Letters to the Editor

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Energy Transfer from Solvent to Solute in Liquid Organic Solutions Under Ultraviolet Excitation

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AGENO *et al.*[1] and Kallmann *et al.*[2] have shown that when certain organic liquid solutions are irradiated with γ rays a transfer of excitation energy from solvent to solute molecules takes place, giving rise to a very efficient conversion of absorbed energy into fluorescent quanta emitted by the fluorescent solute. Such solutions have an important use as scintillation media. There is still much discussion on the mechanism of energy transfer.[3]

In this work the possibility that a similar transfer occurs when the organic solutions are excited by ultraviolet has been examined. The existence of such a transfer would in itself be interesting, and moreover a detailed investigation of such a process might throw new light on the transfer mechanism, since the primary exciting process is much simpler in the case of ultraviolet excitation than in the case of excitation by ionizing radiations.

In a series of preliminary experiments, it was found that a considerable transport of energy from solvent to solute does indeed occur in many organic solutions when excited by light of wavelength 2537A.

For a convincing demonstration of this process, it is necessary that the solvent absorb most of the primary exciting radiation and that the solute absorb very little; on the other hand, the solute concentration should be sufficient to produce detectable fluorescence after transfer. These conditions are satisfied by a dilute solution of *p*-terphenyl (1 g/liter) in benzene, toluene, or xylene, for an exciting wavelength of 2537A. For a particular solute concentration the fraction of primary excitation energy absorbed by the solute was calculated (this was never greater than a few percent) from the relative absorption coefficients of solute and solvent at 2537A. The fluorescence of terphenyl in the aforementioned solvents when excited at 2537A was compared with the fluorescence obtained from a thin layer of solid terphenyl (for which the fluorescent yield is very high) deposited on a quartz slide at the same wavelength. As a further check a comparison was also made with the fluorescence produced by a solution of terphenyl in chloroform, a solvent which does not absorb significantly at 2537A.[4] It was found that the terphenyl fluorescence obtained in the solutions containing the strongly absorbing solvents was very much greater than that expected on the assumption that fluorescence is produced only through direct absorption by the terphenyl. For example, a solution of terphenyl in toluene at a concentration of 1 g/liter showed a fluorescence twenty times as great. The high fluorescent efficiency must be ascribed to transfer of energy from excited molecules of the solvent to molecules of the fluorescent solute. Although most of the measurements have so far been made with terphenyl, qualitative experiments show that transfer effects are obtained if other organic fluorescent materials are used as solutes.

Ageno *et al.*[5] has found evidence showing that fluorescent emission takes place over a region within a few millimeters from a polonium α-particle source immersed in a solution of terphenyl in xylene, and therefore have suggested that energy transfer takes place via long-range secondary radiation emitted by the solvent and absorbed by the solute. In order to see whether such radiative processes are significant in the case of uv excitation, a solution of terphenyl and xylene was placed in a Hilger quartz cell of variable thickness, and the fluorescence measured as a function of the thickness of the cell down to very small thicknesses, for a primary exciting radiation of 2537A. The results show that there is no appreciable radiative transfer over distances greater than 0.01 mm.

A detailed investigation of the dependence of transfer on various parameters such as wavelength and concentration in different liquid systems is being carried out.

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[1] Ageno, Chiozzotto, and Querzoli, Phys. Rev. **79**, 720 (1950).

[2] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950).

[3] For a recent discussion of different points of view see J. B. Birks, *Scintillation Counters* (Pergamon Press, London, 1953).

[4] A reduction of the intensity of the terphenyl fluorescence in chloroform occurs due to partial quenching by the solvent. This reduction, relative to terphenyl in toluene, was found to be about 35 percent, by comparing the two solutions at longer exciting wavelengths, where *both* solvents exhibit negligible absorption relative to the solvent. This quenching was also found to be independent of the exciting wavelength and was taken into account in the comparison at 2537A.

[5] M. Ageno and R. Querzoli, Nuovo cimento **9**, 282 (1952).

Radiation Damage in SiO_2 Structures

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FAST-NEUTRON irradiation of solids in the silicon-oxygen system have produced some interesting results.[1-5] Four phases of this system: (1) quartz, (2) low cristobalite, (3) low tridymite, and (4) glass have been irradiated with fluxes up to 2×10^{20} neutrons/cm^2 at this laboratory and the investigation is still in progress. This is a brief report on some of the results of the investigation.

After a total bombardment of 2×10^{20} neutrons/cm^2, the density of single crystals of quartz are reduced by 14.7 percent. It is somewhat unusual that these crystals reveal no macroscopic defects. The change in density has been traced following progressive irradiations and shows a pronounced structure dependence. The rate of change of density (Fig. 1) is initially small and may be due to the early filling of the *c*-axis interstitial channels with displaced atoms. Long-range order is maintained in single crystals but is gradually diminished until they have suffered a bombardment of approximately 1.2×10^{20} neutrons/cm^2. Following this irradiation the single-crystal x-ray reflections disappear. It is believed that permanent damage is induced in the single-crystal lattice at an early stage $\sim2\times10^{19}$ neutrons/cm^2, since at this

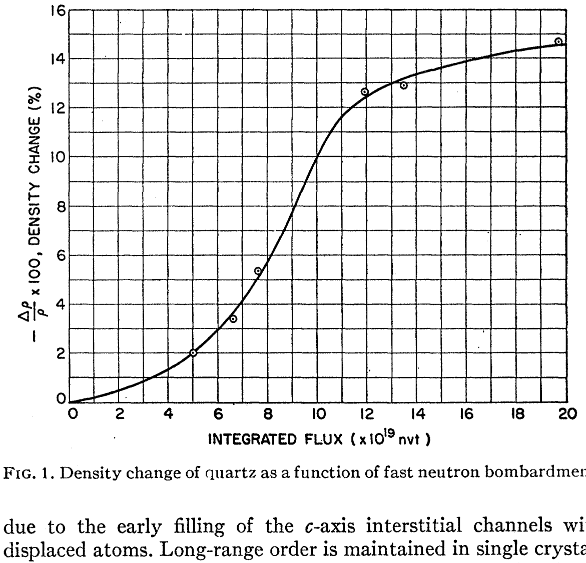

FIG. 1. Density change of quartz as a function of fast neutron bombardment.

point the c/a ratio is lowered below that value which β quartz[6] exhibits at 1000°C. Thermal and electrical evidence supports this view. Crystals bombarded by 5×10^{19} neutrons/cm^2 fail to exhibit the latent heat at the $\alpha\rightleftharpoons\beta$ inversion point and piezoelectric crystals no longer resonate after this irradiation.

Heavy dosages of fast neutron flux reduce all four of these solids to a common phase. This highly disordered material has an x-ray diffraction pattern of a glass, is optically isotropic, and has a density of 2.26. This material was recrystallized by annealing at 930°C for 16 hours and resulted in the formation of polycrystalline α quartz. Debye-Scherrer diffraction patterns taken using monochromatic radiation from a Cu target gave x-ray reflections at angles up to $2\theta=90°$. The fact that x-ray reflections were not observed at larger Bragg angles may be due to incomplete recrystallization, particle-size broadening, or strain. The contributions of each of these factors are being determined.

It appears that the bombardment of any of the above-mentioned phases produces a silica glass, with a density and average refractive index near that of normal low tridymite, which can then be transformed into α quartz in a solid-state reaction. Further annealing studies are necessary to confirm this view unambiguously. Such behavior would be of major interest since investigators[6] have been unsuccessful in their attempts to transform any of the complex silica phases into α quartz by means of a solid-state transformation in the absence of chemical aids.

A detailed report on the results of this investigation will be submitted for publication at an early date.

[1] R. Berman, Proc. Roy. Soc. (London) **A208**, 90 (1951).
[2] R. Berman, Advances in Physics **2**, 5, 103 (1953).
[3] M. Wittels, Phys. Rev. **89**, 3, 656 (1953).
[4] M. Wittels, Unpublished post-deadline paper, Washington D. C. Meeting, American Physical Society, May 2, 1953.
[5] Primak, Fuchs, and Day, Phys. Rev. **92**, 1064 (1953).
[6] R. B. Sosman, *The Properties of Silica* (Chemical Catalogue Company, Inc., New York, 1927).

Experimental Evidence Concerning Degeneracy in Germanium

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IN a recent note by Adams[1] it has been suggested that agreement of theory and experiment for germanium is such as to provide weak but definite evidence that the predicted degeneracy in the band structure[2] does not occur. It is the purpose of this note to point out that more recent measurements have modified substantially the stated points of agreement.

Measurements of lattice mobility taken on purer and presumably more prefect germanium samples show a variation with temperature as $T^{-1.6}$ for electrons,[3] $T^{-2.3}$ for holes,[4] instead of the $T^{-1.5}$ predicted by the deformation-potential theory[5] and other theoretical derivations. Along with other experimental results such as those for magnetoresistance and the anomalous ratio of Hall to drift mobility for holes,[3] this would seem to be explainable only on the basis of a more complicated picture of the band structure,[6] such as that predicted by Herman and Callaway. Such a band structure would result in shifts of the band edges with shear strains as well as dilatation.[5] In the light of these facts, the quantitative agreement found between the value of E_{1G} (the shift of the energy gap per unit dilatation) obtained from pressure experiments and that predicted by the deformation-potential theory for germanium would seem largely fortuitous. For silicon, it is worth noting, agreement was considerably poorer.

Agreement also apparently existed between values of β, the change in energy gap per degree change in temperature, determined from a few different types of experiment. The significance of this agreement is also open to question. One value of β was calculated from the experimental E_{1G} under the assumption that the change in energy gap with temperature was due entirely to thermal expansion. Another value of β is obtained from comparison of the theoretical formula

$$n_i^2=np=4\left(\frac{2\pi m_n^{\frac{1}{2}}m_p^{\frac{1}{2}}kT}{h^2}\right)^3 e^{-E_G/kT} \qquad (1)$$

with n_i^2 calculated from measurements of intrinsic conductivity. With a $T^{-\frac{3}{2}}$ dependence for the lattice mobility and effective masses equal to the free electron mass, this led to a value of 1×10^{-4} ev/°K for β, in good agreement with the value calculated from E_{1G}.[5] Incorporating the changed temperature dependences of the lattice mobilities will change this value and worsen the agreement unless, of course, the effective masses used in (1) are changed. There is, however, a fundamental question as to whether or not these two values of β should agree; it has been shown by Fan[7] that the shift in the energy gap with temperature arises in part from the changing interaction of the electrons with the lattice vibrations.

If the band structure is not the simple kind usually assumed, Eq. (1) must be modified. It may well be that for some particular band structure the modification consists of the insertion of statistical weight factors for the conduction and valence bands as suggested by Adams.[1] The effective masses in the formula for n_i^2 should then represent suitable averages of effective masses over different bands or different directions. Unfortunately, however, the effective mass in other formulas may not be represented by the same average. Thus it appears that, in general, detailed knowledge of the band structure may be required for the determination of β from n_i^2.

A different value of β, 4×10^{-4} ev/°K, is obtained from measurements of infrared absorption.[7] If the band structure of germanium is that calculated by Herman and Callaway, it is not to be expected that this value of β agree with that obtained from thermal transitions.

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[1] E. N. Adams, II, Phys. Rev. **92**, 1063 (1953).
[2] F. Herman and J. Callaway, Phys. Rev. **88**, 1210 (1952).
[3] M. B. Prince, Phys. Rev. **92**, 681 (1953).
[4] W. C. Dunlap, Phys. Rev. **79**, 286 (1950).
[5] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).
[6] Pearson, Haynes, and Shockley, Phys. Rev. **78**, 295 (1950).
[7] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

"Closed" Fountain Effect in Liquid Helium II*†

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THE rise in the liquid level of a closed system of helium II through which a heat current is passing has been observed. The rise is attributed to a stress which is the difference between the thermomechanical tension given by H. London's equation, $\Delta p=\rho S\Delta T$,[1] and a Hooke's law type stress.

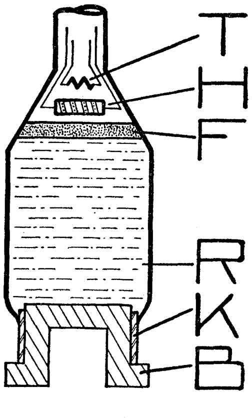

FIG. 1. Diagram of the closed, rouge-packed, glass-metal system.

Figure 1 is a diagram of the apparatus used. It consists of a glass tube which was packed with rouge powder (R) and which