overlap has occurred than before; and (2) the T_c anomaly in the In-Pb case occurs at a slightly lower concentration than in the In-Sn case. We call attention to these features as unsolved problems. One can invent density-of-states curves to account for them, but we have not as yet measured the density of states of any of our samples in any independent way.

The major conclusions then are these: (1) The Fermi surface of In may not resemble the free electron model as closely as had been previously thought; (2) the variation of lattice parameters caused by an expanding Fermi surface interacting with a Brillouin zone is observed unambiguously and confirms the predictions of Goodenough; (3) the structure observed by Tomasch and Reitz in thermopower measurements on In-Pb alloys is confirmed by measurements of other properties and their qualitative interpretations supported; and (4) an anomaly in a plot of T_c vs composition is identified unambiguously with a change in electronic structure occurring with a single crystallographic phase.

The encouragement and counsel of B. T. Matthias, B. R. Coles, and G. O. S. Arrhenius is gratefully acknowledged. Sharon Hillhouse provided valuable experimental assistance.

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*Research supported in part by the U. S. Air Force Office of Scientific Research and the National Science Foundation.

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TRIPLET ENERGY TRANSFER AND TRIPLET-TRIPLET INTERACTION IN AROMATIC CRYSTALS

Joshua Jortner, Sang-il Choi, Joseph L. Katz, and Stuart A. Rice
Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

(Received 6 August 1963)

The purpose of this note is to discuss triplet energy migration and triplet-triplet annihilation leading to fluorescence radiation. The first process has been observed in both ESR[1] and optical spectra[2] of aromatic crystals, and the second process has been invoked to explain laser-induced delayed fluorescence in crystalline anthracene.[3]

The first treatment of exciton-exciton interaction, by Choi and Rice,[4] was concerned with the problem of singlet-singlet bimolecular annihilation to yield a pair of charge carriers. Because of the large magnitude of the intermolecular pair interaction matrix element (i.e., a Coulomb-type interaction), Choi and Rice used a free exciton formalism and did not consider the coupling between the electronic states of the crystal and the intermolecular and intramolecular vibrations. In contrast, the migration of triplet excitons is determined by relatively small exchange interactions (≈5 cm^{-1}), so that the interaction of a triplet exciton with phonons will be strong, the mean free path will be of the order of magnitude of a lattice spacing, and therefore the band description will be inappropriate. The triplet must be treated as a localized exciton. Moreover, as the rate of excitation transfer is small compared with the lattice relaxation time, the triplet exciton is surrounded by a lattice deformation which propagates with it.

Because of lattice vibrations the initial and final states involved in the triplet exciton hopping process are broadened. Consider the initial (0) and final (f) vibronic states of a single molecule,

$$|0\rangle = \Psi_e^{0}\chi_v^{0}, \quad |f\rangle = \Psi_e^{f}\chi_v^{f}, \tag{1}$$

with the energies $\epsilon = \epsilon^v + \epsilon^e$. Time-dependent perturbation theory leads to the transition probability (for transfer of energy from molecule 1 to molecule i)[5]

$$W_{1i}=\frac{2\pi}{\hbar}\int d\epsilon_{iv}{}^{f}\int d\epsilon_{1v}{}^{0}\int d\omega(\epsilon_{iv}{}^{0})\int d\omega(\epsilon_{1v}{}^{f})$$
$$\times\left|\int \mathcal{A}\Psi_{1e}{}^{f}\prod_{j\neq 1}\Psi_{je}{}^{0}V_{1i}\Psi_{1e}{}^{f}\prod_{j\neq 1}\Psi_{je}{}^{0}d\tau\right|^{2}$$
$$\times\left|\langle\chi_{1v}{}^{f}|\chi_{1v}{}^{0}\rangle\right|^{2}\left|\langle\chi_{iv}{}^{f}|\chi_{iv}{}^{0}\rangle\right|^{2}\delta(\{\epsilon_{1v}{}^{f}-\epsilon_{1v}{}^{0}\}$$
$$-\{\epsilon_{iv}{}^{f}-\epsilon_{iv}{}^{0}\}),\qquad(2)$$

where $\omega(\epsilon_v)$ is the probability that a molecule has vibrational energy in the range $d\epsilon_v$ about ϵ_v. In the following treatment, the vibrational spectrum is treated as a continuum. The vibrational overlap cannot, at present, be calculated with any accuracy, and Eq. (2) is therefore simplified to the form[6]

$$W_{1i}=\frac{2\pi}{\hbar}\left|\int \mathcal{A}\Psi_{1e}{}^{f}\prod_{j\neq 1}\Psi_{je}{}^{0}V_{1i}\Psi_{1e}{}^{f}\prod_{j\neq 1}\Psi_{je}{}^{0}d\tau\right|^{2}$$
$$\times\int F(E)f(E)dE,\qquad(3)$$

where $F(E)$ and $f(E)$ are the normalized singlet-triplet ($S\rightarrow T$) absorption function and the triplet-singlet ($T\rightarrow S$) phosphorescence function, respectively.

The interaction responsible for triplet migration involves the exchange term[7]

$$K_{ij}=\langle u_0{}^{i}(1)u_0{}^{j}(1)|r_{12}{}^{-1}|u_f{}^{i}(2)u_f{}^{j}(2)\rangle,$$

where $u_k{}^i$ is the molecular orbital located in the ith molecule and $k=0,f$ refers to the highest filled and lowest empty molecular orbitals, respectively. The molecular orbitals located on different molecules are chosen to be orthogonal.

The exchange integrals have been evaluated numerically[7] for molecular orbitals consisting of linear combinations of carbon $2p\pi$-type orbitals, themselves chosen to be the carbon atom $2p$ *SCF* wave function.[8] The molecular crystals considered are characterized by a monoclinic unit cell containing two molecules, and belong to the symmetry group $C_{2h}{}^{5}$.[9] The basic vectors of the direct lattice are labeled as a, b, and c. The largest values of the exchange integral occur between molecules located at the corner of the unit cell and at the other corner (b) and center of the cell face $[\beta=\frac{1}{2}(a+b)]$ in the ab plane of the crystal (see Table I).

Table I. Electronic matrix elements for triplet excitation transfer in naphthalene and anthracene crystals.

i	K_{1i} (naphthalene) (eV)	K_{1i} (anthracene) (eV)
c	-1.41×10^{-7}	-4.53×10^{-7}
b	9.46×10^{-4}	9.10×10^{-4}
$a+c$	-2.53×10^{-6}	-4.44×10^{-7}
β	-5.62×10^{-4}	-5.37×10^{-4}
$\beta+c$	-1.84×10^{-7}	-6.41×10^{-7}

Because the exchange energy decreases very rapidly with increasing molecular separation, only triplet energy transfer to near neighbors need be considered. The mean lifetime of the triplet excitation on molecule 1, τ_1, the total transition probability, W, and the diffusion coefficient, D, are related by

$$1/\tau_1=\sum_i W_{1i},$$
$$D=\tfrac{1}{6}\sum_i W_{1i}R_{1i}{}^{2},\qquad(4)$$

where R_{1i} is the distance between molecules 1 and i, while the diffusion coefficients along the crystal axes D_a, D_b, and D_c are

$$D_a=(1/\tau_1)_a a^2/2,\quad D_b=(1/\tau_1)_b b^2/2,$$
$$D_c=(1/\tau_1)_c c^2/2.\qquad(4')$$

In the process of executing a random walk, the triplet exciton diffuses a distance $(2DT_0)^{1/2}$, where T_0 is the exciton lifetime. In the case of anthracene, $T_0=10^{-2}$ sec,[3] $a=8.56$ Å, $b=6.04$ Å, $\int F(E)\times f(E)dE\approx0.1$ eV^{-1}, whereupon $\tau_1{}^{-1}\approx3\times10^{9}$ sec^{-1}, $D_{ab}\approx5\times10^{-6}$ cm^2 sec^{-1}. Within the ab plane, the diffusion length is therefore found to be of order 3×10^{4} Å, a value of the same order of magnitude as the diffusion length of singlet excitons. In naphthalene, where the triplet lifetime is longer ($T_0=2.3$ sec) the diffusion length is 5×10^{5} Å in the ab plane. The reader should note that only interactions within the ab plane are of appreciable magnitude.

If there are Z nearest neighbors to a molecule and N molecules per unit volume, the rate of collision of two excitons is

$$RR=Zn^2/2N\tau_1,\qquad(5)$$

with n the number of excitons per unit volume. For anthracene, taking $Z=6$ (i.e., four molecules at distance $|\beta|$ and two molecules at distance $|b|$) and $N=4.22\times10^{21}$ cm^{-3}, $RR=2.1\times10^{-11}n^2$ cm^{-3}-sec^{-1}.[10] When two triplet molecules are adjacent in the *ab* plane, two different exciton-exciton annihilation reactions may take place. It was previously suggested[2] that the annihilation process leads to an excited singlet state, $2T \rightarrow G+S$, but an alternative final state involves the formation of an ion pair with charges on adjacent molecules, $2T \rightarrow G^+ + G^-$. In the case of anthracene the ion pair formation is energetically feasible because the sum of the triplet energies (3.7 eV), the Coulomb interaction energy (2.5 eV), the polarization energy (≈0.5 eV),[11] and the electron affinity (0.6 eV)[12] matches the ionization potential (7.2 eV). The relevant electronic matrix elements are

$$\langle T_i T_j | V | S_i G_j \rangle = (3/2)^{1/2} [\langle u_f^{\,i}(1) u_0^{\,j}(1) | r_{12}^{\;-1} | u_f^{\,i}(2) u_f^{\,j}(2) \rangle - \langle u_0^{\,i}(1) u_0^{\,j}(1) | r_{12}^{\;-1} | u_0^{\,i}(2) u_f^{\,j}(2) \rangle]; \tag{6}$$

$$\begin{aligned} \langle T_i T_j | V | G_i^{\,+} G_j^{\,-} \rangle = (3/2)^{1/2} [& \langle | u_f^{\,j}(1) |^2 | r_{12}^{\;-1} | u_f^{\,i}(2) u_0^{\,j}(2) \rangle + \langle | u_0^{\,i}(1) |^2 | r_{12}^{\;-1} | u_f^{\,i}(2) u_0^{\,j}(2) \rangle \\ & + \langle | u_0^{\,j}(1) |^2 | r_{12}^{\;-1} | u_f^{\,i}(2) u_0^{\,j}(2) \rangle - \langle u_f^{\,i}(1) u_0^{\,i}(1) | r_{12}^{\;-1} | u_0^{\,i}(2) u_0^{\,j}(2) \rangle]; \end{aligned} \tag{7}$$

where G, S, and T refer to the ground state, first excited singlet, and first excited triplet, respectively.

A very cursory examination of Eqs. (6) and (7) indicates that the transition of the double triplet state to an excited singlet is determined by an exchange integral, while the transition to the ion pair is determined by hybrid (ionic integrals). The hybrid integrals between $2p$ wave functions are one to two orders of magnitude larger than the corresponding exchange integrals.[13]

The following set of conclusions is derived:

(1) The mechanism of triplet-triplet annihilation proceeds by charge-pair formation. In general, the matrix element for the formation of charge pairs is 100 times larger than the matrix element for direct singlet formation. If the vibrational overlap factors are about the same for both processes, the transition probabilities are then in the ratio about 10^4:1.

(2) The recombination of the ion pair is very efficient on the time scale of the triplet exciton migration. It is assumed herein that the ion-pair recombination leads to an excited singlet state, thus accounting for the delayed fluorescence observed in these crystals.

(3) The rate-determining step in the triplet-triplet annihilation is the production of two adjacent excited molecules. The annihilation rate is therefore diffusion controlled. Application of the results embodied in Eq. (5) leads to the predicted annihilation rate constant 2.1×10^{-11} cm^{-3} sec^{-1}. This is in excellent agreement with the value $1\times10^{-11} - 4\times10^{-11}$ cm^{-3} sec^{-1} estimated by Kepler et al.[3] The sensitivity of the calculated rate constant to the overlap of the absorption and phosphorescence spectra, and the exchange integrals makes our theoretical estimation uncertain within one order of magnitude.

(4) The triplet-triplet interaction (leading to an ion pair) differs from the singlet-singlet interaction (leading to ionization),[4] in that the rate-determining step in the singlet-singlet interaction leading to ionization is the transition to the state involving a positive ion and a free electron, whereas the rate-determining step in ion-pair formation from triplets is the rate of encounter of the two triplet excitons.

(5) Although it would be tempting to invoke the intermediate ion pair as a precursor to the charge carriers observed in dark conductivity of aromatic crystals, we believe this would be an erroneous deduction. Simple estimates of triplet concentration and charge-carrier concentration show that the ion pair is unlikely to be the source of charge carriers at low field strengths and ordinary temperatures. Investigation of field-induced dissociation and nonequilibrium ion-pair concentrations in systems of the type investigated herein will be of great interest.

This research was supported by grants from the U. S. Public Health Service, the National Science Foundation, and the U. S. Air Force Office of Scientific Research. We have also benefited from the general support of materials research at The University of Chicago by the U. S. Atomic Energy Commission and the Advanced Research Projects Agency.

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CORRECTIONS TO THE PAIRING INTERACTION IN SUPERCONDUCTIVITY*

E. M. Henley and L. Wilets
University of Washington, Seattle, Washington

(Received 12 August 1963)

The theory of superconductivity expounded by Bardeen, Cooper, and Schrieffer[1] is based on a variational wave function involving time-reversed pairs. An alternative formulation given by Bogoliubov[2] is based on the principle of the compensation of dangerous diagrams, following a canonical transformation. The complete statement of the compensation principle can be shown to yield the generalized integral equation for the energy-gap parameter

$$\Delta_{\vec{k}} = -\tfrac{1}{2}\sum\nolimits_{k'} G_{\vec{k}\vec{k}'}\Delta_{\vec{k}'}/(\Delta_{\vec{k}'}{}^2 + \epsilon_{\vec{k}'}{}^2)^{1/2}, \tag{1}$$

where the $\epsilon_{\vec{k}}$ are "renormalized" normal single-particle energies, expressed relative to the Fermi energy, and $G_{\vec{k}\vec{k}'}$ is an "effective" pair interaction. To second order in the interaction V between pairs (after the canonical transformation has been carried out), G is given by[3]

$$G_{\vec{k}\vec{k}'} = \langle\vec{k}, -\vec{k}\,|V|\,\vec{k}', -\vec{k}'\rangle + 2\sum_{\vec{q}\vec{q}'} \frac{u_{\vec{q}}{}^2 v_{\vec{q}'}{}^2 \langle -\vec{k}\vec{q}'\,|V|\,-\vec{q}\vec{k}'\rangle\langle -\vec{q}k\,|V|\,-k'\vec{q}'\rangle - (uv)_{\vec{q}}(uv)_{\vec{q}'}\,|\langle -\vec{k}\vec{q}\,|V|\,-\vec{q}'k'\rangle|^2}{\xi_{\vec{k}} + \xi_{\vec{k}'} + \xi_{\vec{q}} + \xi_{\vec{q}'}}, \tag{2}$$

where, for simplicity, we have here assumed that the potential V acts only in singlet states. The energy $\xi_{\vec{k}}$ is $(\epsilon_{\vec{k}}{}^2 + \Delta_{\vec{k}}{}^2)^{1/2}$, and the u^2 and v^2 are given by

$$\begin{pmatrix} u_{\vec{k}}{}^2 \\ v_k{}^2 \end{pmatrix} = \frac{1}{2}\left(1 \pm \frac{\epsilon_{\vec{k}}}{\xi_{\vec{k}}}\right). \tag{3}$$

The second-order term in Eq. (2) proportional to $(u^2)(v^2)$ dominates over the $(uv)(uv)$ term and corresponds to intermediate scattering of a particle-hole pair. We note that for an attractive interaction (negative V) the second-order correction is effectively repulsive and tends to reduce the energy gap.

Bogoliubov, Tolmachev, and Shirkov[2] have argued that the ratio of the second-order terms in G to the first-order one are proportional to the energy gap, and are thus negligible. We have investigated this point in some detail, and find instead that this ratio is proportional to the strength of the interaction in the limit of small gaps. The second-order term can, in fact, be numerically very significant and in some instances no solution of Eq. (1) with Eq. (2) obtains.

We wish to draw a distinction between solving the integral equation (1) for the energy gap and an alternative perturbation procedure.[4] In the latter case one introduces a canonical transformation, the parameters of which (i.e., $\Delta_{\vec{k}}{}^0$) are determined by solving the lowest order (BCS) integral equation. The quasiparticle energies can then be evaluated by a perturbation treatment of