisation in amorphous V_2O_5

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Abstract. ESR experiments performed on crystalline and amorphous WO_3 -doped V_2O_5 indicate different behaviours of both spectra with temperature and microwave frequency. A line broadening is observed for the crystalline oxide as the temperature increases while the ESR spectrum of amorphous V_2O_5 remains well resolved up to 300 K. This suggests that the electron hopping frequency between V^{4+} and V^{5+} ions is much smaller in the amorphous oxide. A strong frequency dependence of the ESR linewidth is observed for the amorphous sample, but not for the crystalline one. This has been attributed to a distribution of g -values among the different vanadium sites caused by a fluctuation of the local crystal field Δ . An analysis of the ESR linewidth as a function of the microwave frequency leads to a value $\delta\Delta = 0.24$ eV of the crystal field fluctuations. Such a random distribution of Δ contributes to increase the activation energy of the hopping process and thus to the localisation of the charge carriers in the amorphous oxide.

1. Introduction

Vanadium pentoxide is a non-stoichiometric compound in which oxygen deficiency is compensated by the reduction of some vanadium ions to a low oxidation state, namely V^{4+} (Dziembaj 1978). Such an oxide behaves as a mixed-valence semiconductor. Its electrical properties arise from the hopping of unpaired electrons between V^{4+} and V^{5+} ions (Patrino and Ioffe 1965, Scott *et al* 1971, Haemers *et al* 1973). A strong electron-phonon coupling is observed in V_2O_5 . The unpaired electrons are strongly bound in their own polarisation wells and the charge carriers are actually small polarons (Ioffe and Patrino 1968). At room temperature, the conductivity is dominated by the thermally activated hopping of these small polarons. It follows an exponential law $\sigma = \sigma_0 \exp(-W_h/kT)$ where the activation energy W_h is approximately equal to half the polaron binding energy (Austin and Mott 1969).

Amorphous V_2O_5 can be obtained by vapour deposition (Allersma *et al* 1967), RF sputtering (Koffyberg and Benko 1978) or splat cooling (Rivoalen *et al* 1976). It also exhibits semiconducting properties due to a hopping process similar to that of crystalline V_2O_5 (Koffyberg and Benko 1978) but, the random glass structure leads to a disorder energy term W_D that has to be taken into account in the expression for the activation energy. Austin and Mott (1969) showed that at high temperature ($T > \Theta/2$, Θ is the Debye temperature) the activation energy W can be expressed as $W = W_h + \frac{1}{2}W_D$. The disorder energy W_D represents the energy difference between 3d electrons located at different

vanadium sites. As a result of the structural disorder, a localisation of the charge carriers may occur when W_D becomes large enough (Anderson 1958). The conductivity of amorphous V_2O_5 appears to be about two or three orders of magnitude smaller than in crystalline V_2O_5 (Allersma *et al* 1967).

The electrical properties of amorphous semiconductors depend strongly on the disorder energy term W_D , so it is very important to be able to measure it. Electrical conductivity experiments have already been performed on V_2O_5 -based glasses (Chandhari and Li 1974, Frazier *et al* 1976, Greaves 1973, Linsley *et al* 1970, Sayer *et al* 1971, Sayer and Mansingh 1972), or V_2O_5 amorphous thin films (Koffyberg and Benko 1978). They would allow a good determination of W_D if the measurements could be made over a large temperature scale, below $\Theta/4$, when the activation energy W turns from $W_h + \frac{1}{2}W_D$ to $\frac{1}{2}W_D$. Unfortunately, the resistivity of amorphous V_2O_5 usually becomes too high to allow accurate measurements at very low temperature. So the values of W_D reported in the literature spread from 0.18 eV (Koffyberg and Benko 1978) up to 0.38 eV (Allersma *et al* 1967). The disorder energy W_D arises from a distribution of the vanadium $3d^1$ energy levels due to random fluctuations of the local crystal field Δ . Such fluctuations of Δ would also lead to a distribution of the V^{4+} g -values among the different vanadium sites in amorphous V_2O_5 . A line broadening is then observed in the ESR spectra (Sperlich *et al* 1973) from which the random disorder can be estimated.

An analysis of the ESR linewidth as a function of temperature and microwave frequency is presented in this paper. Experiments have been performed on crystalline and amorphous WO_3 -doped V_2O_5 . It has previously been shown that in both phases, the unpaired electron is trapped on a single vanadium site, allowing a straightforward comparison between ESR spectra (Kahn *et al* 1974, Livage *et al* 1980). This is not the case for pure V_2O_5 where the unpaired electron is delocalised over two vanadium sites in the crystalline oxide (Gillis and Boesman 1966) while it remains localised on a single vanadium in the amorphous phase. It will be shown that the ESR spectrum of the crystalline oxide depends on the temperature but not on the microwave frequency while the reverse is observed with the amorphous oxide. These observations are attributed to a localisation of the charge carriers due to the structural disorder. An analysis of the linewidth as a function of the microwave frequency will allow an estimation of the crystal field fluctuation contribution to the disorder energy term W_D .

2. Experimental

Amorphous vanadium pentoxide was prepared by splat-cooling from the melt at rates of about 10^6 °C s⁻¹. The oxide is melted at 800°C in an induction-heated platinum crucible which has a hole 1 mm in diameter in the bottom. High-pressure argon is suddenly admitted into a 'gun' placed above the crucible. It forces the liquid oxide through the hole and spreads it onto a glass plate placed a few centimetres below the crucible. This ultrafast quenching yields dark blue glossy platelets a few micrometres thick. X-ray diffraction measurements showed that the splat-cooled oxide was amorphous. Chemical analysis indicates that it contains about 0.5% of V^{4+} ions. Polycrystalline samples were easily made by slow cooling of the melt. All crystalline and amorphous samples were doped with 0.5 mol % of WO_3 . This doping was obtained by adding the corresponding amount of WO_3 before melting the mixture (Livage *et al* 1980). ESR experiments were performed on a Varian spectrometer at 9.5 GHz and 35 GHz. An Oxford Instrument cryostat was used to make measurements down to liquid helium temperature.

3. Results

Figures 1 and 2 show the X-band ESR spectra of polycrystalline and amorphous WO_3 -doped V_2O_5 . The low-temperature spectra (1a, 2a) both exhibit a well-resolved hyperfine structure indicating that the 3d unpaired electron ($S = \frac{1}{2}$) is localised on a single vanadium site $^{51}V(I = \frac{7}{2})$. The parallel and perpendicular features seen on the spectrum suggest that

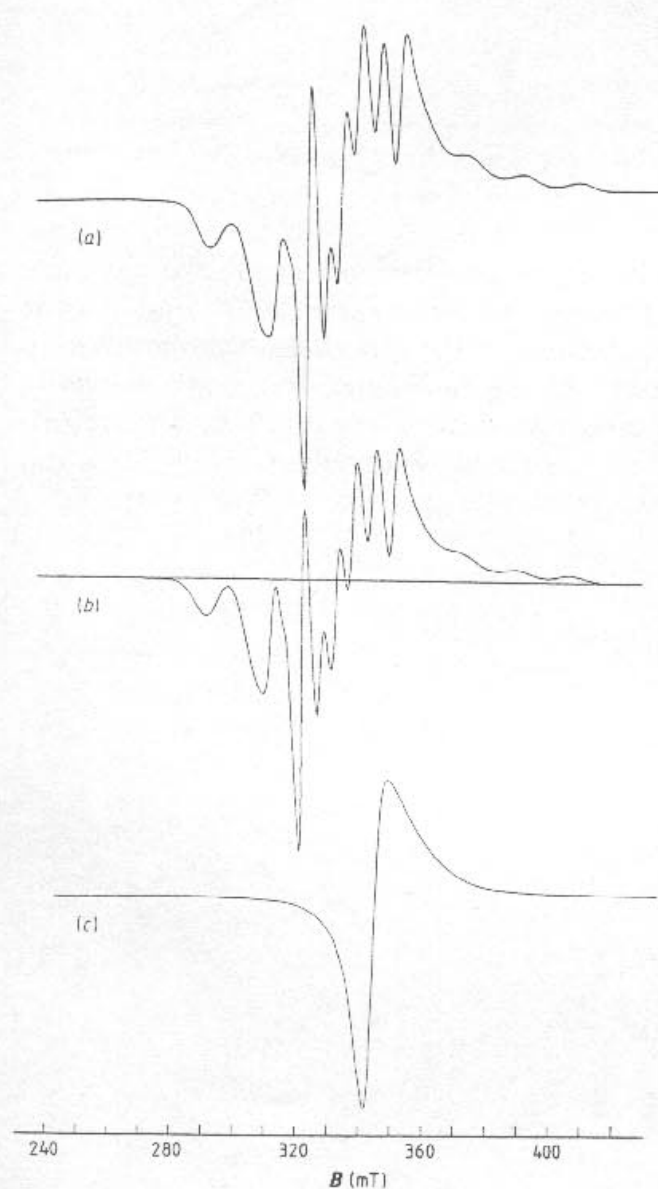


Figure 1. X-band ESR spectra of polycrystalline WO_3 -doped V_2O_5 ($WO_3 = 0.5$ mol %). (a) experimental spectrum recorded at 4 K; (b) simulated spectrum; (c) experimental spectrum recorded at 300 K.

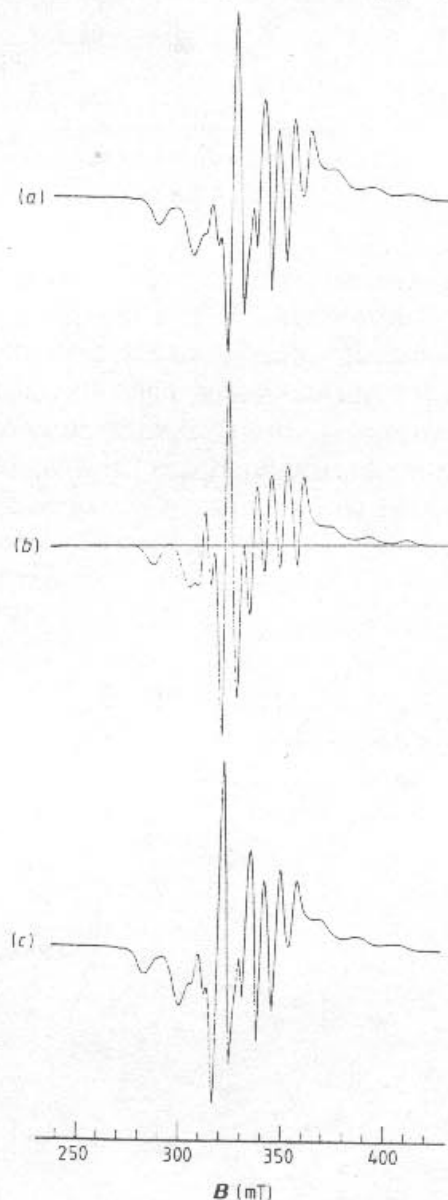


Figure 2. X-band ESR spectra of amorphous WO_3 -doped V_2O_5 ($WO_3 = 0.5$ mol %). (a) experimental spectrum recorded at 4 K; (b) simulated spectrum; (c) experimental spectrum recorded at 300 K.

the V^{4+} ion lies in an axially distorted crystal field. The ESR spectrum can then be described with the usual spin Hamiltonian:

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

where z is taken along the main axis of the axially symmetric \mathbf{g} and \mathbf{A} tensors. The parallel

Table 1. ESR parameters of crystalline and amorphous WO_3 -doped V_2O_5 .

	Polycrystalline		Amorphous	
	X band	Q band	X band	Q band
g_{\parallel}	1.887 ± 0.001	1.887 ± 0.002	1.913 ± 0.001	1.913 ± 0.002
g_{\perp}	1.980 ± 0.002	1.980 ± 0.001	1.981 ± 0.002	1.981 ± 0.001
$A_{\parallel}(\text{G})$	161 ± 0.5	161 ± 2	176 ± 0.5	176 ± 2
$A_{\perp}(\text{G})$	53 ± 1	53 ± 0.5	66 ± 1	66 ± 0.5
$\Delta H_{\parallel}(\text{G})$	70 ± 2	70 ± 5	80 ± 2	150 ± 5
$\Delta H_{\perp}(\text{G})$	30 ± 2	30 ± 1	36 ± 2	50 ± 1

All measurements were performed at low temperature (44 K and 77 K), in a temperature range where no broadening due to electron hopping is observed.

lines can easily be seen on each side of the spectrum where they correspond to a maximum in the derivative curve, allowing a straightforward determination of A_{\parallel} and g_{\parallel} . The perpendicular lines cross the base line in the middle of the spectrum where they overlap with the parallel lines. Their position cannot be accurately measured and a computer simulation was undertaken in order to get all ESR parameters. The best fit between experimental and simulated spectra was obtained for the values reported in table 1. The g and A parameters are almost the same as those previously reported for WO_3 -doped V_2O_5 .

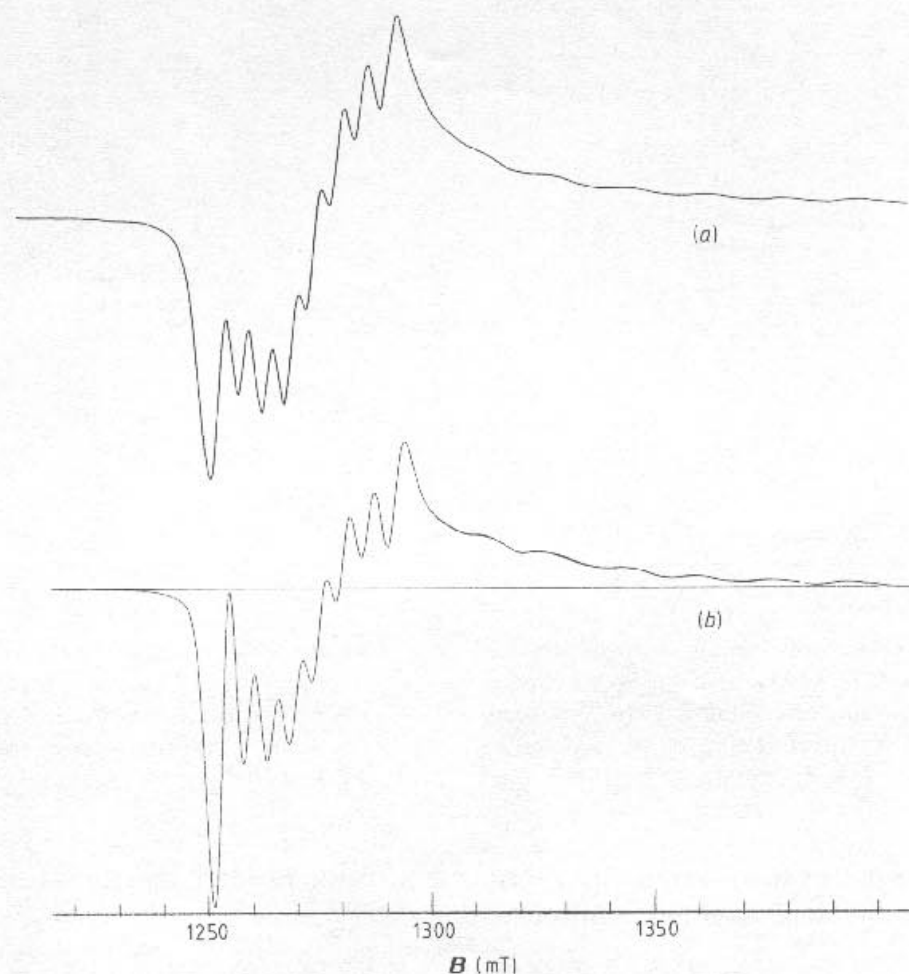


Figure 3. Q-band ESR spectra of polycrystalline WO_3 -doped V_2O_5 ($\text{WO}_3 = 0.5 \text{ mol } \%$). (a) experimental spectrum recorded at 77 K; (b) simulated spectrum.

single crystals (Livage *et al* 1980). The ESR spectra described in this paper were performed on polycrystalline samples making an accurate determination of the ESR parameters more difficult. That is the reason why the slight orthorhombic distortion observed on single crystals has been neglected here. The powder ESR spectra can be correctly described with an axially symmetric spin Hamiltonian. We verified by computer simulation that the orthorhombic \mathbf{g} and \mathbf{A} tensors previously found for single crystals did not give a better fit with experimental spectra. The ESR spectrum of amorphous V_2O_5 (figure 2) does not vary with temperature in the range 4–300 K. On the other hand, a line broadening is observed in the case of the crystalline oxide. As the temperature increases, the hyperfine lines begin to broaden over 100 K, then overlap and collapse around 200 K giving a single broad line (figure 1c).

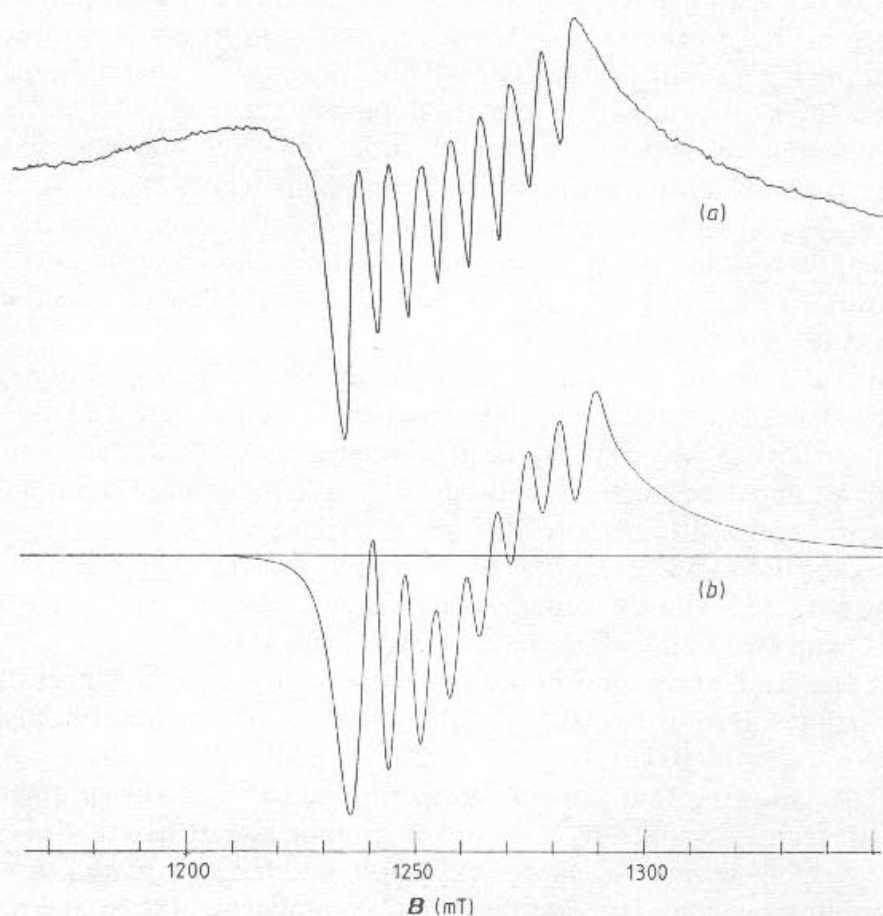


Figure 4. Q-band ESR spectra of amorphous WO_3 -doped V_2O_5 ($WO_3 = 0.5$ mol%). (a) experimental spectrum recorded at 77 K; (b) simulated spectrum.

Figures 3 and 4 show the Q-band ESR spectra of polycrystalline and amorphous WO_3 -doped V_2O_5 , both recorded at 77 K. They mainly show the perpendicular hyperfine lines, so that A_{\perp} and g_{\perp} can be directly measured from the spectrum. The other ESR parameters can be obtained from a computer simulation, and are reported on table 1. For the crystalline oxide, these parameters are the same as those previously found at X-band. This is not the case for the amorphous sample: the g and A tensors have not been modified, but the linewidth appears to be strongly frequency dependent. It is almost twice as large at 35 GHz than at 9.5 GHz. The hyperfine lines have been broadened so much that the parallel lines can no longer be seen on the wings of the spectrum (figure 4).

4. Discussion

4.1. Electron localisation

The eight hyperfine lines observed in the ESR spectra of amorphous and crystalline WO_3 -doped V_2O_5 indicate that in both cases the unpaired electron is localised on a single vanadium site. Previous studies performed on WO_3 - V_2O_5 single crystals (Livage *et al* 1980) showed that at low temperature the unpaired electron is trapped on one vanadium ion situated near the W^{6+} along the b direction. Defects like $\text{W}^{6+}-\text{O}-\text{V}^{4+}$ are observed. The unpaired electron and the doping impurity are associated, leading to the ESR parameters reported in table 1.

The ESR spectra of the amorphous oxide are also typical of V^{4+} ions, but the \mathbf{g} and \mathbf{A} tensors are noticeably different from those observed in the corresponding crystalline oxide. The measured g -values are, on the other hand, quite identical to those reported for pure crystalline V_2O_5 (Gillis and Boesman 1966). This suggests that the unpaired electron does not remain in the Coulomb field of the doping impurity. It should rather be trapped in a deep potential well due to structural disorder. This hypothesis is reinforced by the fact that the \mathbf{g} and \mathbf{A} tensors characterising paramagnetic defects in doped amorphous V_2O_5 do not depend on the nature of the doping impurity (Livage *et al* 1977).

The analogy between the \mathbf{g} tensors of crystalline and amorphous V_2O_5 indicates that short-range order is conserved. The local crystal field around vanadium should be almost the same in both compounds.

The linewidth of the ESR spectrum of crystalline WO_3 -doped V_2O_5 is strongly temperature dependent (figure 1). It increases with temperature and all the hyperfine lines collapse above 200 K. This can be attributed to a lifetime broadening effect due to the hopping of unpaired electrons between V^{4+} and V^{5+} ions. The hopping frequency increases with temperature according to an exponential law $\nu_h = \nu_0 \exp(-W_h/kT)$ where W_h is the activation energy of the thermally activated hopping process. All the lines collapse at 200 K when ν_h becomes of the same order of magnitude as the hyperfine parameters expressed in frequency units, i.e. $\nu_h \simeq 400$ MHz.

The ESR spectrum of the amorphous oxide does not vary with temperature (figure 2). It remains well resolved up to 300 K showing that the hopping frequency is smaller than the linewidth, i.e. $\nu_h < 100$ MHz. Such a result agrees with DC electrical conductivity measurements, showing that at room temperature the resistivity of amorphous V_2O_5 ($\rho = 5 \times 10^4 \Omega \text{ cm}$) is about two orders of magnitude larger than that of the crystalline oxide ($\rho = 5 \times 10^2 \Omega \text{ cm}$). Assuming that such a difference mainly arises from the electron mobility, we may estimate the hopping frequency of the unpaired electron in amorphous V_2O_5 to be about 4 MHz. Such a value is much smaller than the observed linewidth and cannot lead to any broadening effect.

4.2. Crystal-field fluctuations

One of the most striking features of the ESR spectra of amorphous V_2O_5 comes from their strong frequency dependence. According to our measurements (table 1), this appears to be mainly due to a broadening of the hyperfine lines with the microwave frequency. As suggested by Sperlich *et al* (1973), this could be due to a distribution of \mathbf{g} among the different vanadium sites. For an orbitally non-degenerate ground state, the g -factor can be expressed as $g = g_e(1 - n\lambda/\Delta)$ where $g_e = 2.0023$ is the free-electron g -value, λ the V^{4+} spin-orbit coupling constant, Δ the crystal-field parameter and n a constant depend-

ing on the ground-state wavefunction of the unpaired electron. This expression shows that a distribution of g could result from a distribution of Δ . The frequency dependence of the observed ESR linewidth could then be interpreted as a g -factor distribution δg due to crystal field fluctuations $\delta\Delta$.

Analogy between g -tensors in amorphous and orthorhombic V_2O_5 suggests that short-range order is almost the same in both compounds. The crystal-field symmetry around V^{4+} can then be approximated to C_{4v} (Bachman *et al* 1961) and the unpaired electron lies in a $3d_{xy}$ orbital (Ballhausen and Gray 1962). The ground state being 2B_2 , the g -factor can be expressed as:

$$g_{\parallel} = g_e(1 - 4\lambda/\Delta_1) \quad (1)$$

$$g_{\perp} = g_e(1 - \lambda/\Delta_2) \quad (2)$$

where

$$\Delta_1 = E_{b_1} - E_{b_2} = 10Dq$$

$$\Delta_2 = E_e - E_{b_2} = -3D_s + 5D_t.$$

According to Ballhausen and Gray (1962), Δ_1 corresponds to the octahedral crystal-field splitting while Δ_2 indicates the degree of tetragonal distortion along the z axis. A random distribution $\delta\Delta_1$ and $\delta\Delta_2$ would lead to a random distribution $\delta\Delta$ (Sperlich *et al* 1973).

$$\delta\Delta = \frac{1}{2}[(\delta\Delta_1)^2 + (\delta\Delta_2)^2]^{1/2} \quad (3)$$

which can be estimated from ESR experiments at X and Q band. The powder spectrum obtained with amorphous V_2O_5 results from the superposition of randomly distributed V^{4+} axial crystal fields over all orientations. It is then characterised by the four ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} and the linewidth ΔH . Dipolar interactions lead to a dependence of ΔH on θ (angle between the applied magnetic field and the distortion axis z of each site). Our experiments show that the linewidth also depends on the microwave frequency ν . The measured linewidth $\Delta H_{\text{exp}}(\theta, \nu)$ can then be expressed as (Sperlich *et al* 1973):

$$\Delta H_{\text{exp}}^2(\theta, \nu) = \Delta H_{\text{DD}}^2(\theta) + \Delta H^2(\theta, \nu) \quad (4)$$

where $\Delta H_{\text{DD}}(\theta)$ corresponds to the dipolar contribution:

$$\Delta H_{\text{DD}}(\theta) = \frac{1}{3}(\Delta H_{\parallel} + 2\Delta H_{\perp}) + \frac{1}{3}(\Delta H_{\parallel} - \Delta H_{\perp})(3 \cos^2 \theta - 1).$$

It does not depend on the microwave frequency and a comparison between X and Q band spectra will leave it out. From the Zeeman term $h\nu = g(\theta) \beta H(\theta, \nu)$ we can calculate

$$\Delta H(\theta, \nu) = \frac{h \delta g(\theta)}{\beta g^2(\theta)} \nu$$

where

$$g^2(\theta) = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$$

and

$$\delta g(\theta) = [1/g(\theta)](g_{\parallel} \cos^2 \theta \delta g_{\parallel} + g_{\perp} \sin^2 \theta \delta g_{\perp}).$$

According to (1) and (2), then neglecting $\delta\lambda/\lambda$ we can write:

$$\delta g_{\parallel} = \frac{4g_e\lambda}{\Delta_1} \left(\frac{\delta\Delta_1}{\Delta_1} - \frac{\delta\lambda}{\lambda} \right) \simeq (g_e - g_{\parallel}) \frac{\delta\Delta_1}{\Delta_1}$$

$$\delta g_{\perp} = \frac{g_e\lambda}{\Delta_2} \left(\frac{\delta\Delta_2}{\Delta_2} - \frac{\delta\lambda}{\lambda} \right) \simeq (g_e - g_{\perp}) \frac{\delta\Delta_2}{\Delta_2}.$$

This leads to the general relationship:

$$\Delta H(\theta, \nu) = \frac{h\nu}{\beta} \frac{1}{g^3(\theta)} \left((g_e - g_{\parallel})g_{\parallel} \cos^2 \theta \frac{\delta\Delta_1}{\Delta_1} + (g_e - g_{\perp})g_{\perp} \sin^2 \theta \frac{\delta\Delta_2}{\Delta_2} \right).$$

For the parallel ($\theta = 0$) and perpendicular ($\theta = \pi/2$) hyperfine lines we then have:

$$\Delta H_{\parallel}(\nu) = \frac{h\nu (g_e - g_{\parallel})}{\beta g_{\parallel}^2} \frac{\delta\Delta_1}{\Delta_1} \quad H_{\perp}(\nu) = \frac{h\nu (g_e - g_{\perp})}{\beta g_{\perp}^2} \frac{\delta\Delta_2}{\Delta_2}.$$

Δ_1 and Δ_2 can be deduced from optical spectra. According to Ragle (1963) the electronic transition ${}^2B_1 \leftarrow {}^2B_2$ and ${}^2E \leftarrow {}^2B_2$ occur at 13000 cm^{-1} and 10300 cm^{-1} respectively. These values were obtained for V_2O_5 single crystals, but the identity of \mathbf{g} tensors in amorphous and crystalline V_2O_5 suggests what we can, with a good approximation, use these values in our calculations. This leads to $\beta\Delta_1 = 0.35 \pm 0.04 \text{ eV}$, $\delta\Delta_2 = 0.33 \pm 0.06 \text{ eV}$ and $\delta\Delta = 0.24 \pm 0.04 \text{ eV}$. This value of $\delta\Delta$ gives an estimation of the crystal-field fluctuations due to the random disorder in amorphous V_2O_5 .

5. Conclusion

The ESR spectra of amorphous and crystalline WO_3 -doped V_2O_5 are quite similar when recorded at low temperature and 9.5 MHz. This is due to the fact that in both cases, the unpaired electrons are localised on a single vanadium site giving rise to V^{4+} ions. Their behaviour with temperature and microwave frequency is, on the other hand, very different. The ESR linewidth of the crystalline oxide appears to be strongly temperature dependent due to a hopping process of the unpaired electrons between V^{4+} and V^{5+} ions. An 'Anderson localisation' of the charge carriers is observed in amorphous V_2O_5 whose ESR spectrum does not vary with temperature. This localisation can be attributed to energetic fluctuations W_D of the V^{4+} unpaired electron ground state caused by the random glass structure. This disorder energy term W_D can be expressed as (Sperlich *et al* 1973):

$$W_D = [(\delta E_c)^2 + (\delta\Delta)^2]^{1/2}$$

where δE_c and $\delta\Delta$ represent the Coulomb energy and the crystal-field fluctuations. The ESR spectra are influenced by the crystal-field fluctuations $\delta\Delta$ which give rise to a strong frequency dependence of the linewidth. A value of $\delta\Delta = 0.24 \pm 0.4 \text{ eV}$ can then be estimated from a careful analysis of the ESR linewidth. On the other hand, no information can be obtained about the Coulomb energy δE_c . We can thus only give a minimum value of the disorder energy W_D .

Rather few electrical conductivity measurements have been published on amorphous V_2O_5 . Most of them concern V_2O_5 -based glasses to which a glass former has been added. A straightforward comparison between our ESR experiments and conductivity measurements is then rather difficult. The only reported data found in the literature deal with V_2O_5 thin films where the V^{4+} concentration must be much higher than in our samples. Most of these works report values of W_D ranging between 0.18 eV and 0.40 eV (Allersma *et al* 1967, Linsley *et al* 1970, Lynch *et al* 1971, Sayer *et al* 1971, Sayer and Mansingh 1972, Greaves 1973, Sperlich *et al* 1973, Chandhari and Li 1974, Frazier and France 1977, Koffyberg and Benko 1978).

Our ESR results agree with those values. In any case, the main point remains to know whether the total ground-state energy fluctuation influences the activation energy of the hopping process or whether the charge carriers rather look for easy hops between vanadium sites having almost the same potential energy.

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