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# Study on microstructural lattice deformation of polypyrrole by positron annihilation lifetime spectroscopy

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Microstructural defects (polarons, bipolarons), responsible for conduction in polypyrrole (PPy) has been studied using positron annihilation lifetime (PAL) spectroscopy, conductivity and electron spin resonance (ESR) measurements. Pyrrole, oxidized at different oxidizing strengths [0.13(N)–2.0(N)] by ammonium ferric sulphate has been used for the preparation of PPy. It is observed from the PAL measurement that of the two lifetime components the longer one originates from annihilation of positron in the defect (polaron and bipolaron) sites and the corresponding intensity is a measure of the defect concentration. Further it is evident from the ESR spectra that the dominant defects are polarons at lower oxidizing strengths [ $\leq 0.75(N)$ ] and bipolarons at strengths  $\geq 1.0(N)$ . Conductivity data corroborate the findings. © 1999 American Institute of Physics. [S0021-9606(99)50406-6]

## I. INTRODUCTION

Polypyrrole (PPy) has attracted much experimental and theoretical attention because it is one of the most stable conducting polymers and easy to synthesize.<sup>1–3</sup> The effect of doping on electronic states, conductivity and optical properties of such polymers have been widely investigated over the past several years leading to the proposition that these properties are considerably affected by the polaron or bipolaron type of defects generated in the neutral polymer chain.<sup>3–5</sup> Typically, PPy possesses a nondegenerate ground state. A polaron is produced upon extraction of a negative charge from a neutral segment of the chain (via partial oxidation) accompanied by lattice relaxation. Formation of polaron, a radical cation, introduces two states within the band gap which are bonding and antibonding in character. Subsequent removal of further negative charges from the PPy chain that already contains a polaron, may yield more polarons or the existing polaron may be ionized to form a bipolaron (via additional oxidation). Theoretical calculations done by Bredas *et al.*<sup>6</sup> suggest that the latter process is favored energetically. Although contradictory arguments exist,<sup>7</sup> it is now evident that bipolarons play a fundamental role in the charge transport within the PPy chain. As more bipolarons are generated, their energies overlap leading to bipolaron bands within the forbidden gap. Electronic energy levels of such a system have been suggested by Bredas *et al.*<sup>6</sup> Since polypyrrole is insoluble and infusible, the experimental investigations are partially hampered. Recently, microstructural changes in the conducting polymer matrix has been extensively studied through positron annihilation lifetime (PAL) measurements.<sup>8–10</sup> Because of its nondestructive nature and sensitivity to electron density fluctuations within a material, PAL measurements are being conducted widely to identify the nature of the defects, particularly the open volume defects. Doyle *et al.*<sup>8</sup> have studied the PAL in PPy at different

temperatures and observed weak temperature dependence and they attributed positron trapping to polarons only. Later on Sharma *et al.*<sup>11</sup> suggest that positron localization takes place in the bipolaronic environment. Pethrick<sup>12</sup> has recently published an extensive review on the use of PAL measurements in polymers and has pointed out the suitability and importance of this technique for using it as a probe to study defects in polymers. The aim of the present work is to study the effects of reagent concentration used to synthesize polypyrrole on the microstructural lattice deformation of the resulting polymer. We have assessed this using PAL spectroscopy, ESR spectroscopy and 4 probe conductivity measurements.

## II. EXPERIMENT

### A. Materials

Pyrrole (E. Merck, Germany) is purified twice by fractional distillation under nitrogen atmosphere immediately before use. Ammonium ferric sulphate  $[(NH_4)Fe(SO_4)_2]$ , 12 H<sub>2</sub>O (E. Merck, Germany) is used as the oxidizing agent with conductivity water as its solvent.

### B. Polymer synthesis

PPy is synthesized by mixing pyrrole solutions with solutions of the oxidizing agent of different strengths viz., 0.13(N), 0.25(N), 0.5(N), 0.75(N), 1.0(N), 1.5(N) and 2(N). In each case, pyrrole is added to such an extent that the molar ratio of an oxidizing agent to pyrrole is 50:1. This ratio is maintained to ensure complete conversion of the pyrrole monomer to PPy.<sup>13</sup> In each case polymerization is allowed to proceed for 1 h. PPy, formed as a black precipitate, is collected by filtration in a sintered bed crucible. The polymer thus obtained is rinsed thoroughly with water and dried for 24 h at room temperature *in vacuo*. Dried polypyrrole

TABLE I. PAL spectroscopic parameters of different PPy samples.

Oxidizing agent	Strength	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_B$ (ps)	$I_2$ (%)
	(N)				
(NH <sub>4</sub> )Fe(SO <sub>4</sub> ) <sub>2</sub>	0.13	180 ± 3	403 ± 5	201 ± 2	19 ± 1.5
	0.25	180 ± 3	400 ± 5	202 ± 2	20 ± 1.5
	0.50	180 ± 3	401 ± 5	206 ± 2	22 ± 1.5
	0.75	180 ± 3	401 ± 5	209 ± 2	25 ± 1.5
	1.00	160 ± 3	351 ± 5	191 ± 2	30 ± 1
	1.50	154 ± 3	343 ± 5	191 ± 2	35 ± 1
	2.00	150 ± 3	330 ± 5	197 ± 2	43 ± 1

powder doped with an oxidizing agent at different strengths as stated above is subjected to 6 ton/cm<sup>2</sup> pressure for 10 min to make pellets which are subsequently used for conductivity as well as PAL measurements. Dried PPy powder is used to take the ESR spectra.

### C. PAL measurements

The positron annihilation lifetime has been measured with a fast-slow coincidence assembly. The detectors are 25 mm diam, 25 mm long cylindrical BaF<sub>2</sub> scintillators coupled to Philips XP2020Q photomultiplier tubes (PMT). The negative pulses from the anodes of the PMTs are fed directly to constant fraction differential discriminators and then to the inputs of a time-to-amplitude converter. The resolving time (FWHM) measured with a <sup>60</sup>Co source and with the windows of the slow channels of the fast-slow coincidence assembly set to select pulses corresponding to 300 keV to 550 keV in one channel and 700 keV to 1.32 MeV in the other is 190 ps.

The experimental positron source is prepared from carrier free <sup>22</sup>NaCl solution in water by depositing a drop of the solution and then drying it on a thin nickel foil 2 μm thick to obtain a source strength to 10 μCi. A similar nickel foil is placed on the source to cover it.

The contribution of the source in the lifetime spectrum, which has been ascertained by referring to the measured value of the lifetime of positrons in an Al single crystal sample is ≲2%.

The lifetime and the relative intensities have been extracted from the recorded spectra using the PATFIT-88 program.<sup>14</sup>

### III. RESULTS AND DISCUSSIONS

Each of the positron lifetime spectrum is resolvable into only two lifetime components  $\tau_1$  and  $\tau_2$ . The lifetime and their relative intensities are given in Table I. The lifetime component  $\tau_1$  originates from the annihilation at the perfect sites of the bulk of the material. But it is modified by the rate by which the positrons are localized at the defect sites.<sup>15</sup> In the present case the trapping rate of positrons are different and this will have some bearings on  $\tau_1$ . Explicitly,  $\tau_1$  cannot be related with annihilation from a particular site unlike for  $\tau_2$  which arises from annihilation in the defect sites. In fact  $\tau_1$  becomes the bulk lifetime ( $\tau_B$ ) in the absence of any defect in the material. According to the theory of two state trapping model<sup>16</sup>  $\tau_2$  originates from the annihilation at the

defect sites, i.e., the distorted part of the lattice. In this context Sharma *et al.*<sup>11</sup> suggest that trapping sites for the positrons in the samples are created as a consequence of spatially localized dopant ions. These dopants create local lattice distortion in such a way so as to create local negatively charged domain that localize positrons. Further, it appears certain that the presence of the dopant anion is strongly associated with the process of negative charge extraction from the PPy chain (i.e., formation of polarons and bipolarons). So it seems instructive to consider the trapping sites for positrons as the dopant anions having polaronic or bipolaronic environment, i.e.,  $\tau_2$  originates from positron annihilation at the dopant site with polaronic or bipolaronic environment. Since the lifetime components  $\tau_1$  and  $\tau_2$  are affected by the structure of the anion, we have chosen the oxidizing agent with SO<sub>4</sub><sup>2-</sup> as the dopant ion in all the cases.

Doyle *et al.*<sup>8</sup> who have used CH<sub>3</sub>CN as the solvent and have prepared PPy by electrochemical means have reported two lifetime components having values higher than the corresponding ones obtained in the present experiment. Machida *et al.*<sup>17</sup> have found that PPy shows poor conductivity when CH<sub>3</sub>CN is used as a solvent to prepare it. They have also demonstrated that the conductivity of PPy is severely controlled by the solvent. For example, the conductivity is 190 S cm<sup>-1</sup> with methanol as the solvent and <5 S cm<sup>-1</sup> with CH<sub>3</sub>CN. This finding indicates a similar solvent dependence of PAL in PPy and should account for the difference in the lifetime values obtained by Doyle *et al.*<sup>8</sup> and in the present work. They have also predicted that positrons interact via excited state polarons.<sup>8</sup> However, when polypyrrole is prepared using a concentrated solution of an oxidizing agent the major defect in the PPy chain is bipolaron.<sup>6</sup>

In this context, the work of Lei *et al.*<sup>13</sup> who have used FeCl<sub>3</sub> as an oxidizing agent provides some useful observations which can help explain the nature of the variation in the value of  $\tau_1$  observed in the present work with a change in strength of an oxidizing agent such as (NH<sub>4</sub>)Fe(SO<sub>4</sub>)<sub>2</sub>. Accordingly, when it is used at lower strengths say up to 0.75(N), some chemical defects originate from overoxidation and from the *sp*<sup>3</sup> hybridized carbon atom (nonplanar) in the PPy chain apart from polarons and bipolarons, because of the low formal reduction potential of the Fe<sup>+3</sup>/Fe<sup>+2</sup> system. At the same time, the associated short chain length also reduces the effective mobile electron density. On the other hand at strengths ≥ 1.0(N) the chemical defects no longer exist and the chain length increases.<sup>13</sup> As a result of this sharp change in the physicochemical environment,  $\tau_1$ , which remains almost constant up to a strength 0.75(N), drops down abruptly to a smaller value at a strength 1.0(N) (Table I). A similar abrupt change in dc and optical conductivities reported by Lei *et al.*<sup>13</sup> at a strength lying somewhere within 0.5(N) to 1.0(N), supports this finding.

As mentioned earlier  $\tau_2$  originates from the annihilation at the dopant site.<sup>8,9,11</sup> According to the theory of the two state trapping model  $\tau_2$  is a constant.<sup>16</sup> But the experimental results render the situation quite unusual. The results exhibit a small variation of  $\tau_2$  in the region of lower [≲0.75(N)] and higher (≥ 1.0(N)) oxidizing strengths while it reduces drastically in the concentration region 0.75(N) to 1.0(N). This

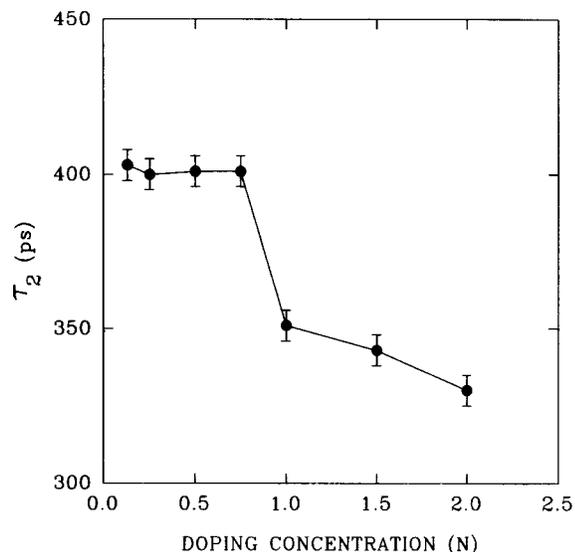


FIG. 1. Variation of  $\tau_2$  as a function of strength of the oxidizing agent, ammonium ferric sulphate.

apparent unusual situation can be explained in the following way. At the lower strengths of the oxidizing agent [ $\leq 0.75(N)$ ] polarons are formed along with the chemical defects while at the higher strengths of the oxidizing agent [ $\geq 1.0(N)$ ], chemical defects cease to exist and the number of bipolaron increases in the PPy chain. It has been demanded by Christensen *et al.*<sup>18</sup> that the bipolaronic environment is effectively more negative than the polaronic environment, which in turn leads to the fluctuation in electron density around the dopant ions and as a consequence a sudden quenching of  $\tau_2$  value is observed in the doping concentration from 0.75(N) to 1.0(N) as shown in Fig. 1.

We discuss our findings based on the two state trapping model.<sup>16</sup> The model suggests that the net disappearance rate of the delocalized positrons can be written as

$$\lambda_1 = \lambda_B + \mu_D C_D, \tag{1}$$

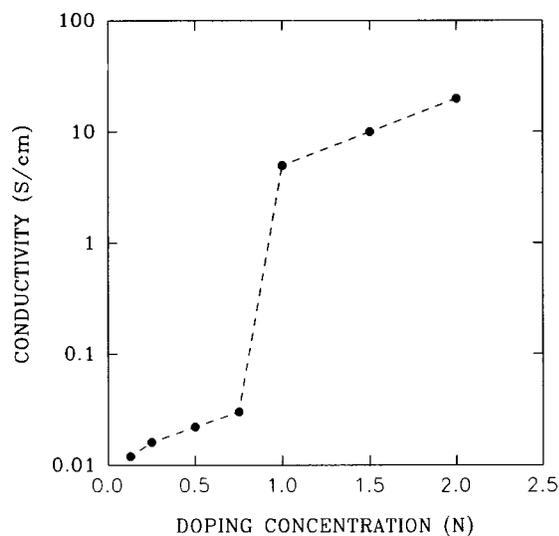
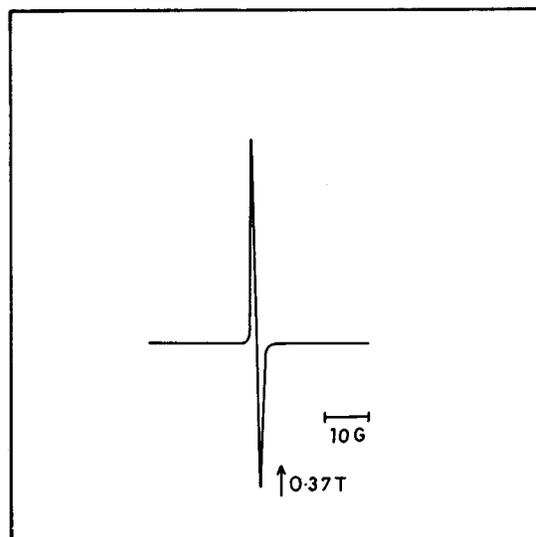
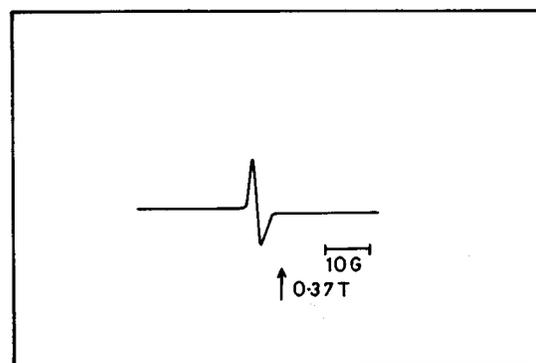


FIG. 2. Plot of conductivity of polypyrrole with the strength of the oxidizing agent.



(a)



(b)

FIG. 3. Typical ESR spectra of polypyrrole prepared by using ammonium ferric sulphate solution as an oxidizing agent with strength (a)  $\leq 0.75(N)$  and (b)  $\geq 1.0(N)$ .

where  $(\lambda_B)^{-1}$  is the lifetime of the positrons annihilating in the bulk and is given by the expression

$$\tau_B = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1} (I_1 + I_2). \tag{2}$$

$\mu_D$  is the trapping rate per unit dislocation density and  $C_D$  is the dislocation density. The model further suggests that the bulk lifetime ( $\tau_B$ ) would be a constant.<sup>19</sup> From the experimental results (Table I) it is clearly evident that  $\tau_B$  is not a constant, rather it shows a slight variation.

The conductivity data at different strengths of the oxidizing agent presented in Fig. 2 shows that with  $(NH_4)Fe(SO_4)_2$  as an oxidizing agent, the conductivity linearly increases with strength up to 0.75(N) and then rises sharply (by 170 times) at a strength of 1.0(N) and thereafter again takes a slow linear rising course upto 2.0(N). The variation of  $\tau_1$  and  $\tau_2$  shows an identical trend as that obtained from the corresponding conductivity measurement.

In Figs. 3(a) and 3(b) typical ESR spectra of polypyrrole samples synthesized by using lower [ $\leq 0.75(N)$ ] and higher [ $\geq 1.0(N)$ ] strengths of the oxidizing agent  $(NH_4)Fe(SO_4)_2$  respectively have been presented. The ESR spectra of the

samples have been taken under the identical experimental conditions, (e.g., gain setting  $4 \times 10$  in both the cases). ESR spectrum of PPy is a matter of controversy over the last two decades. Different explanations have been put forward to explain the nature of ESR signal in such samples. In a recent review article Saunders *et al.*<sup>20</sup> have ascribed the ESR activity of PPy to polarons and not to accidental defects. An ESR spectrum of a sample having polaronic defects would show a signal with high intensity. However, as the bipolaron to polaron ratio increases in a sample, the corresponding spectrum would have small intensity under the same set of experimental conditions. Since the approximate relative intensity of an ESR signal is proportional to the peak to peak derivative amplitude and to the square of the peak to peak width, a comparison of the spectra of Figs. 3(a) and 3(b) reveals that a sample prepared by using  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$  as an oxidizing agent is comprised mostly of polarons at lower strengths [ $\leq 0.75(\text{N})$ ] while predominantly of bipolarons at strengths  $\geq 1.0(\text{N})$ . Genoud *et al.*<sup>21</sup> support this view and suggest that the probability of bipolaron (a spinless entity) formation is appreciably small at a low oxidation level. So one may conclude that  $\tau_2$  is a consequence of the annihilation of the positron at the dopant site with the polaronic environment at lower strengths ( $\leq 0.75$ ) and the bipolaronic environment at higher strengths [ $\geq 1.0(\text{N})$ ].

The nature of variation of the relative intensity ( $I_2$ ) pertaining to the lifetime component  $\tau_2$  (Fig. 4) in the respective samples also lends support to the above view. The values of the  $I_2$  in samples prepared by using  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$  shows a large rate of increase with increasing oxidizing strength which indicates that number of defects increases with the increasing oxidizing strength. At very low level of oxidation only polarons are generated and as the doping level increases both carriers are produced until polaron recombination results in bipolarons being the dominant species in the highly oxidized PPy. The doping levels at which bipolarons start to be generated and polaron recombinations commences will depend on the average PPy chain length. At higher oxidizing strengths the average chain length is somewhat larger than it

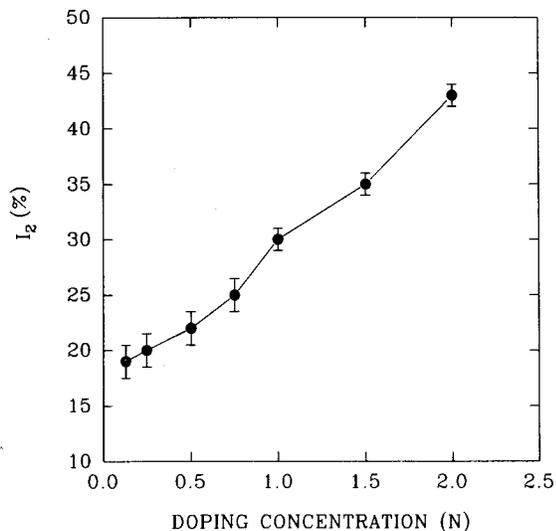


FIG. 4. Variation of intensity  $I_2$  with doping concentration.

is at lower oxidizing strengths. As a consequence the relative intensity  $I_2$  shows a large rate of variations. The lifetime data analysis along with ESR spectroscopic studies reveal that the value of  $I_2$  is a measure of defect concentration in the polaronic environment up to strength  $0.75(\text{N})$  and of that in the bipolaronic environment (predominantly) at strengths starting from  $1.0(\text{N})$  to  $2.0(\text{N})$ .

#### IV. CONCLUSIONS

In summary we have presented the detailed results from a series of experiments by which we have investigated the role of the oxidizing strength used to prepare PPy on the microstructural environment of the same. The major findings of these experiments are (i) the unusual variation of the second lifetime component ( $\tau_2$ ) which indicates that the local electronic environment of the dopant ion has a profound effect on the annihilation lifetime, (ii) the PAL spectroscopic studies coupled with ESR measurements clearly establish the fact that the environment of the dopant ion is polaronic in the lower strength region [ $\leq 0.75(\text{N})$ ] while it is predominantly bipolaronic in the higher strength region [ $\geq 1.0(\text{N})$ ] and (iii) from the experimental data one may infer that the effective mobile electron density in the bipolaronic environment is greater than that in the polaronic environment. Finally it is expected that further investigations will be carried out so as to clarify the unusual variation of  $\tau_2$  and to observe the saturation in the lifetime components and the relative intensities.

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- <sup>1</sup>G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.* **83**, 253 (1982).
- <sup>2</sup>A. Z. Diaz and J. Bargon, in *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 1, pp. 81–115.
- <sup>3</sup>J. H. Kaufman and N. Colaneri, *Phys. Rev. Lett.* **53**, 1005 (1984).
- <sup>4</sup>J. C. Scott, P. Pfluger, M. Krounbi, and G. B. Street, *Phys. Rev. B* **28**, 2140 (1983).
- <sup>5</sup>P. Pfluger and G. B. Street, *J. Chem. Phys.* **80**, 544 (1984).
- <sup>6</sup>J. L. Bredas, J. C. Scott, K. Yakushi, and G. B. Street, *Phys. Rev. B* **30**, 1023 (1984).
- <sup>7</sup>M. Nechtschein, F. Devreux, F. Genoud, E. Vieil, J. M. Pernat, and E. Genies, *Synth. Met.* **15**, 59 (1986).
- <sup>8</sup>S. E. Doyle, G. M. B. Mahoubin Jones, and R. A. Pethrick, *Polym. Commun.* **26**, 262 (1985).
- <sup>9</sup>Z. L. Peng, S. Q. Li, Y. Q. Dai, B. Wang, S. J. Wang, H. Lin, and H. Q. Zie, *Synth. Met.* **64**, 33 (1994).
- <sup>10</sup>A. J. MacKinnon, R. A. Pethrick, S. D. Jenkins, and P. T. McGrail, *Polymer* **35**, 5319 (1994).
- <sup>11</sup>S. C. Sharma, S. Krishnamoorthy, S. V. Naidu, C. I. Eom, S. Krichene, and J. R. Reynolds, *Phys. Rev. B* **41**, 5258 (1990).
- <sup>12</sup>R. A. Pethrick, *Prog. Polym. Sci.* **22**, 1 (1997).
- <sup>13</sup>J. Lei, Z. Cai, and C. R. Martin, *Synth. Met.* **46**, 53 (1992).
- <sup>14</sup>P. Kirkegaard, N. J. Pedersen, and M. Eldrup, Report of Riso National Laboratory, Riso-M-2740, 1989.
- <sup>15</sup>R. N. West, *Adv. Phys.* **22**, 263 (1977).
- <sup>16</sup>A. Seeger, *J. Phys. F* **3**, 248 (1973).
- <sup>17</sup>S. Machida, S. Miyata, and T. Techagumpuch, *Synth. Met.* **31**, 311 (1989).
- <sup>18</sup>P. A. Christensen and A. Hamnett, *Technique and Mechanism in Electro-*

*chemistry* (Chapman and Hall, New York, 1994), p. 344.

<sup>19</sup>P. Hautojärvi and C. Corbel, in Proceedings of the International School of Physics "Enrico Fermi," Positron Spectroscopy of Solids, edited by A. Dupasquier and A. P. Mills Jr., 1995 (unpublished).

<sup>20</sup>B. R. Saunders, R. J. Fleming, and K. S. Murray, *Chem. Mater.* **7**, 1082 (1995).

<sup>21</sup>F. Genoud, M. Guglielmi, M. Nechtschein, E. Genies, and M. Salmon, *Phys. Rev. Lett.* **55**, 118 (1985).