Transport of magnetization in inhomogeneously broadened spin systems

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We consider the transport of magnetization in general and especially the transport of magnetization to isolated relaxation centers in spin systems where the inhomogeneous distribution of resonant frequencies is much broader than the interspin dipolar interaction. The results relate to T_1 and T_2 relaxation and to hole burning in a number of amorphous systems including those which are deuterated.

I. INTRODUCTION

In most solid nuclear-spin systems the magnetization is readily transported via mutual spin flips induced by the dipolar interaction. By a mutual spin flip we mean the spin conserving process whereby one spin flips up (down) and a neighboring spin flips down (up). Such a spin system thermalizes in a time of order ω_d^{-1}, where ω_d is the frequency characterizing the magnitude of the dipolar interaction. Further, a band with a width[1] of order ω_d is formed about the Larmor frequency ω_0 of an individual spin. The transport of magnetization and the formation of a band of states is relatively unaffected by inhomogeneous line broadening on a scale that is small compared to ω_d.

However, the above mechanism cannot operate if the resonant Larmor frequencies $\omega_0(i)$ of the individual spins i are inhomogeneously broadened by an amount large compared to ω_d. One can picture this as the failure of the mutual spin-flip transition of frequency $\omega_0(i)-\omega_0(j)$ to conserve Zeeman energy to within ω_d or as the transition lying outside of the dipolar band. In this paper we shall explore the transport of magnetization and especially the transport of magnetization to relaxation centers in the limit of large inhomogeneous broadening. We shall consider only the case of spin $I=\frac{1}{2}$ although in practice inhomogeneous broadening often arises from electric field gradients acting on the quadrupole moments of nuclei with $I>\frac{1}{2}$. However, by specializing to the relatively simple $I=\frac{1}{2}$ case we shall be able to concentrate on the essential mechanisms without having to manipulate all of the extra operators[2] that are introduced if $I>\frac{1}{2}$.

Magnetic resonance has been very useful as a probe of structural and dynamical properties of many materials. Recently NMR has been applied to a number of amorphous and/or glassy systems. Because of their noncrystalline nature, atomic sites in these materials experience a distribution of electric field gradients, and therefore $I>\frac{1}{2}$ nuclear spins in these systems typically experience substantial inhomogeneous broadening. Our results will describe hole burning[3] as well as the transport of magnetization in such systems. Further, a number of interesting amorphous semiconductors contain D. Our results can describe the thermalization as well as the transport of magnetization to D_2 relaxation centers in these systems.[4]

In the remainder of this section we shall argue that there is no residual dipolar order in a severely inhomogeneous broadened system. Section II contains a dynamical treatment of two interacting spins that can also be coupled to the lattice. This simple model makes clear the basic physical ideas of this paper and suggests how to study the N-spin problem. The generalization to the N-spin problem and a discussion of the results is contained in Sec. III.

It is sometimes thought that various "isochromats" or spectral regions of similar frequency shifts can form a dipolar reservoir for the z component of the magnetization in a badly inhomogeneously broadened system. The following construction will show that this is not true in a system where the distribution of inhomogeneous broadening is random and thus uncorrelated from site to site. Consider a spin system with a distribution of Larmor frequencies $\omega_0(i)$. The width of this distribution is characterized by ω_q. Further, consider interactions among the spins that are proportional to $\omega_d(r/r_0)^{-n}$, where r is the distance between the spins, r_0 is a nearest-neighbor distance, ω_d is an interaction strength, n is the dimensionality of the interaction, and $\omega_q \gg \omega_d$. Now suppose that an isochromat of width Δ forms a "dipolar" reservoir or a thermal system of interacting spins. Let c be the concentration or fraction of spins in that isochromat of width Δ. Since c must scale as r^{-3}, where r is the average distance between spins in the isochromat,

$$\Delta=c^{n/3}\omega_d \ . \tag{1}$$

Also, since c is the concentration or the fraction of spins in the isochromat,

$$c=\Delta/\omega_q \ . \tag{2}$$

Equations (1) and (2) can then be solved for Δ. However, there is no solution for Δ if $n<3$ (and, of course, $c \ll 1$). Thus there is no thermal subsystem in the usual sense. There are systems $\omega_q \gg \omega_d$ which do not satisfy the assumptions used in the above argument. For example, a random distribution of a small concentration of point defects yields a distribution of electric field gradients that are very correlated from site to site in an otherwise perfect lattice.

II. SPIN PAIR

In this section we consider a pair of spins interacting via the truncated dipolar Hamiltonian[1]

$$H_d = \hbar\omega_d \{ S_z(1)S_z(2) - \tfrac{1}{4}[S_+(1)S_-(2)+S_-(1)S_+(2)]\} , \quad (3)$$

where $S_\alpha(i)$ is the α component of the spin operator at the site i. Further,

$$\omega_d = \omega_d(1,2) = \gamma^2\hbar(1-3\cos^2\theta_{12})/r_{12}^3 , \quad (4)$$

where the two spins are separated by the distance r_{12}, θ_{12} is the angle that $\mathbf{r}_{12}$ makes with the direction of an external magnetic field that defines the z direction, and γ is the gyromagnetic ratio of the spins. Each spin experiences a slightly different magnitude of magnetic field H_i, and thus the Larmor frequency of the ith spin is $\omega_0(i)=\gamma H_i$. It is also convenient to define a difference frequency

$$\omega_q = \omega_q(1,2) = \omega_0(1) - \omega_0(2) . \quad (5)$$

One can easily diagonalize the Hamiltonian for the system of two spins. However, this yields no information that is useful for our purposes. Instead we form equations of motion for $S_z(i)$ and for all of the operators that couple to it. Besides the Zeeman Hamiltonian and the interaction Hamiltonian given by Eq. (3), we also include longitudinal and transverse spin relaxation that arise from as yet unspecified mechanisms. The relaxation rate for $S_z(i)$ is denoted by $\Gamma_1(i)$ and the rate for $S_+(i)$ is denoted by $\Gamma_2(i)$. These correspond to T_1 and T_2 processes, respectively. By assuming that all $S_\alpha(i,t)$ have an $\exp(-i\omega t)$ dependence, and by using the Heisenberg equations of motion one can easily derive the equations

$$[\omega + i\Gamma_1(1)]S_z(1) = \tfrac{1}{4}\omega_d[S_-(1)S_+(2) - S_+(1)S_-(2)] ,$$
$$[\omega - \omega_q - i\Gamma_2(s)]S_+(1)S_-(2) = \tfrac{1}{4}\omega_d[S_z(2)-S_z(1)] , \quad (6)$$

where the argument s refers to the sum of 1 and 2 as in

$$\Gamma_2(s) = \Gamma_2(1) + \Gamma_2(2) . \quad (7)$$

There are two more equations that are the same as Eqs. (6) with 1 and 2 interchanged and with ω_q replaced by $-\omega_q$. These four equations form a complete dynamical description of the part of the two-spin system that conserves S_z. It is convenient to interpret these equations as a set of four normal mode equations where the real and imaginary parts of ω yield the frequencies and decay rates for the modes.

It is worth investigating the solutions to Eq. (6) in several limiting cases. For example, if all of the Γ's are zero, one of the modes,

$$\omega S_z(s) = 0 , \quad (8)$$

describes the conservation of the total magnetization. Further, if $\omega_q \ll \omega_d$, the other three modes are given approximately by the equations

$$\omega[S_+(1)S_-(2)+S_-(1)S_+(2)] = 0 ,$$
$$(\omega - \tfrac{1}{2}\omega_d)[2S_z(\delta) - S_+(1)S_-(2) + S_-(1)S_+(2)] = 0 , \quad (9)$$
$$(\omega + \tfrac{1}{2}\omega_d)[2S_z(\delta) + S_+(1)S_-(2) - S_-(1)S_+(2)] = 0 ,$$

where δ refers to the difference of 1 and 2 as in

$$S_z(\delta) = S_z(1) - S_z(2) . \quad (10)$$

These equations describe the start of the formation of a dipolar band.

Our main interest, however, is the limit where ω_q is much greater than ω_d or any of the Γ's. In this limit two of the four modes have frequencies of order ω_q. These modes correspond to $S_+(1)S_-(2)$ and $S_-(1)S_+(2)$ and are of no further interest here. By keeping terms only to lowest order in $\omega/[\omega_q + i\Gamma_2(t)]$ one obtains equations for the other two modes

$$[\lambda - \Gamma_1(1)]S_z(1) + \beta[S_z(2) - S_z(1)] = 0 ,$$
$$[\lambda - \Gamma_1(2)]S_z(2) + \beta[S_z(1) - S_z(2)] = 0 , \quad (11)$$
$$\beta = \beta(1,2) = \omega_d^2\Gamma_2(s)/8[\omega_q^2 + \Gamma_2^2(s)] ,$$

where $\omega = -i\lambda$. Thus λ describes a decay rate.

The solutions to Eqs. (11) are

$$\lambda = \beta + \tfrac{1}{2}\Gamma_1(s) \pm [\beta^2 + \tfrac{1}{4}\Gamma_1^2(\delta)]^{1/2} , \quad (12)$$

where $\Gamma_1(\delta)$ is defined in analogy with $S_z(\delta)$ in Eq. (10). In the limit $\beta \ll \frac{1}{2}\Gamma_1(\delta)$ the solutions approach

$$\lambda_1 = \Gamma_1(1) + \beta ,$$
$$\lambda_2 = \Gamma_2(2) + \beta , \quad (13)$$

and the eigenvectors are $S_z(1)$ and $S_z(2)$, respectively. In the opposite limit $\beta \gg \frac{1}{2}\Gamma_1(\delta)$, the solutions approach

$$\lambda_1 = 2\beta ,$$
$$\lambda_2 = \tfrac{1}{2}\Gamma_1(s) , \quad (14)$$

and the eigenvectors are $S_z(\delta)$ and $S_z(s)$, respectively.

In the limit where $\beta \ll \Gamma_1(\delta)$, the S_z of each spin decays with its own longitudinal decay rate and the coupling is unimportant. However, suppose that $\Gamma_1(2)$ is zero. In that case λ_2 equals β and the z component of spin 2 undergoes longitudinal or T_1 decay via the transverse (or T_2-like) fluctuations of the pair of spins. If $\Gamma_2(2)$ is zero then the transverse fluctuations of spin 1 induce the longitudinal decay of spin 2 in a manner in which spin 1 acts like a paramagnetic impurity.[5,6] However β depends on $\Gamma_2(s)$, and thus the mechanism also is operative if $\Gamma_2(1)=0$ and $\Gamma_2(2)\neq 0$. Thus it is the transverse fluctuations of the pair of spins that is important.

The other limit where $\Gamma_1(\delta) \ll \beta$ is also interesting. In this limit the two spins "thermalize" at a rate β and then decay with the average decay rate of the two spins. The transverse fluctuations of the spins induce the mutual spin flips that thermalize the pair and cause the pair to decay as a single system. In a larger system this would correspond to the spin temperature limit. In any case the z component of the magnetization is transported from one spin to the other via mutual spin flips where the transverse fluctuations take up the energy imbalance. If all of the relaxation rates are zero, there is virtually no transport of magnetization.

III. EXTENDED SYSTEMS

In the last section we considered a pair of inhomogeneously shifted spins interacting via the truncated dipolar Hamiltonian. Here we generalize the ideas to extended systems. In an extended system with a distribution of inhomogeneous splittings, there will always be some pairs of spins (i,j), where by chance $\omega_q(i,j)$ will not be greater than $\omega_d(i,j)$. However, since we are considering systems where typical ω_q's are much greater than nearest-neighbor ω_d's, the incidence of such pairs (i,j) is relatively small. For our purposes these tightly bound spin pairs can be ignored since they will contribute very little to the transport of magnetization.

First we consider a system of spins where all spins have identical or nearly identical Γ_1 and Γ_2. These relaxation rates arise from spin-lattice relaxation, or Γ_2 could arise from spin-spin interactions with another reservoir of spins. It cannot, of course, be associated with the spin-spin interactions that are under consideration. This is the regime where $\beta \gg \frac{1}{2}\Gamma_1(\delta)$ for any pair and is thus described by Eqs. (14). The relaxation of the total magnetization is Γ_1 but the transport of the z component of the magnetization between members of a pair of spins at sites i and j is described by $\beta(i,j)$ instead of $\omega_d(i,j)$. Consider, for example, a hole-burning experiment with a hole narrow compared to the inhomogeneous linewidth. Since magnetization can be transported from one spin to another spin at a site with different resonant frequency, the hole will evolve into a broader-shallower hole with a rate of order β, where β is an average $\beta(i,j)$ over nearest-neighbor pairs. Since S_z is conserved by this process, the area of the hole will not be changed by this process. Assuming that $\Gamma_1 \ll \beta$, the hole will fill in with the much smaller rate Γ_1.

Next consider the relaxation of a set of inhomogeneously broadened spins by a number of relaxation centers. An example of such a systems is bonded D in a-Si:D with effectively dilute D_2 impurities. The D_2 nuclear spins relax reasonably quickly to the lattice via their electronic shell, while the atomic D relaxes very slowly to the lattice directly. Since Γ_1 and Γ_2 are only nonzero for the relaxation centers, the spins cannot interact with each other except via the relaxation centers.

One might suppose that some spin (labeled 3) is very far from a relaxation center (labeled 1) and thus is only very weakly connected to it. Such a spin may couple to the relaxation center via an intermediary spin (labeled 2). However, this coupling is very weak. A calculation similar to, but more tedious than, the one described in Sec. II shows that, through an intermediary, $\beta(1,3)$ is replaced by $\beta(1,3;2)$ where

$$\beta(1,3;2)=[\omega_d^2(1,2)\omega_d(2,3)/32\omega_q^2(2,3)] \times(\tfrac{1}{4}\{\Gamma_2/[\omega_q^2(1,3)+\Gamma_2^2]\} +\{\Gamma_1/[\omega_q^2(2,3)+\Gamma_1^2]\}) \ . \tag{15}$$

Now consider a simplified problem of N particles which includes one sink and $N-1$ other particles. The equations describing the decay are easily seen to be

$$\begin{aligned}&[\Gamma_1+\beta(s)-\lambda]S_z(1)-\sum_j \beta(j)S_z(j)=0 \ , \\ &[\beta(i)-\lambda]S_z(i)-\beta(i)S_z(1)=0, \quad i\neq 1 \ ,\end{aligned} \tag{16}$$

where $i=1$ is the sink spin,

$$\begin{aligned}&\beta(i)=\beta(i,1) \ , \\ &\beta(s)=\sum_i \beta(i) \ ,\end{aligned} \tag{17}$$

and, $\beta(1)=0$. Equations (16) can be combined to yield the single eigenvalue equation

$$\lambda-\Gamma_1-\beta(s)-\sum_i \beta^2(i)/[\lambda-\beta(i)]=0 \ . \tag{18}$$

An exact solution to the above equations can only be obtained by numerical methods with specific sets of $\beta(i)$. However, we have been able to obtain quasianalytical solutions that have been verified by numerical solutions. It is useful to view Eq. (18) as an eigenvalue equation for the decay mode of the sink spin 1 and any other spins that are in thermal equilibrium with it. Further, it is convenient to order the labeling on the rest of the spins so that

$$\beta(2)>\beta(3)> \cdots >\beta(N) \ . \tag{19}$$

Next, in Eq. (18), we make the following approximation:

$$\beta^2(i)/[\lambda-\beta(i)]=\begin{cases}-[\beta(i)+\lambda] \ \text{ if } \beta(i)>\lambda & \text{(20a)}\\ \beta^2(i)/\lambda \ \text{ if } \beta(i)<\lambda \ . & \text{(20b)}\end{cases}$$

Now suppose that $M-1$ of the spins have $\beta(i)>\lambda$ and the remaining $N-M$ spins have $\beta(i)<\lambda$. Then, by substituting Eq. (20) into Eq. (18) we obtain the approximate eigenvalue

$$\lambda_M=\Gamma_1/M \tag{21}$$

for the mode involving the sink spin. Further, from Eqs. (18) and (19), it is clear that M is determined by the condition that

$$\beta(M)>\lambda_M>\beta(M+1) \ . \tag{22}$$

This obtains because using Eqs. (20) one finds that terms i with $\beta(i)>\lambda$ contribute significantly to the summation in Eq. (18) but terms i with $\beta(i))<\lambda$ do not. If Eq. (22) does not uniquely determine M, the solution with the largest M is appropriate. Thus, Eqs. (21) and (22) determine M, the number of spins that are in thermal equilibrium with the sink spins. For completeness, $\beta(1)$ is defined as infinity and $\beta(N+1)$ is defined as zero. The rest of the spins i have relaxation rates that are approximately $\beta(i)$.

The arguments leading to Eqs. (21) and (22) are quite crude. In particular, the approximations described in Eqs. (20a) and (20b) are mathematically (not physically) motivated and are really only valid if $\beta(i)\gg\lambda$ and $\beta(i)\ll\lambda$, respectively. However, extensive numerical work shows that the results are quite good. That is, we have solved Eqs. (16) or Eq. (18) by numerical methods for specific sets of $\beta(i)$ that describe random distributions of inhomogeneous broadening and different distances from the sink spin 1. We found that Eqs. (21) and (22) and the description following them gave a good account of the situation as Γ_1 was changed. That is, the fraction of $S_z(s)$ that decays with a single rate is pretty well given by M/N and λ_N is a good estimate for that decay rate. Further, the spins i not included in the thermal reservoir decay with rates $\beta(i)$. The reason that the approximation described in Eqs. (20) works is that for most of the spins it is actually a valid approximation.

Figure 1 depicts a possible scenario for relaxation as a function of temperature. In this figure Γ_1 and Γ_2 are sketched as a function of the temperature. The functional dependence of $\Gamma_{1,2}$ on T, of course, depends on the specific relaxation mechanism in question. Rather than a specific mechanism, the figure describes a situation where $T_2=\Gamma_2^{-1}$ increases as T does and where there is a minimum in T_1 as a function of T. This would, for example, pertain to D_2 in a-Si:D. In any case, Γ_1/N is also sketched while the shaded region corresponds to the range of values of $\beta(i)$. The dashed line corresponds to the average value of the longitudinal relaxation rates of the spins. At high temperatures, where Γ_1 is greater than all of the $\beta(i)$'s, each spin relaxes independently with its individual rate $\beta(i)$. In this limit there is a broad distribution of relaxation rates. As the temperature is lowered more and more spins become thermalized with the sink spin and they tend to relax as a whole.

The situation when one has a sprinkling of relaxation centers in a sea of otherwise noninteracting spins is quite similar. The equations describing the decay can easily be derived and are conveniently expressed as

$$[\lambda-\Gamma_1-\beta(\alpha)]S_z(\alpha)+\sum_\beta \beta(\alpha,\beta)S(\beta) = \sum_j \beta(\alpha,j)S_z(j)=0 \; ,$$

$$[\lambda-\beta(i)]S_z(i)+\sum_\alpha \beta(i,\alpha)S_z(\alpha)=0 \; , \tag{23}$$

where Latin letters denote nonsink sites, Greek letters denote sink sites, and

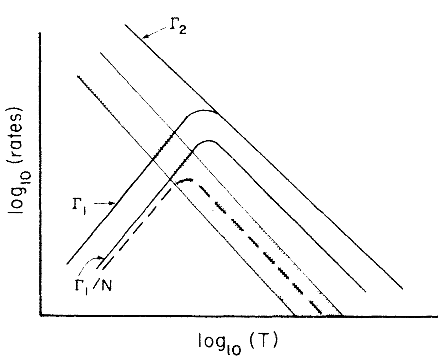

FIG. 1. Possible scenario for relaxation as a function of temperature. The shaded region corresponds to the range of values of $\beta(i)$ and the dashed line is the average value of Γ_1.

$$\beta(i)=\sum_\alpha \beta(i,\alpha) \; , \quad \beta(\alpha)=\sum_i \beta(\alpha,i)+\sum_\gamma \beta(\alpha,\gamma) \; . \tag{24}$$

Equations (23) can be combined to yield an equation analogous to Eq. (18),

$$\left[\lambda-\Gamma_1+C(\alpha)-\sum_\gamma D(\alpha,\gamma)\right]S_z(\alpha)+\sum_\beta D(\alpha,\beta)S_z(\beta)=0 \; ,$$

$$C(\alpha)=\sum_j \lambda\beta(\alpha,j)/[\beta(j)-\lambda] \; , \tag{25}$$

$$D(\alpha,\gamma)=\beta(\alpha,\gamma)+\sum_j \beta(\alpha,j)\beta(j,\gamma)/[\beta(j)-\lambda] \; .$$

In comparing Eq. (25) to Eq. (18), $C(\alpha)$ take the place of $\beta(s)$ for the sink α. The quantity $D(\alpha,\gamma)$ describes the effective coupling between the sites α and β. As can be seen, there is a direct coupling described by $\beta(\alpha,\gamma)$ and in indirect coupling via all of the nonsource spins. The size of this second coupling mechanism depends on the eigenvalue λ itself. We have not found any analytical tricks like Eqs. (20) that make Eqs. (25) easier to understand. Therefore, we have run numerical solutions for a number of different distributions of spins and sinks. What happens is that when an appreciable fraction of the $\beta(\alpha,i)$ becomes large enough so that a number of spins i thermalize with a given sink α, the sinks themselves begin to experience appreciable interactions among themselves. In general, our numerical work shows that Eqs. (16)–(22) are a good representation to the infinite spin system if N equals the ratio of the number of spins divided by the number of sources. This, perhaps, should not be too surprising.

Throughout this work we have assumed that the relaxation centers are each described by a single relaxation rate, and thus, without the other spins, these relaxation centers would exponentially relax. However, since the rates of the relaxation center need not all be equal, the total decay of magnetization need not be described by a single exponential. Thus the equations are valid where one locally has relaxation by a single relaxation rate even though globally one does not. We believe that the equations could be generalized to the case where the local relaxation rates are not exponential, but we have not yet tried to do so.

At present, there is very little experimental data to compare to our theory. However, we believe that the major result of this work is in showing that inhomogeneous systems can relax with a single exponential and in obtaining the conditions under which this can occur. We have also analyzed how spins can relax even if magnetization cannot diffuse to relaxation centers. Experiments on D nuclei in a-Si:D shows that the bonded D does relax to D_2 relaxation centers even though the inhomogeneous broadening is very large compared to a typical dipolar interaction.[4] Further it appears that at least some thermalization of the bonded D can take place. On the other hand, other experiments[7] on bonded D exhibit a range of T_1's that vary over 5 orders of magnitude and appear to correspond to the limit where each spin decays independently. Since $B(i,j)$ is proportional to $\omega_d^2(i,j)$ and $\omega_d(i,j)$ is proportional to the inverse cube of the distance between i and j, the range of $\beta(i,j)$ should be proportional to c^2, where c is the number of sinks divided by the number of spins. Further, the distribution of β's or relaxation rates should be heavily weighted toward the smaller rates as is observed in the experiments. Further experiments and quantitative calculations to describe them are currently in progress. In particular, the shape of the nonexponential relaxation of magnetization is being measured and calculated in a-Si:D. Finally, experiments on hole burning on D in amorphous metal deuterides show hole shape changes that are in at least qualitative and semiquantitative agreement with our theory.[3] However, more detailed experiments and a theory for $I > \frac{1}{2}$ are needed for a better comparison. In addition, further work is needed to see how the mechanism operates in rotating-frame experiments.

ACKNOWLEDGMENTS

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[1]See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. IV.

[2]P. A. Fedders, Phys. Rev. B **11**, 995 (1975).

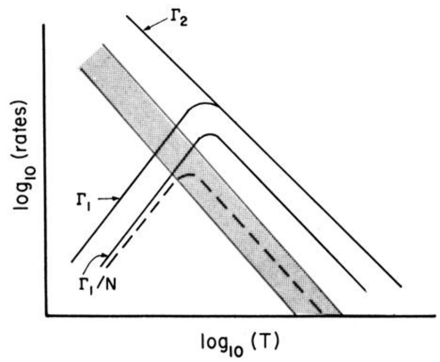
[3]V. P. Bork, P. A. Fedders, R. E. Norberg, R. C. Bowman, and E. L. Venturini, in *Amorphous Hydrides*, edited by G. Mabbakidis and R. C. Bowman (Plenum, New York, 1986).

[4]D. J. Leopold, P. A. Fedders, and R. E. Norberg, Phys. Rev. B **31**, 5642 (1985).

[5]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. IX.

[6]I. J. Lowe and D. Tse, Phys. Rev. **166**, 279 (1968).

[7]V. P. Bork, P. A. Fedders, R. E. Norberg, K. D. Mackenzie, and W. Paul, *Proceedings of the 11th International Conference on Amorphous and Liquid Semiconductors, Rome, August, 1985* [J. Non-Cryst. Solids (to be published)].



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