On the temperature dependence of excited triplet state spin sublevel populations of shallow traps in molecular crystals

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Since the first experimental observation of the ESR spectrum of an excited triplet state of an organic molecule in a molecular host crystal,[1] factors affecting relative triplet spin sublevel populations have become increasingly important. Optical detection[2a] of ESR in zero magnetic field (ODMR)[2b] of both pure[3] and mixed crystals[4] at low temperatures, where in general a Boltzmann distribution of populations does *not* exist,[5] has yielded valuable information pertaining to many aspects of molecular excited states and has made still more important the nature of mechanisms which affect the non-Boltzmann spin sublevel population distribution.

For a guest molecule in a host crystal, the steady state population of a triplet spin sublevel at low temperature is determined by the populating rate, i.e., the intersystem crossing rate, divided by the rate constant for decay to the ground state. The ratio of spin sublevel populations is dependent on temperature through the temperature dependence of the spin–lattice relaxation rates[6] which will produce a Boltzmann distribution of populations at sufficiently high temperature. Here we wish to report a temperature dependent mechanism distinct from spin–lattice relaxation which can strongly affect the ratio of spin sublevel populations of shallow traps such as those formed by isotopic impurities. Unlike spin–lattice relaxation which tends to equalize the populations, the considerations discussed below can cause the spin polarization to invert. In an ODMR experiment this can result not only in a change in magnitude of the signal but also in a change in the signal's sign.

For a system composed of a host crystal containing shallow traps, the ratio of trap spin sublevel populations will be influenced by the temperature dependent partitioning of excitations between the traps and the host crystal's triplet exciton bands. Since in general the exciton spin sublevels will have lifetimes which are different than those of the trap, rapid exchange of population between the band and trap will result in trap decay times which are weighted averages of the band and trap lifetimes. The weighting factor is determined by the probability of finding an excitation in the trap.

If we consider the case where the principal axes system of the trap's zero field splitting tensor coincides with that of the host crystal's, as in traps formed by isotopic impurities, and where energy transfer between translationally inequivalent molecules is unimportant, then the trapping and detrapping processes themselves will not mix the spin sublevels, and in the absence of spin–lattice relaxation the sublevel populations may be treated independently. For a system composed of a host crystal and one type of trap species in thermal equilibrium, the probability of finding an excitation of the system in the trap is given by $\chi(T) = 1/Z(T)$, where $Z(T)$, the partition function, is identical for all spin sublevels.[7] Thus the ith spin sublevel of the trap will have population N_T^i given by

$$N_T^i = \frac{K_{isc}^i \chi}{K_T^i \chi + K_E^i (1-\chi)} . \tag{1}$$

K_{isc}^i is the total rate for intersystem crossing into the trap and band ith spin sublevel and K_T^i and K_E^i are the rate constants for decay to the ground state from the ith spin sublevel of the trap and band, respectively. Thus the ratio $R^{ij}(T)$ of the populations of two trap spin sublevels i and j is

$$R^{ij}(T) = \frac{N_T^i}{N_T^j} = \frac{K_{isc}^i}{K_{isc}^j}\left(\frac{K_T^j \chi + K_E^j (1-\chi)}{K_T^i \chi + K_E^i (1-\chi)}\right) . \tag{2}$$

For a system in which K_T^j/K_T^i is equal to K_E^j/K_E^i, the ratio $R^{ij}(T)$ would not be affected by the temperature dependent band-trap population distribution. However, when the ratio of the trap sublevel lifetimes is markedly different than the ratio of the band sublevel lifetimes, even a very small change in $\chi(T)$, the trap probability, can produce a large change in $R^{ij}(T)$. For a system with more than one type of trap species, the appropriate partition function and trap probability[7a] are used in Eq. (2) while for a system which is not in thermal equilib-

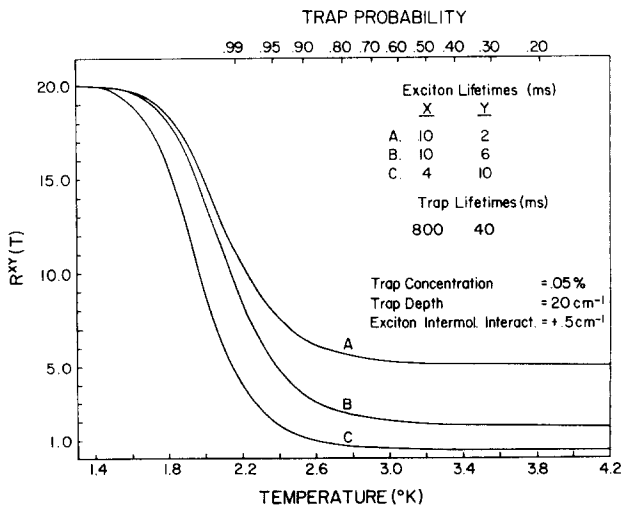

FIG. 1. Temperature dependence of the ratio of triplet spin sublevel populations for shallow traps in molecular crystals produced by population exchange between exciton and trap states. Curves A, B, and C illustrate the importance of the relative lifetimes. Note that at 2.6 °K curve C passes through 1, i.e., the spin polarization changes sign.

rium, a similar procedure can be applied by solving the coupled differential equations for band and trap spin sublevel populations including terms for trapping and detrapping.[7a]

To illustrate the above considerations the temperature dependence of $R^{xy}(T)$, the ratio of trap spin sublevel populations [Eq. (2)] is displayed in Fig. 1 for a model "one dimensional" host crystal, i.e., for a system such as 1,4-dibromonaphthalene[8a] or 1,2,4,5-tetrachlorobenzene[8b] in which the intermolecular interactions responsible for triplet exciton transport occur between translationally equivalent molecules along a single crystallographic axis. A 20 cm^{-1} trap depth, a $+0.5$ cm^{-1} intermolecular interaction matrix element, and a trap concentration of 0.05% were employed to determine $\chi(T)$. The ratio of the intersystem crossing rates, a multiplicative constant, was set equal to 1. Trap lifetimes $1/K_T^y$ and $1/K_T^x$ were chosen to be 40 and 800 msec, respectively. These numbers are similar to reported values of trap sublevel lifetimes in a one dimensional solid.[5a,7b] The curves in Fig. 1 are calculated using several sets of exciton lifetimes which are on the order of those reported for the one dimensional solid, 1,2,4,5-tetrachlorobenzene, mentioned above.[9] These are tabulated in the figure. The trap probability as a function of temperature $\chi(T)$ is indicated along the top axis.

Two important features of the curves should be noted. First, there is a substantial change in $R^{xy}(T)$ in a temperature range (1.4–2.2 °K) in which there is a very small change in the trap probability. The large change in the ratio of spin sublevel populations for a small change in $\chi(T)$ occurs when the ratio and magnitude of the intrinsic trap lifetimes is considerably different than the ratio and magnitude of the intrinsic exciton lifetimes. Curve C illustrates the second important point. With only a small change in trap probability (1.0–0.85), the ratio $R^{ij}(T)$ can fall below one for a system in which $K_T^i/K_T^j \gg 1$ and $K_E^i/K_E^j \ll 1$. The low temperature spin polarization first shrinks as the temperature is raised, passes through zero $[R^{ij}(T)=1]$ and then begins to grow in the opposite direction. In an ODMR experiment, the signal would become smaller, go to zero, and then grow, but with opposite sign, as the temperature is increased through this region. Recently there have been a number of temperature dependent ODMR experiments performed on systems composed of shallow traps in communication with exciton bands.[10] The mechanism described here will strongly affect signal strengths and will add to the overall complexity of temperature dependent ODMR experiments in this type of system.

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