Excitons in molecular physics

This report summarizes the proceedings of the Symposium on Excitons in Molecular Crystals, held on October 11 and 12 under the sponsorship of E. I. duPont deNemours and Company, in Wilmington, Delaware. The authors are both at the University of California at Berkeley.

By *A. Suna* and *J. J. Hopfield*

Pleasant fall weather added to the high spirits and congeniality of a group of physicists and chemists attending a symposium on molecular excitons as guests of duPont's Central Research Department. Their common interest in excitons had attracted participants from academic and research institutions across the country, and from Canada as well. Welcoming the visitors, Central Research Director P. L. Salzberg announced that the symposium marked the belated dedication of the site of the meeting, duPont's newly constructed Physical Research Building.

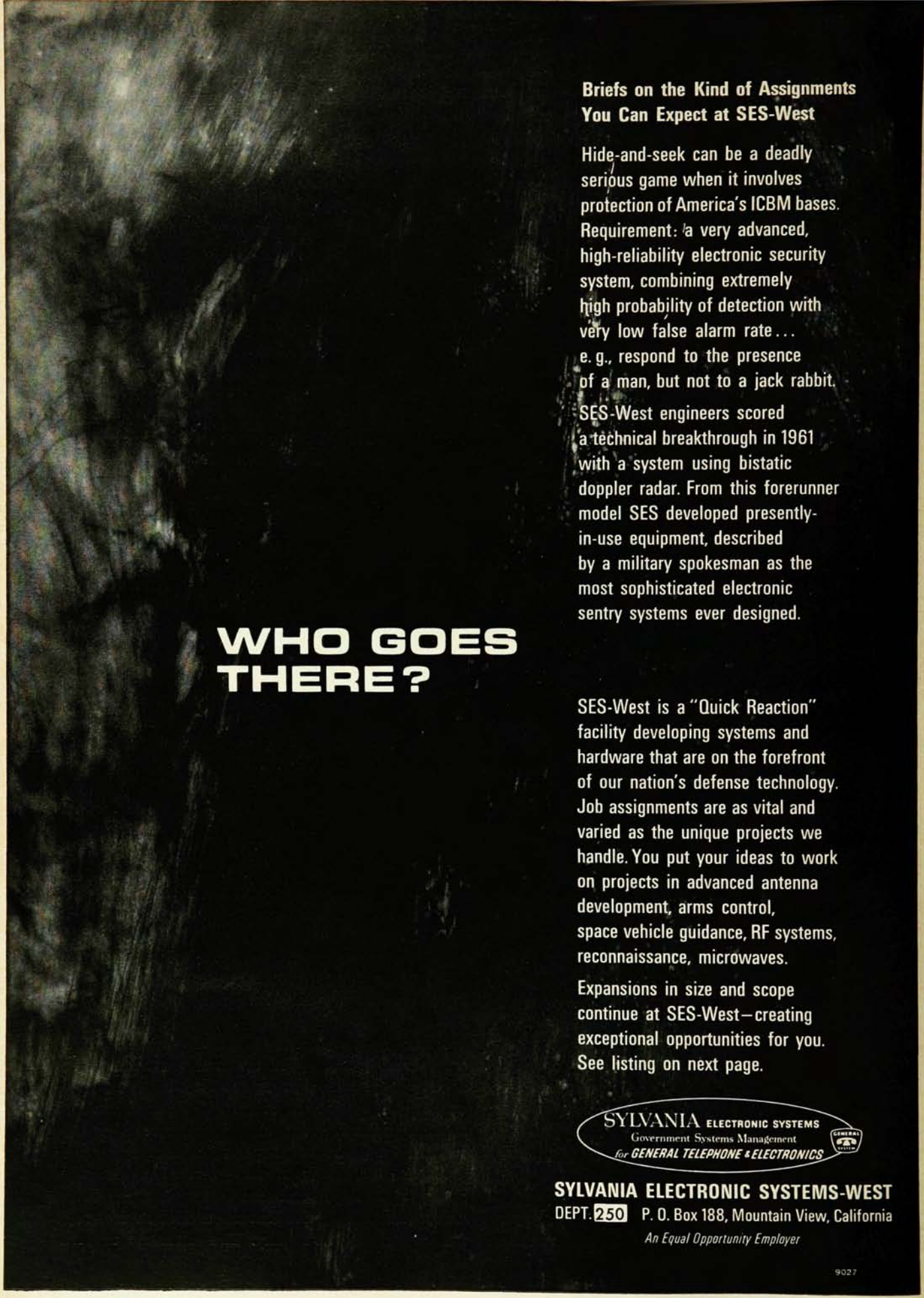
Excitons, neutral quasiparticles arising as fundamental modes of electronic excitation in insulating crystals, are perhaps more familiar in semiconductors and alkali halides where they can be characterized simply as bound electron-hole pairs. The type of exciton which was the center of interest of the symposium has the electron so tightly bound to the hole that the resulting entity is more appropriately described as a mobile excited state of the individual molecules composing the crystal. Nevertheless, basic similarities pervade studies of all types of excitons, as was pointed out in the opening talk by J. J. Hopfield. Thus, the determination of the nature of the energy dispersion of a mode of excitation being studied is essential in ascertaining whether or not this mode can justifiably be called an exciton. The talk stimulated an animated discussion of differences between the two basic kinds of exciton, weakly and tightly bound. It was agreed that excitons play a greater role in the spectrum of excitations of molecular crystals than of other solids; Hopfield's remark that properties of weakly bound excitons can in large measure be predicted from independent measurements on the constituent electron and hole was countered by statements pointing out that a knowledge of the excited states of isolated molecules can similarly lead to an accurate description of molecular excitons.

Following this introduction the participants were treated to a detailed analysis of several instructive special examples of molecular excitons, as R. M. Hochstrasser described the electronic spectra of crystals of perylene and of the anthracene-trinitrobenzene charge transfer complex. The study of tightly bound excitons has long been a meeting ground between physicists and chemists; more recently, it has attracted biological interest as well. In this context, W. C. Rhodes reviewed the application of exciton theory in the treatment of electronic interactions in helical polymers.

The proceedings took a more theoretical turn when R. E. Merrifield outlined a calculation applicable to the effects, on an exciton, of internal vibrations of the molecules carrying the exciton. The simple one-dimensional model employed in this work was also treated in the subsequent talk by a method quite different from Merrifield's variational procedure. A. Suna approached the problem by using the many-body Green's function which seems to be quite the vogue in solid-state physics these days; the calculation was presented as part of a general discussion of the relevance and usefulness of Green's function to treating problems of excitons interacting with phonons.

The symposium was quite successfully balanced between theory and experiment of varying degrees of sophistication. Merrifield's and Suna's formal presentations were followed up, on the second day of the meeting, with a description of some ingenious experiments by G. W. Robinson. By introducing known amounts of one or more types of isotopic impurities into deuterated benzene crystals, Robinson (together with G. C. Nieman) has achieved the creation of shallow traps which do not perturb the geometry of the crystal; measurements related to the motion of excitons between these traps then provide an indirect determination of a number of otherwise elusive properties of the excitons—e.g., the band width for triplet excitons.

One of the most appealing features of the symposium was the abundance of uninhibited discussion, facilitated by the limitation of the number of participants to about fifty. The exchange of opin-



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ion seemed especially lively during Saturday's morning session. Enthusiasm rose during the discussion of Robinson's talk and reached a peak following the description, by P. Avakian, of some remarkable experiments which have recently created quite a stir in the literature. The experiments in which Avakian had participated involved the observation of blue fluorescence upon irradiation of anthracene crystals with intense red light. The evidence presented—e.g., the observation of delayed fluorescence—pointed toward an exciton-exciton annihilation mechanism as being responsible for the observed phenomena. A theoretical description of the annihilation mechanism was suggested by S. A. Rice, who in addition described some painstaking calculations related to this and other exciton-exciton annihilation processes. Exciton-exciton interactions were also the subject of D. B. Chesnut's presentation; a simplified model of this interaction yielded a qualitative description of observed anomalous magnetic behavior of several ion-radical salts.

A nonelectronic type of exciton arises when the excited molecular state responsible for its existence is a state of vibrational excitation. Observations of such vibrational excitons in the infrared spectra of molecular crystals were described by R. M. Hexter.

Not all the exciton physics that transpired during the symposium did so in the formal talks and the discussions following them. A number of short presentations of recent results were interspersed between the talks. Moreover, there was ample opportunity for exchange of ideas and information on a more personal basis. All of Friday evening was set aside for this purpose, with cocktails and an informal dinner without after-dinner speeches.

Though hardly the most popular field in solid-state physics, the study of excitons in molecular crystals is fast coming into its own as was amply evidenced at this symposium. The richness and variety of probems in this field of research were stressed in the inspiring closing statements by J. A. Wheeler. He pointed to many ideas in exciton physics which also arise in seemingly unrelated areas, such as elementary particle physics and nuclear physics. Professor Wheeler emphasized the role of the chemists who prepare the molecular crystals used in the study of tightly bound excitons. Forecasting an exciting technological future for exciton research, he added that Wilmington physicists, who work near the largest concentration of PhD chemists in the world, are in a unique position to take advantage of the potentialities in a field which of necessity involves the cooperation of physics and chemistry.