crystal B was quenched to the dark value by infrared but the attenuation effect in crystal A was unaffected by infrared.

A semiquantitative spectrographic analysis revealed little difference between the two crystals. In Table I are included some properties of the two crystals A and B and also those of a third crystal, C, upon which qualitative measurements have been made.

Two types of mechanisms are being considered as possible explanations of the ultrasonic attenuation changes: (1) relaxation associated with electron or hole trapping at impurity or vacancy sites, or with electron transitions at sulfur photoactivation sites, and (2) changes in thermoelastic attenuation losses due to heat conduction by photoactivated electrons. It is believed that the ultrasonic attenuation effect may be found in other photosensitive crystals and may be a useful tool for solid state investigation of photoconductors.

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[2]D. R. Boyd and Y. T. Sihvonen, J. Appl. Phys. 30, 176 (1959).

EXPERIMENTAL PROOF OF THE EXISTENCE OF A NEW ELECTRONIC COMPLEX IN SILICON

J. R. Haynes
Bell Telephone Laboratories, Murray Hill, New Jersey
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Recombination radiation from silicon crystals containing one of the group III or group V elements as an added impurity has recently been examined using a spectroscope of high resolution. Extremely sharp lines appear at low temperatures. It will be shown that these lines can only be interpreted as the radiation produced by the recombination of an electron and a hole both of which are bound in an immobile four-particle complex consisting of an impurity ion and three electronic particles.

Excess electrons and holes were produced in silicon single crystals by illumination with a high-intensity light beam.[1] These carriers recombine in thermal equilibrium with the crystal lattice giving recombination radiation. The intensity of this radiation as a function of photon energy is shown in Fig. 1 for two different silicon specimens at 25°K: (1) a crystal containing a negligible amount of impurity, shown by the dashed line; (2) a crystal containing arsenic added to the melt in the crystal growing process, shown by the solid line.

The dashed trace is essentially all intrinsic recombination radiation produced by the recombination of excitons with simultaneous photon and phonon emission. The energy of the exciton, E_0,

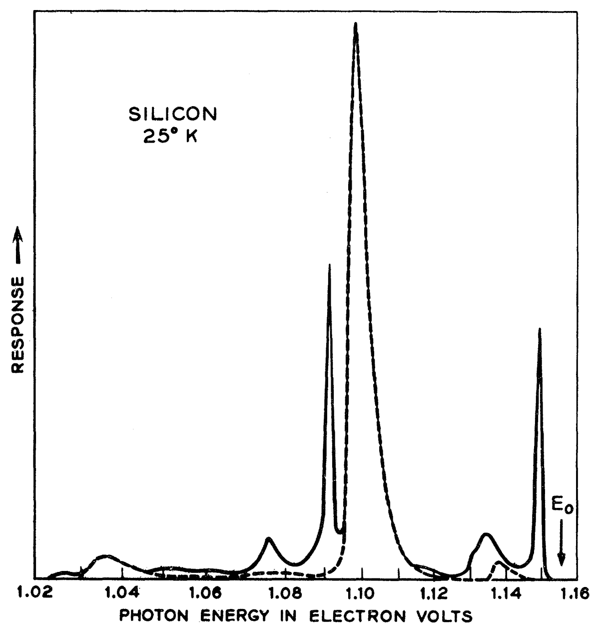

FIG. 1. Spectrometer response (nearly proportional to the number of photons/unit energy interval) as a function of the energy of the photons for two silicon crystals: (1) A specimen containing a negligible amount of impurity, shown by the dashed trace. (2) A specimen containing 8×10^{16} cm^{-3} arsenic atoms, shown by the solid trace.

is shown at 1.156 ev which is less than the energy gap by an amount equal to the exciton binding energy. The principal line is produced by the recombination of excitons that conserve crystal momentum by the emission of a transverse optical (TO) phonon. The line width is primarily due to differences in thermal velocities of the excitons. The line shape is given by a Boltzmann energy distribution with a small amount of broadening produced by exciton collisions with the crystal lattice.

The result of adding 8×10^{16} cm^{-3} arsenic atoms to the silicon in the crystal-growing process is shown in Fig. 1 by the solid trace. The prominent change produced by adding the arsenic is to introduce two new sharp lines at 1.091 and 1.149 ev. These lines are actually much narrower than shown in Fig. 1 since their half-intensity width, W, is the effective slit width of the spectrometer. By narrowing the spectrometer slit, at the expense of signal to noise ratio, it has been found that $W < 0.0005$ ev. Evidently the lines are produced by the recombination of an electron and hole both of which are immobilized, since if either were free to move the lines would have the width of a Boltzmann energy distribution.

The ratio of the integrated intensity in the sharp lines to that in the principal exciton line is found to be proportional to the amount of arsenic added. Therefore, the recombining hole and electron responsible for the sharp lines are bound in some kind of complex to single arsenic atoms.

The energy difference of the two sharp lines is the energy of the TO phonon. Evidently recombination proceeds both with and without phonon emission. In the latter case the crystal momentum is conserved with negligible energy loss by giving it to the crystal as a whole via the arsenic atom with which the hole and electron are associated.

The energy, E_D, required to free the bound electron and hole as an exciton from the complex has been measured from the energy displacement of the lines. Since the sharp line at 1.091 ev and the main exciton line are both produced by emission of the same phonon, E_D is the energy difference between the center of the sharp line and the radiation produced by recombining excitons having zero thermal energy (obtained by a Boltzmann energy curve fit to the exciton line). This energy has also been calculated from measurements of the amount that the sharp lines shrink with respect to the exciton line as the temperature of the silicon crystal is increased.[2] Both ways of obtaining E_D give values very close to 0.0065 ev.

These same sharp lines appear when other group V donors are substituted for arsenic as an impurity. The lines, however, are displaced in energy in a regular way. The dissociation energies of the complex produced by adding donors are shown in Fig. 2 plotted as a function of the ionization energy of the donor, E_i (open circles). To a good approximation $E_D = 0.1E_i$.

This energy relationship identifies the complex as a hole bound to a positive donor ion by an electron pair bond, since the other two possibilities are eliminated as follows: (1) It cannot be a hole bound by a single electron to the donor ion since then $E_D = E_i - E_x + E_h$, where E_h is the binding energy of the hole, and the binding energy of the exciton, $E_x \approx 0.007$ ev.[3] Therefore, $E_D \gtrapprox E_i$ for this model. (2) It cannot be an exciton trapped at a neutral donor by mutual polarization since then E_D would decrease as E_i increases.

These sharp lines are also produced by adding group III acceptors to silicon. The dissociation energies of the complex responsible for the lines are also shown in Fig. 2 as a function of the ionization energy of the acceptor introduced (solid circles). Again it is found that $E_D = 0.1E_i$. Therefore, this complex is identified by iden-

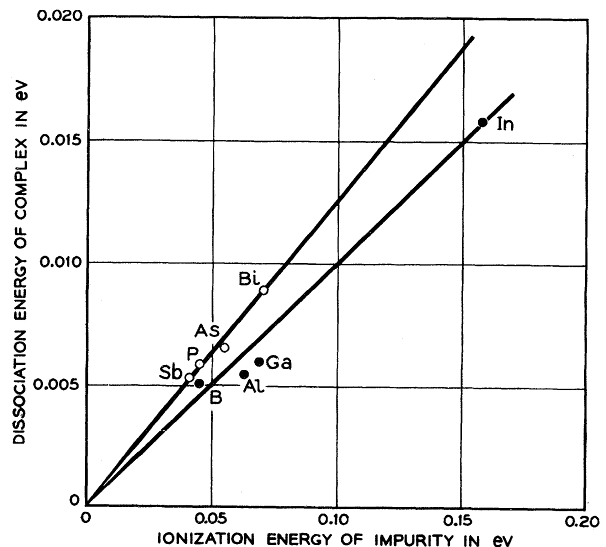

FIG. 2. Energy required to remove an exciton from the complex as a function of the ionization energy of the impurity involved.

tical reasoning as the same complex that was obtained by adding donors, except for complete charge sign reversal. It is an electron bound to a negative acceptor ion by a hole pair bond.

The existence of this complex was pointed out by Lampert[4] who estimated its dissociation energy for equal masses of electrons and holes from Ore's calculation[5] of the minimum dissociation energy of a positron bound to a negative hydrogen ion. However, since Ore's calculated value is more than an order of magnitude too low,[6] Lampert's estimate of E_D is correspondingly in error. This is shown by a simple argument by Kohn[7] who is able to place E_D between $0.055E_i$ and $0.35E_i$ in satisfactory agreement with experiment.

It is a pleasure to thank M. Lax for helpful discussions and W. F. Flood for the specimens and data.

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[1]J. R. Haynes, Methods of Experimental Physics, edited by K. Lark-Horovitz and V. A. Johnson (Academic Press, Inc., New York, 1959), Vol. 6, Part B, p. 322.

[2]The equation used is $R_1/R_2 = (T_2^{3/2}/T_1^{3/2}) \exp(E_D/kT_1 - E_D/kT_2)$, where R is the ratio of the area under the sharp lines to that under the exciton line at temperature T. A factor N_1/N_2 should be included if the neutral donor population changes significantly between T_1 and T_2.

[3]G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958).

[4]M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).

[5]A. Ore, Phys. Rev. 83, 665 (1951).

[6]Using the experimentally determined value of $E_D = 0.1E_i$ and reversing Lampert's argument, we obtain a value for the dissociation energy of a positron bound to a negative hydrogen ion (or an electron bound to an antiproton by two positrons) of $0.1(13.6) = 1.4$ ev. This is 20 times as large as Ore's calculated value.

[7]Walter Kohn (personal communication). His reasoning follows: For donor impurities the minimum energy of the complex will occur when the effective mass of the hole, $m_h \ll m_e$, the effective mass of the electron. For this condition the "Bohr radius" of the hole is so much larger than that of the two electrons that the system can be considered as consisting of a hole bound to a single negative electronic charge of relatively infinite mass. The dissociation energy $E_D = E_1 + E_2 - E_x$, where E_1 is the energy required to remove the hole, E_2 is the energy required to remove one of the electrons, and E_x is the energy gained in forming an exciton out of the freed electron and hole. But $E_1 = E_x$ so that $E_D/E_i = E_2/E_i$, where E_2 is the energy required to remove an electron from a negative hydrogen ion (0.75 ev) and E_i is the ionization energy of hydrogen (13.6 ev). Thus, the minimum energy of $E_D/E_i = 0.055$. The value of E_D/E_i will increase monotonically with m_h/m_e, reaching (when $m_h \gg m_e$) the asymptotic value E_D/E_i = (dissociation energy of a hydrogen molecule)$/E_i = 4.5/13.6 = 0.33$.

SEARCH FOR DOUBLE-QUANTUM EMISSION IN THE DECAY OF Xe^{131m}

Torsten Alväger and Hans Ryde
Nobel Institute of Physics, Stockholm, Sweden
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As a competing process to the single-quantum decay of an excited nuclear state there is a double-quantum transition in which two gamma rays or conversion electrons are emitted simultaneously.[1,2,3] This second order process gives rise to a continuous distribution of the emitted gamma rays. The structure of this distribution depends mainly on the multipolarity of the two transitions. To date no experimental evidence has been found for the existence of two-quantum emission.

The possibility for detecting two-quantum emission should be largest when the single quantum transition is suppressed. This is, for example, the case in the $0+ \to 0+$ transition in Zr^{90}, where a single gamma transition is forbidden. The intense bremsstrahlung from the decay of Y^{90} seems, however, to make the observation of the double-quantum emission difficult. Another possibility for studying the double-quantum emission is in connection with a transition of high multipolarity. In this case the de-excitation can occur also by the emission of two quanta of lower multipolarities. This should be the situation in the decay of the isomeric $h_{11/2}$ level in Xe^{131} to the ground state by the 164-kev $M4$ transition. The relative intensity of any other gamma ray in this decay is estimated to be very low. Using an harmonic oscillator potential, Eichler and Jacob[3] have calculated the ratio between the transition probabilities for double- and single-quantum emission in the decay of Xe^{131m}. They obtained the ratio 5×10^{-5}. The weak, two-quantum distribution is very difficult to observe di-