at about 8°K, and pointed out that it can be considered as an indication of the occurrence of a lower transition which had been known in deuterated methanes but not in methane until then. Now it may not be pertinent to identify the observed anomaly with the predicted lower transition of our normal mixture at about 14°K, since this is somewhat too high and this should be sharp as it is in deuterated methanes. On the other hand, it does not seem unreasonable to suppose that the anomaly reflects collectively all the effects due to possible transitions and interspecies conversion below the upper transition in our equilibrium mixture.

Quite recently Hopkins et al.[9] have reported that nmr intensity in solid methane increases with time when the sample is maintained at various temperatures between 4.2 and 10°K, if it contains a small amount of oxygen, but that no appreciable change is exhibited if the sample is pure. According to their interpretation that this is evidence for the oxygen catalysis of nuclear-spin species conversion, our normal mixture is nothing but pure methane and our equilibrium mixture corresponds to methane containing oxygen. Consequently it is highly desired to carry out further experiments, by means of samples of controlled oxygen content, with the purpose of testing our predictions presented in this note.

Details of the present calculations will be published elsewhere in a series of papers.

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[1]K. Clusius, Z. Physik. Chem. (Leipzig) B3, 41 (1929); J. H. Colwell, E. K. Gill, and J. A. Morrison, J. Chem. Phys. 39, 635 (1963), and 42, 3144 (1965).

[2]For spectroscopic studies see G. B. Savitsky and D. F. Hornig, J. Chem. Phys. 36, 2634 (1962); A. Anderson and R. Savoire, ibid. 43, 3468 (1965). For nmr studies see G. A. de Wit, thesis, University of British Columbia, 1966 (unpublished); G. A. de Wit and M. Bloom, Phys. Letters 21, 39 (1966). For neutron inelastic scattering experiments see B. Dorner and H. Stiller, Inelastic Scattering of Neutrons in Solids and Liquids (International Atomic Energy Agency, Vienna, Austria, 1965), Vol. II, p. 291; Y. D. Harker and R. M. Brugger, J. Chem. Phys. 46, 2201 (1967). For theoretical studies see T. Nagamiya, Progr. Theoret. Phys. (Kyoto) 6, 702 (1951); K. Tomita, Phys. Rev. 89, 429 (1953).

[3]L. Pauling, Phys. Rev. 36, 430 (1930).

[4]H. M. James and T. A. Keenan, J. Chem. Phys. 31, 12 (1959).

[5]One step in this direction has already been marked by M. J. Freiser, thesis, Purdue University, 1956 (unpublished), in which he has discussed some quantum effects in the upper transition in both light and heavy methanes.

[6]E. Bartholomé, G. Drikos, and A. Eucken, Z. Physik. Chem. (Leipzig) B39, 371 (1938).

[7]J. S. Rosenshein and W. M. Whitney, in Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt et al. (Plenum Press, New York, 1965), p. 1114.

[8]J. H. Colwell, E. K. Gill, and J. A. Morrison, J. Chem. Phys. 36, 2223 (1962).

[9]H. P. Hopkins, Jr., P. L. Donoho, and K. S. Pitzer, J. Chem. Phys. 47, 864 (1967). See also R. P. Wolf and W. M. Whitney, in Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt et al., (Plenum Press, New York, 1965), p. 1118.

DIRECT, TWO-PHOTON PHOTOCARRIER GENERATION IN ANTHRACENE

F. C. Strome, Jr.
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650
(Received 1 December 1967)

We wish to report evidence for the generation of mobile charge carriers in anthracene crystals by a direct, two-photon transition to a conducting or autoionizing state. We have measured the intensity dependence of photocurrent and prompt fluorescence excited by 40-nsec pulses of light at 597 nm (2.07 eV), 571 nm (2.16 eV), and 525 nm (2.35 eV). We find a square-law dependence for both quantities. Since the prompt fluorescence is directly proportional to the number of singlet excitons,[1] our results are not consistent with singlet-photon or singlet-singlet mechanisms for carrier generation.

Figure 1 shows the experimental data. The excitations at 597 and 525 nm were obtained as the first and second anti-Stokes stimulated Raman lines when a giant-pulsed ruby laser beam from 10- to 20-MW peak power was focused by a 5-cm lens into liquid nitrogen.

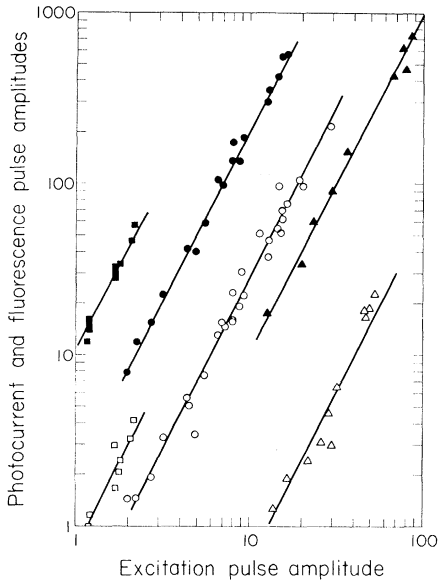

FIG. 1. Photocurrent (open symbols) and fluorescence (solid symbols) pulse amplitudes plotted against excitation pulse amplitudes at 597 (triangles), 571 (squares), and 525 nm (circles). One unit of photocurrent is 0.34 nA cm^{-2}; fluorescence, 5.7 W cm^{-3}; excitation, 3400, 3000, and 2500 W cm^{-2} at 597, 571, and 525 nm, respectively. The crystal was 1.1 mm thick and 6 mm diam, and was biased at 900 V.

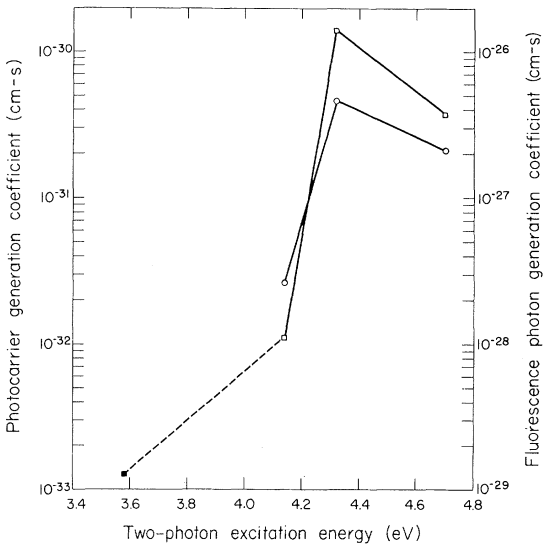

FIG. 2. Photocarrier (circles) and prompt fluorescence (squares) generation coefficients at the wavelengths of measurement. The solid square represents data of J. L. Hall, D. A. Jennings, and R. M. McClintock [Phys. Rev. Letters 11, 364 (1963)] with ruby laser excitation.

The emerging radiation was filtered as required and directed through the crystal by a second lens after being monitored by the use of a beam-splitting reflector and a biplanar photodiode. The excitation at 571 nm was obtained similarly from liquid oxygen. The intensity at 571 nm was relatively low because of an absorption band in the oxygen.

Figure 2 shows the two-photon charge-carrier and fluorescence photon generation coefficients as functions of the two-photon energy. The data are consistent with a photocurrent generation threshold near 4 eV, as found by one-photon absorption.[2-4] Because of uncertainties in the distribution of exciting light at the crystal and the quadratic intensity dependence, the carrier generation coefficients may be in error by a factor of the order of 3. Because of additional uncertainties in the fluorescence collection efficiency, the fluorescence generation coefficients may be in error by an order of magnitude. However, relative magnitudes at the three wavelengths are believed to be in error by less than 30%.

Another process which could explain the observed intensity dependence of the current is the production of triplet excitons by one-photon absorption, followed by triplet photoionization. The fluorescence could then be an independent, two-photon excitation of a nonconducting state. To check this hypothesis, a second ruby laser, operated in the burst mode, was used to produce triplets in the crystal, the burst ending about 100 μsec before an excitation pulse at 525 nm. The delayed fluorescence was monitored by a gated photomultiplier tube to avoid saturation effects from prompt fluorescence. Its intensity at the time of the 525-nm pulse was 50 times greater than that generated by the 525-nm pulse alone. Because the delayed fluorescence intensity is proportional to the square of the triplet density, the auxiliary exposure therefore produced 7 times more triplets than were produced by the 525-nm pulse alone. In spite of this increased triplet density, no obvious increase was observed in the photocurrent pulse caused by the 525-nm excitation, indicating that triplet ionization was not a significant factor.

A large number of repetitions of the experiment indicated that a very small increase in photocurrent might be associated with the enhanced triplet density. From an estimate of an upper limit for this increase, together with a triplet density of 2.8×10^{13} cm^{-3}, calculated from the observed delayed-fluorescence

decay rate, an upper limit of 5×10^{-22} cm^2 was calculated for the triplet photoionization cross section at 525 nm. This value is 20 times smaller than the one reported by Holzman et al.,[5] but these authors used excitation which extended down to about 472 nm. Perhaps the smaller available kinetic energy, relative to a threshold at 4 eV, with two 525-nm photons results in more loss of carriers by immediate recombination than at the shorter wavelengths.

Crystals were also exposed to stimulated Raman pulses at 467 and 421 nm, which are the third and fourth anti-Stokes lines from liquid nitrogen. At both wavelengths, the fluorescence was essentially a linear function of the intensity, indicating that one-photon excitation from a vibronic level of the ground state was dominant. The photocurrent had an approximate square-law dependence, which is expected for either singlet-photon or singlet-singlet interaction mechanisms for carrier production. From Nakada's values[6] for the absorption coefficient at 421 nm and Kepler's singlet photoionization cross section,[7] the expected photocarrier generation at this wavelength was calculated to be 3×10^6 cm^{-2} for an excitation intensity of 110 W cm^{-2}. A measured value of 3.2×10^6 cm^{-2} was found. Calculations based on the exciton-exciton interaction mechanism and the measured generation coefficient of Silver et al.[8] yielded currents larger by factors from 15 to 75, depending upon the polarization.

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[1]S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, J. Chem. Phys. 42, 330 (1965). This paper includes a discussion of the origins of prompt and delayed fluorescence in anthracene, with references to earlier work.

[2]G. Castro and J. G. Hornig, J. Chem. Phys. 42, 1459 (1965).

[3]R. F. Chaiken and D. R. Kearns, J. Chem. Phys. 45, 3966 (1966).

[4]N. Geacintov and M. Pope, J. Chem. Phys. 45, 3884 (1966).

[5]P. Holzman, R. Morris, R. C. Jarnagin, and M. Silver, Phys. Rev. Letters 19, 506 (1967). The reported cross section should be multiplied by 2.5 to account for a new determination of 0.02 for the singlet-triplet intersystem crossing fraction instead of the value of 0.05 used in this paper.

[6]I. Nakada, J. Phys. Soc. Japan 20, 346 (1965).

[7]R. G. Kepler, Phys. Rev. Letters 18, 951 (1967).

[8]M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters 10, 12 (1963).

ULTRASONIC PROPAGATION IN $RbMnF_3$ NEAR THE MAGNETIC CRITICAL POINT

Brage Golding*
Bell Telephone Laboratories, Murray Hill, New Jersey
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Measurements of the ultrasonic attenuation and velocity near the magnetic critical point in the cubic Heisenberg antiferromagnet $RbMnF_3$ have been performed over a wide range of frequencies. The ultrasonic attenuation coefficient α is divergent at T_C and obeys the law $\alpha\propto\omega^2(T-T_C)^{-0.32\pm0.02}$ for two decades of reduced temperature T/T_C-1.

Considerable theoretical attention has been focused recently on the behavior of the ultrasonic propagation near the magnetic critical point.[1-5] As the transition temperature of a magnetic solid is closely approached, the fluctuations of the magnetization give rise to an increasing cross section for spin-phonon scattering. This manifests itself physically as a growth of the absorption of the ultrasonic waves. Although most theories predict the attenuation coefficient α to be singular at the critical temperature T_C there appears to be no agreement as to the strength of the singularity. Furthermore, it is not yet clear what differences, if any, exist between the critical behavior of α for the ferromagnet and antiferromagnet. The experimental data on these quantities have been sparse. In antiferromagnetic MnF_2 an investigation[6] showed a frequency-dependent anomaly at T_C but no quantitative conclusion could be drawn about the existence of a singularity. Quite recently, measurements of α in the metallic ferromagnet gadolinium[7] have indicated a singularity of the form $\alpha\propto(T-T_C)^{-1.2}$. We