Introduction

ALL FORMS OF MATTER NORMALLY RESIDE IN their lowest or ground energy states, unless excited to higher energy states by mechanical impact; bombardment of particles; or radiation of heat, light, X-rays, and γ-rays. The higher energy states, called excited states, can be continuous or discrete in their energy structure depending on the specific nature of matter and their external influences. The occupation of an excited state has a characteristic lifetime of its own. This time is usually rather short, but it can sometimes be metastably long, unless a steady state is reached for the substance when excited by an external source. If the excitation is of an impact or pulse type, then the excited state usually decays in an exponential manner with time t as $I_{o}e^{-t/T}$, where I_o is the initial intensity and T is called the lifetime of the state.

It is interesting and important to study the discrete energy states of matter. Microscopic constituents of matter such as electrons, nuclei, atoms, molecules, etc. all have mostly discrete energy states, which are more frequently dealt with in atomic and molecular problems. Consequently, we will assume in this paper that all energy states are quantized as either nondegenerate (single) or degenerate (more than one state having the same energy) quantum energy levels or as a band of not clearly resolvable quantum states.

Excitation from the ground state of atoms or molecules is usually accomplished either by electromagnetic radiation such as optical X- or γ-rays or by particles, most commonly electrons. Different forms of excitation have different selection rules governing the quantum transition probabilities. Generally speaking, electromagnetic radiation excitation has simpler selection rules and requires easier experimental techniques than particle (e.g., electron) excitation which has much less discriminating selection rules and for which the experimental techniques are often considerably more involved. In the case of photoexcitation, it is customary to characterize this process as one of "pumping."

The transformation of an atomic or molecular species from a higher energy state to a lower energy state is achieved by a radiative transition accompanied by the emission of light radiation known as photons or by a nonradiative transition accompanied by the emission of quantized vibration waves known as phonons. The relatively rare case of excitation from a lower state being promoted to a higher energy state can only be accomplished by the presence of an extra source of excitation energy. The radiative and nonradiative transitions, each having their own characteristic lifetimes, can form a very complicated multiconnected network of pathways which some scientists playfully refer to as resembling "bed springs." With respect to a given impulsive pumping, all excitations in the whole system will eventually decay in magnitude and each will return to its original ground state.

Whether the radiative and/or nonradiative transition pathways are considered individually or collectively, they represent excitation energy transfers taking place in a partial or whole system. This kind of physical phenomenon is generally too complicated and difficult to be comprehensively described theoretically, particularly when scientific rigor is required. Experimental techniques can be of great value in the study of energy transfer phenomena.

This paper describes some experimental examples of excitation energy transfer in atoms and molecules in a solid-state environment as studied by a microwave-optical double resonance method.

Modulated Transfer of Excitation Energy

A system that is initially in the ground state

The advent of laser science and technology has given considerable impetus to new and comprehensive studies of excited states in various forms of matter, especially in solids. Much attention has been given to the dynamic changes in population and energy of excited states by radiative and nonradiative quantum transitions. A number of experiments have been conducted at The Applied Physics Laboratory on atoms (chromium ion) or molecules (naphthalene) in (single crystalline) solid environments by the method of microwave-optical double resonance. Several examples of the double resonance method are given as well as a suggestion for a possible application to studies of excitons in crystalline solids.

can be continuously or impulsively pumped to a set of excited energy levels. Subsequent transfers of excitation to other sets of excited energy levels and eventually back to the ground level will take place in a steady-state manner or in a time-decaying way involving different time constants. We will call this an *unmodulated* state of excitation energy transfer.

Some parts of the energy system may have sublevels having spacings of quantum energy $h\nu$ corresponding to the microwave frequency ν (broadly speaking, between radio-frequencies and high millimeter-wave frequencies). These sublevels may represent the Zeeman energy separation in a magnetic field, fine-structures in an atom or molecule, or hyperfine structures due to interactions between the nuclear moments and the extra-nuclear fields. A resonant absorption of microwaves will transfer some of the population from the lower energy level to the higher energy level. This transfer of population may be either a steady-state or impulsive type, depending upon the nature of the microwave waveform as a function of time. Quite analogous to the optical* excitation, the continuous microwave waveform will produce a steady-state transfer of population, whereas an impulsive microwave waveform will produce a transfer of population which decays exponentially with time.

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* For brevity, we will hereafter use the expression "optical" to represent either the ordinary optical range or higher energy ranges such as those of X-rays, γ-rays, etc.

A resonant transfer of population induced by microwaves between two sublevels in a state can generate a corresponding change of population transfer between that state and another state with an optical energy separation. This is so because the given sublevels may have different optical transition probabilities. Thus, a change in population in a given sublevel by microwave resonance would affect the optical absorption. Hence the microwave resonance between the sublevels would produce an incremental transfer of excitation between optical levels. If the microwave resonance takes place in the ground state and there are optical excitations from the ground state to higher states, then the effect of microwave resonance at the ground level would amount to a modulation on the transfer of excitation of the entire system. If, however, the microwave resonance is applied to a given excited optical state, then its effect will act only on the transitions between that excited optical state and other states all the way down to the ground state. In any case, this type of incremental change in the transfer of excitation energy can be characterized as that of a *modulated* state.

In recent years, techniques using some form of modulation to gain knowledge of the selection rules, the transition probabilities of radiative or nonradiative transitions, the total or differential lifetimes of states, the various pathways of the excitation energy transfers, etc. have begun to be extensively used. The name *modulation spectroscopy* has been introduced to denote the use of such techniques. This naming of a new branch of spectroscopy is itself an indication of the fruitfulness of employing these methods of study.

In many studies of the afore-mentioned type, both microwave and optical resonances are used simultaneously; this is commonly known as *microwave-optical double resonance* (MODR). In some special cases where the microwave resonance is applied to an excited optical state, most often in the form of an electron spin resonance (ESR), direct detection of the ESR effect may often be too difficult because of the weak intensity changes owing to the smallness of population in the excited optical state. On the other hand, the effect of ESR on the fluorescence or phosphorescence radiation from the excited optical state to the ground state may be much more easily detectable on account of the higher detector efficiency at optical frequencies. This kind of approach is

known in the literature as the method of *optical detection*.

Concrete Examples of Excitation Energy Transfer in Solids

Case A: Chromium atomic ion Cr^{3+} in Al_2O_3 (ruby)[1,2]

Figure 1 shows one "molecule" of Al_2O_3 in the rhombohedral crystal structure of aluminum oxide, known in mineralogy as corundum. Each rhombohedral unit has a center of inversion between two "molecules" of Al_2O_3 lying along the C-axis which is a three-fold rotational axis C_3. Each group of Al_2O_3 has a triad of O^{2-} ions in a plane perpendicular to the C-axis and two Al^{3+} ions placed on each side of the triad on the C_3 axis. The aluminum oxide crystal becomes a ruby when a very small percentage of the aluminum Al^{3+} ions are substituted by the chrominum ions Cr^{3+}.
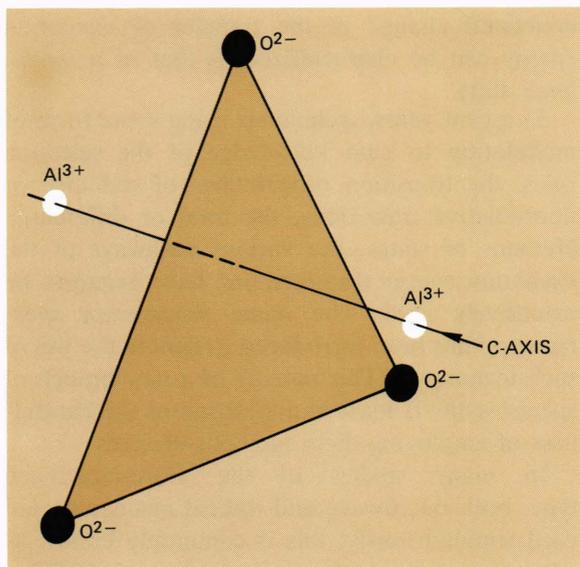
Fig. 1—Configuration of "molecule" Al_2O_3 in rhombohedral crystal structure of aluminum oxide; the center of inversion (not shown) lies on the C-axis.

Figure 2 shows only a small part of the ruby energy diagram near its ground state $^4A_2$, which

[1] C. K. Jen, J. C. Murphy, and L. C. Aamodt, "ESR Population-Modulation Spectroscopy of Optical Transition Processes in Dilute and Concentrated Ruby," *International Symposium on Electron and Nuclear Magnetic Resonance*, Melbourne, Australia, Aug. 11–15, 1969.
[2] J. C. Murphy, L. C. Aamodt, and C. K. Jen, "Energy Transport in Ruby Via Microwave-Optical Experiments," *Phys. Rev. B 9*, Mar. 1, 1974, 2009–2022.
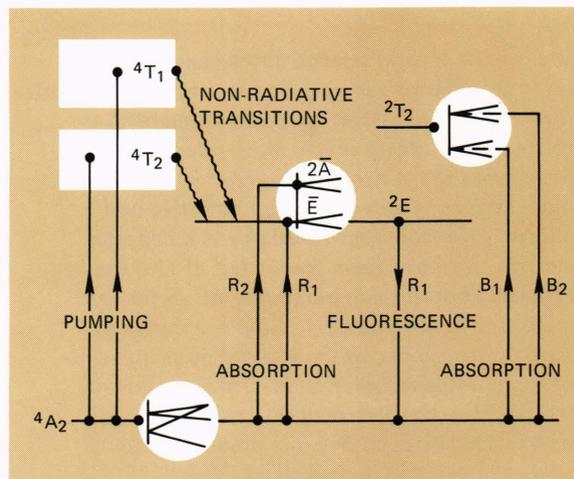
Fig. 2—Energy diagram of Cr^{3+} in Al_2O_3 (ruby) showing the ground state, some excited states, optical transitions, and Zeeman energy splittings.

is a spin quartet state signifying the parallelism of three d-electron spins, each with a spin angular momentum of $\hbar/2$. The inset circle at $^4A_2$ shows the Zeeman splitting of 4 sublevels under a magnetic field which from here on will be assumed to be along the C-axis. If a ruby crystal is irradiated by a visible light source, the energy state of the Cr^{3+} ion will be raised to either one or both of the broad-band excited quartet states ($^4T_1$ and $^4T_2$). From the broad-band states, the excited ions will relax nonradiatively to many lower energy levels and, most important of all, to the $\bar{E}(^2E)$ state. The lifetime of Cr^{3+} ions in the $\bar{E}$ state is a few milliseconds, and a fluorescent radiation (sometimes known as the R_1 light around 6,940Å) is emitted, which is the well-known red light of ruby. One quickly notes that $\bar{E}$ is a doublet state that can be split into two Zeeman levels in a magnetic field. In fact, the fluorescent radiation from one Zeeman sublevel is circularly polarized in one sense and that from the other Zeeman sublevel is circularly polarized in the opposite sense, with respect to the C-axis. When not individually resolved, the sum of the two components of radiation would seem to be linearly polarized.

Now if the original light source has adequate intensity around the R_1 fluorescent light wavelength, there will be absorption at this wavelength. The increased population at the $\bar{E}$ level will be re-emitted as R_1 fluorescence. If, in addition, there is a high enough concentration of Cr^{3+}
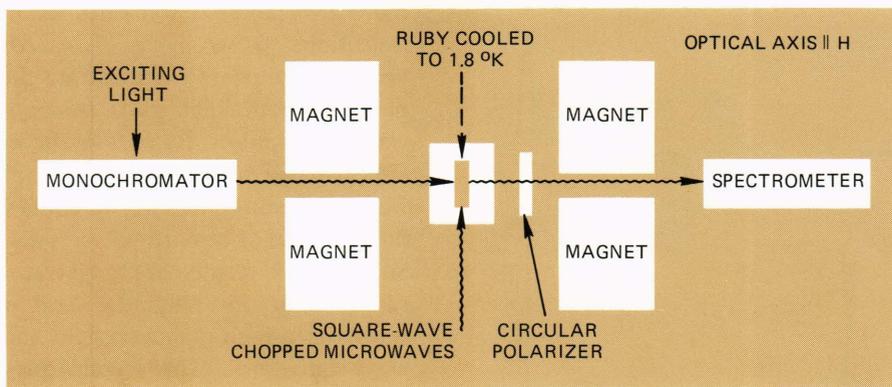
Fig. 3—Diagrammatic experimental setup for studying microwave-optical double resonance (MODR) at liquid helium temperatures. (The APL Microwave Physics Laboratory is equipped with such a setup.)

ions or the sample is fairly thick, then the emitted R_1 light can be self-absorbed by the sample and re-emitted again. This process can be repeated many times.

The above is a description of the steady-state dynamics of excitation energy transfer for Cr^{3+} ions in ruby when pumped by a light source. Experimentally, all these happenings can be observed by the set-up shown in Fig. 3. The components include a light source, liquid helium cooling of the ruby sample, circular polarizer and an optical spectrometer. There also is an additional equipment of microwave radiation incident on the ruby sample in a microwave cavity and a magnetic field. This means we can use electron spin resonance as a means to investigate: (a) the transition probabilities of quantum transitions among the Zeeman sublevels in the ground state $^4A_2$; (b) the transition probabilities of optical
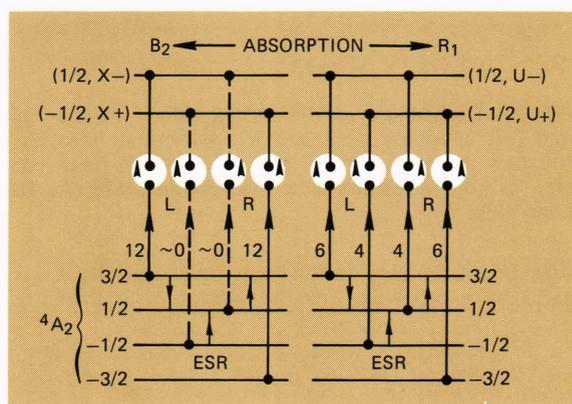
Fig. 5—Circularly polarized absorption transitions (R denotes right and L denotes left) from ground state $^4A_2$ Zeeman quartet levels to $^2T_2$ doublet levels (B_2 lines) and E doublet levels (R_1 lines).

transitions from $^4A_2$ Zeeman levels to the Zeeman levels of an upper state like $^2T_2$ (the B_2 lines) as affected by the electron spin resonance in the ground state; and (c) the transition probabilities of the absorption of the circularly polarized components of the R_1 line as affected by the electron spin resonance in the ground state. The experimental results for the above three cases as obtained at APL are shown in Figs. 4, 5, and 6. There are, however, two remaining questions to be answered: (a) what are the spin selection rules and transition probabilities between the quartet band energy states and the metastable doublet state (often referred to as "intersystem crossing"), say, the $\bar{E}$ state? and (b) What are the spin selection rules and transition probabilities between the Zeeman sublevels in the $\bar{E}$ doublet state? The

Fig. 4—Electron spin resonance (ESR) curve of the ground state $^4A_2$ as a function of the magnetic field.
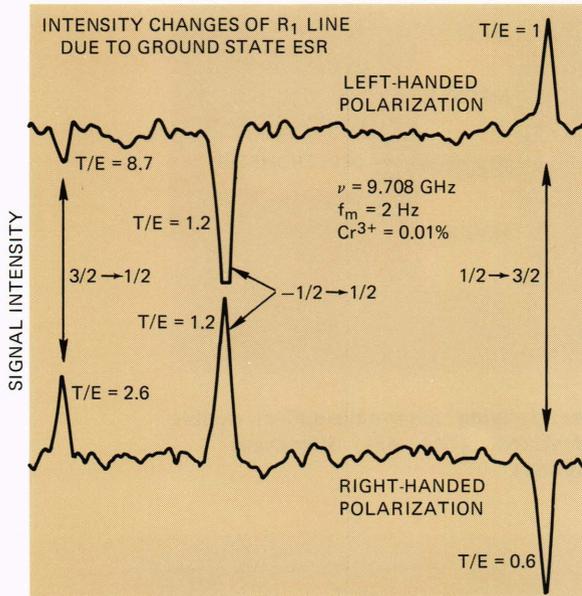
Fig. 6—Recordings of the MODR effect on the right and left circularly polarized R_1 absorption lines as a function of the magnetic field; the MODR lines coincide in field positions with the ground state $^4A_2$ ESR lines (Fig. 5).

first question was tentatively answered by G. F. Imbusch et al.[3] by a "spin memory effect;" i..e.,

there are spin selection rules for the nonradiative transitions, shown in Fig. 7. At APL we have devised a method to demonstrate this that involves pumping both light short pulses and microwave wave short pulses. By putting the microwave pulse either ahead or behind the pumping light pulse, we had reason to believe we could definitely prove the presence or absence of the *spin memory* effect. So far, our results are negative, but we would rather defer our judgment until we can test the results at a high magnetic field and a high microwave frequency. The second question was originally settled by Geschwind et al.[4] and the results are fully confirmed in our investigations using our method of detecting the changes of the light intensities of the circularly polarized components of the R_1 lines when the excited E doublet state is subjected to electron spin resonance. The results are shown in Fig. 8. It is noticed there that by producing an electron spin resonance, the population is increased in the upper excited state as much as the population is decreased in the lower excited states. But, since the intrinsic transition probability for the right-handed polarization of R_1 fluorescence is higher for the case of $\Delta m = \pm 1$ than for the case of $\Delta m = 0$, there

[3] G. F. Imbusch and S. Geschwind, "Optical Detection of EPR in the $\bar{E}(^2E)$ State of $(3d)^3$ Ions in Al_2O_3 and Spin Memory Effects in the Optical Pumping of Ruby," *Optical Properties of Ions in Crystals*, Wiley-Interscience, New York, 1967, 171–186.

[4] S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn, "Orbach Relaxation and Hyperfine Structure in the Excited $\bar{E}(^2E)$ State of Cr^{3+} in Al_2O_3," *Phys Rev. A* 137, Feb. 15, 1965, 1087–1100.
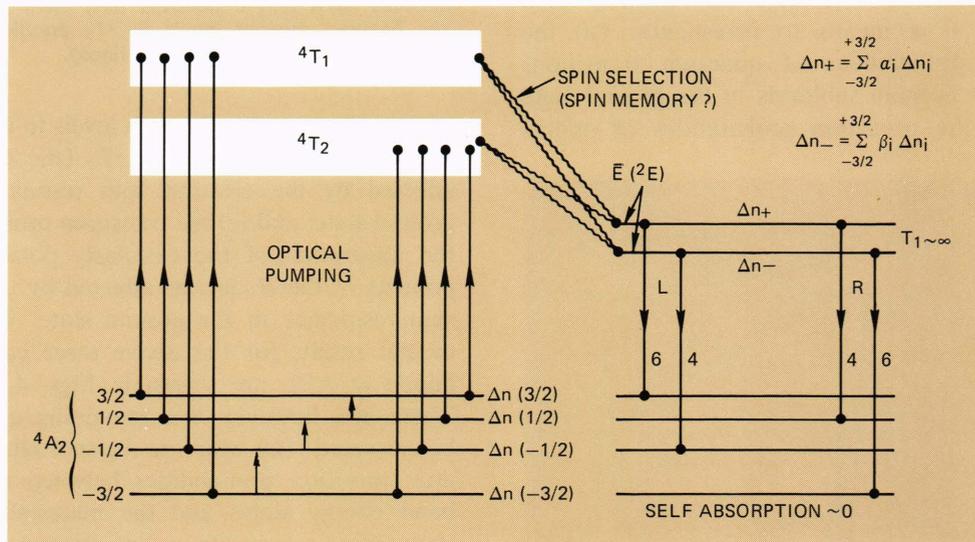
Fig. 7—The wavy lines in this diagram denote "intersystem crossing" nonradiative transitions. The question of spin selection rules should be decided by the coefficients α_i and β_i in the displayed equations when they are evaluated experimentally.
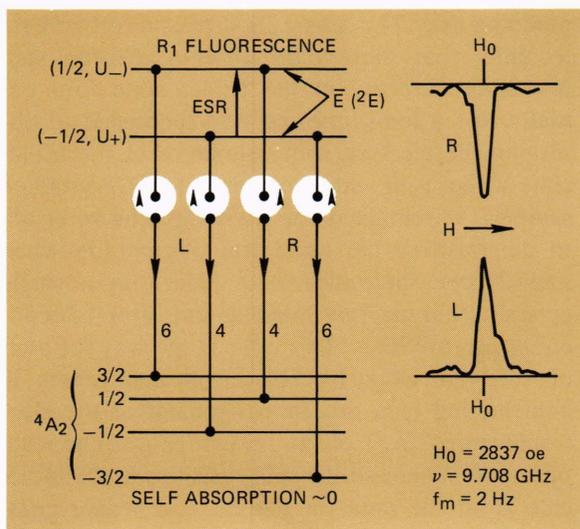
Fig. 8—Recordings of the MODR effect on the R_1 fluorescence intensity when ESR is applied to the $\bar{E}$ excited state.

would be a net decrease of R_1 intensity for the right-handed polarization, as shown in the diagram. Here, m denotes the electron spin quantum number of a sublevel either in the excited $\bar{E}$ (^2E) state or in the ground $^4A_2$ state. Following this nomenclature, Δm means the difference between the m value in the $\bar{E}(^2E)$ state and the m value in the $^4A_2$ state for the quantum transition under consideration. Similarly, there should be a net increase for the intensity of the left-handed polarization in agreement with the experimental result. (The sense of circular polarization is here defined as that observed when looking in the direction of propagation of the fluorescent light.)

The microwave-optical results on the $\bar{E}(^2E)$ doublet state gave definitive information of the g-factor of that state which turned out to be highly anisotropic, resulting in $g\| = 2.45$, $g\perp = 0.06$. (The quantity g-factor is a dimensionless number which is proportional to the ratio of the magnetic moment to the spin angular momentum.) This result of $g\|$ and $g\perp$ should be valuable for studies on the $\bar{E}$ excited state wavefunctions and other purposes.

It seems interesting to mention a very well-known fact that T. H. Maiman in 1960 first succeeded in making a ruby laser by optically pumping a ruby crystal so hard that the population in $\bar{E}$ state was larger than that in the ground state, thus fulfilling the condition of *population inversion*. Not surprisingly, pulsed pumping light

has to be used under these circumstances because of the heating of the crystal. Nowadays, however, because of improved techniques, there are also steady-state ruby lasers at low powers.

Case B: Naphthalene molecules in a durene crystal[5]

Figure 9 shows a unit cell with one naphthalene ($C_{10}H_8$) planar molecule replacing one of the two durene molecules. A naphthalene molecule would ordinarily be in a singlet ground state, since it does not have any unpaired electrons. A simplified energy diagram of the naphthalene
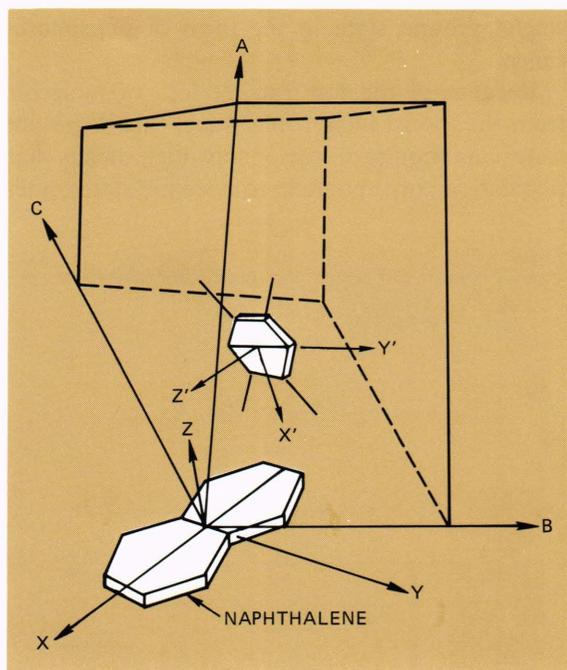
Fig. 9—A naphthalene molecule with X, Y, and Z coordinates axes replacing one of the two durene molecules in a unit cell.

molecule in a durene crystal is shown in Fig. 10. Optical pumping raises the energy level of naphthalene molecule (D_{2h} symmetry) from its singlet ground state to higher singlet states as shown. Through intersystem crossing by nonradiative transitions, the naphthalene molecule is transformed into triplet states (each of which has two parallel unpaired electron spins), but finally settles down to the lowest lying metastable triplet state

[5] C. K. Jen, L. C. Aamodt, and A. H. Piksis, "Changes Induced in the Phosphorescence Radiation of Aromatic Molecules by Paramagnetic Resonance in Their Metastable Triplet States," *The Triplet State*, Cambridge University Press, New York, 1967, 143–162.

$^3B_{2u}$. The lifetime of this metastable triplet state for naphthalene in durene is approximately two seconds, with the result that the naphthalene molecules slowly de-excite themselves from the triplet state back to the singlet ground state. Strictly speaking, the lowest lying triplet state could be perfectly stable if it were not for the existence of a small spin-orbit coupling in the molecule. But there is a small amount of spin orbit coupling that causes the triplet state to acquire a small admixture of the singlet state character. This is the reason for the emission of light from the metastable triplet state back to the singlet ground state in the form of phosphorescence.

Because of the low rate of loss of molecules from the lowest lying triplet state, this metastable state can acquire a reasonably high steady-state population corresponding to a steady-state optical pumping rate. This was a good reason for workers to think that they could observe electron spin resonance directly on the triplet state. But actually, for a long time, no one succeeded in observing the electron spin resonance in the triplet state when using either powder or polycrystalline samples. It remained for Clyde Hutchison et al.[6] to demonstrate the successful observation when naphthalene molecules were placed in a single crystal of durene, thus avoiding anisotropic broadening spectral lines. This opened the way for a lot of splendid work by Hutchison and others in contributing to a precise assignment of the electronic state ($^3B_{2u}$) of the lowest-lying triplet state of naphthalene and the spin densities in the molecule from the data on the g-factor tensor components and characteristics of the hyperfine structure. They, of course, extended their work to many other molecules.
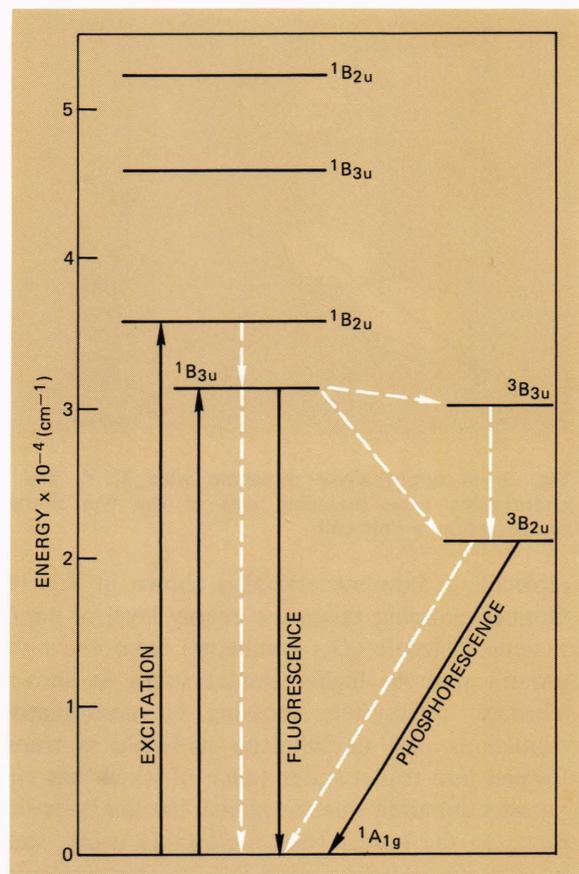
Having learned of and repeated some of Hutchison's fine work we became interested in the possibility of optically detecting the effect of electron spin resonance on the differently polarized components of the phosphorescent radiation. When we voiced this possibility in the Magnetic Resonance meeting at Padua, Italy, in September 1965,[7] J. H. Van der Waals, the Chairman of that session, thought it was too difficult to do and wished us a lot of luck. Figure 11 shows the expected polarization of the emitted phosphorescent light when the magnetic field (H_0) is parallel to the X-axis of the molecule and Fig. 12 shows the expected polarization when the magnetic field is parallel to the Y-axis of the molecule. These expectations were predicated upon assuming certain forms of spin orbit coupling and the extent that they agreed with the experiment would be taken as a criterion for judging the correctness of the assumption. At the February meeting on the Triplet State in Beirut, Lebanon, we again reiterated the theory but our experiments up to that time were unsuccessful. Neither did the Van der Waals' group have any luck with it. But fortunately, Mark Sharnoff[8] of the University of Delaware had succeeded in making the microwave-

Fig. 10—A simplified energy level diagram of naphthalene in a durene single crystal. Level positions are shown appropriately to scale. Dashed lines signify nonradiative transitions.

[6] C. A. Hutchison, Jr. and B. W. Mangum, "Paramagnetic Resonance Absorption in Naphthalene in its Phosphorescent State," J. Chem. Phys. 34, Mar. 1961, 908–922.
[7] C. K. Jen, "Discussion," Seventh International Symposium on Free Radicals, Padua, Italy, Sept. 10, 1965.
[8] M. Sharnoff, "Discussion," The Triplet State, Cambridge University Press, New York, 1967, 175–178.
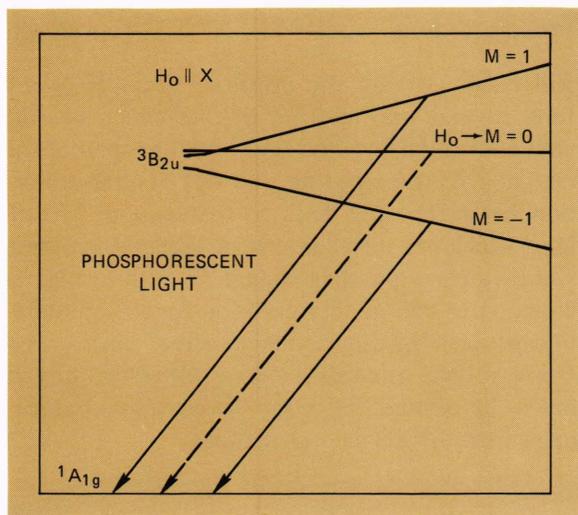
Fig. 11—The energy diagram of a naphthalene mole-cule in a durene crystal showing the polarization of the phosphorescent emission from the triplet state to the ground state for the case of $H_0 \| X$-axis: (—) for X-polarized radiation ($^1B_{3u}$ admixture) and (— — —) for Z-polarized radiation ($^1B_{1u}$ admixture).

Fig. 12—The energy diagram of a naphthalene mole-cule in a durene crystal showing the polarization of the phosphorescent emission from the triplet state to the ground state for the case of $H_0 \| Y$-axis: (—) for X-polarized radiation ($^1B_{3u}$ admixture) and (— — —) for Z-polarized radiation ($^1B_{1u}$ admixture).

optical double resonance for deuterated naph-thalene in a biphenyl single crystal just days before the Beirut meeting took place. Later on, Van der Waals expanded his work at the University of Leiden and made some very nice experimental and theoretical investigations on the microwave-optical double resonance of some spe-cial aromatic molecules in organic crystalline lat-tices.

A parenthetical remark may be made on the role of some organic dye molecules in solutions that are used for making dye lasers. These dyes are organic molecules having conjugated double bonds which have similar properties to the aroma-tic molecules we have just discussed, particularly with regard to the transfer of excitation from ex-cited singlet states to triplet states through inter-system crossing. Referring to Fig. 10, an excited singlet state such as $^1B_{3u}$ can transfer its excitation to the triplet state like $^3B_{2u}$ through a nonradiative transition, but it can also return to the ground state $^1A_{1g}$ while emitting a fluorescent radiation. Particularly for the purpose of making excited dye molecules perform as laser light generators, we have to discourage excited dye molecules from making transitions to triplet states. On the con-trary, we need to promote the probability of ex-cited dye molecules returning to the upper vibra-

tional energy levels in the ground state, which are not heavily populated. This objective can be best accomplished by using exceedingly short pulses in light pumping and also sometimes using other molecules as inhibitors to prevent excited dye molecules from being transferred to triplet states. In this way, the fluorescent radiation from excited singlet states to various higher vibrational levels in the ground electronic state plays the role of promoting stimulated emission in dye lasers. The resulting laser radiation tends to form a broad band of lines, from which a much narrower line can be tuned in by using a grating. This is the principle by which tunable dye lasers are made.

Case C: Microwave probing in the annihilation process of positronium

This is a classic experiment carried out by M. Deutsch of M.I.T. and others years ago.[9] We

[9] M. Deutsch, "Three-Quantum Decay of Positronium," *Phys. Rev.* **83**, Aug. 15, 1951, 866–868. For the original survey, see S. DeBene-detti and H. C. Corben, "Positronium," *Annual Review of Nuclear Science*, Annual Reviews, Inc. 1954, 191–218. For a recent survey, see R. N. West, "Positron Studies of Condensed Matter," *Advances in Physics* **22**, 1973, 263–383.

want to recall this beautiful experiment because it has a close kinship with our microwave-optical double resonance approach.

Suppose one has a radioactive source line Na^{22} which emits positrons (also simultaneously γ-rays). Let these positrons impinge upon a metal such as silver or copper, or an insulator such as quartz crystal or teflon. The positrons will travel in a given material until they have lost most of their kinetic energy. Then there is a good chance that quasi-stable atoms are formed, each of which contains a positron and an electron; the latter may be a conduction electron in a metal or a valence electron of an atom in the insulator. This quasi-stable atom, known as positronium, may be in the singlet state ($J = 0$) with the spin of the positron and electron antiparallel (parapositronium) or in the triplet state ($J = 1$) with the two spins parallel (orthopositronium). There should be a difference in energy between the triplet and singlet states $\Delta W = W(J = 1) - W(J = 0)$, which is the fine structure energy difference.

By theory and experiment, the annihilation of a singlet positronium must result in the emission of two γ-rays (each with energy about mc^2) going in opposite directions in order to conserve momentum. The annihilation of a triplet positronium must result in the emission of three γ-rays with a resultant angular momentum of $J = 1$. If it were possible to apply a very high frequency microwave to cause a transition from the $J = 0$ state to $J = 1$ state, there would be an increase of three quanta emission due to triplet positronium annihilation over the two-quanta emission due to singlet positronium annihilation because of the effect of the microwaves. It turned out, however, that the fine structure energy ΔW is of the order of 200 GHz ($\lambda = 1.6$ mm), which is practically too high a frequency for the present day millimeter wave source.

Deutsch and others turned their attention to a very ingenious solution for the problem. They noted that the Zeeman effect of the triplet state of the positronium is quadratic, as shown in Fig. 13. They also noted that the $M = \pm 1$ sublevels are unaffected by the magnetic field, but the $M = 0$ level rises as the function $(1 + X^2)^{1/2}$ where $X = \dfrac{2e\hbar H}{mc\Delta W}$. The $M = 0$ level is in fact a mixture of singlet and triplet character of positronium. Suppose microwave radiation is used to produce

resonance as $h\nu = \dfrac{\Delta W}{2}(1 + X^2)^{1/2}$. Two effects will result: (a) for the transition from $M = \pm 1$ level to that part of $M = 0$ level which has the character of triplet, nothing should happen to the emission of three-quanta and (b) for the transition from $M = \pm 1$ level to that part of $M = 0$ level which has the character of singlet, then there will be a corresponding change from three quanta emission to two quanta emission for the annihilation process. In this resonance effect, since ν and H are known, one can solve for ΔW which turned out to be around 202 GHz—in very good agreement with theoretical calculations.
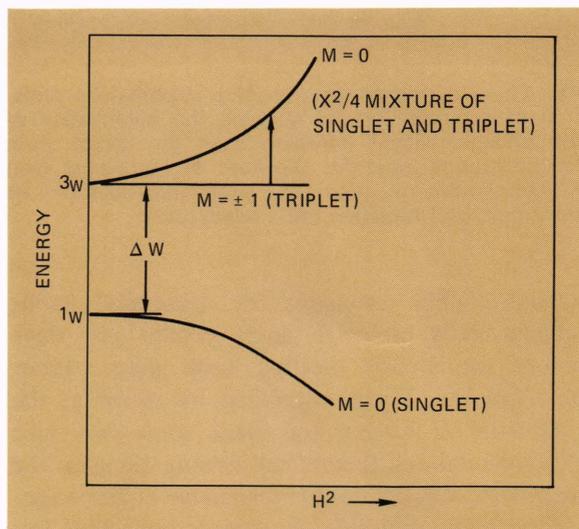
Fig. 13—The splitting of positronium triplet energy (^{3}W) and positronium singlet energy (^{1}W) in a magnetic field. (After DeBenedetti and Corben—Ref. 9.)

Case D: Speculative microwave probing of excitons[10]

Let us consider a perfectly homogeneous and uniform organic or inorganic single crystal. According to the band theory of the solid state, the conduction and valence bands are separated by a band gap as shown in Fig. 14. For simplicity, it is assumed that the wave vector **K** is zero. If the crystal is irradiated by a light source, then there is usually a very strong and sharp fundamental absorption band starting from the photon energy equal to the band gap. The electron from the valence band is lifted to the conduction band, thus causing photoconductivity.

[10] For general reference, see C. Kittel, *Introduction to Solid State Physics*, 2nd ed., John Wiley & Sons, Inc., New York, 1956, 504–512.
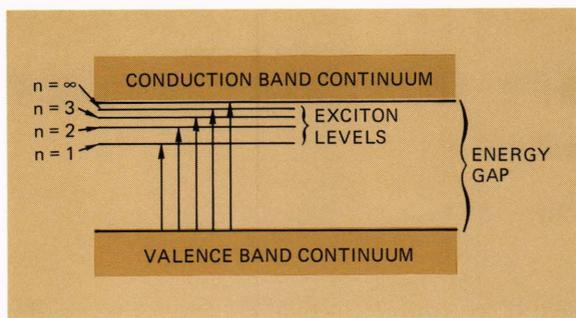
Fig. 14—Energy levels of an exciton with its center of mass at rest. Optical transitions from the top of the valence band (assumed to be at wave vector K = 0) are shown by the arrows. (After Kittel—Ref. 10.)

In some cases, however, there seem to be some energy levels below the bottom edge of the conduction band to which electrons from the valence band can be excited. The excitation of an electron to such a level would leave a hole in the valence band. A hole in the solid-state band theory is supposed to have the property analogous to that of a positron, in that it is assumed to have a positive charge numerically equal to that of an electron and a spin angular momentum of one-half $\hbar$. In a solid body, neither the electron nor the hole (pseudo-positron) should have a mass equal to that of a free electron. Each one of them should have an effective mass of its own (the electronic effective mass is not necessarily equal to the effective mass of the pseudo-positron).

An electron and a pseudo-positron must have a Coulomb interaction energy between them and can form a bond as in a hydrogen atom, which can now be called a pseudo-positronium. This physical entity is known as an exciton. In the literature, if an exciton has relatively low binding energy and the electron pair components are separated by a fairly large distance, it is known as the Wannier exciton. But if an exciton has relatively high binding energy and its components are separated by a fairly small distance, then it is known as the Frenkel exciton.

An exciton, whether of the Wannier or Frenkel type, owing to the translational symmetry and long-range interaction forces, can migrate in the crystal until something causes the exciton components to recombine, thus resulting in the disappearance of the hole and an emission of radiation. Hence, one may say an exciton can exhibit a spatial transfer of excitation but no net transfer of charge. Practically speaking, a Wannier exciton may have a longer range of migration, whereas a Frenkel exciton may be more localized and has a short range of migration.

Just like a positronium, an exciton can have both singlet and triplet states, i.e., paraexciton for antiparallel spins and orthoexciton for parallel spins. The fine structure energy difference can be calculated if one has information on the effective masses, the distance of separation between the components and the dielectric constant of the medium (the concept of dielectric constant may not hold true for the short distances involved in the Frenkel exciton). From a private communication,[11] we learn that the fine-structure energy separation for a Wannier exciton may be of the order of a few cm^{-1} and the fine-structure energy separation for a Frenkel exciton should be appreciably larger. The fine structure of the Wannier exciton may be directly excitable by microwave or millimeter waves, while the Zeeman effect may be a suitable means for studying the Frenkel exciton.

Concluding Remarks

In this paper, an introduction is given on the subject of excitation energy transfer in solids. It is hoped that the reader can catch the qualitative fundamentals of the subject without having to delve into technical aspects of the problem. As APL workers were among the originators of applying microwave-optical double resonance, we have employed many original techniques in comprehensively studying two interesting and important cases of excitation energy transfer in solids, one concerning a substituted atomic ion and the other a substituted molecule in an otherwise homogeneous crystalline environment. To show that the double resonance method is also extensively used elsewhere, a most notable case of positronium experiment is cited. A possible use of the method in the study of excitons in crystalline solids is given as a speculative suggestion.

Acknowledgment

[11] Indebted to Kishin Moorjani, APL, private communication.