LUMINESCENCE of ORGANIC and INORGANIC SYSTEMS

A conference report by **Grace Marmor Spruch** *and* **Felix H. Brown**

LAST October the Physics Department of New York University at Washington Square played host to about 300—shall we call them luminaries?—in the field of luminescence at a five-day international conference. It was the first time an attempt was made, on a large scale, to bring together researchers in the luminescence of organic systems and those investigating inorganic systems. As the chairman of the conference, Professor Hartmut P. Kallmann of NYU, one of the rare few who work in both fields, said: "I feel a little like a man who has two very good friends, but these two friends don't speak to one another."

The conference was held in the Eisner and Lubin Auditorium of NYU's Loeb Student Center. It was sponsored by the Air Force Aeronautical Research Laboratory, the Army Research Office at Durham, the Office of Naval Research, and New York University. It opened Monday, October 9, with a welcome by Professor Morris Shamos on behalf of the Physics Department and by Dean James Hester representing the University.

The meeting was open, with thirty-four half-hour talks presented by invitation and shorter communications offered from the floor. Speakers came from France, Great Britain, Germany, Israel, Japan, the Netherlands, Puerto Rico, and Spain. Italy and Poland were represented by papers which will be published in the conference *Proceedings*. Three scientists from the Soviet Union had been invited but failed to respond. Several of the heads of foreign laboratories were given the opportunity to bring one or two of their students or younger co-workers, in the belief that these younger people, who do not ordinarily get to attend international conferences, might very well derive the most from them. Each talk was followed by a short discussion. In addition, Thursday afternoon was devoted to a general discussion of organic systems and Friday afternoon to a general discussion of inorganic systems. Successive half-day sessions were devoted alternately to inorganics and to organics—one can provide for togetherness but cannot legislate it—and it was thought that an occasional half day off might be welcomed by those overwhelmed by forays into strange territory. There was an official half day off for all at the midway point, Wednesday afternoon, when the territory surveyed was Manhattan Island, from a boat which toured around it.

THE first session was a memorial to Michael Schön and Georges Destriau, two of the outstanding workers in the field who were born in the same year, 1903, and who died within months of one another a year ago. Professor Kallmann said that it grieved him to act as sole chairman of the conference, since the idea of the conference was a joint one, his and Schön's, it having originated the previous summer at a smaller meeting in Munich. N. Riehl of the Technische Hochschule in Munich, a long time co-worker and personal friend of Schön, delivered the "In Memoriam" address. He traced Schön's career from its start in theology and philosophy, and discussed his work in luminescence which led to a qualitative explanation of the common effects in crystal phosphors. He spoke of Schön's "unhappy love affair" with zinc sulfide, which resisted his direct quantitative advances although it responded quite willingly to his more subtle qualitative approach. Riehl also spoke of Schön the man, characterizing him as a decided opponent not only of Nazism but of all forms of dictatorship, and a firm believer in the ultimate triumph of democracy despite temporary defeats.

The address in memory of Georges Destriau was given by his long time colleague, J. Mattler of the Faculté des Sciences de Paris. Mattler told how, through more than fifteen years of direct collaboration with Destriau, he had had the opportunity to appreciate his human qualities as much as the richness and originality of his scientific work, which encompassed such diverse topics as eagres * and the electroluminescence for which he is most famous and which bears his name as the Destriau effect. Mattler told of accompanying him on his last trip to the US in May 1959, of Destriau's feeling that it was to be his last, and of how moved he was to see, at the Westinghouse Research Laboratories, the first practical realization of electroluminescence, "an expression of his long and patient researches".

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Most of the talks were on experimental work. F. E. Williams of the University of Delaware, however, opened the Monday afternoon session with some "Theoretical Considerations of the Luminescence of Alkali Halide and Zinc Sulfide Phosphors". He discussed the problem of the relative oscillator strengths for the principal impurity absorption bands in alkali halides and emphasized the effect of crystalline interactions on the pure spin states. He gave a theoretical analysis of the optical properties of zinc sulfide prepared with Zn^{65} which forms Cu by K capture. He then discussed the general characteristics common to both alkali halide and zinc sulfide phosphors, stating that the broad absorption and emission bands and the Stokes shift arise in both classes of phosphors from the difference in electronic configuration of the activator system in the ground and excited states, from the polar character of the medium, and from the orbital electron or hole motion being rapid compared to lattice vibrations.

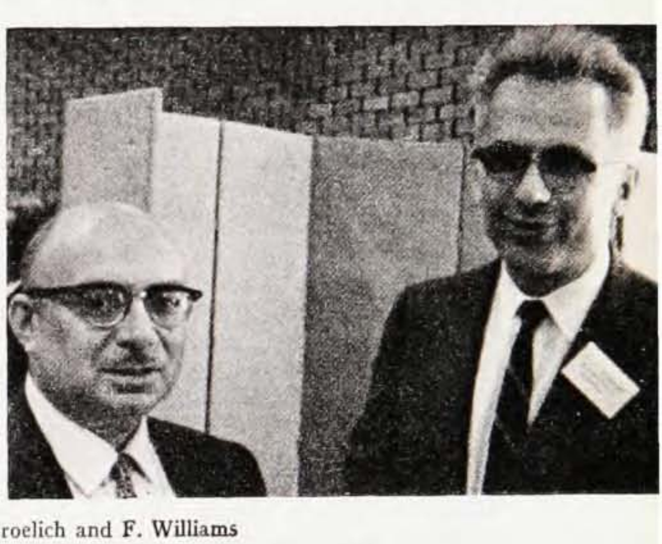
One of the highlights of the meeting was the talk by James Franck of the University of Chicago Tuesday morning, "A Discussion of the Assumption that Photoionization Plays a Decisive Role in Photosynthesis". Franck opened by saying that he was very pleased to be able to give this talk at a conference on luminescence, because for most physics meetings there was too much biology in it and for most biology meetings there was too much physics. Two theories for the photochemical steps of photosynthesis were compared. The one held by Franck and his co-workers assumes that light absorbed by the chloroplast pigments is utilized according to the usual rules of photochemistry. The second, most recently presented in detailed form by Calvin and his co-workers, is based on the assumption that a photo-induced ionization of chlorophyll molecules and the migration of charges play an essential role in photosynthesis. Calvin was this year's recipient of the Nobel Prize in chemistry. Franck received the Nobel Prize in physics some years ago. The discussion is obviously Olympian.

Tuesday afternoon belonged to zinc sulfide, with three talks on its luminescence centers. N. Riehl ascribed the blue luminescence centers in ZnS: Cu phosphors to an association of an interstitial Cu^+ ion with a Cu^+ ion on a lattice site. When the temperature is raised, blue centers are converted into green centers either by a reversible or by an irreversible process. The irreversible process occurs only under conditions which permit chemical reactions on the crystal surface. The reversible process was used to obtain equilibrium blue-to-green ratios at different temperatures. These were frozen in by rapid cooling, and measured. Information was also obtained about the fate of the coactivator during the conversion, and a value of 0.76 ev was determined for the reaction enthalpy of the green-blue association.

At the Wednesday morning session, which was devoted largely to time constants of fluorescence in solu-

H. Kallmann (conference chairman), G. Marmor Spruch (conference secretary), and N. Riehl.

J. Mattler and F. Gans



H. C. Froelich and **F. Williams**

N. Riehl, A. Halperin, and J. B. Birks (*photos by Erwin Cohen*)

E. J. Bowen and F. Wilkinson (in front); W. Van Gool and S. Shionoya in background.

tions, Th. Förster of the Technische Hochschule in Stuttgart discussed some higher aromatic aldehydes, which are nonfluorescent in inert solvents, but which fluoresce in hydroxylic or acidified hydrocarbon solvents. This solvent activation of fluorescence was ascribed to the small difference between the π,π^* and n,π^* excited singlet states which allows solvent effects to alter their relative position. A quantitative study of shifts in absorption and emission spectra with solvent composition and with temperature makes it possible to distinguish two mechanisms in the case of pyrene-3-aldehyde. Strong proton donors activate mainly by stabilizing the nonbonding n electron, thus raising the n,π^* excitation energy, while weak proton donors or solvent molecules of sufficient polarity activate by a solvent relaxation process which stabilizes the excited π,π^* state. In the case of moderately activating agents, solvent rearrangement during the lifetime of the excited molecule is most important, while ground-state interaction prevails with strong activators at low concentration.

E. J. Bowen of Oxford University opened the Thursday morning session, which dealt largely with energy transfer in organic systems, with a talk on solvent effects on fluorescence yields. He stated that the fluorescence yields of 1- and 2-naphthylamines and certain of their sulfonates increase with a lowering of temperature to a limiting value which in many cases is less than unity. The deviation from unity occurs because, during the rapid loss of excess vibrational energy, a fraction of the excited molecules crosses over to the triplet level by a "single-chance" process. The probability of this crossover appears to be correlated to the separations between absorption and fluorescence band maxima, which are a measure of the extent of solute-solvent interactions of the excited state.

He was followed by F. Wilkinson of Oxford who reported on his work with G. Porter of Sheffield University on energy transfer from the triplet state. He discussed the mechanism of electronic excitation energy transfer in fluid solvents from the triplet state of a donor molecule to an acceptor molecule. This process results in quenching of the excited donor and elevation of the acceptor molecule to its triplet state. He stated that it is diffusion controlled when the energy of the acceptor is considerably lower than that of the donor, but there is no evidence for long-range resonance transfer of the kind found in the analogous singlet energy-transfer processes. As the triplet energies become comparable, the transfer probability is reduced and no quenching is observed by molecules with triplet levels higher than that of the donor.

THURSDAY evening, at the conference dinner, James Franck gave an extremely moving address entitled, "Reminiscences on Personalities and Problems in the Era of the Development of Modern Science". Franck, whose experience spans all the major upheavals of modern physics, and who participated actively and significantly in several of them, spoke of the difference in the atmosphere surrounding physics and physicists in his student days compared to that of today. In that era, a career as a research physicist offered little opportunity either for making a living or for gaining public recognition. University positions were exceedingly rare, and job opportunities in industry had reached the staggering total of something like one physicist hired every ten years. As a result, the small community of physicists showed, in general, more devotion to the search for truth and less to personal ambition than is possible under the altered conditions of today. Franck said that to attain the greatest objectivity still remains the goal for which we all must strive.

Sitting by his side as Franck spoke of those days was Richard Courant of NYU's Courant Institute of Mathematical Sciences, a member of the Göttingen

Th. Förster and J. Franck

F. Williams answering a question during the last session of the luminescence conference, the general discussion of inorganic systems.

trio of lifelong friends, Born, Courant, and Franck, which dates back to that time.

Franck laid claim to being the first person in his native Hamburg to receive a local x ray, when he was a boy of fourteen. Having read with utter fascination of the discovery of x rays, he was absolutely delighted when the arm he had just broken meant he could be regarded as a suitable subject for x-ray photography. He rushed to a small physics laboratory owned by the city to learn whether they might have an x-ray tube available. It turned out that they had acquired one that very day and were as eager to take a picture of the arm as was young Franck. The question "Don't you have to ask your parents?" was apparently squared away, for the picture was taken. It showed that the bones had not been set correctly by the doctor. Thus did Franck's scientific curiosity benefit his health.

He ended his warm, modest speech by saying that the great men (Einstein, Planck, Bohr, and Nernst) opened paths: "We went along and picked flowers to the right and to the left and made a bouquet for ourselves."

AT the last session H. Kallmann gave some raisons d'être for this organic-inorganic union. He asserted that in three of the main aspects of fluorescence there are similarities between organic and inorganic systems: in the types of states which are excited, in the way these states can be excited, and in charge transfer. In both organic and inorganic materials there are exciton states, states in the bulk material which may not be exciton states, highly emissive impurity states, and impurity states with forbidden transitions. The differences between the states in the two types of materials arise from the fact that the binding forces between neighbors are so much smaller in organic materials. Energy differences are therefore much smaller and can be detected only at lower temperatures, but the states themselves are similar. He took his evidence from the conference itself, pointing out that W. Van Sciver had described the exciton in alkali halides, while several days earlier H. Sponer had given a talk on exciton states in naphthalene. Kallmann drew an analogy between Förster's picture of fluorescence of a solute influenced by the surrounding solvent, and the influence of the surroundings on impurity states in inorganic materials. The difference arises from the stronger fields in the inorganic materials. Excitation by radiative coupling occurs in both systems. A solution with two components can have one component excited by the radiation of the other. This corresponds to an inorganic phosphor with two activators and two emission bands. Nonradiative transfer, which is more significant, also occurs in both types of systems, especially when the acceptor has only a small absorption probability. He went from one analogy to another.

After this scientific windup by Kallmann, N. Riehl stood up to say a few words, his characteristic footlong cigar dangling from his lips in flagrant defiance of gravity. He reiterated the importance of the unification of organic and inorganic solid-state physics: "It is certainly necessary to make an attempt in this direction. I believe the attempt we have made in the last few days was not completely unsuccessful because I have observed that while the organic people were sitting here in the auditorium the inorganic people were sitting in cafeterias not very far from here." (For direct evidence of organic impurities in an inorganic session, see the photo above, taken at the very last session, the general discussion of inorganic systems.)