

ESR study at various microwave frequencies of amorphous and polycrystalline $\text{ZnO} \cdot x\text{V}_2\text{O}_5$ system

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The study of the system $\text{ZnO} \cdot x\text{V}_2\text{O}_5$ has shown that the various phases obtained by different cooling rates have ESR line-shapes which are very dissimilar. It has been shown that the amorphous phase is characterized by a well resolved hyperfine structure and that the ZnV_2O_6 phase has a very asymmetrical line-shape which closely resembles those studied in the magnetic resonances in metals. To verify the role played by the skin depth in causing this asymmetry, the measurements have been carried out at various microwave frequencies particularly in the low range of frequencies where the lines become symmetrical. This behaviour can be explained by assuming that the low frequency skin depth of the samples containing a high amount of ZnV_2O_6 is of the same order of the sample size. The use of this assumption permits an evaluation of the sample conductivity (about $5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$) which is close to the measured values (about $10^{-3} \Omega^{-1} \text{cm}^{-1}$).

1. Introduction

Glasses and polycrystalline materials containing V_2O_5 exhibit semiconducting properties due to the hopping of an electron between V^{4+} and V^{5+} sites. The more studied systems are the P_2O_5 – V_2O_5 mixtures but also compositions of the kind MO – V_2O_5 can give materials of high electrical conductivity [1, 2].

It has been shown, for example, that the equimolar system PbO – V_2O_5 has an electric conductivity which is strongly dependent on the thermal treatment of the material [2]. Moreover the intimate connection between the ESR line-shape and the hopping frequency of the polarons has been made evident [2, 3].

The appearance of a well resolved hyperfine structure is a distinctive feature of the amorphous phase in which the mean energy difference

between adjacent sites, W_D , is high, i.e. $W_D \gg kT$. In this case the electric conductivity is very low.

In crystalline or polycrystalline materials the contribution of W_D to the term $\exp(-W/kT)$, which is proportional to the electron jumping rate, is low. As a consequence, the hopping frequency will be higher and the material will have a higher conductivity. In these cases the ESR lines show a tendency to lose the hyperfine structure and for a very high hopping rate they assume a symmetrical Lorentzian shape.

The system $\text{ZnO} \cdot x\text{V}_2\text{O}_5$, particularly for $x = 2$, shows an even more pronounced dependence of the jumping rate on the phases present in the material. Although it has been impossible, in many cases, to make direct measurements of the conductivity, because most compounds have been obtained as a polycrystalline material, the

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ESR spectra give a clear insight to the various phases obtained.

As will be shown later, some of the spectra can be easily interpreted. On the contrary the polycrystalline samples of the composition $\text{ZnO} \cdot 2\text{V}_2\text{O}_5$, for which X-ray diffraction indicates the presence of a great amount of ZnV_2O_6 , are characterized by ESR spectra (see Fig. 1) which are very similar to those observed by Feher and Kipp [4] in the case of conduction electrons in metals and by Bloembergen [5] for the NMR (nuclear magnetic resonance) of metals.

These spectra are strongly dependent on the ratio of the skin depth (i.e. the distance inside the material at which the microwave field is attenuated by a factor e) and the sample size. In fact, if the skin depth is larger than the sample size the electrons will be subjected to a microwave field which is roughly constant and the resulting ESR spectrum is a Lorentzian or Gaussian symmetrical line, a situation which is always varified when performing the ESR of a non conducting material.

If, on the contrary, the skin depth is smaller than the sample size, the electrons are subjected to different RF (radio frequency) fields and each electron will be irradiated by microwave pulses, the length of each pulse being given by the time the electron takes to cross a distance of the order of the skin depth. The ratio of the skin depth and the sample size will be equal to the ratio of the time during which the electron is subjected to the microwave field and the time spent in the interior of the material. This situation gives rise to asymmetrical ESR line-shapes.

From an experimental standpoint, the more direct method for verifying this hypothesis is that of performing the ESR experiments at different microwave frequencies, particularly at low frequencies where the skin depth becomes larger and in which a larger section of material is irradiated.

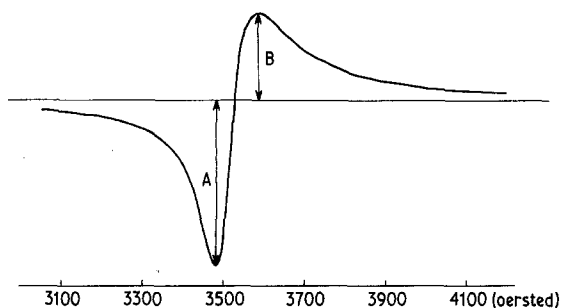


Figure 1 X band spectrum of the polycrystalline $\text{ZnO} \cdot 2\text{V}_2\text{O}_5$ sample.

This is particularly true in the case of low conductivity materials in which the skin depth is of the same order as that of the sample size.

The purpose of the present paper is to present the results obtained by the ESR study at various microwave frequencies of the system $\text{ZnO} \cdot x\text{V}_2\text{O}_5$. For the polycrystalline samples $\text{ZnO} \cdot 2\text{V}_2\text{O}_5$, which exhibit a line-shape very different from those previously obtained, a full discussion of the line-shape is given which accounts for the differences experimentally observed at the various microwave frequencies and which can provide an evaluation of the sample conductivity.

2. Experimental set-up

Most of the experiments have been performed at frequencies between 1 and 4 GHz, a frequency range which is not usual in commercial instruments. For this reason the spectrometer of Fig. 2 was built up. The most distinctive part is the sample cavity, which by means of replaceable rings can be put to work at any frequency between 1 and 4 GHz. In the present case this range was covered with intervals of 300 MHz. For a detailed description of the resonator the reader is referred to [6].

The microwave power is obtained by two cavity-stabilized oscillators, model Engelmann CC 12 for frequencies between 1 and 2 GHz and Engelmann CC 24 for frequencies between 2 and 4 GHz which can deliver 50 mW on the whole range. The oscillator was locked to the cavity frequency by means of an automatic frequency control (AFC).

The microwave power reached the cavity through a continuously variable attenuator and a circulator. A diode detector and a lock-in amplifier completed the spectrometer.

The X band spectra were obtained on a commercial spectrometer, model Bruker spectrospin ER 200 D, which utilized a rectangular TE_{102} cavity and a field modulation frequency of 100 kHz.

3. Preparation and characterization of the samples

The samples were prepared by melting, for two hours, the appropriate quantities of ZnO and V_2O_5 (Carlo Erba reagent grade) in an electrically heated muffle furnace under an air atmosphere.

In order to obtain different cooling rates, the melts were quenched on materials with various thermal conductivities, i.e. liquid nitrogen cooled graphite and stainless steel. A very slow cooling

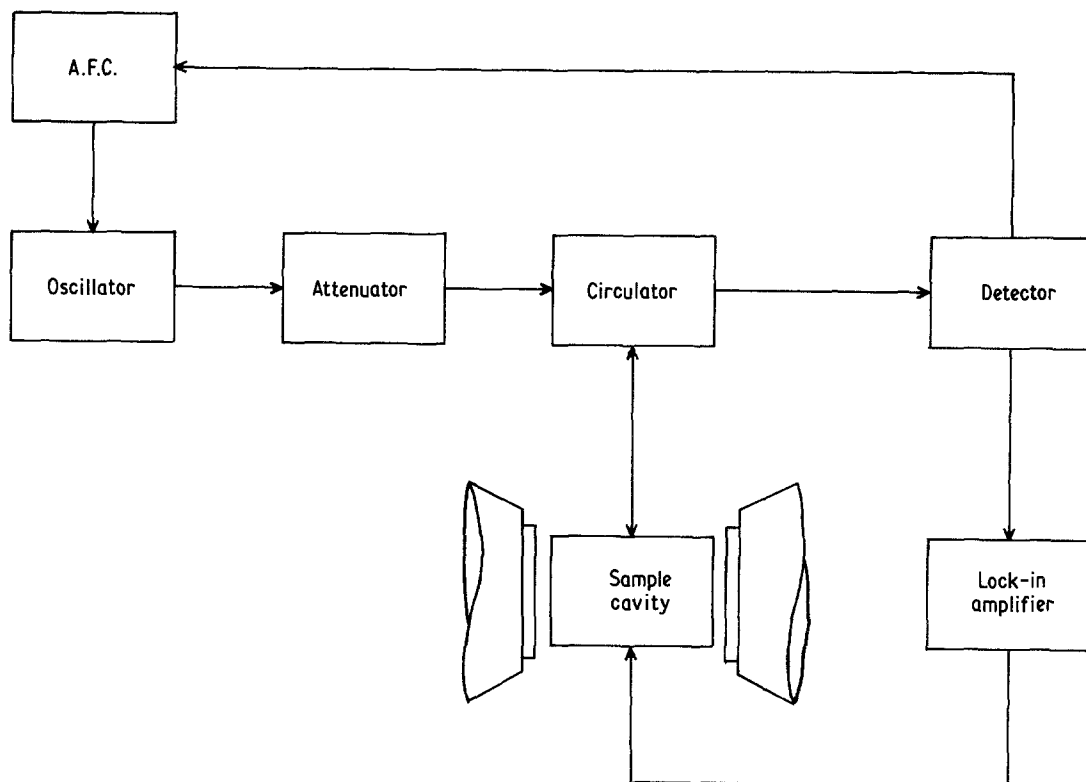


Figure 2 Block diagram of the low frequency ESR spectrometer.

rate (2°Ch^{-1}) was obtained by connecting an electronic programmer with the muffle furnace. The composition of the samples and the quenching characteristics are reported in Table I.

The characterization of the material was performed by means of powder X-ray diffraction. The recorded patterns were compared with theoretical ones calculated by a computer program on the basis of presumable crystalline structures. In

this way it was possible to check if the material was amorphous and/or eventually identify the crystalline phases. The characterization results are also summarized in Table I.

In every case except in the $\text{ZnO}\cdot\text{V}_2\text{O}_5$ composition the quenching on graphite gave rise to a completely amorphous material, confirming the considerable glass-forming capability of the V_2O_5 -based systems. Slower cooling rates have, on the

TABLE I Sample characterization

Sample	Composition	Main phase	Traces	Cooling rate
1	$\text{ZnO}\cdot\text{V}_2\text{O}_5$	amorphous	ZnV_2O_6 V_2O_5 $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	fast
2	$\text{ZnO}\cdot\text{V}_2\text{O}_5$	amorphous	V_2O_5 $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	very fast
3	$\text{ZnO}\cdot\text{V}_2\text{O}_5$	ZnV_2O_6	V_2O_5 $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	very slow
4	$\text{ZnO}\cdot 2\text{V}_2\text{O}_5$	ZnV_2O_6 V_2O_5	—	fast
5	$\text{ZnO}\cdot 2\text{V}_2\text{O}_5$	amorphous	—	very fast
6	$\text{ZnO}\cdot 1.5\text{V}_2\text{O}_5$	amorphous	V_2O_5 ZnV_2O_6 $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	fast
7	$\text{ZnO}\cdot 1.5\text{V}_2\text{O}_5$	amorphous	—	very fast
8	$\text{ZnO}\cdot 2.5\text{V}_2\text{O}_5$	amorphous	—	very fast

contrary, originated crystalline phases embedded in the amorphous matrix. Only samples 3 and 4 of Table I did not show the presence of the amorphous matrix.

It should be noted that whereas sample 4 was composed only of V_2O_5 and ZnV_2O_6 , in accordance with the $ZnO-V_2O_5$ phase diagram [7], the other polycrystalline materials always showed the presence of $\alpha-Zn_2V_2O_7$ which could not be predicted on the basis of the phase diagram.

Moreover even the very slow cooling in the furnace of the melt of the $ZnO \cdot V_2O_5$ composition did not give rise to a single ZnV_2O_6 phase, as expected from a thermodynamic basis. The presence of $\alpha-Zn_2V_2O_7$ can be explained by supposing a crystallization rate higher than that of ZnV_2O_6 .

Preliminary electrical conductivity measurements were carried out on some of the amorphous and polycrystalline samples at room temperature. Whereas no particular problem was encountered with the amorphous samples, it was impossible to isolate single crystals of ZnV_2O_6 and $\alpha-Zn_2V_2O_7$ of such a size to perform the conductivity measurements in a meaningful way. Hence, it was necessary to measure the conductivity of the bulk polycrystalline samples. However we are trying to grow single crystals of ZnV_2O_6 and $\alpha-Zn_2V_2O_7$ of sufficient quality.

Density measurements of the amorphous $ZnO \cdot 2V_2O_5$ sample permitted the evaluation of the absolute concentration N of the vanadium atoms inside the material ($N = 1.48 \times 10^{22} \text{ cm}^{-3}$); hence we could obtain by standard relationships [8] the distance R between the transition metal ions ($R = 0.408 \text{ nm}$).

Standard wet analyses performed on the same sample gave the concentration n of the V^{4+} charge carriers ($n = 6.8 \times 10^{20} \text{ cm}^{-3}$).

4. ESR spectra discussion

All the samples show ESR spectra which can be surely attributed to the V^{4+} species formed during

high temperature melting. In particular, each time the amorphous phase was present in a sufficient amount, the ESR spectrum was characterized by a well defined hyperfine structure which can be described by a spin Hamiltonian of the kind [9]:

$$H = g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

where the spin Hamiltonian parameters have the values $g_{\parallel} = 1.920$, $g_{\perp} = 1.973$, $A_{\parallel} = 188$ oersted and $A_{\perp} = 69$ oersted.

These values were found to be completely insensitive to variations of the batch composition and they are characteristic of the VO^{2+} ion in a glassy matrix [9–11].

The composition $ZnO \cdot 2V_2O_5$ when obtained as an amorphous compound showed again the VO^{2+} spectrum to which a very broad line is superimposed (see Fig. 3). The measure of the width of this line cannot be very accurate because of the superimposed hyperfine structure but a value of about 350 oersted can be assumed. The presence of two, so different ESR spectra in a material which is characterized by an amorphous X-ray pattern can be explained by assuming that inside the material there are regions of different jumping rates.

The hyperfine spectrum must, in fact, be assigned to regions in which the jumping frequency is smaller or, at the most, equal to the linewidth of the observed hyperfine lines which means a jumping frequency of the order of 30 MHz.

The broad line on the other side must originate in regions in which the jumping rate exceeds the value of A_{\parallel} and must be comparable with the linewidth thus giving a hopping frequency whose lower limit is between 0.6 and 1 GHz.

An attempt to evaluate the conductivity of the different regions has been done by using these values for the hopping rate P . In fact, from the relationships $\mu = (eR^2/kT)P$ and $\sigma = en\mu$ [12] the value of $5.4 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$ was obtained. This

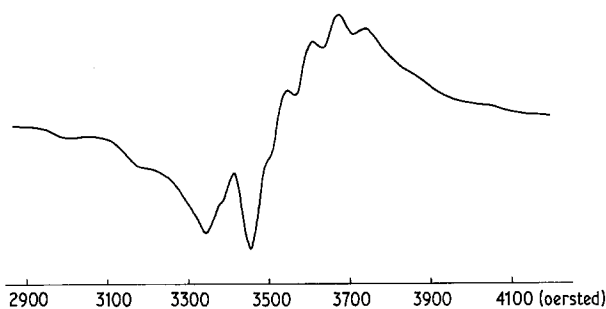


Figure 3 X band spectrum of the amorphous $ZnO \cdot 2V_2O_5$ sample.

value is very similar to those obtained in glasses but does not agree with the preliminary conductivity results (about $10^{-7} \Omega^{-1} \text{cm}^{-1}$). It must be remembered that the ESR data can only give the lower limit of the conductivity.

When the samples were cooled at a slower cooling rate a polycrystalline mixture resulted which consisted mainly of ZnV_2O_6 . In this case the X band ESR spectrum shown in Fig. 1 results, which is characterized by a very asymmetric line-shape. The low frequency spectrum of the same sample is shown in Fig. 4 and it is easy to verify that it has a nearly symmetric shape and a line-width of 82 oersted.

As previously said line-shapes, as that shown in Fig. 1, were observed in the case of paramagnetic centres in metals. The ratio A/B (see Fig. 1) can be used to distinguish between the various paramagnetic centres involved [13]. In fact if the signal is due to conduction electrons and the skin depth is smaller than the sample size, it will always be $A/B \geq 2.7$. A lower value of the A/B ratio is possible in the case of slowly diffusing localized electrons. If they are at the sample surface, the ratio will be $A/B = 1$ and if they are uniformly distributed through the sample volume $A/B \cong 2.7$ for a Lorentzian shape and $A/B = 2$ for a Gaussian line. In the present case an A/B ratio of 2 was obtained.

In an attempt to obtain a more homogeneous material some samples were prepared at a very low cooling rate. In this case an A/B ratio of 2.3 was obtained.

These values of the A/B ratio can be explained in these cases when the time necessary to cross the sample T_T is longer than the time necessary to cross the skin depth T_D and when both times are longer than the relaxation time T_2 , i.e. $T_T > T_D > T_2$.

Moreover, it is necessary to assume a Gaussian line-shape, a case which has not been explicitly

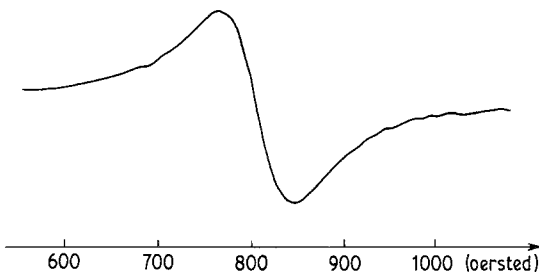


Figure 4 L band spectrum ($\nu = 2.15 \text{GHz}$) of the polycrystalline $\text{ZnO} \cdot 2\text{V}_2\text{O}_5$ sample.

treated in the study of conduction electrons for which the line is supposed to be homogeneously broadened, and hence Lorentzian.

In this case the RF power absorbed by the sample can be put in the form [5]:

$$W = 3/4\omega^{1/2}c(8\pi\sigma)^{-1/2}H_0^2R^2[1 + 2\pi(\chi' + \chi'')] \quad (2)$$

where ω is the microwave frequency, σ is the sample conductivity, R is the sample radius and H_0 is the RF field. χ' and χ'' are as usual the two components of the complex susceptibility. Equation 2 shows that in this case both components of the susceptibility contribute to the power absorption.

By putting $k = 3/4c(8\pi\sigma)^{1/2}H_0^2R^2$ in Equation 2 and using the usual formulae for χ' and χ'' [14], i.e.

$$\begin{cases} \chi' = -1/2\pi\chi_0\omega_0(\omega - \omega_0)T_2f(\omega - \omega_0) \\ \chi'' = 1/2\pi\chi_0\omega_0f(\omega - \omega_0) \end{cases} \quad (3)$$

where χ_0 is the static component of the magnetic susceptibility and $f(\omega - \omega_0)$ is a normalized shape function, the power absorption will become:

$$W = k\omega^{1/2}\{1 + \pi^2\chi_0\omega_0f(\omega - \omega_0) \times [1 - (\omega - \omega_0)T_2]\}. \quad (4)$$

To evaluate the derivative of this line, which is the experimentally observed quantity, the further assumption that the frequency or field sweep is much lower than the observing frequency or field, i.e. $\omega^{1/2} \sim \omega_0^{1/2}$, must be done.

In this case it will be:

$$\begin{aligned} \partial W/\partial\omega &= k\pi^2\chi_0\omega_0^{3/2}\{f'(\omega - \omega_0) \\ &\times [1 - (\omega - \omega_0)T_2] - T_2(\omega - \omega_0)\} \end{aligned} \quad (5)$$

In the case in which the original line has a Gaussian shape it will be:

$$\begin{cases} f(\omega - \omega_0) = [T_2/(2\pi)^{1/2}] \exp[-T_2^2(\omega - \omega_0)^2/2] \\ f'(\omega - \omega_0) = -T_2(\omega - \omega_0)f(\omega - \omega_0) \end{cases} \quad (6)$$

and substituting in Equation 5

$$\begin{aligned} \partial W/\partial\omega &= -G\{[1 - T_2(\omega - \omega_0)]T_2(\omega - \omega_0) + 1\} \\ &\times \exp[-T_2^2(\omega - \omega_0)^2/2] \end{aligned} \quad (7)$$

where $G = (k\pi^2\chi_0T_2^2\omega_0^{3/2})/(2\pi)^{1/2}$.

By using Equation 7 it is possible to obtain line-

shapes which closely resemble the ESR spectra of Fig. 1.

Equation 7 has been evaluated starting from a Gaussian line-shape whilst in the study of ESR of paramagnetic centres in metals Lorentzian line-shapes are normally used.

In glasses and in disordered materials, however, in which the line broadening is mainly due to a spread of the spin Hamiltonian parameters the assumption of a Gaussian line-shape is fully justified.

On the other hand, the more homogeneous phase obtained at a low cooling rate tends to have a more regular environment and the results are more similar to those obtained on metals.

In passing from *X* band to *L* band the skin depth increases considerably. In this case the RF absorption of the sample is independent of the diffusion rate of the paramagnetic centres.

Also in the case of samples obtained at a very low cooling rate the low frequency spectra have always a symmetrical shape without any appreciable variation.

The assumption of a low frequency skin depth comparable with the sample size can be used to make an evaluation of the electrical conductivity. In fact using the standard formula for the skin depth $\delta = (2/\omega\mu_0\sigma)^{1/2}$ it is possible to obtain $\sigma \sim 5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$, a value which is of the same order of magnitude as that obtained in the case of fast conducting glasses and which agrees with the preliminary results obtained by d.c. conductivity measurements ($10^{-3} \Omega^{-1} \text{cm}^{-1}$).

5. Conclusions

From the study of the line-shapes of the ESR spectra it is possible to gain a useful insight on the motional processes taking place inside the studied materials. In particular it is possible to obtain an evaluation of the hopping rate of the unpaired electrons responsible for the electrical conductivity. The estimated values of the hopping rate are then inserted in the usual formulae [12] and evaluations of the drift mobility and the d.c. conductivity are hence obtained.

In spite of the substantial agreement between the values calculated in this way and the direct measurements of the d.c. conductivity presently performed, caution should be exercised when

correlating the ESR data with the d.c. conductivity. In fact the ESR line-shapes can be affected by motional processes which are localized in confined regions of the materials and which do not contribute to the d.c. conduction. Such a situation can easily be met in an amorphous phase separated matrix.

The comparison of the ESR line-shapes obtained at low (*L* band) and high (*X* band) frequency has given the possibility of making some evaluation of the skin depth for crystalline samples. Apart from this particular situation, the low frequency experiments can give a better resolved ESR spectra because all the field dependent broadenings are strongly reduced.

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