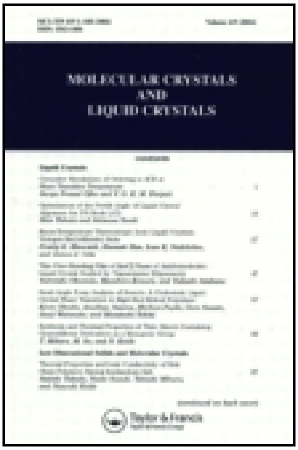

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Tunneling Processes in Doped Polymer Glasses Below 1° K

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TUNNELING PROCESSES IN DOPED POLYMER GLASSES BELOW 1° K

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Abstract We have performed optical hole-burning experiments in the temperature range between $25mK$ and $500mK$ and found a linear temperature law which we ascribe to spectral diffusion. Also the time evolution of the holes was investigated. A broadening of the holes on a logarithmic time scale, which we attribute to longtime relaxation processes of two level systems (TLS) was measured. Implications on the theory of TLS are discussed.

INTRODUCTION

Photochemical and photophysical hole burning is a well established technique for eliminating the large inhomogeneous broadening of electronic transitions, which dominates the optical spectroscopy of amorphous solids. With the possibility of measuring the quasi-homogeneuos width Γ_{qh} of electronic transitions, dye molecules can be used as probes for dynamical processes in amorphous solids[1,2]. The temperature dependence of the electronic linewidth of a given dye molecule in a crystalline lattice as compared to its linewidth in an amorphous solid shows large differences in both, its absolute value and its broadening behavior. This is due to the different origin of the dominant line broadening mechanisms: Interaction with phonons in a crystalline host and with two level systems (TLS) in an amorphous solid.

For different dye molecules in amorphous, organic matrices the quasihomogeneous linewidths have been measured as $\Gamma_{qh} \propto T^{\alpha}$ with $1 \leq \alpha \leq 2$ in the temperature range between $0.3K$ and $20K$ [3,4,5]. This is in contrast to temperature dependencies scaling with T^4 or exponentially like $\exp(-\Delta E/k_BT)$ [3,5]; the latter has been observed for similar dye molecules in crystalline matrices.

Various theories have been proposed for explaining the different exponents of the measured temperature dependencies. They differ in the model assumptions concerning the nature of the coupling between the TLS and the phonon bath on one hand and the coupling between the TLS and the electronic system on the other hand.

In order to decide which of these theories, if any, describes the boadening mechanism in amorphous solids it is important to investigate the behavior of optical linewidths at very low temperatures, at which the differences between phonon-like and TLS-like exicitations are expected to become very significant. For this reason we have constructed a ^{3}He/^{4}He dilution refrigerator with optical windows for transmission spectroscopy. With this cryostat we were able to perform experiments on optical linewidths down to $25mK$, a temperature regime in which only very few optical data exist [6,7].

Ref. 7 for instance contains the only published hole burning data in the temperature regime below $300mK$. These data exhibit a very puzzling temperature dependence, where the authors claim two crossovers of the exponent α in one temperature decade. Furthermore a dependence of this exponent upon the location in the inhomogeneous absorbtion band was observed. In contrast to this, our measurements show no sign of a crossover and yield a linear dependence over the hole temperature range and no dependence of α upon the wavelength. These new results should be quite relevant in the discussion of the multitude of theoretical models which have been suggested.

EXPERIMENTAL PART I: TEMPERATURE EFFECTS OF SD

We investigated polystyrene (PS) doped with free-base phthalocyanine (H_2Pc) and polymethylmethacrylate (PMMA) doped with tetra-4-tert-butyl phthalocyanine (H_2Pc^*). The samples had optical densities of 0.55 and 0.42 respectively at a typical thickness of $3.3mm$ and $2mm$ respectively. The samples were prepared by bulk polymerisation of the solution of the dye in the monomer. The temperature dependence of the hole width is shown in figure 1 on a linear plot. Two observations are worth mentioning and are reported with good experimental evidence:

First, the systems exhibit a linear temperature dependence over the whole temperature range down to $25mK$ and no crossover to a constant linewidth is seen. This indicates that dynamical processes occur in amorphous systems even at these ultra-low temperatures.

Second, a residual linewidth is found which is nearly the same for both systems, reconfirming that in an amorphous system the linewidth reaches the lifetime limited value $\Gamma_h = 1/2\pi T_1$ (Heisenberg limit) of the electronic transition only in the limit $T \rightarrow 0K$. This limit is reached within 10% !

It is commonly assumed that the homogeneous linewidth of a dye molecule embedded in a solid matrix can be described as [2]:

$$\Gamma_h = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2^*} \tag{1}$$

In equation 1 the parameter T_1 contains all energy relaxation processes and is assumed to be constant at low temperatures. The temperature dependence is

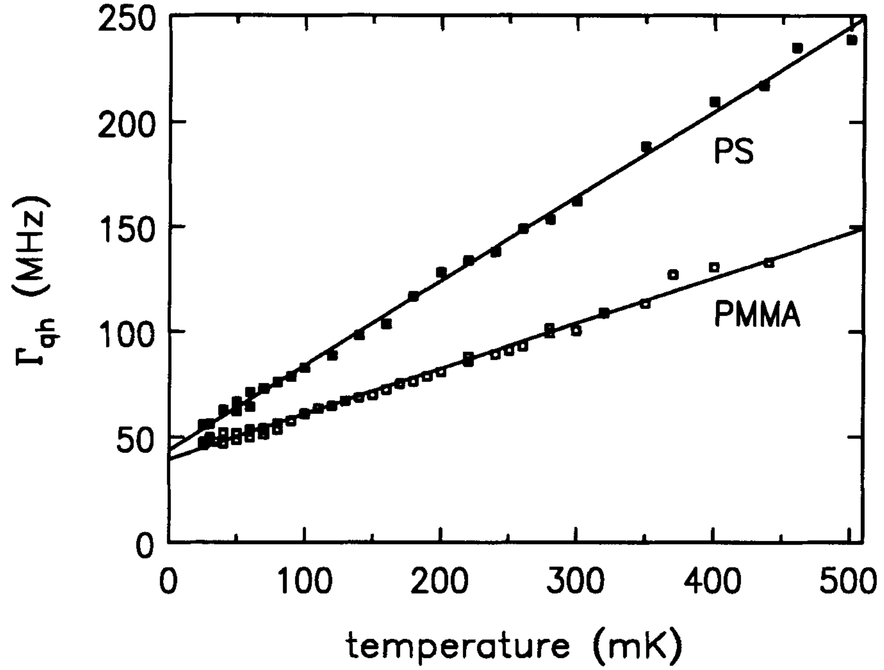

FIGURE 1 Temperature dependence of the quasi-homogeneous hole width Γ_{qh} for the $S_1 \leftarrow S_0$ transition of H_2Pc and H_2Pc^* in the amorphous polymers PS and PMMA between 25 mK and 500 mK [10].

therefore caused by the dephasing time T_2^*. In oder to explain hole-burnig data at temperatures between 1 K and 20 K in the polymer matrices PMMA, PS, and PE dephasing via local modes was assumed [8]. The measured holewidth can therefore be written as:

$$\Gamma_{qh} = 2\Gamma_h + \Gamma_{SD} \tag{2}$$

where Γ_{SD} is the spectral diffusion part of the linewidth. The factor of two in equation 2 indicates that hole burning can be considered as a tandem two photon process, yielding twice the homogeneous linewidth [2]. Using our own experimental data we could verify this factor by comparing $\Gamma_{qh}(T \rightarrow 0K) = 2\Gamma_h$ with the fluorescence lifetime of the electronic excitation. If we take the model of Black and Halperin [9] we can derive the following temperature and time dependence [10]:

$$\Gamma_{SD} = \frac{2\pi^2}{3\hbar} \langle |C_{ij}| \rangle \overline{P}(\lambda - \lambda_{min}) k_B T \ln(r_{max} t) \tag{3}$$

Here C_{ij} is an average coupling constant between the TLS and the electronic system of the dye molecules. $\overline{P}(\lambda - \lambda_{min})$ is a density of states which, if considered constant for tunneling parameters $\lambda > \lambda_{min}$, yields a linear temperature law. Eq.(3) shows a logarithmic time dependence for times $t \gg r_{max}^{-1}$, where r_{max} is the maximum tunneling rate. This logarithmic time behavior is a consequence of the specific rate distribution of the TLS in the regime of small rates.

EXPERIMANTAL PART II: TIME EFFECTS OF SD

We performed a long time experiment at the temperature T=50mK, where a hole was observed for 100 hours. The curve with the index $t_B = 0h$ in figure 2 is the result of the above described experiment. A pronounced logarithmic time evolution could be detected. We consider this result as a verification of the predicted time evolution of the spectral holes.

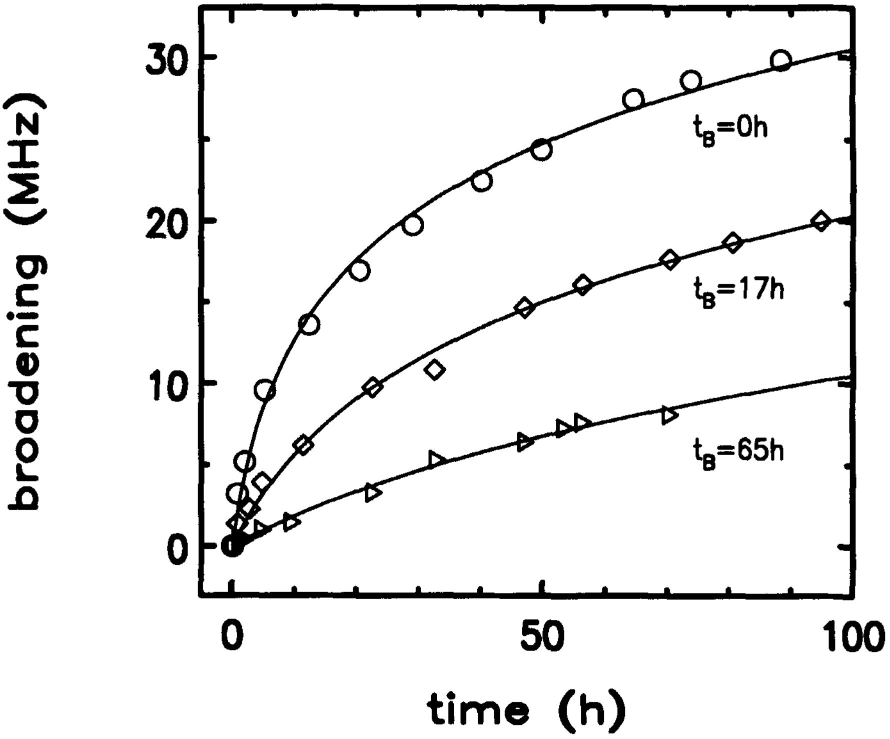

FIGURE 2 Time evolution of three different holes. The index t_B marks the respective burning times after reaching a temperature of T=50mK.

Finally we discovered an additional relaxation phenomenon which, in our opinion, can only be measured in the ultra low temperature regime. The holes, burnt at a variable time interval t_B *after* reaching the minimal temperature of 50mK, showed a smaller broadening during the 100 hour observation period. This result could be attributed to long relaxation times of TLS in the millikelvin regime. During the cooling of the cryostat the tunneling systems remain thermally "charged". The broad distribution of relaxation rates causes the existance of TLS in the thermally excited state even after the finite time which is necessary for the cooling of the sample; i.e. the pseudo spin system of the TLS is not in the thermal equilibrium. This relaxation can be understood in terms of single TLS flips. Therefore, an additional broadening of the spectral holes is observed. The number of TLS in the thermally excited state decreases as a function of time and consequently the magnitude of the broadening effect. Figure 2 confirms this model assumption. These holes, which were burnt 17h and 65h, respectively, after the cooling show a reduced broadening as compared to the first experiment at $t_B = 0h$.

CONCLUSION

In summary, we report the existance of two different phenomena in the very low temperature regime, which can both be linked to TLS dynamics of the amorphous host. We observed spectral diffusion due to tunneling processes involving *two level systems* and a decrease of the hole broading effect, which shows a long time decay of thermally charged TLS. The latter result can be looked upon as an optical analogue to *long time heat release* experiments [11,12,13] performed in amorphous solids.

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REFERENCES

1. J.Friedrich and D.Haarer, Angew. Chem., 96 96 (1984); Angew. Chem. Int. Ed. Engl., 23 113 (1984).
2. W.E. Moerner (ed.) Persistent Spectral Hole-Burning: Sience and Applications, Springer N.Y. (1987).
3. A.A.Gorokhovskiĭ, Ya.V. Kikas, V.V. Pal'm, and L.A. Rebane, Sov. Phys. Solid State, 23(4) 602 (1981).
4. A. Burkhalter, G.W. Suter, U.P. Wild, V.D. Samoilenko, N.V. Rasumova, and R.I. Personov, Chem. Phys. Lett., 94(5) 483 (1983).
5. H.P.H. Thijssen, R.E. van den Berg, and S. Völker, Chem. Phys. Lett., 103(1) 23 (1983).
6. M.M. Broer, B. Golding, W.H. Haemmerle, J.R. Simpson, and D.L. Huber, Phys. Rev. B, 33(6) 4160 (1986).

7. A. Gorokhovskiĭ, V. Korrovits, V. Palm, and M. Trummal, Chem. Phys. Lett., 125(4) 355 (1986).
8. G. Schulte, W. Grond, D. Haarer, and R. Silbey, J. Chem. Phys., 88(2) 679 (1988).
9. J.L. Black and B.I. Halperin, Phys. Rev. B, 16, 2879 (1977).
10. K.-P. Müller and D. Haarer, Phys. Rev. Lett., 66 2344 (1991)
11. J. Zimmermann, G. Weber, Phys.Rev.Lett., 46 661 (1981)
12. M. Schwark, F. Pobell, M. Kubota, and R.M. Müller, J. Low. Temp. Phys. 58 171 (1985).
13. M. Deye and P. Esquinazi, Zeitschr. f. Phys. B 76 283 (1989).