

Quantitative EPR Spectroscopy in Solid State Chemistry*

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Error sources in quantitative EPR spectroscopy of solid state materials associated with sample shape and sample packing procedure have been analyzed. It was found that: The differences in the shape of bulky, solid state materials (despite being of identical material, volume, and sample mass) can cause EPR signal intensity differences of 200–500 %. The differences in the sample tube packing procedure of the powdered/polycrystalline materials (despite being of identical material, volume, and sample shape) can cause the EPR signal intensity differences of 17–21 %.

Essential difficulties in quantitative EPR spectroscopy were clearly demonstrated in the results obtained from international experiments carried out in 1962 [1] and 1991–1992 [2]. In principle, experimental errors in quantitative EPR measurements for a given laboratory and a given EPR spectrometer may be reduced in carefully performed experiment to 2–5 % [3]. However, experimental data on the same sample obtained in different laboratories were found to be incompatible, and can produce an uncertainty of 100–200 % [1], and others up to 500 % [3]. No satisfactory explanation for this discrepancy has been found at present.

A multitude of error sources influence the accuracy and reproducibility of quantitative EPR spectroscopy (see [3–8] for review). The essential problem is that some of these error sources may cause significant systematic and/or nonsystematic errors in quantitative EPR measurements. *Warren and Fitzgerald* [6] have classified the error sources to the two large groups: i) instrumental factors, and ii) sample associated factors. The majority of mentioned error sources can be controlled by the EPR spectrometer operator. However, some sample associated factors, mainly sample shape in the case of bulky, solid state materials, and sample packing procedure in the case of the powdered/polycrystalline materials, could be partially influenced and/or controlled directly by the quantitative measurement applicant, who is only an EPR spectroscopy user, but not an EPR spectroscopy specialist/operator.

The aim of this paper presented is: i) calling to the large community of the solid state chemists/physicists, who are the producers/applicants of solid state samples, and ii) make known the error sources in solid

state quantitative EPR spectroscopy, which are associated with the sample shape and sample packing procedure.

EXPERIMENTAL

The samples were prepared and measured according to the same procedures as were described in the experimental section of our previous paper [9]. A short recapitulation with specific reference to the preparation and measurement of cylindrical samples with various shapes is described.

The cylindrical samples with various shapes were prepared as follows: The original tube (o.d. \approx 4 mm) with the powdered Varian strong pitch standard sample was opened under an inert atmosphere, and the material was reloaded to thin-walled quartz EPR tubes, with various internal diameter (i.d.) and identical length (60 mm). The pairs of the identical cylindrical samples with various material column diameter (d), from 0.75 mm to 4 mm and sample length (L), from 1.3 mm to 50 mm, were prepared. This basic procedure for filling of the sample tubes was used: The powdered material was poured in the sample tube, shaken, and pressed carefully by lightly knocking the tube on the laboratory table ten times.

All samples were accurately inserted in the centre of the microwave cavity, using our original device for precision positioning of line-like sample in the rectangular cavity. In this case the sample alignment procedure was modified for cylindrical samples with various diameter, as was described in our previous paper [10].

Spectra were recorded using a Bruker ER 200 D-SRC EPR spectrometer with Aspect 2000 computer and with the original double TE₁₀₄ rectangular cavity.

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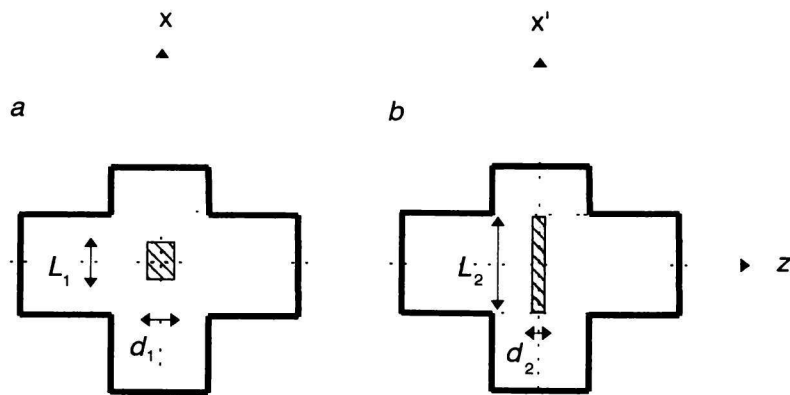


Fig. 1. Schematic diagram of the cross-section of the microwave rectangular cavity, in the centre of which the solid state cylindrical samples with identical volume, but different shape were inserted. (For more details see text.)

Identical instrumental parameters were used to those described in our previous paper [9]. The temperature of the EPR laboratory room was air-conditioned at 16°C. In all cases the intensity of the EPR signal was characterized by the peak-to-peak height of the first derivative EPR signal.

RESULTS AND DISCUSSION

The error sources in quantitative EPR experiments associated with different shape of bulky, solid state samples have been investigated. The experimental results obtained are illustrated on a simple example.

Fig. 1 shows the schematic diagram of the cross-section of the microwave rectangular cavity, in the centre of which the solid state cylindrical samples were positioned. The material, volume, and mass of these samples was identical, however, the sample shapes were different: In the case (a) $d_1 = 4$ mm, $L_1 = 5$ mm, and in the case (b) $d_2 = 2$ mm, $L_2 = 20$ mm. This fact caused that the EPR signal intensity obtained for the sample with the shape (a) was about 200 % higher than the one for the sample with the shape (b). The comparison of the other pairs of the samples with identical volumes but different sample shapes, have shown the signal intensity differences of 200–500 %. However, when the sample shapes were identical, the differences were found between 3–5 %, which is in accordance with the literature data [3].

It is clear that the different sample shapes (in spite of identical sample material, volume, and also sample mass) could be responsible for the essential difficulties in quantitative EPR spectroscopy of bulky, solid state materials.

The detailed analysis of error sources associated with various sample shape will be a subject of our next paper in preparation.

The error sources in quantitative EPR experiments

associated with different packing procedures of the sample tube by powdered/polycrystalline state materials have been investigated. The experimental results obtained are again illustrated in a simple example.

The three sets of line-like powdered samples ($L = 30$ mm, i.d. = 1.3 mm) were prepared by the following different packing procedures: a) The powdered material was poured into the sample tube, neither shaking, nor pressure was applied. b) The powdered material was poured into the sample tube, shaken, and pressed carefully by lightly knocking it ten times on the laboratory table. c) The powdered material was poured into the sample tube, shaken carefully, and pressed hard by the small piston. The material, volume, and shape of these samples was identical, however, the sample volume densities were different. Mainly, the increase in the volume mass was: i) about 13 % between (b) and (a), and ii) about 22 % between (c) and (a) packing procedure. This fact caused an increase in the corresponding EPR signal intensity about 17 % and 20 %, respectively. (For more details see our previous paper [9].)

It is evident that the different sample tube packing procedures (in spite of identical sample material, volume, and shape) could be responsible for the essential difficulties in quantitative EPR spectroscopy of powdered/polycrystalline materials.

To our knowledge, the importance of the influence of both error sources on the accuracy and reproducibility of quantitative EPR spectroscopy of the bulky and powdered/polycrystalline solid state materials has not been analyzed in the literature with satisfactory precision, and more attention to the investigation of this phenomenon will be needed in the future.

CONCLUSION

It can be concluded that both the mentioned phe-

nomena may be serious sources of significant errors in quantitative EPR spectroscopy if: i) the bulky samples (crystals, rows, etc.) with identical material, volume, and sample mass, but different shapes; or ii) the powdered/polycrystalline samples with identical material, volume, and sample shape, but with EPR sample tubes filled by different packing procedures, are under comparison. Accordingly, any quantitative conclusions from the experimental EPR data in the solid state chemistry/physics have to be drawn with a great deal of caution.

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