Volume 9, Number 4
1009-1963/2000/09(04)/0290-04
CHINESE PHYSICS
April, 2000
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# ELECTRON PARAMAGNETIC RESONANCE STUDIES OF DIMENSIONALITY OF POLYANILINE FILMS*

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(Received 21 September 1999)

The line shape analysis of electron paramagnetic resonance (EPR) spectra for low-dimensional solids are calculated. A comparison is carried out between the experimental EPR results of polyaniline samples and theoretical calculation. The dimension evolution of the samples from nonconducting to conducting states is obtained. It is found that the dimensional properties determined by EPR are in good accordance with those obtained using previous ellipsometric methods.

**PACC:** 6140K; 7630

## I. INTRODUCTION

Polyaniline is a family of polymers that is known for its remarkable insulator-to-conductor transition as a function of protonation. Upon protonation of the emeraldine form of polyaniline, its conductivity increases by about 10 orders of magnitude, reaching $1\,\mathrm{S/cm}$[1] while the number of electrons on the polymer chains remains constant. Because of their novel properties, e.g., the absence of Peierls instability, which usually appears in low-dimensional anisotropic system, the metallic behavior of conducting polyaniline has been investigated theoretically and experimentally by many authors[2−5]. The results reveal that the dimensionality is important in the determination of the properties of polyaniline. However, up to now details of the electronic structure and the dimension evolution of polymer changing from insulator to conductor have not been clearly obtained.

Electron paramagnetic resonance (EPR) is a powerful tool for probing spin interaction in low-dimensional systems. From the EPR spectrum one can extract detailed information including line shape, linewidth and g factor.

In this paper, to study the line shape of EPR spectra we propose a new method based on the fractional dimensional space model, which is especially suitable for studying general anisotropy systems. The line profiles for solids with different fractional dimensions are calculated. The EPR absorption of both insulating and conducting samples are measured, from which we obtain the dimensionality of differently doped samples. Comparing the experimental results with theoretical calculation, we find that the fractional dimensionality determined by EPR quantitatively describes the degree of anisotropy in low-dimensional system.

## II. THEORETICAL CALCULATION

In their linear-response theories, Kubo *et al.*[6] and Abragam[7] have derived the general expression of decay function of the transverse magnetization which may be approximated by

$$\phi(t) = \exp\left[-\int_0^t (t-\tau)\psi(\tau)\mathrm{d}\tau\right], \qquad (1)$$

where $\psi(\tau)$ is a correlation function of the magnetization of the system in the full local field, this generally means the sum of contributions from many spins.

While at high-temperature approximation the line profile $I(\omega)$, which is the Fourier transform of the correlation function $\psi(\tau)$ at an arbitrary frequency, can be expressed as

$$I(\omega) = A\int_0^\infty \phi(t)\cos\omega t\mathrm{d}t. \qquad (2)$$

Therefore, the line shape may be computed numerically once the interchain coupling of the system is defined.

Usually, in order to obtain the line shape and the corresponding parameters of EPR spectra for solids with various structures, we have to compute the EPR Hamiltonians. In this work, we perform the calculation by using a phenomenological theory, in which we do not calculate the specific spin interactions and EPR Hamiltonians, but use the phenomenological expressions of correlation functions.

An accurate calculation of the correlation function $\psi(\tau)$ is extremely difficult and it has been customary to approximate it by finding the leading terms in

* Project supported by the National Science Foundation of China (Grant No. 19874081).

a short-time expansion and using the results to characterize an assumed form for $\psi(\tau)$. But in the high-temperature limit and in a range of enough large $\tau$, $\psi(\tau)$ can be defined by a simple function. For one-dimensional systems, Hennessy *et al.*[8] concluded

$$\psi(\tau) = B\tau^{-1/2}, \tag{3}$$

and for three-dimensional system in exchange-narrowing theory, Gulley *et al.*[9] gave

$$\psi(\tau) = B'\tau^{-3/2}. \tag{4}$$

We extend the above equations to the fractional-dimensional case, and propose the following equation:

$$\psi(\tau) = C_n\tau^{-n/2}, \tag{5}$$

where $n$ is an assumed parameter of a physical model, which implies the dimension that can be fractional, and $C_n$ is the constant for the $n$ case. Equation (5) can be regarded as a definition of the fractional dimension that is related to an isotropic property of spin diffusion as well.

From Eqs.(5) and (1) we can acquire the decay of the transverse magnetization as a function of $t$:

$$\phi(t) = \exp(-D_n t^{2-n/2}), \tag{6}$$

where $D_n$ is a constant related with the dimensionality $n$. Figure 1 shows the decay of transverse magnetization for different fractional dimensionalities ($n$=0, 0.5, 1, 1.5, 2, 2.5 and 3) calculated by using Eq.(6).

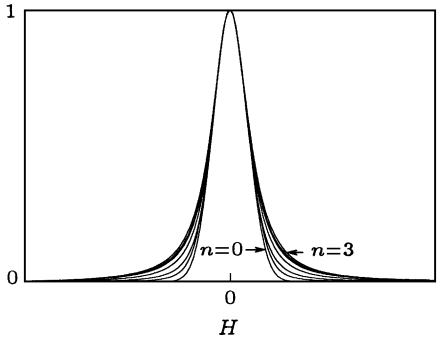



**Fig.2.** (a) Normalized line shapes of EPR spectra of different dimensionality.

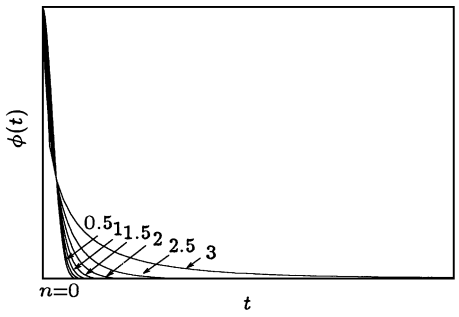



**Fig.1.** Decay of transverse magnetization for different dimensionality.

From Eqs.(6) and (2), the line shapes of EPR for various dimensional cases are computed and shown in Fig.2(a). The line shapes of solids with different dimensionality are nearly the same in the linewidth region, but show appreciable differences far out in the wings of the resonance line center $H_0$. Therefore, by studying EPR absorption $I(H)$ far from the line center $H_0$, we can analyze the dimensional effect on the line shape of EPR. The line shapes of EPR for various fractional dimension cases are illustrated in Fig.2(b), in which the quantity $I(H_0)/I(H)$ as the function of $[(H - H_0)/\Delta H_{1/2}]^2$ is used to express the line shape. $\Delta H_{1/2}$ is the half line width of a resonance line and $H_0$ is the value of the field $H$ at resonance.

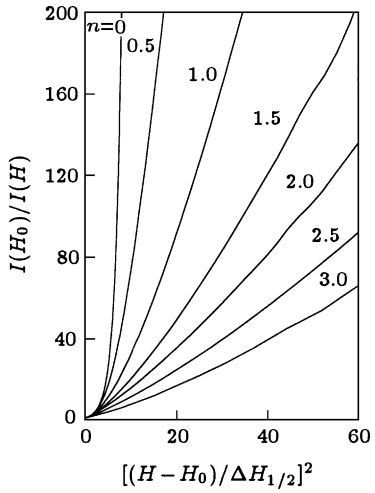



**Fig.2.** (b) Theoretical EPR line shapes for various dimensional solids.

## Ⅲ. EXPERIMENTAL

To examine the validity of the above-derived relationship of line shape with dimensionality, the EPR spectra of polyaniline were measured. Polyaniline is selected as the model system because (1) it is a class of anisotropy; (2) it is an insulator in its intrinsic state and becomes high conductive when it is protonated by acidic process. The change of the conductivity can be described as the dimensional change caused by inter-chain interaction after protonation.[10,11]

The emeraldine base of polyaniline(PAN-ES) was

prepared by chemical means and cast into films. The conducting polyaniline samples were obtained by dipping the insulating films into acid solution of different HCl concentrations for 72 h. After this treatment of protonation, the polyaniline samples were dried for EPR measurements. The measurement of EPR absorption was performed at room temperature in dark with a JEOL JES-FE3X spectrometer at the $X$-band with a field modulation frequency 6.4 GHz. All resonance signals were averaged using a digital storage oscilloscope and sent to a computer for analyses. A typical first derivative absorption line of the conducting polyaniline sample is shown in Fig.3. For both the insulating and conducting samples, $g$ factor held constant ($g$=2.0034).

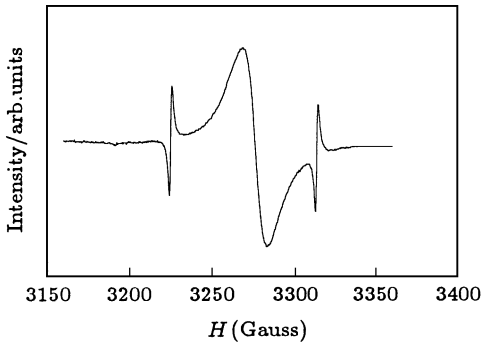



**Fig.3.** A typical first derivative of EPR absorption line of HCl-doped polyaniline.

## IV. RESULTS AND DISCUSSION

By performing the simple integral calculus of EPR derivative signals without the $Mn^{2+}$ standard, we obtain the line shapes. The evolution of EPR spectrum from non-conducting to conducting polyaniline films is shown in Fig.4, in which curve A stands for non-conducting state, curves B to D for different doping concentrations. Here the $y$-axis is the reciprocal intensity normalized to its central value and the $x$-axis is the square of the static magnetic field measured from the center of the EPR line and normalized to the half-power linewidth. By fitting the experimental line shapes of various samples with the theory, the values of fractional dimension n for differently doped samples are derived. The $n$ values of sample A, B, C, D are 1.1, 1.5, 1.9, 2.7, respectively. The result is basically in agreement with the metallic bundle model,[4] which proposed the film consists of 3-dimensional (3D) conducting region and 1-dimensional (1D) amorphous region. Our derived $n$ value of fully conducting polyaniline is 2.7, which is a little smaller than 3, implying the results are reasonable.

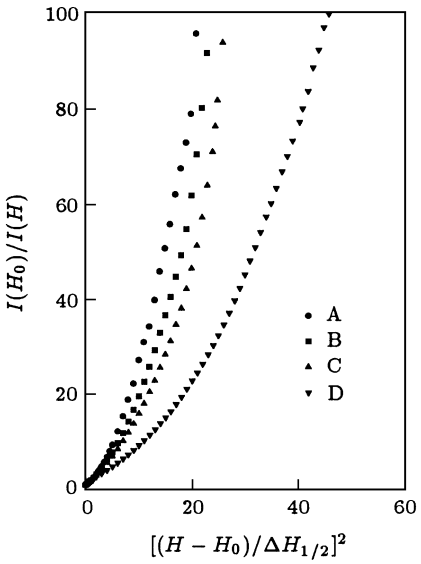



**Fig.4.** The line shapes of insulating and different protonated conducing polyaniline.

On the other hand, Mo *et al.* have investigated the dimensional crossovers of electron states of polyaniline in the doping process by the ellipsometric spectra and obtained the effective dimension of the electron states.[10,11] The fractional dimension of polyaniline determined by spectroscopic ellipsometry is from 0.9 for insulting state to 2.6 for fully conducting state. The results of dimension determined by the two methods are consistent.

In conclusion, by using the phenomenological expression method, EPR can be a potentially efficient technique for probing electron dimensional behavior in low-dimensiond solids. It has been demonstrated that it is an efficient approach in determining the dimensionality of conducting polyaniline.

## ACKNOWLEDGEMENTS

We are grateful to Prof. K. C. Gong of South China University of Technology for his help in sample preparation.

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