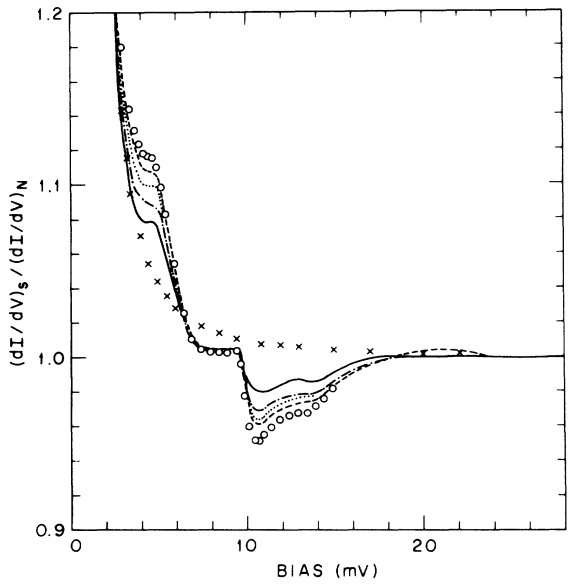

FIG. 2. Curves of $(dI/dV)_S/(dI/dV)_N$ vs V for four Si-Pb junctions with Pb negatively biased, together with the BCS density of states (crosses) and the density of states of superconducting Pb (circles). The notations and experimental conditions are given under Fig. 1.

fabricated on As-doped Si, Sb-doped Si, and Sb-doped Ge as well. We conclude that the breakdown of the usual tunneling expression is a common feature of semiconductor-superconductor junctions, being independent of dopant in Si and Ge.

I am most greatful to W. L. McMillan and J. M. Rowell for helpful discussions and to G. Kaminsky for technical assistance.

[1]J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964).

[2]W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 11.

[3]M. N. Alexander and D. F. Holcomb, Solid State Commun. 6, 355 (1968). These authors also identify a second characteristic donor concentration $n_{cb} \approx 2 \times 10^{19}$ cm^{-3}, at which the Fermi level passes into the conduction band of pure Si.

[4]T. F. Tao and Y. Hsia, Appl. Phys. Lett. 13, 291 (1968); J. W. Conley, C. B. Duke, G. D. Mahan, and J. J. Tiemann, Phys. Rev. 150, 466 (1966).

[5]This small increase in conductance at $T > T_c$ in high biases can be accounted for by thermal excitation of electrons over the Si surface barrier.

[6]D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. 148, 263 (1966).

[7]D. C. Tsui and L. N. Dunkleberger, Appl. Phys. Lett. 18, 200 (1970); L. B. Schein and W. D. Compton, Appl. Phys. Lett. 17, 236 (1970).

Spin Memory in the Trapping of Triplet Excitons*

Mark Sharnoff and Elsa B. Iturbe
Department of Physics, University of Delaware, Newark, Delaware 19711
(Received 6 July 1971)

By using optical methods to detect paramagnetic resonance signals from triplet excitons and from trapped triplet excitations in benzophenone, we have shown that spin angular momentum is conserved in triplet-triplet energy transfer.

Some years ago, Dexter pointed out[1] that spin-forbidden processes occurring in the sensitized luminescence of solids should proceed primarily via the quantum-mechanical exchange interaction and hence be conservative of spin angular momentum. While subsequently investigating energy transfer in rigid organic media, Ermolaev and Terenin discovered[2] that transfer of energy from a donor in a triplet state to an acceptor initially in a singlet state was of very short range and concluded that the exchange interaction was responsible for the transfer. Since that time, Davydov splitting in the singlet-triplet absorption spectra of organic crystals has been extensively studied[3,4] and found to be roughly consistent in magnitude, if not always in sign,[5] with calculations based on the exchange mechanism.

While today it is widely held that the exchange interaction is the principal mechanism of triplet-triplet energy transfer, a severe test of the spin-conserving properties of this transfer has not yet been reported. And while the types of experiments[6-8] which are capable of providing the necessary spin discrimination are noteworthy in themselves, the evidence which they provide is indirect and not unexceptionable. The present note provides direct indication that spin angular momentum is indeed conserved in a typical triplet-triplet energy-transfer process. The process chosen for this study is the capture of free

excitons by intrinsic traps in a nominally pure crystalline lattice, the orthorhombic phase of benzophenone.

Benzophenone crystals prepared in our laboratory have consistently been pure enough to show phosphorescence from free excitons, and at 4.2°K the optical emission spectrum begins with a sharp line at 4133.3 Å which coincides with the 0-0 band of the crystalline $S_0 \rightarrow T_1$ absorption spectrum.[9] When this emission line is isolated by means of a high-resolution scanning spectrometer and used for photoelectric detection of EPR, a pair of exciton resonances identical to those we have previously described[10] is observed. Resonances from trapped excitations may be observed by appropriate selection of the wavelength illuminating the exit slit of the spectrometer. The emission from traps begins at 4143 Å. There are two varieties[11] of trapped excitation, one having a lifetime of about 5×10^{-3} sec and the other a lifetime of about 2×10^{-5} sec. The two varieties have overlapping EPR and optical emission spectra (Fig. 1).

Two properties of the exciton signals[10] and of the trap signals[10,11] require attention here. Firstly, the optically detected exciton EPR signals are all positive, in the case of the low-field $\Delta m = \pm 1$ transitions, but negative for all the high-field $\Delta m = \pm 1$ transitions. The optically detected signals from the traps were *never* observed to be negative, either in our earlier work in which virtually unfiltered phosphorescence was used, or in our present wavelength-selective work. Secondly, the spin-lattice relaxation times[10] of the excitons are exceedingly short[12] ($\lesssim 2\times10^{-7}$ sec) at 4.2°K, while the spin-lattice relaxation times of the trapped excitations are longer than the lifetimes of the excitations themselves.[10,11] The latter circumstance ensures that cross relaxation between excitons and traps can have no important influence on the spin dynamics of either system. It also implies that, once an exciton has become trapped, it does not reappear as a mobile excitation. The spins of the exciton system thus have no way of sensing the spins of the trapped excitations. But the trapped excitations *are* able to sample, exactly once during their lifetimes, the condition of the exciton spins. For each trapped excitation is influenced at birth by the spin of the exciton which engendered it and, because of its slow spin-lattice relaxation, must carry that influence throughout its life.

The lifelong persistence of the magnetization of each trapped excitation makes possible an experimental inquiry into the spin selectivity of the trapping mechanism, and typical results of such an investigation are shown in Fig. 2. Of particular interest in that figure are the diminution, with increasing microwave modulation frequency, of all EPR signals detected via emission from traps and the absence, in signals detected via emission from excitons, of any trace of trap EPR. The former feature eliminates any possi-

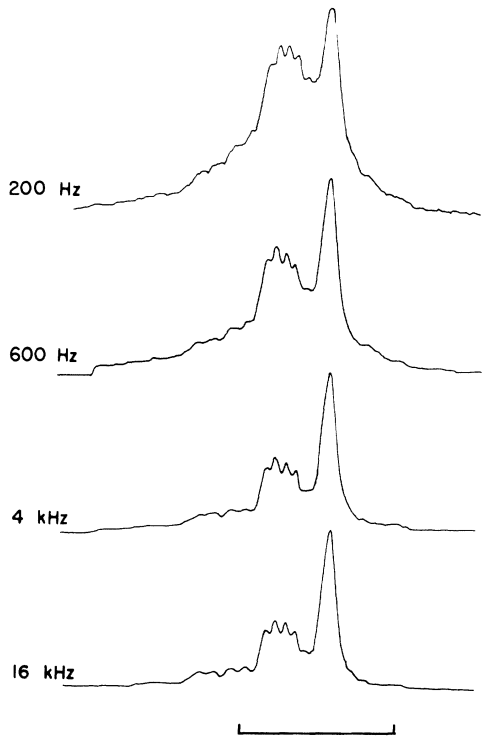

FIG. 1. Optically detected magnetic-resonance signals from triplet excitons (smooth peak) and trapped triplet excitations (bumpy shoulder) in crystalline benzophenone at 4.2°K. Microwaves are pulsed on and off at the repetition rate shown at the left of each tract. Ordinates represent the difference between phosphorescence intensity with microwaves on and phosphorescence intensity with microwaves off. Peak signal amplitude corresponds to a change of approximately 1.5% in the total emission received by the photomultiplier. Abscissas represent magnetic field, which increases linearly towards the right. Bracketed interval = 200 G. Note that the amplitude of the exciton resonance is independent of the microwave modulation frequency, but that the signal from traps diminishes continuously between 200 Hz and 4 kHz. This diminution arised because the spin-lattice relaxation times of the long-lived traps exceeds 5×10^{-3} sec, preventing the populations of their spin states from following the more rapid pulsations in microwave power. The signal from the short-lived traps persists to modulation frequencies as high as 40 kHz.

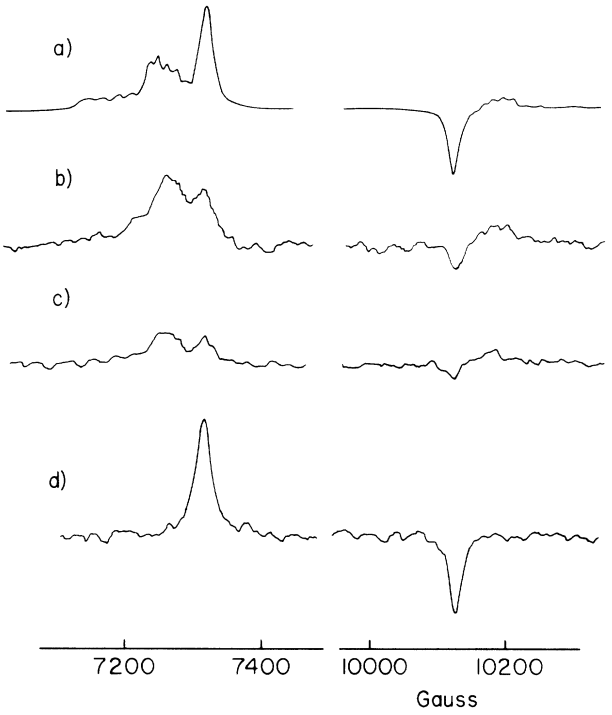

FIG. 2. Optically detected signals obtained with $\vec{H} \| \vec{b}$ axis. Microwave frequency, 24.58 GHz. Sample temperature 4.2°K. (a) Phosphorescence filtered only by CS 4–72 and 5–58 filters. Microwave modulation frequency, 4 kHz. The exciton resonances are the positive peak at 7330 G and the negative peak at 10 120 G. The trap resonances are the bumpy, positive shoulders (see Ref. 10). (b) Phosphorescence filtered by scanning spectrometer. Spectrometer set at 4502 Å, a wavelength common to the emission spectrum of both types of traps. Spectrometer bandwidth 3 Å; modulation frequency, 200 Hz. (c) Same as (b), but with microwave modulation frequency raised to 4 kHz. Amplifier gain is the same as for trace (b). The reduction in signal amplitude may be understood by reference to Fig. 1. (d) Phosphorescence filtered by scanning spectrometer set at 4134 Å (exciton 0-0 band). Bandwidth 3 Å. Microwave modulation frequency, 4 kHz. The signal shape and amplitude were not detectably different when 200-Hz modulation was used.

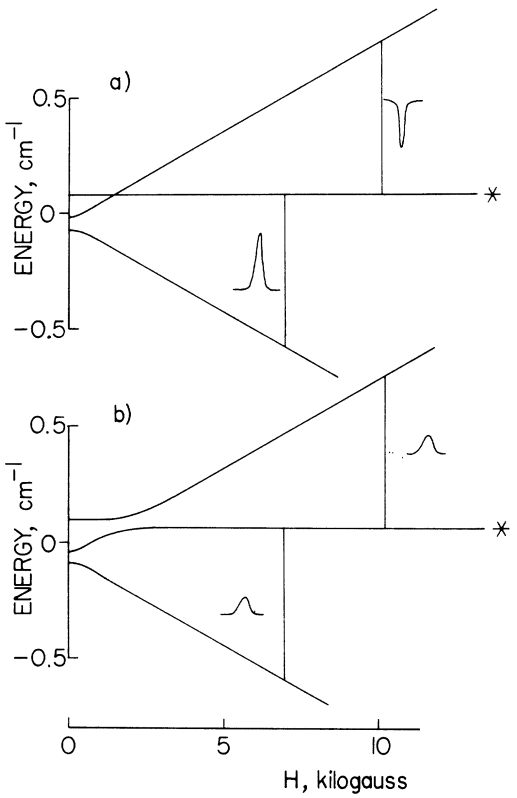

FIG. 3. Energy level and emission diagram for (a) excitons and (b) trapped excitations with $\vec{H} \| \vec{b}$. Emissive level designated by asterisk. The microwave transitions represented by the vertical lines produce the signal patterns indicated. In (b) the solid lines represent the effects of saturating the trap EPR, and the dotted lines the effects of saturating the exciton EPR.

bility that excitonic EPR appears because the trap emission selected by the spectrophotometer is contaminated with luminescence from excitons; the excitonic signals appearing during such detection must accordingly arise from the transcription of exciton magnetization into trap magnetization. The latter feature underwrites our earlier statement concerning the influence of cross-relaxation and de-trapping phenomena.

The third and most interesting feature of Fig. 2—that the excitonic EPR detected via the trap emission has the same sign as excitonic EPR detected directly—requires a more lengthy explanation. In the interests of clarity, we shall here present a simplified version which ignores the difference in orientation[10,13] between the principal axis system of the exciton EPR and that of the trap EPR. (That the effects of this oversimplification are not severe can be judged from the fact that less than 20° separate the excitonic b axis, which is associated with about 75% of the excitonic emission,[10] from the molecular z axis,[13] which is associated with about 90% of the emission[8] from trapped excitations.[10]) The excitons and the traps are then represented by nearly equivalent energy-level emission diagrams,[14] as shown in Fig. 3. Because the excitonic spin-lattice relaxation times are short[10] compared to the phosphorescence lifetime, the relative populations of the excitonic spin sublevels will be nearly Boltzmannian even though the phosphorescence tends to prevent the establishment of such a distribution. Hence when $\vec{H} \| \vec{b}$, saturation of the

low-field exciton resonance will increase, and saturation of the high-field exciton resonance will decrease, the population of the $m = 0$ level. When $\vec{H} \| \vec{b}$, this is the most strongly radiative level, and hence the exciton emission will increase upon saturation of the low-field resonance but decrease when the high-field resonance is excited.

Thus far we have ignored the redistribution in populations which the trapping mechanism might produce. In consistency with the exchange model for energy transfer, however, we shall assume that the trapping mechanism is spin conservative and does not favor any particular spin orientation. When this is the case, not only will the indications of Fig. 3(a) continue to apply, but the relative populations of the spin sublevels of the traps, Fig. 3(b), will be closely dependent upon the populations of the corresponding exciton levels. If the phosphorescence from the traps were not spin selective, the relative populations of the trap levels would assume steady-state values which were identical with those of the corresponding exciton levels. But, because the spin-lattice relaxation times of the traps are long, and because (for $\vec{H} \| \vec{b} \approx \| z$) the $m = 0$ trap levels are strongly radiative, these levels will become underpopulated in comparison with the $m = \pm 1$ levels. Direct saturation of either of the trap resonances will increase the population of this level, effecting a corresponding increase in the trap emission, as indicated. Considering now the effect which saturation of the *exciton* resonances will have upon the trap populations, we note that any process which decreases the relative population of $m = 0$ exciton states will, via trapping, ultimately decrease the relative population of $m = 0$ trap levels. In this way the observation of negative exciton signals in a detection channel in which trap signals are exclusively positive may be rationalized.

The argument outlined above may be repeated for other directions of $\vec{H}$ and leads to the prediction that any exciton resonance detected via the trap emission will have the same sign as when detected via the exciton emission. We have tested this prediction for $\vec{H} \| \vec{a}$ and $\vec{H} \| \vec{c}$, and find it well fulfilled. The results are qualitatively similar to those illustrated in Fig. 2.

Although our description of the transfer has been couched in terms of populations, energy transfer by exchange should also preserve any coherence previously established in the exciton spin system. It should be possible to determine, by observing Larmor modulation[15] in both the exciton and trap channels, whether *all* elements of the excitonic spin-density matrix are conserved during trapping processes. Such an experiment would best be done at very low external magnetic fields, where hyperfine interactions have only second-order influence on the dynamics of the triplet spins.

In summary, we interpret our results as providing a quantitative indication that triplet-triplet energy transfer proceeds predominantly via the exchange interaction. It is evident that the experiments we have described, in which the populations of the donor's spin states are monitored as well as those of the acceptor, are capable of quantitative assessment of the degree to which any spin-nonconserving interaction (magnetic dipole-dipole interaction, for instance) might participate in this process.

---

*Work supported under the National Science Foundation Grants No. GP-10929 and No. GP-29519.

[1]D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

[2]V. L. Ermolaev and A. N. Terenin, J. Chem. Phys. 55, 698 (1958).

[3]D. M. Hanson and G. W. Robinson, J. Chem. Phys. 43, 4174 (1965).

[4]D. M. Burland, G. Castro, and G. W. Robinson, J. Chem. Phys. 52, 4100 (1970).

[5]R. H. Clarke and R. M. Hochstrasser, J. Chem. Phys. 46, 4532 (1967).

[6]M. A. El-Sayed, D. S. Tinti, and E. M. Yee, J. Chem. Phys. 51, 5721 (1969).

[7]R. H. Clarke, Chem. Phys. Lett. 6, 413 (1970).

[8]I.-Y. Chan and J. Schmidt, Symp. Faraday Soc. 3, 156 (1969).

[9]S. Dym, R. M. Hochstrasser, and M. Schafer, J. Chem. Phys. 48, 646 (1968).

[10]M. Sharnoff, Symp. Faraday Soc. 3, 137 (1969).

[11]M. Sharnoff, in Proceedings of the Fifth Molecular Crystals Symposium, Philadelphia, Pennsylvania, 1970 (to be published), p. 127.

[12]In addition to the direct saturation measurements of T_1 reported in Ref. 10, we have carried out a partial series of saturation-recovery measurements which show that T_1 for excitons is certainly less than 5×10^{-6} sec.

[13]M. Sharnoff, J. Chem. Phys. 51, 451 (1969).

[14]The signs and magnitudes of the zero-field splittings in these diagrams have been taken from Refs. 10 and 13.

[15]L. L. Chase, Phys. Rev. Lett. 21, 888 (1968).