absorption edge in rutile is due to the partici-
pation of different energy phonons in the fun-
damental absorptions of the two polarizations
of the light. Clearly, the impurity observed
here is capable of affecting the degree of di-
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EXPERIMENTAL OBSERVATION OF THE EXCITONIC MOLECULE

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The purpose of this Letter is to present ex-
perimental observations of the excitonic mole-
cule, a stable complex in Si consisting of two
electrons and two positive holes. It is hoped
that this information will provide the impetus
for the discovery of its effects in a wide va-
riety of other materials.

The history of excitonic molecules goes back
to 1946 when Wheeler[1] gave theoretical evidence
for the existence of entities composed entire-
ly of electrons and positrons. He considered
an electron bound to a positron, an electron
bound to two positrons, and two electrons bound
to two positrons. He concluded that the first
two entities should be stable against dissocia-
tion but not the last. The next year Hylleraas
and Ore[2] showed that this entity should also
be stable and gave it the name "positronium
molecule." While evidence for the existence
of the first of Wheeler's entities, positronium,[3]
was found by Deutsch[4] and later by many others,
no evidence for the existence of the positro-
nium molecule has been reported.

In 1958 Lampert[5] pointed out that Wheeler's
entities should exist in nonmetallic solids with
positive holes in the role of positrons. He named
the entity produced by binding two positive holes
to two electrons an "excitonic molecule."

The binding energy of the excitonic molecule
can be estimated in two ways. (1) From the
binding energy of the exciton in silicon, E_X
$= 8 \times 10^{-3}$ eV,[6] and the calculated value of the
ratio of the dissociation energy of positronium,[1]
$E_{Ps} = 6.8$ eV, to that of the positronium mole-
cule,[7] $E_{Ps_2} = 0.135$ eV, $E_{Ps}/E_{Ps_2} = E_X/E_{X_2}$,
$E_{X_2} = 0.16$ meV. (2) It has been shown[8] that
binding energy of an exciton trapped at a neu-
tral donor (or acceptor) is ~0.1 the ionization
energy of the donor (or acceptor), so that E_{X_2}
$= 0.1E_X$ ~0.8 meV.

Evidence for the existence of the excitonic
molecule was obtained from the recombination
radiation from Si at low temperatures. The
Si specimen was immersed in liquid He which
was pumped below λ transition. High concen-
trations of excess electrons and holes were
produced by focusing the light from a mercury
arc[9] on one side of the specimen. Recombina-
tion radiation from the opposite side was an-
alyzed with a spectrometer, detected by a lead
sulfide cell, and recorded on a chart.

All of the detectable intrinsic recombination

radiation from Si at 18°K is produced by the recombination of excitons with phonon emission.[10] A reproduction of a recorder trace of recombination radiation at ~3°K is shown in Fig. 1. The radiation at E is due to exciton recombination with emission of the transverse optical (TO) phonon. Radiation due to exciton recombination with emission of the transverse acoustical (TA) phonon and that due to simultaneous emission of two TO phonons, seen at 18°K, is not visible here since the amplitude of these lines is much less. New radiation which dominates the spectrum occurs at M_1, M_2, and M_3. The maxima of these lines all fall 15 meV below the intrinsic exciton phonon replicas mentioned above. Even the relative amplitudes of analogous lines are the same within a factor of 2.

The equivalence of the phonons involved to conserve crystal momentum in the recombination of both excitons and the new radiation shows that the band structure involved is the same in both cases and, therefore, the radiation cannot be a surface phenomenon but must occur in the volume of Si.

The radiation from seven specimens has been examined. These had resistivities in the range

10^3 to 10^4 Ω cm. They include both n and p type obtained from three different sources of supply. All showed the new radiation below ~10°K. Evidently the radiation is an intrinsic property of pure Si.

The definitive test of the origin of this radiation is its dependence on carrier concentration. The carrier concentration was changed by changing the exciting light intensity.[10] The result is shown in Fig. 2. The exciton recombination radiation, which is proportional to the exciton concentration n_X, increases linearly with light intensity. This is the expected result for constant carrier lifetime, since at this low temperature essentially all of the excess electrons and holes are bound as excitons so that $n_X = n = p$ where n and p are the total excess electron and hole concentrations including those bound as excitons. Most importantly, the amplitude of the line M_1 increases as the square of the exciton line, showing that two excitons are required for its production.[11] Two free excitons, however, cannot be involved. Much higher concentrations of excitons are produced at 18°K than at 3°K, as shown by the exciton recombination-line amplitudes,[12] yet no detectable radiation occurs at M_2. It is, therefore, evident that the effect of the low temperature is to permit the binding of two
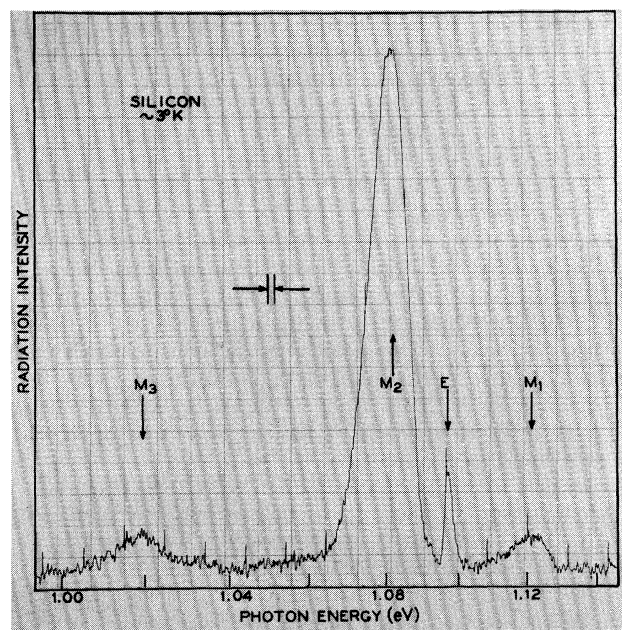

FIG. 1. Spectrogram of a Si specimen at ~3°K. The horizontal axis is the energy of the emitted photons in eV. The vertical response is nearly proportional to the number of photons per unit energy interval. The specimen resistivity at room temperature was 9×10^3 Ω cm.
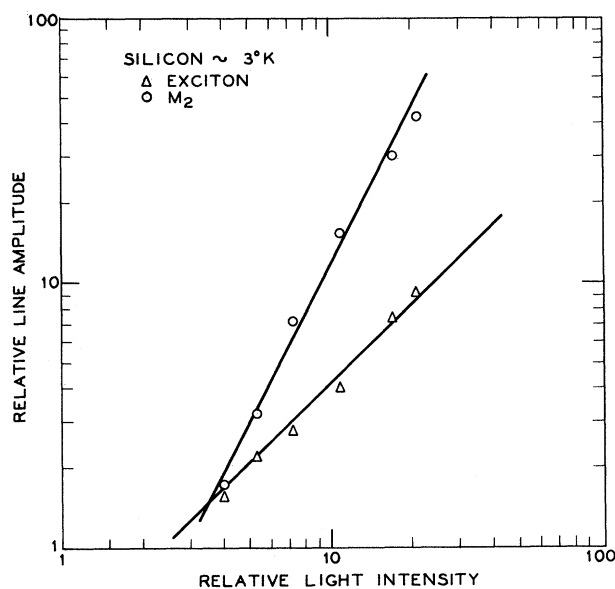

FIG. 2. Relative amplitude of the line M_2 and the exciton line E as a function of the relative light intensity. The lines are drawn with slopes of 1 and 2.

excitons together into a single complex. This complex is called the excitonic molecule.[13]

The energies and shapes of the lines show that the radiative transitions occur by the recombination of an electron and hole with phonon emission, and that the remaining electron and hole are ejected to the conduction and valence bands. The energy of the emitted photon is

$$h\nu = E_g - 2E_X - E_{X_2} - E_K - \hbar\omega + E_T, \tag{1}$$

where E_g is the energy band gap, E_X the exciton binding energy, E_{X_2} the excitonic molecule binding energy, E_K the kinetic energy of the ejected electron and hole in the conduction and valence bands, $\hbar\omega$ the energy of the emitted phonon, and E_T the thermal translational energy of the excitonic molecule. The line shapes are qualitatively in agreement with Eq. (1). The rapid rise on the high-energy side is due to the increase in the number of states available to the ejected electron and hole, while the drop on the low-energy side is produced by the decreasing probability that the transition includes electrons and holes of increasing kinetic energy. The line is broadened by E_T. A small amount of tailing appears on the high-energy side. This is at least mostly due to recombination of excitons trapped on impurities since this tailing varies between specimens.

A crude measure of the binding energy can be obtained by extrapolating the high-energy side of both the excitonic-molecule and the exciton lines to zero. By this construction $E_K \rightarrow 0$. For exciton recombination the emitted photon has energy

$$h\nu_X = E_g - E_X - \hbar\omega + E_T, \tag{2}$$

where E_T is the thermal translational energy of the exciton and E_T of Eq. (1) $= E_T$ of Eq. (2) by equipartition of energy. Subtracting Eq. (1) from Eq. (2) gives $\Delta h\nu = E_X + E_{X_2}$. Experimentally, $\Delta h\nu = 10$ meV, so that if $E_X = 8$ meV the value of E_{X_2} is 2 meV, but the uncertainty in E_X is ~2 meV. Therefore, at present, the best experimental value is $E_{X_2} \lesssim 2$ meV, but Eq. (1) is justified.

Further details will be included in a paper intended for publication elsewhere.

It is a pleasure to acknowledge helpful conversations with M. Lax and W. L. Brown, and the essential experimental assistance of W. F. Flood.

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[10]This experiment presented experimental problems since the radiation M is strongly temperature dependent. The exciting light power used in obtaining the spectrogram of Fig. 1 was ~1 W. The temperature of the He was 1.9°K but the temperature of the Si was higher due to the Kapitza resistance. The exciting light intensity was, therefore, reduced by defocusing the light spot so that the total energy on the specimen was held constant and the Si temperature change was small. The intensity of the light spot at the place on the Si "seen" by the spectrometer was calibrated by increasing the Si temperature to liquid N_2 and measuring the exciton-line amplitudes as a function of defocusing-lens turns. Previous measurement showed that at this temperature and excitation the amplitude of the exciton line increases as the square of the light intensity which was changed with a diaphragm and calibrated with a thermocouple. This is the expected result for constant carrier lifetime since few excess holes and electrons are bound as excitons and $n_X \propto n_p$.

[11]Since the ratio of the amplitudes of lines M_1, M_2, and M_3 remain fixed, as expected of phonon replicas, they also increase as the square of the exciton line.

[12]This fact is explained by a decrease in lifetime of the excess carriers between 18 and 3°K, so that the equilibrium concentration of n and p is much less at 3°K. In Si, carrier lifetime is controlled by processes involving phonon emission.

[13]It cannot be an electron bound to two holes (or a hole bound to two electrons) since then $M \propto n_X^{3/2}$. Also it would be impossible to explain the line position since the binding energy of two excitons is required by Eq. (1).
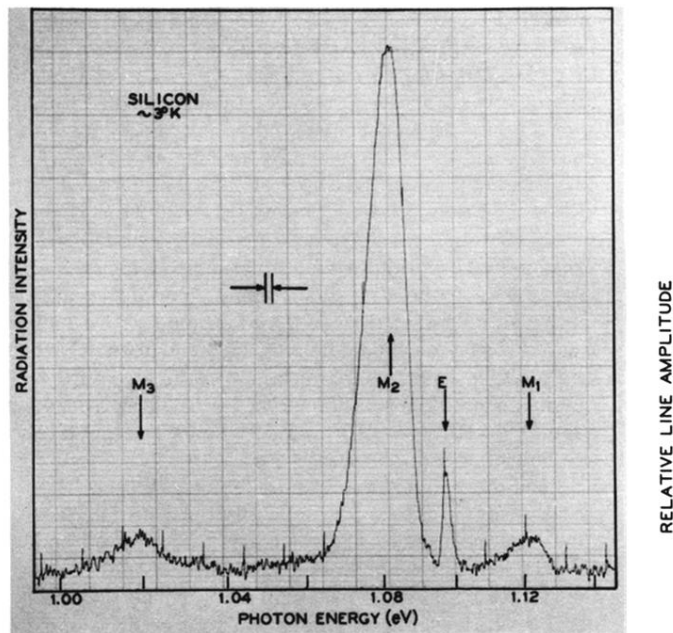
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