Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

X-Band Optically Detected Magnetic Resonance (ODMR) Study of C_{60}-Doped π-Conjugated Polymers

P. A. Lane [a] , J. Shinar [a] , K. Yoshino [b] , Y. W. Ding [c] & T. J. Barton [c]
[a] Ames Laboratory - USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011
[b] Faculty of Engineering, Osaka University, Yamada-Oka 2-1, Suita, Japan
[c] Ames Laboratory - USDOE and Chemistry Department, Iowa State University, Ames, IA, 50011
Version of record first published: 04 Oct 2006.

To cite this article: P. A. Lane , J. Shinar , K. Yoshino , Y. W. Ding & T. J. Barton (1994): X-Band Optically Detected Magnetic Resonance (ODMR) Study of C_{60}-Doped π-Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 327-334

To link to this article: http://dx.doi.org/10.1080/10587259408039263

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 327–334
Reprints available directly from the publisher
Photocopying permitted by license only

X-BAND OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR) STUDY OF C_{60}-DOPED π-CONJUGATED POLYMERS

P. A. Lane, and J. Shinar
Ames Laboratory - USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011.
K. Yoshino
Faculty of Engineering, Osaka University, Yamada-Oka 2-1 Suita, Japan.
Y. W. Ding and T. J. Barton
Ames Laboratory - USDOE and Chemistry Department, Iowa State University, Ames, IA 50011.

Abstract The X-band ODMR of 0.1 - 10 mol.% C_{60}-doped 2,5-dihexoxy poly(*p*-phenylenevinylene) (DHOPPV) and 2,5-dibutoxy poly(*p*-phenylene-acetylene) (DBOPPA) is described. As invariably observed in undoped π-conjugated polymers, it includes a narrow PL-enhancing polaron resonance at $g \approx 2.002$, and full- and half-field triplet exciton powder patterns. The polaron resonance is surprisingly weak in undoped DHOPPV, but its intensity increases twentyfold at 0.1 mol.% C_{60}, and then decreases one hundredfold at 10 mol.%. In undoped DBOPPA the narrow resonance is intense and initially decreases with C_{60} content.
C_{60} doping generally drastically weakens the full- and half-field triplet exciton resonances. The results are discussed in relation to the role of positive (p^+) and negative (p^-) polarons and bipolarons as nonradiative singlet and triplet quenching centers; the polaron resonance is then attributed to their removal by spin-dependent p^+ - p^- recombination, which may also generate radiative singlet excitons. .

I. INTRODUCTION

The rapid advances in the development of π-conjugated polymer-based light-emitting diodes (LEDs)[1,2] have drawn wide attention to the optoelectronic processes in these systems.[3-15] The plethora of excited states that have been invoked to account for the observed phenomena include the low-lying antisymmetric 1^1B_u and 1^3B_u and symmetric m^1A_g and 1^3A_g singlet and triplet excitons, resp., and positive and negative polarons (p^+ and p^-, resp.), and bipolarons (bp^{++} and bp^{--}, resp.). However, even as higher-energy neutral and charged excitations should also be considered, in view of their possible generation by UV excitation or charge carrier injection, the role of the lower-energy excitations is still actively debated. Among the studies of these lower-energy states, the

various types of optically detected magnetic resonance (ODMR) techniques have proven to be powerful tools in providing striking signatures of polarons and triplet excitons.[5-11] This paper describes new results on the ODMR of C_{60}-doped 2,5-dihexoxy poly(*p*-phenylenevinylene) (DHOPPV) and 2,5-dibutoxy poly(*p*-phenyleneacetylene) (DBOPPA). The effects of doping on the resonance lineshapes are minor, but their effects on the intensities are dramatic. In particular, light doping of highly ordered DHOPPV sharply increases the intensity of the otherwise surprisingly weak narrow polaron resonance. However, heavy doping drastically weakens it, and it is barely observable at 10 mol.% C_{60}. On the other hand, the relatively intense narrow polaron resonance of undoped DBOPPA gradually decreases with the C_{60} concentration [C_{60}]. The intensities of the full- and half-field triplet exciton powder patterns are drastically reduced upon doping, and they are almost unobservable at 10 mol.% C_{60} in DBOPPA. The results are all consistent with a scenario in which charged spin 1/2 carriers relax to polaron states, probably stabilized by structural defects. Like-charged polarons may also form bipolarons.[3,4,10,11] These polarons and bipolarons then effectively quench singlet and triplet excitons, but the recombination of oppositely charged polarons may generate radiative 1^1B_u excitons. The ramifications of these scenarios are discussed in section IV below.

II. EXPERIMENTAL PROCEDURE

The synthesis of highly ordered DHOPPV has been previously described.[16] The synthesis of DBOPPA has also been previously described;[17] previous studies, however, have all indicated that the PPAs are relatively disordered and contain a high density of defects. The polymers and C_{60} were dissolved in toluene. After the solution was placed in a quartz tube, the solvent was evaporated, the doped polymer films were cooled to 77K, and the tube was pumped and sealed with a torch. The ODMR system was previously described.[5-7]

III. RESULTS

The PL yield of DHOPPV and DBOPPV decreased from 8% and 19%, resp., to 0.5% and 0.2%, resp., as [C_{60}] increased from 0 to 10 mol.%. These observations are consistent with those of Yoshino et al.[18] and with previous studies,[4] which have indicated that bipolarons and defect-stabilized polarons, whether doping- or photo-induced, are efficient singlet exciton quenching centers.

The narrow polaron resonance of C_{60}-doped DHOPPV and DBOPPA at 20K, excited by 25 mW at 488 nm and 40 mW at 9.35 GHz, is shown in Figures 1 and 2. The resonance lineshapes were excellently fit to the sum of a broad and a narrow Gaussian in all cases. The [C_{60}]-dependence of the intensity $\Delta I_{PL}/I_{PL}$ of each component and of the sum is shown in Figure 3. Several striking observations should be addressed:

(i) The narrow resonance of the undoped highly ordered DHOPPV (Fig. 1) is surprising-

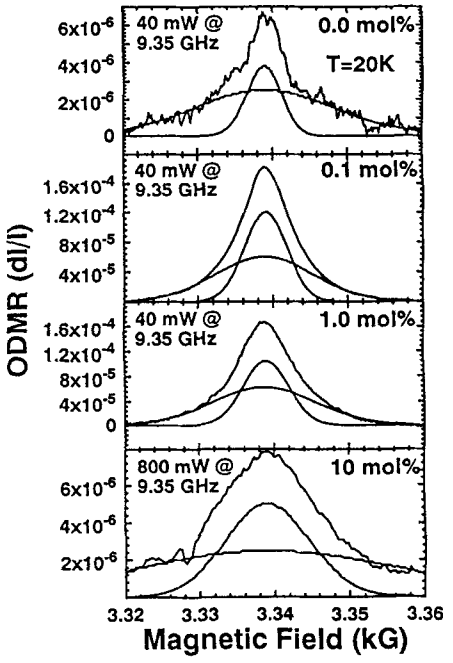

Figure 1. *The narrow polaron ODMR of C_{60}-doped 2,5-dihexoxy-PPV at several doping levels, excited by 25 mW at 488 nm and the denoted microwave power. The Gaussian components which add to fit the observed spectra are also shown.*

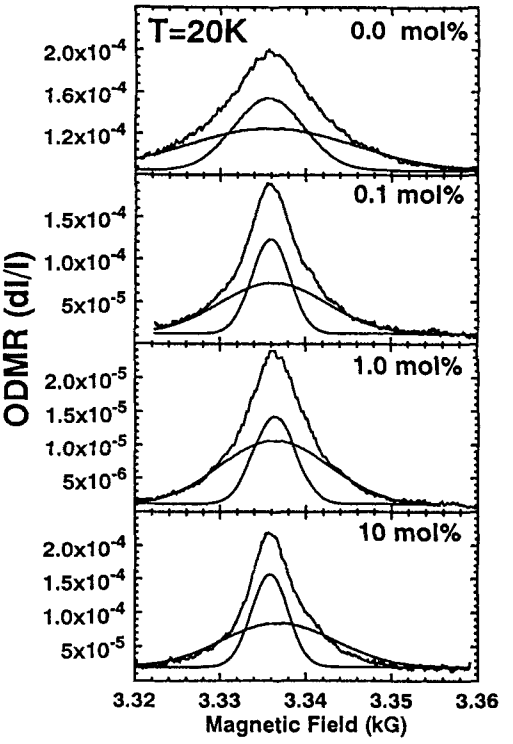

Figure 2. *The narrow polaron ODMR of C_{60}-doped 2,5-dibutoxy-PPA at several doping levels, excited by 25 mW at 488 nm and the denoted microwave power. The Gaussian components which add to fit the observed spectra are also shown. Note the splitting of the components at 10 mol.% (see text)*

ly weak, as its amplitude is only $\Delta I_{PL}/I_{PL} \sim 7x10^{-6}$, as compared to amplitudes of 10^{-4} - 10^{-3} displayed by polythiophenes, PPAs, and other samples of PPV or its derivatives.[5-7]

(ii) The amplitude of the polaron resonance dramatically increases from ~$7x10^{-6}$ to ~$2x10^{-4}$ upon light 0.1 mol.% doping (Figs. 1 and 3).

(iii) Heavy 10 mol.% doping of DHOPPV then sharply reduces the observed intensity of the polaron resonance, down to ~$8x10^{-6}$ at a microwave power of 800 mW, or ~$1.8x10^{-6}$ at 40 mW (Figs. 1 and 3).

(iv) Light 0.1 mol.% doping has only a minor effect on the intensity of the polaron resonance in DBOPPA (Figs. 2 and 3), but heavier doping strongly reduces its intensity. The surprising rise of its intensity at 10 mol.% is not clear, but it may possibly be related to the following observation.

(v) Whereas the g-values of the narrow and broad Gaussian components that fit the narrow resonance are the same in all other cases, in 5 and 10 mol.% C_{60}-doped DBOPPA they are split by $\Delta g \sim 8x10^{-4}$ (~1.3 G). This effect may be instrumental in the 5 mol.% doped film since a relatively high microwave power of 250 mW, which probably broad-

ens the observed resonance, was needed to obtain the spectrum. Figure 1 indeed shows the broadening effect of an 800 mW microwave field. In the 10 mol.% film, however, the microwave power was only 40 mW. Thus, the observed splitting of the Gaussian components was probably not instrumental in that case. Results (iv) and (v) are therefore addressed in section IV below, and the possibility that they are due to polarons localized on the Fullerene molecule is discussed.

(vi) Figures 4 - 6 clearly show that the full- and half-field triplet exciton resonances are dramatically reduced by doping. Indeed, the relatively intense half-field resonance of undoped DBOPPA[7] was completely quenched by 0.1 mol.% doping.

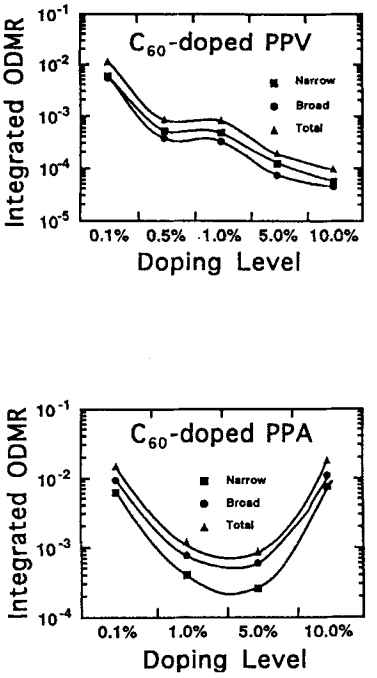

Figure 3. *The C_{60}-content dependence of the amplitude $\Delta I_{PL}/I_{PL}$ of the polaron resonance in DHOPPV and PBOPPA under the same conditions use to obtain the spectra shown in Figs. 1 and 2.*

IV. DISCUSSION

Before discussing each of the foregoing observations, we reexamine the previous interpretation of the ODMR results. That interpretation suggested that the polaron resonance is due to magnetic resonance enhancement of the spin-dependent p^+ - p^- recombination. Previously, however, it was believed that the PL-enhancing mechanism is singlet exciton generation by p^+ - p^- fusion.[5-7,10,11] The results of this work, however, as well as those of UV-excited ODMR described elsewhere in this volume,[18] should also be considered within the role of polarons as nonradiative singlet and triplet exciton quenching centers, as first suggested by Wei et al.[19] Thus, the polaron resonance may also be due to the reduction in the density of these nonradiative singlet quenching centers as a result of the spin-dependent p^+ - p^- recombination. The results of this work, as well as the UV-ODMR,[18] appear to be consistent with this revised picture, if it is also assumed that the polarons are stabilized by structural defects and they also quench triplet excitons. However, heavy doping should rapidly increase the bipolaron content. These excitations are probably more detrimental to the PL than polarons, since their formation clearly removes polarons from the system, and their decay probably occurs by trapping of an additional oppositely charged polaron. We now discuss the foregoing results described in paragraphs (i) - (vi) of section III within this revised picture.

(i) If the density of structural defects in the undoped DHOPPV studied in this work is re-

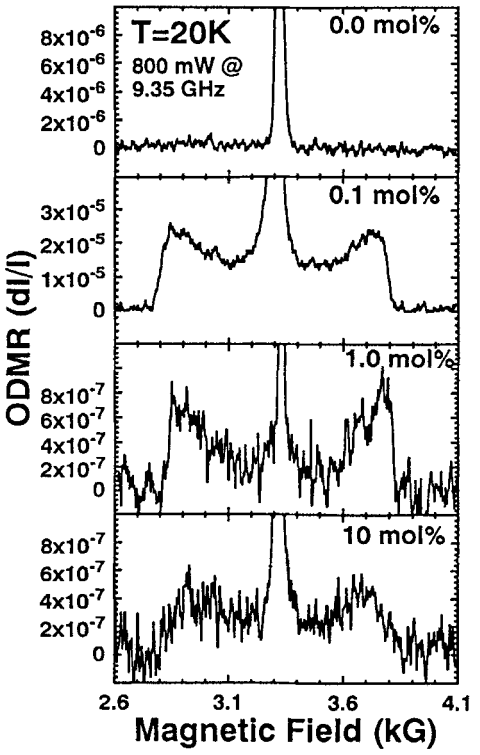

Figure 4. *The full-field triplet exciton resonance of 0.1, 1, and 10 mol.% C_{60}-doped DHOPPV excited by 25 mW at 488 nm and 800 mW at 9.35 GHz. Note the sharp reduction in the intensity at 1 and 10 mol.%.*

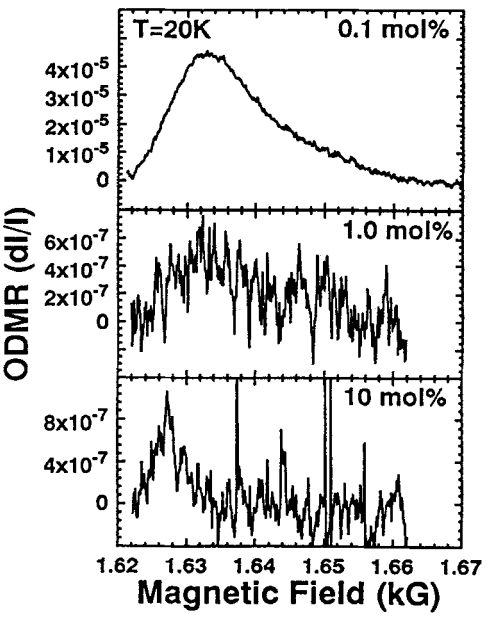

Figure 5. *The half-field triplet exciton resonance of 0.1, 1, and 10 mol.% C_{60}-doped DHOPPV excited by 25 mW at 488 nm and 800 mW at 9.35 GHz. Note the sharp reduction in the intensity at 1 and 10 mol.%.*

latively low, then the density of polarons is also low, resulting in a weak resonance (Fig. 1). Indeed, the first ODMR study of PPV and its derivatives[6] already yielded narrow resonances that were weaker but triplet exciton resonances that were stronger than those observed in, e.g., polythiophenes.[5] It is now clear that both of these observations are consistent with the revised scenario, if the density of structural defects in the PPV films was lower.

(ii) The dramatic increase of the amplitude of the polaron resonance from ~7x10^{-6} to ~2x10^{-4} upon light doping of DHOPPV by 0.1 mol.% C_{60} (Fig. 1) is again consistent with the foregoing model, as the charges induced by the doping then relax into polar-on states stabilized by the structural defects, and magnetic resonance conditions then re-sult in a much larger increase of spin-depen-dent p^+ - p^- recombination, and consequent-ly far stronger enhancement of the PL.

(iii) The sharp decline of the polaron resonance intensity of DHOPPV at higher doping levels is clearly accountable by the rapid increase in the density of C_{60}-induced bp^{++}. This results in a greater rate of spin-independent nonradiative capture and decay of p^{-} by bp^{++}, resulting in a weaker $\Delta I_{PL}/I_{PL}$. At the highest doping levels, the bipolaron content clearly increases at half the rate of the doping level, resulting in a weaker reduction of $\Delta I_{PL}/I_{PL}$.

(iv) The moderate effect of initial C_{60} doping on the polaron resonance of DBOPPA is now clearly consistent with the foregoing picture, as several studies on PPAs have indicated that the structural disorder in this system is generally much greater than in PPV.[7,11,17] Hence, if visible excitation of PPAs generates far more polarons, by fission of singlets, than PPVs, then the initial undoped polaron resonance will be much more intense. Thus, the effects of light doping on the polaron ODMR in PPAs would be much weaker than on well-ordered PPVs.

(v) The surprising sharp increase of the intensity $\Delta I_{PL}/I_{PL}$ of the polaron resonance of DBOPPA at 10 mol.% C_{60} is due to the rapid decrease in I_{PL} rather than to an increase in ΔI_{PL}. This behavior may be related to observation (v), which is the slight splitting of the g-values of the narrow and broad Gaussians the sum of which very closely reproduces the observed lineshape. A common scenario for both observations is the localization of polarons on the C_{60} molecule at this high doping level. The ODMR of these polarons has been described,[20] albeit within the previous model of singlet generation by polaron fusion, but recent results are described elsewhere in this volume in relation to the revised scenario.[21]

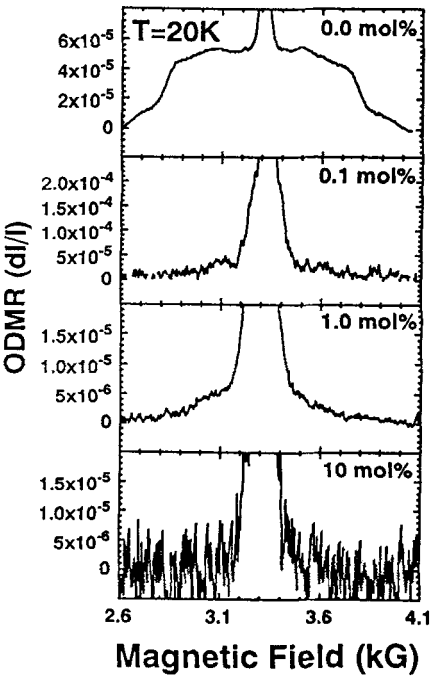

Figure 6. *The full-field triplet exciton resonance of 0.1, 1, and 10 mol.% C_{60}-doped DBOPPA excited by 25 mW at 488 nm and 800 mW at 9.35 GHz. Note the sharp reduction in the intensity at 1 and 10 mol.%. The half-field resonance was unobservable at these doping levels.*

(vi) Finally, the nearly complete quenching of the full- and half-field triplet exciton resonances (Figs. 4 - 6) by C_{60} doping are obviously consistent with their effectively spin-independent quenching by polarons and bipolarons.

SUMMARY AND CONCLUDING REMARKS

In summary, the behavior of the X-band ODMR of 0.1 - 10 mol.% C_{60}-doped 2,5-dihexoxy poly(*p*-phenylenevinylene) (DHOPPV) and 2,5-dibutoxy poly(*p*-phenylene-acetylene) (DBOPPA) was described. The salient observations included the sharp rise of the intensity of the polaron resonance upon light doping of DHOPPV, the subsequent sharp decrease of the intensity at higher doping levels in this polymer and in DBOPPA, and the nearly complete doping-induced quenching of the triplet exciton resonance in both. These results were all shown to be consistent with polaron stabilization by structural defects and generation of bipolarons, which efficiently quench singlet and triplet excitons, and nonradiatively recombine with polarons, at high doping levels. The narrow polaron resonance is then believed to result from magnetic resonance enhancement of $p^- - p^+$ recombination, which both yields singlet excitons, and eliminates nonradiative singlet quenching centers. The possibility that the nonradiative recombination of polarons with bipolarons generates defects in processes similar to the Staebler-Wronski effect in hydrogenated amorphous Si should also warrant consideration.[22]

ACKNOWLEDGEMENTS

JS thanks Drs. Z. V. Vardeny and D. D. C. Bradley for valuable discussions. Ames Laboratory is operated by Iowa State University for the US Department of Energy under contract W-7405-Eng-82. The work at Ames was supported by the Director for Energy Research, Office of Basic Energy Sciences. Supported by NSF grant DMR-9202981.

REFERENCES

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **347**, 539 (1990).
2. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, **357**, 477 (1992).
3. R. H. Friend, D. D. C. Bradley, and P. D. Townsend, J. Phys. D **20**, 1367 (1987).
4. D. D. C. Bradley and R. H. Friend, *J. Phys. Cond. Matt.*, **1**, 3671 (1989); K. E. Ziemelis, A. T. Hussain, D. D. C. Bradley, R. H. Friend, J. Ruhe, and G. Wegner, *Phys. Rev. Lett.*, **66**, 2231 (1991).
5. L. S. Swanson, J. Shinar, and K. Yoshino, *Phys. Rev. Lett.*, **65**, 1140 (1990).
6. L. S. Swanson, P. A. Lane, J. Shinar, and F. Wudl, *Phys. Rev. B*, **44**, 10617 (1991).
7. Q.-X. Ni, L. S. Swanson, P. A. Lane, J. Shinar, Y. W. Ding, S. Ijadi-Maghsoodi, and T. J. Barton, *Syn. Met.*, **49-50**, 447 (1992).
8. X. Wei, B. C. Hess, Z. V. Vardeny, and F. Wudl, *Phys. Rev. Lett.*, **68**, 666 (1992).
9. G. S. Kanner, X. Wei, B. C. Hess, L. R. Chen, and Z. V. Vardeny, *Phys. Rev. Lett.*, **69**, 538 (1992).
10. L. S. Swanson, J. Shinar, A. R. Brown, D. D. C. Bradley, R. H. Friend, P. L.

Burn, A. Kraft, and A. B. Holmes, *Phys. Rev. B*, **46**, 15072 (1992).
11. L. S. Swanson, J. Shinar, Y. W. Ding, and T. J. Barton, *Syn. Met.*, **55-57**, 1 (1993).
12. E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman, and H. H. Horhold, *Phys. Rev. B*, **46**, 9320 (1992).
13. H. A. Mizes and E. M. Conwell, *Phys. Rev. Lett.*, **70**, 1505 (1993).
14. J. M. Leng, S. Jeglinski, X. Wei, R. E. Benner, Z. V. Vardeny, F. Guo, and S. Mazumdar, *Phys. Rev. Lett.*, **72**, 156 (1994).
15. J. W. P. Hsu, M. Yan, T. M. Jedju, L. J. Rothberg, and B. R. Hsieh, *Phys. Rev. B*, **49**, 712 (1994).
16. I. Murase,T. Ohnishi, T. Noguchi, and M. Hirooka, *Polymer Comm.*, **28**, 229 (1987).
17. L. S. Swanson, F. Lu, J. Shinar, Y. Ding, and T. J. Barton, in *Electroluminescence: New Materials for Devices and Dis-plays*, edited by E. M. Conwell, M. Stolka, and M. R. Miller, *SPIE Conf. Proc.*, **1910**, 101 (1993).
18. J. Shinar, A. V. Smith, P. A. Lane, K. Yoshino, Y. W. Ding, and T. J. Barton, *this volume.*
19. X. Wei, J. M. Leng, and Z. V. Vardeny, *Bull. Am. Phys. Soc.*, **38**, 258 (1993).
20. P. A. Lane, L. S. Swanson, Q. X. Ni, J. Shinar, J. P. Engel, T. J. Barton, and L.Jones, *Phys. Rev. Lett.*, **68**, 887 (1992).
21. P. A. Lane and J. Shinar, *this volume.*
22. M. J. Thompson, Y. Hamakawa, P. G. LeComber, A. Madan, and E. Schiff, editors, *Amorphous Silicon Technology - 1992*, Mat. Res. Soc. Symp. Proc. **258** (1992).
23. M. J. Thompson, Y. Hamakawa, P. G. LeComber, A. Madan, and E. Schiff, editors, *Amorphous Silicon Technology - 1992, Mat. Res. Soc. Symp. Proc.*, **258** (1992).