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Author

Haller, E.E.

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E.E. Haller

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Hydrogen in Crystalline Semiconductors

Eugene E. HALLER

University of California at Berkeley

and

Materials Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720 USA

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1. Introduction

The role of hydrogen has attracted significant interest from many members of the broad semiconductor research community in recent years. The reasons for this rise in research activity can be traced to the rich spectrum of interactions of hydrogen with impurities and defects in crystalline semiconductors. The ease of creating many of these interactions, the vast arsenal of characterization techniques which can be brought to bear, and last but not least, the theoretical contributions, both predictive and confirmative, have led rapidly to a rather mature state of understanding.

After an "incubation" period in the 1970's and early 80's, during which the first hydrogen related centers were discovered and characterized in ultra-pure germanium (1-4), a sharp increase of research activity occurred after the discovery of shallow acceptor passivation in crystalline silicon (5-7). In the meantime many hydrogen related centers and effects have been found in several III-V compound semiconductors and their alloys. Little activity regarding hydrogen in other semiconductors, e.g. II-VI compounds and their alloys, has been reported. Is this due to experimental and/or theoretical difficulties or have these communities simply not yet entered the field?

The aim of this review is to convey an insight into the rich, multifaceted physics and materials science which has emerged from the vast variety of experimental and theoretical studies of hydrogen in semiconductors. In order to arrive at the current understanding of

HYDROGEN IN CRYSTALLINE SEMICONDUCTORS

EUGENE E. HALLER

*Lawrence Berkeley Laboratory
and
University of California at Berkeley
Berkeley, California 94720 USA*

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ABSTRACT

The state of the current understanding of hydrogen in elemental and compound semiconductors is reviewed. The results of new experimental and theoretical studies of the microscopic structure of acceptor-hydrogen and donor-hydrogen complexes are presented. Questions regarding hydrogen tunneling in some of the acceptor and donor complexes in elemental semiconductors, as well as the problem of electronic states of isolated hydrogen, are discussed in light of the most recent experimental findings. Also, some promising areas of future research are indicated.

1. Introduction

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After an "incubation" period in the 1970's and early 80's, during which the first hydrogen related centers were discovered and characterized in ultra-pure germanium (1-4), a sharp increase of research activity occurred after the discovery of shallow acceptor passivation in crystalline silicon (5-7). In the meantime many hydrogen related centers and effects have been found in several III-V compound semiconductors and their alloys. Little activity regarding hydrogen in other semiconductors, e.g. II-VI compounds and their alloys, has been reported. Is this due to experimental and/or theoretical difficulties or have these communities simply not yet entered the field?

The aim of this review is to convey an insight into the rich, multifaceted physics and materials science which has emerged from the vast variety of experimental and theoretical studies of hydrogen in semiconductors. In order to arrive at the current understanding of

hydrogen related phenomena in a logical way, each chapter will start with a brief review of the major experimental and theoretical advances of the past few years. These will be followed by succinct summaries of some of the unanswered questions which will in turn point to areas for future research. It is not possible to give a complete and detailed review of the field in the space available. Those who are interested to learn more about this fascinating area of semiconductor research are referred to reviews (8,9), to a number of conference proceedings volumes (10), and to an upcoming book (11) which will contain authoritative chapters on most aspects of hydrogen in crystalline semiconductors.

As is the case for much semiconductor research, the study of hydrogen has been stimulated by both basic scientific curiosity as well as technological interest. Some of the early art of semiconductor device processing can finally be put on a scientific foundation and new ways of arriving at advanced device structures begin to use what we have learned from the basic studies of hydrogen in semiconductors (12).

This review is structured along the hydrogen related phenomena, not according to the semiconductor materials types. This makes for direct and easy comparison of the properties of hydrogen-containing impurity and defect complexes, of isolated hydrogen and of the dynamic aspects of hydrogen in the various semiconductors. Where appropriate, I will also draw comparisons to other interstitial impurities which were shown to passivate acceptors a long time ago. The long hoped for analogy between hydrogen and its light counterpart muonium has recently been established, furthering the understanding of the properties of both particles in semiconductors.

This survey will intentionally not cover phenomena produced by hydrogen implantation, radiation defect and deep level hydrogen interactions, and amorphous materials. Research in these areas is vigorous and much interesting physics has been learned, but the limited

space simply does not allow a discussion of all these experiments and theoretical contributions. I apologize to all my colleagues whose important contributions I am not able to properly address and reference in this text.

2. Hydrogen Containing Complexes

2.1 Neutral shallow acceptor- and donor-hydrogen complexes

Because the shallow acceptor-hydrogen and shallow donor-hydrogen complexes in Si are the most thoroughly studied centers, I will begin this section with a brief review of the major experimental and theoretical results which have led us to today's level of understanding. The experimentalists working with acceptor- and donor-hydrogen complexes in Si and III-V semiconductors made excellent use of a number of fortuitous circumstances. These include the possibility of forming high concentrations of these complexes which allows the application of many analytical tools; the ease of introducing hydrogen from the crystal surface at low temperatures to depths of a few μm ; the completeness of the reactions forming neutral dopant hydrogen complexes (especially for the case of acceptors in Si) which eliminates interference from residual electrically active dopants; and the existence of deuterium with twice the mass of hydrogen which increases the sensitivity of secondary ion mass spectrometry by a factor of 500 and allows unambiguous identification of hydrogen local vibrational modes through isotope shifts.

Perhaps the greatest impetus for the rise in interest in hydrogen in semiconductors came from the discovery of the deactivation of acceptors near the Si-SiO₂ interface in MOS structures by Sah *et al.* (5), followed by the direct hydrogen plasma exposure experiments of Pankove *et al.* (6,7). Hydrogen was implicated by both groups as the cause for the removal of free holes in the p-type silicon. Secondary ion mass spectrometry (SIMS) of deuterium RF plasma exposed p-type silicon wafers showed that the acceptor and the

deuterium concentrations were identical in the deactivated region (13). The deactivation of acceptors by another impurity immediately reminds us of the well known lithium compensation and passivation of acceptors in Si and Ge (14). The fact that one did not observe donors compensating acceptors but the formation of neutral acceptor-hydrogen complexes was established through a series of elegant far infrared local vibrational mode (LVM) spectroscopy experiments by Stavola *et al.* (15). The strong dependence of the hydrogen stretch vibration frequency on the mass of the acceptor clearly indicates that hydrogen is bound directly to the acceptor. The ratio of hydrogen and deuterium LVM frequencies lies close to $\sqrt{2}$, establishing the observation of a single vibrating hydrogen atom. The fact that the frequency ratio is not precisely equal to $\sqrt{2}$ is related in most cases to the reduced mass of the complete set of atoms involved in the local vibration. Newman (16) interprets the deviation from $\sqrt{2}$ for the Sn-H and Sn-D stretch vibrations in GaAs with anharmonicity of the vibrational mode.

The early results were supported and complemented by a vast series of experiments making use of various characterization techniques, as well as by theoretical models and calculations. Ion beam channeling, making use of specific nuclear reactions, established the precise location of the passivated boron acceptor (17) and of the hydrogen bound near a bond center (BC) position (18). Uniaxial stress LVM spectroscopy by Bergman *et al.* (19) unambiguously showed the acceptor-hydrogen complexes to have trigonal symmetry (Fig. 1).

Theoretical efforts have been successful in explaining, and in some cases in predicting, the experimental findings. The hydrogen stretch vibration frequency ($\nu_{\text{stretch}}=1875 \text{ cm}^{-1}$) of the B-H complex in Si was reproduced by DeLeo and Fowler (20) who also predicted the LVM frequency of the Al-H center ($\nu_{\text{stretch}}=2201 \text{ cm}^{-1}$) with excellent accuracy. Several calculations lend strong support to the trigonal acceptor-hydrogen complex model

with a proton (H^+) residing near a bond center (BC) site in one of the four acceptor bonds (21-24) and we may safely conclude that this model is definitive.

This does not mean, however, that all the details are understood. The Al-H and Ga-H LVM spectra in Si show low energy sidebands whose origins are still not fully understood (15). A further problem is related to the absence of wagging modes of the acceptor-hydrogen complexes. Such vibrations have not been found in the expected frequency range between 600 and 800 cm^{-1} . Pajot *et al.* (25) discovered an unusual difference between the effect of the substitution of ^{10}B with ^{11}B on the hydrogen and deuterium stretch vibrations. The D stretch frequency shifts by 3.3 cm^{-1} , whereas the H frequency moves only by 0.8 cm^{-1} . Watkins *et al.* (26) have recently proposed an explanation of this difference on the basis of a Fermi resonance.

In closing the discussion on acceptor-hydrogen complexes in p-type Si, I would like to draw the reader's attention to an informative theoretical comparison of the structures of boron in Si compensated by hydrogen, lithium and copper. Calculations by Estreicher (27) show the stable position for H^+ to be BC while Li^+ and Cu^+ occupy an antibonding (AB) site (Fig. 2). This work was stimulated not only by the hydrogen related findings but also in part by the well established passivation of acceptors by Li (14); an effect which had been used extensively for many years in the fabrication of large volume lithium drifted germanium gamma ray detectors (28) and lithium drifted Si X-ray and particle detectors, (29) and by the very recent observation that boron and other shallow acceptors are passivated in Si by polishing wafers (30). The theoretical findings together with perturbed angular correlation (PAC) position decay experiments (31) and additional experimental evidence (32) show that polishing related passivation is not hydrogen related but most likely due to rapidly diffusing interstitial copper.

Deactivation of shallow donors was discovered in Si by Johnson *et al.* (33). Donor passivation escaped experimental observation for several years due in part to the lower degree of passivation, to some difficulties in introducing H into n-type Si, and to the lower thermal stability of these complexes. Spectroscopic studies by Bergman *et al.* (19) showed that the H-stretch and wag vibrations have frequencies which are almost donor mass independent. Uniaxial stress measurements produce orientational splittings which are fully consistent with trigonal hydrogen-donor complexes (19). These experimental results are supported by model calculations which have improved much over recent years. They strongly suggest that H⁻ binds to a Si atom in the antibonding position which is in a straight extension of the Si-donor bond (Fig. 3). The recent models can reproduce LVM frequencies with reasonable accuracy. Zhang and Chadi (34) obtain $\nu_{\text{stretch}} = 1290 \text{ cm}^{-1}$ and $\nu_{\text{wag}} = 715 \text{ cm}^{-1}$, while Denteneer *et al.* (35) arrive at $\nu_{\text{stretch}} = 1460 \text{ cm}^{-1}$ and $\nu_{\text{wag}} = 740 \text{ cm}^{-1}$, as compared to the experimental values for the P-H complex of $\nu_{\text{stretch}} = 1555 \text{ cm}^{-1}$ and $\nu_{\text{wag}} = 809 \text{ cm}^{-1}$, respectively.

The understanding of hydrogen-acceptor and -donor complexes in GaAs, Al_xGa_{1-x}As, GaP, and InP has also progressed significantly in recent years. Comprehensive reviews have been written by Pajot (36). Though the studies in III-V semiconductors are less extensive than in Si and mostly limited to LVM spectroscopy, deuterium SIMS, and C/V measurements, it has been shown unambiguously that hydrogen can passivate group II acceptors (37,38,39) and group IV donors and acceptors (9,40,41,42). All these centers have trigonal symmetry, as determined by uniaxial stress experiments (43,44). It is interesting to note that H-related infrared absorption peaks have been found in bulk InP and in epitaxially grown InP layers which were capped with InGaAs (36). In the former case the hydrogen source is traced to wet B₂O₃ which acts as an encapsulation layer during crystal growth, while the latter effect can be traced to AsH₃ used to grow the capping layer.

From the values of ν_{stretch} and ν_{wag} found in GaAs:Si it has been concluded that hydrogen binds directly to the Si_{Ga} donor and lies in an AB location opposite a broken bond between Si_{Ga} and one of its As neighbors (Fig. 4). Further evidence comes from two small, higher frequency absorption peaks which are assigned to the stable isotopes of ^{29}Si and ^{30}Si , both present at concentrations of a few percent in natural silicon (43). Both the peak heights and the LVM frequencies support this assignment. Arsenic forms three bonds and has a lone electron pair, a configuration which is common for this group V element. Similar observations have been made for Sn_{Ga} donors. *Ab initio* calculations support the AB site for an H^- compensating the donor (45).

There exists little direct experimental evidence for passivation of shallow acceptors and donors by hydrogen in germanium. Ultra-pure germanium crystals which are H_2 atmosphere grown exhibit a strong radial net-dopant gradient, often called "coring" (46), which has been explained with the passivation of residual shallow acceptors by hydrogen. Near the crystal surface the excess hydrogen can out-diffuse during the cooling down cycle and acceptors do not become passivated in the near surface region. This in turn leads to the often observed p-type "skin", the thickness of which can range from a fraction of a mm to a few mm. Long term annealing at moderate temperatures (300-400°C) removes the radial gradient supposedly by homogenizing the hydrogen concentrations. From the limited information available one can conclude that the shallow level impurity-hydrogen complexes have low thermal stability and that other more stable complexes compete for the available interstitial hydrogen.

2.2 Partially passivated centers

Multivalent dopants, e.g. double acceptors, can be partially passivated under appropriate circumstances. For a double acceptor this means that one of the negative core charges is screened by a nearby proton while the second core charge still binds a hole. The proton effectively reduces the two acceptor levels of the double acceptor to one level which is typically shallower than either of the levels of the isolated double acceptor. A number of such centers have been studied in Si and in Ge. An interesting facet of these centers is the possibility of studying the symmetry of the structure via optically induced ground state to bound excited state transitions of the remaining hole.

Far infrared Fourier transform spectroscopy has produced high resolution spectra of the acceptors A(Be,H) and A(Zn,H) in Ge (47,48,49) and A(Be,H) in Si (50,51). The latter exhibits a spectrum which has been interpreted with tunneling hydrogen. We will return to this topic in section 3. Recent spectroscopic studies of zinc in hydrogen or deuterium containing silicon samples by Merk *et al.* (52) give strong indications that a single acceptor A(Zn,H) exists.

The dipole formed between the negatively charged double acceptor core and the nearby positive proton splits the fourfold degenerate s-like ground state of the remaining hole into two components. Kahn *et al.* (53) used uniaxial stress spectroscopy to show that these centers have trigonal symmetry. They found it convenient to model the ground state splitting with an equivalent uniaxial stress S at the impurity core. This local stress only affects the s-like states but leaves p-like bound excited states unchanged. Using this approach, it is very simple to evaluate the effects of external uniaxial stress on the optical transition spectrum. Fig. 5 (Fig. 6 in Kahn *et al.* (53)) shows the splitting of the ground state of A(Be,H) in Ge under compressional uniaxial stress in the [111] direction.

An internal stress $S = -0.81$ kbar leads to an excellent fit of the theory to the data. The experimentally determined line positions correspond precisely to the theoretical prediction.

The concentrations of the acceptors $A(\text{Be},\text{H})$ and $A(\text{Zn},\text{H})$ amount to about 1% of the isolated dopant concentration in Ge single crystals grown in a 1 atm H_2 ambient. The thermal stability of both centers has been determined using variable temperature Hall effect and annealing. Fig. 6 displays the free hole freeze-out curve of a beryllium doped Ge single crystal for various annealing cycles. The high temperature section in which the free hole concentration drops from $\sim 10^{15} \text{ cm}^{-3}$ to $\sim 10^{13} \text{ cm}^{-3}$ is due to the freezing out of the $E_v + 25 \text{ meV}$ level of $\text{Be}^{0/-}$ (48,49). A shallow acceptor with a concentration close to $\sim 10^{13} \text{ cm}^{-3}$ freezes out at a shallower slope in the "AS GROWN" sample. Spectroscopy shows that this is mainly the acceptor $A(\text{Be},\text{H})$. Annealing cycles at temperatures between 600 and 700°C are required to break up this complex. Haegel (49) determined the dissociation energy E and the prefactors ν of $A(\text{Be},\text{H})$ and $A(\text{Zn},\text{H})$. She found: $\nu(A(\text{Be},\text{H})) = 3 \times 10^8 \text{ s}^{-1}$ and $E(A(\text{Be},\text{H})) = 2.1 \pm 0.6 \text{ eV}$; $\nu(A(\text{Zn},\text{H})) = 3 \times 10^{12} \text{ s}^{-1}$ and $E(A(\text{Zn},\text{H})) = 3.0 \pm 0.3 \text{ eV}$. These values show that the double acceptor-hydrogen complexes in Ge are bound much more strongly than shallow acceptor-hydrogen complexes.

A further center which has yielded much interesting physics is the triple acceptor copper-dihydrogen complex $A(\text{Cu},\text{H}_2)$. Like $A(\text{Be},\text{H})$ in Si this center shows dynamic effects of hydrogen and will be discussed further in section 3.

Our knowledge of the interaction between double donors and hydrogen is rather limited. Full passivation of chalcogen double donors in Si has been reported by Pensl *et al.* (54). Recently Peale *et al.* (55) have reported five new donor levels in sulfur doped silicon into which hydrogen was diffused at 1280°C. Three of these donors exhibit isotope shifts

upon substitution of hydrogen with deuterium, providing direct proof of the presence of hydrogen in these impurity complexes. Further studies are required to determine the composition and structure of these new centers.

2.3. Activation of neutral impurities by hydrogen

The first centers in semiconductors which were proven to contain hydrogen were discovered in ultra-pure Ge single crystals after rapid quenching from around 400°C.² It was shown that specific crystal growth conditions are necessary to obtain crystals which contain these centers (4). The typical ultra-pure Ge crystal is grown by the Czochralski technique from a melt contained in a silica crucible and in a H₂ ambient. The residual net-dopant concentration in these crystals can be as low as 10¹⁰ cm⁻³ but the neutral impurities Si, O and H are present at concentrations close to 10¹⁴ cm⁻³. At 400°C a small number of hydrogen atoms becomes mobile (H₂ molecules may dissociate) and upon quenching the isolated hydrogen atoms diffuse to shallow potential wells formed by Si and O. The acceptor A(H,Si) and the donor D(H,O) which reach concentrations of up to 3×10¹¹ cm⁻³ exhibit a number of interesting properties which will be summarized briefly. The acceptor A(H,C) which forms during Ge crystal growth from a graphite crucible has properties which are similar to those of A(H,Si).

The acceptors A(H,Si) and A(H,C) were the first shallow acceptors in Ge which exhibited a split 1s-state manifold (4). Such a splitting is unusual because the top of the valence band is fourfold degenerate and has Γ_8 symmetry. Kahn *et al.* (53) showed that both acceptors are static complexes which have trigonal symmetry. The splitting can be modeled just as in the case of A(Be,H) and A(Zn,H) with a local built-in stress which originates from the electric dipole at the core of the complexes. Fig. 7 shows the transitions from the split

ground state of the acceptor A(H,Si) and the normal shallow acceptor Al for uniaxial compressional stress applied along the [111] orientation. Whereas the Al D line splits symmetrically into two components of about equal strength, the D lines of A(H,Si) split in a 1:3 ratio with intensities 3:1 as expected for a trigonal complex.

It is interesting to note that the built-in stress S for A(H,Si) has a positive value while the partially passivated Be and Zn complexes require a negative S . This difference in sign has been explained with the orientations of the internal electric dipole. Calculations of Denteneer *et al.* (56) showed that Si in Ge indeed binds a H^- in an antibonding position. The calculated binding energies are very small, in agreement with the very low thermal stability of A(H,Si) which anneals already at room temperature. It would be interesting to obtain theoretical results for A(H,C) which is much more strongly bound.

Table I contains the 1s-state energies for the trigonal acceptors A(H,Si), A(H,C), A(Be,H) and A(Zn,H) in Ge. The average energy of the 1s-state components lies very close to the ground state energy of 11.2 meV obtained from effective mass theory (57,58).

During annealing of A(H,Si) in rapidly quenched ultra-pure Ge a donor D(H,O) forms (59). Substitution of H with D leads to an isotope shift of 51 μeV , a direct proof of the presence of hydrogen in this complex (3). The exceptionally sharp lines in the far infrared optical transitions spectrum of D(H,O) are due to the fact that the ground- and the bound excited states are stress insensitive and that the crystals are very pure. Navarro *et al.* (60) used this donor for magnetospectroscopic linewidth studies and found that the line broadening approaches closely the ultimate limit given by final state mixing. A second unusual property of D(H,O) is the abrupt appearance of a lower energy set of transition lines at a critical uniaxial stress.

Fig. 8 schematically shows an energy level series which accounts for all the experimentally observed splittings and thermal population of higher lying states of D(H,O). The labeling of the states is derived from the tunneling hydrogen model (59). This model is based on the rapid motion of the hydrogen bound to oxygen between four equivalent antibonding positions. The nuclear tunneling leads to splitting of the 1s- and the np-states. A competing model (61,62) proposed a static, trigonally distorted complex. Both models can explain a majority but not all of the properties of D(H,O) and only additional experiments appear to be able to determine which of the two models is the correct one.

The detailed studies of the partially hydrogen passivated and of the hydrogen activated centers could not have been performed without a spectroscopic technique which combines spectral resolution with very high sensitivity. The photothermal ionization spectroscopy (PTIS) which was discovered by Lifshits and Ya'Nad (63), relies on a two-step ionization process of an impurity-bound carrier at low temperatures. The first step is the usual optical transition which occurs when an electron (hole) is excited from the groundstate to one of the bound excited states. If the electron (hole) resides in the excited state for a long enough time a phonon may transport it into the conduction band (valence band). In this case the conductivity will change and this change can be detected with modern lock-in techniques with extremely high sensitivity. The PTIS technique works especially well for pure and lightly doped semiconductors in which the bound excited state lifetimes are long and which have very small free carrier concentrations at low temperatures. Grimmeiss *et al.* (64) have used PTIS and absorption in the continuum of shallow levels for the study of deep level centers with effective mass-like bound excited states in silicon. Our group has made

extensive use of PTIS in the study of residual impurities and defect complexes primarily in ultra-pure Ge (4,65).

The major findings from the detailed studies of hydrogen containing complexes are the following:

- Isolated hydrogen is an amphoteric impurity
- Hydrogen can passivate, partially passivate and activate impurities
- Most complexes are static with trigonal symmetry, some are dynamic
- H^+ resides near a BC position next to the acceptor it passivates
- H^- assumes an AB position, bound either to the donor directly (e.g. GaAs:Si_{Ga},H) or to one of the host atoms next to the donor (e.g. Si:P,H)
- All the static, partially passivated and activated centers display a 1s-state splitting which is due to the electric dipole produced between H and the impurity
- Theoretical models which reproduce most properties with good accuracy exist for most of these complexes

3. Isolated Hydrogen

The majority of information on isolated hydrogen has come so far from muon spin resonance (μ SR) studies (66) and from theoretical calculations. The early models focussed on the tetrahedral interstitial site T_d as the most likely position of isolated hydrogen. The study of anomalous muonium (Mu^*) in semiconductors led Cox and Symons (67) to propose the BC site as the most stable position for this light hydrogen analogue ($m_{Mu} \approx 1/9 m_H$). In the meantime a number of theoretical calculations have arrived at the same conclusion for hydrogen (68-71). The total energy contour plot computed by Van de Walle *et al.* (72) for H^+ in Si is shown in (Fig. 9). Contour plots for H^+ , H^0 , and H^- show large differences for the low and the high electron density regions. H^+ placed at BC produces a global minimum. The H^+ at BC should not be viewed as a bare proton. The missing charge resides in a region near the neighboring Si atoms and corresponds to the antibonding state in the silicon energy gap. H^0 also produces a global minimum when placed at BC though the minimum is less deep than for H^+ . A very different behavior is observed for H^- which prefers the T_d site. These calculations describe the static situation at $T=0K$. Each energy value for a given set of coordinates of the energy surfaces is obtained by moving the specific hydrogen charge species infinitesimally slowly to this coordinate and fully relaxing all neighboring silicon atoms. Rapid hydrogen motion which does not allow relaxation of the silicon atoms would lead to very different energy surfaces.

There exists very little experimental information on the states of isolated hydrogen in semiconductors. The obvious search for EPR signals of H^0 remained fruitless until the recent discovery of a signal in low temperature hydrogen implanted silicon. This so-called AA9 spectrum reported by Gorelinski and Nevinnyi (73) displays hyperfine interactions which can be interpreted with hydrogen occupying a BC site. Further information comes from experiments with the hydrogen analogue, muonium. Polarized positive muons (μ^+)

can be implanted, one at a time, into semiconductor crystals. The muon lifetime ($\tau = 2.2 \mu\text{s}$) is long enough for them to thermalize and to find a minimum energy position. When μ^+ binds an electron it forms muonium, a low mass hydrogen analogue. The precession frequency of the muon spin is used as a probe of the local magnetic field and has been developed into a powerful spectroscopy tool called muon spin resonance (μSR) (66). Kiefl and Estle (74) have summarized the μSR studies in semiconductors. They report that in most semiconductors one observes normal and anomalous muonium. They propose that the anomalous muonium spectrum (Mu^*) and AA9 EPR signature of hydrogen in silicon are due to isostructural centers of muonium and hydrogen, respectively.

Whether the analogy between H and Mu can be extended further to impurity-hydrogen complexes is still an open question. The normal muonium (Mu) has full tetrahedral symmetry and is most likely occupying a tetrahedral interstitial site. This site is metastable as predicted by theory and in agreement with the absence of any signals from isolated hydrogen at the T_d site.

This summarizes what is experimentally known at the present time about the structure of isolated hydrogen and muonium. Information on charge states and energy levels in the bandgap of isolated hydrogen in semiconductors is also rather sparse. From electric field drift experiments which will be discussed in section 3.3., we know that hydrogen exists in silicon as H^+ and H^- . This is consistent with the most advanced theoretical calculations (72) which show that H^+ is the energetically preferred state in p-type crystals while H^- dominates in n-type crystals. It is generally assumed that energy levels corresponding to $\text{H}^{0/-}$ and $\text{H}^{+/0}$ lie close to the center of the gap in the case of silicon but so far no precise experimental determination has been made.

The first direct determination of an energy level of $H^{0/+}$ in GaAs appears to have been made by Clerjaud *et al.* (75) in the study of the formation of carbon-hydrogen complexes. Using local vibrational mode spectroscopy they report that the complexes only form in p-type crystals and have been able to localize the energy level of $H^{0/+}$ near $E_v+0.5$ eV. This assignment may only be valid if isolated hydrogen forms a positive U center, i.e., if the $H^{-/0}$ level lies above the $H^{0/+}$ level.

Johnson and Herring (76) have observed a strong deuterium build-up to large concentrations beyond the depletion layer in a reverse biased, hydrogenated n^+ -p-Si junction. H^+ ions drifting through the depletion layers form this large concentration which has been measured as a function of depth by SIMS. No experimental information exists regarding the structure of hydrogen in this region. The most likely form may be interstitial H_2 molecules which are not much larger than hydrogen atoms and can easily fit into the tetrahedral interstitial space.

The most important points regarding isolated hydrogen in semiconductors are:

- Theory and experiment find the BC site to be the stable position for H^+ and H^0 . This also appears to be the stable position of the anomalous muonium (Mu^*).
- There exist two charged hydrogen species, H^- and H^+ . The energy levels of $H^{-/0}$ and $H^{0/+}$ in Si lie close to the gap center but our present knowledge does not allow us to determine if hydrogen is a negative or a positive U center.
- Evidence of the energy level of $H^{0/+}$ in GaAs near $E_v+0.5$ eV.

- H₂ molecules may form the bulk of all the hydrogen in a crystal but no experimental proof exists for this assumption.

4. H Motion

4.1 Dynamic complexes

A number of impurity-hydrogen complexes exist which indicate that hydrogen does not reside statically in one lattice position. The shallow acceptor complexes A(Cu,H₂) in Ge and A(Be,H) in Si and the shallow donor D(H,O) in Ge all exhibit special properties which suggest hydrogen to be in a dynamic state. Our information on these centers comes from high resolution far infrared spectroscopy of the optical transitions of the bound carrier. Muro and Sievers (50) and later Peale *et al.* (51) used Falicov's tunneling hydrogen model (77) to explain the large isotope shift in the ground state upon substitution of H with D and the 1s- and np-state splittings of A(Be,H) and A(Be,D) in Si. The tunneling of hydrogen between four equivalent real space positions leads to nuclear Γ_1 singlet and Γ_5 triplet states. Hydrogen-hole interaction leads to a 1s-state manifold with a total of sixteen components. These sixteen states are grouped into three quadruplets ($3 \times \Gamma_8$) and two doublets (Γ_6, Γ_7). Uniaxial stress splits the Γ_8 states into two doublets while Γ_6 and Γ_7 are spin doublets (Kramer's doublets) which do not split under stress. The analysis of the piezospectroscopy data of A(Be,H) and A(Be,D) is fully consistent with hydrogen tunneling.

The acceptor A(Cu,H₂) in Ge is the only center which has been proven to bind two hydrogen atoms. This proof comes from crystals containing both H and D leading to three centers when copper is introduced. These are identified as A(Cu,H₂), A(Cu,H,D), and A(Cu,D₂) shown in Fig. 10. Kahn *et al.* (78) analyzed these centers and created further complexes with the radioactive isotope tritium (T). All these copper related centers show simple hydrogenic sets of lines except A(Cu,H₂) which has a very complicated 1s manifold

with eleven and perhaps more components. Kahn *et al.* used the Devonshire model of the hindered rotor (79) to explain qualitatively the difference between A(Cu,H₂) and the complexes containing heavier hydrogen isotopes.

The third center which has been modeled using tunneling hydrogen is the shallow donor complex D(H,O). The special properties of this donor have been described in section 2.3. There still exists controversy as to the necessity to invoke tunneling to explain the experimental observations. Recent magnetospectroscopic studies by Gel'mont *et al.* (80) give support to the tunneling model but additional high stress experiments will be required to decide in favor of the static or the dynamic model.

4.2. Reorientation of the static B-H complex in Si

At the low temperatures where LVM spectroscopy of the H passivated acceptors in Si is performed, the H⁺ is frozen in a BC position. Stavola *et al.* (81) showed that the trigonal symmetry axis of the B-H complexes can be oriented along one of the <111> axes at room temperature using high uniaxial stresses. Cooling down a sample under the applied stress freezes all B-H centers in one preferred <111> orientation which in turn leads to a stress induced dichroism of the hydrogen stretch LVM absorption coefficient for the polarization orientation of the light parallel or perpendicular to the axis of the complex (Fig. 11). The orientation induced dichroism decays with a certain time constant τ at a given temperature. Stavola *et al.* (82) derived an activation energy for the randomization of the B-H complexes of 0.19 eV with a prefactor of $\tau_0 \cong 10^{-11}$ s. The value of this activation energy is surprisingly close to the energy barrier between two neighboring BC sites obtained from the static calculations of the total energy surfaces by Denteneer *et al.* (23). Is this close agreement between the experimental result and the static energy barriers accidental? This

question belongs to the key issues which have to be resolved before we can claim understanding of hydrogen in semiconductors.

4.3. Hydrogen diffusion and electric field drift

The importance of diffusion data is reflected by the fact that the earliest studies of hydrogen in silicon were the permeation experiments by Van Wieringen and Warmoltz (83) yielding the solubility and diffusion coefficient of H in Si at high temperatures. Similar experiments with higher accuracy were performed by Frank and Thomas for Ge (84). We begin to understand why later diffusion experiments performed at lower temperatures disagreed in some cases by orders of magnitude. The migration of hydrogen strongly depends on the charge state which in turn depends on the Fermi level position. The static energy surfaces may serve as a guide in understanding the microscopic migration path. The energy barriers along a low energy path are only about 0.2 eV, lower than the experimentally determined value at high temperatures.

DeLeo *et al.* (71) and Beall Fowler *et al.* (85) performed semiempirical calculations which included the relaxation of the silicon host atoms upon motion of H^0 and H^+ from one BC site to another. Their energy barriers for both species are estimated to be ≤ 1 eV. These results emphasize the importance of the silicon motion. The hydrogen essentially has to wait until the "door opens" to let it pass to the neighboring BC site. According to this model the large mass of the silicon host atoms dominates H migration. This is equivalent to thermally activated motion excluding tunneling. In the negative charge state, hydrogen prefers the T_d site. Migration from T_d to T_d site requires less Si relaxation and opens the possibility for tunneling.

It should be possible to differentiate between migration of the H^+ and the H^- species with electric field drift experiments. Such experiments have been performed recently by Johnson *et al.* (76), Zundel *et al.* (86), Zhu *et al.* (87) and Tavendale *et al.* (88,89) in Si and by Tavendale *et al.* (90) in GaAs. The published results do not yield direct information on the diffusion coefficient of H^- because of recombination and dissociation of H^- and positively charged donors.

The most sophisticated calculations of high temperature diffusion of H^+ in Si have been performed by Buda *et al.* (91) who used *ab initio* molecular dynamics simulations. In these calculations the motions of H^+ and the Si atoms in a cluster are followed in time steps of 6×10^{-4} ps! In view of the enormous computational effort only high temperature diffusion ($T > 1000^\circ\text{C}$) has been simulated where H^+ moves over finite distances in a time of 1.5 ps. Close examination of the result of such a calculation (Fig. 12) shows that H^+ does not stay on a low energy path. This is due to the large mass ratio between H and Si. The host Si atoms simply cannot follow the rapid hydrogen motion. This makes it clear that dynamic or quantum mechanical effects such as zero point vibration, Si relaxation, etc., must be included in theoretical models which shall give an accurate and complete description of H in semiconductors. Since *ab initio* molecular dynamics simulations cannot be carried out in their present form at low temperatures, other theoretical models have been proposed to explain hydrogen diffusion. Chang and Chadi have investigated hydrogen bonding and diffusion using *ab initio* self-consistent pseudo-potential methods (92,93). From the comparison of the energy of several hydrogen-impurity and hydrogen-hydrogen complexes they find a new metastable H_2^* species which is used to explain the differences of hydrogen diffusion at low temperatures in n- and p-type silicon.

Blöchl *et al.* (94) have used rate theory to calculate the temperature dependent diffusion coefficient of H^+ in Si using static total energy surfaces. The results agree to within a factor of three at high temperatures with Buda *et al.* (91) calculations and with the experimental results of Van Wieringen and Warmoltz (83). It will be interesting to find out how the results of this approach for other charge species of hydrogen will compare with experiments at low temperatures.

Hydrogen diffusion affecting the motion of other impurities, in this case oxygen, has been observed by Newman *et al.* (95,96). They report on an enhancement of the rate of oxygen thermal donor formation in Si catalyzed by hydrogen. The normal oxygen diffusion activation energy of 2.5 eV drops to ~ 1.5 eV in the temperature range of 250 – 500°C in the presence of hydrogen. A mobile H concentration of 10^8 cm^{-3} and a heat of solution of solution of ~ 1.0 eV is derived from the enhanced oxygen diffusion model. The authors further show that earlier studies of thermal donor formation in preheated wafers may have been influenced by hydrogen contamination.

The catalysis of enhanced motion of an impurity has been observed some time ago by Hansen *et al.* (97) who showed that the presence of copper in Ge increases the out-diffusion rate of tritium by large factors. The model for this case of catalyzed motion is based on the dissociation of H_2 in Ge by the formation of transient Cu-H species.

5. Summary and Discussions

The first discovery of hydrogen containing impurity complexes in Ge in the mid-70's and early 80's followed by the vast amount of work on various aspects of H in Si and to a lesser degree in III-V compound semiconductors have taught us much about the spectrum of interactions of the lightest element in the structurally most perfect solids. The many

paths towards today's understanding are characterized by the usual driving forces: scientific curiosity, optimal scientific gain to effort ratio, and to some degree technological significance. The easy experiments and calculations have been performed. However, the remaining problems will require larger efforts.

The dynamic aspects of isolated hydrogen are perhaps the ones most difficult to understand. Work on hydrogen in metals has been in progress for a very long time and we may be able to learn from the work on diffusion of hydrogen in metals which was discussed by Fukai and Sugimoto (98). They consider coherent tunneling or hopping at the lowest temperatures followed by adiabatic and nonadiabatic transitions at higher temperatures. The over-barrier jump mode or thermal motion leads to fluid-like motion at sufficiently high temperatures. Will we observe all these modes for H in semiconductors? It appears that the theorists can look forward to interesting work and discussions!

Our understanding of complexes is well advanced. The models for neutral acceptor-hydrogen and donor-hydrogen complexes seem definitive. While all the acceptor-hydrogen complexes in Si and III-V semiconductors share the same general trigonal structure, donor-hydrogen complexes in Si differ from the ones in III-Vs in the location of H^- . That H^- resides in an AB position makes sense in view of the necessity to accommodate two electrons near the dopant atom. We have a detailed understanding of several partially passivated multivalent acceptors, however, less is known about multivalent donor hydrogen complexes. Regarding deep level defects and impurities we know that hydrogen passivates many of them, but we have no information on their structure. This group of phenomena may have technical implications and it should be studied further.

No hydrogen related effects have been reported in II-VI semiconductors. The cause for this is unknown to the author. Since hydrogen has been studied in alkali halide crystals

and is known to play active roles in III-V semiconductors one may expect to find some interesting interactions in II-VI materials.

Let me close this survey by complimenting all the researchers who have contributed in a very efficient way to this exciting field of semiconductor research. Though much has been learned from experiments and theory up to now I would still like to encourage colleagues outside this area to join and help us complete our understanding of this marvelously complex picture produced by the simplest element in close to perfect crystalline solids.

6. Acknowledgments

I would like to thank my many friends and colleagues who have collaborated with our group, who stimulated the research with discussion, and who brought important work to my attention.

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TABLE I
ACCEPTOR COMPLEXES WITH TWO 1S-LIKE LEVELS^a (Ref. 53)

Acceptor Complex	Level Designation and Binding Energy (meV)		Energy Splitting (meV)	Average Energy (meV)
	Ground State	Excited State		
A(H,Si)	A(H,Si) ₂ 11.66	A(H,Si) ₁ 10.59	1.07	11.13
A(H,C)	A(H,C) ₂ 12.28	A(H,C) ₁ 10.30	1.98	11.29
A(Be,H)	A(Be,H) ₁ 11.29	A(Be,H) ₂ 10.79	0.50	11.04
A(Zn,H)	A(Zn,H) 12.53	b -----	-----	-----

^aThis list includes only those acceptor complexes with hole binding energies in the range 8.4 ~ 12.6 meV. Although some species might possess more than two 1s-like levels, no more than two have been detected for those which are included here.

^bA second 1s-like level has not been detected, but is expected to exist: see text.

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Figure Captions

- Fig. 1 BC configuration of the B-H complex in Si. (From Ref. 19)
- Fig. 2. Fraction of the {110} plane showing the lowest-energy configurations of the {H,B}, {Li,B}, and {Cu,B} pairs in *c*-Si. The thin vertical lines indicate the positions of the two substitutional sites in the perfect lattice. The bond lengths are in Å, and the "degrees of bonding" (0.00 for a purely ionic bond, 1.00 for a perfect 2 electron bond) are given in parentheses. Bonds amounting to less than 7% of a two-electron covalent bond are not drawn. The solid circle is the boron atom, the shaded circles are Si host atoms, and a tetrahedral interstitial site (*T*) is indicated. (From Ref. 24)
- Fig. 3. Configuration of the As-H complex in Si. (From Ref. 19)
- Fig. 4. Configuration of a group IV donor-H complex in GaAs. (From Ref. 36)
- Fig. 5. PTIS spectra of the *D* transitions of A(Be,H), boron, and aluminum, under [111] uniaxial compression. The Be-H complex shows orientational splitting and in square brackets, the numbers 1 and 2 refer to A(Be,H)₁ and A(Be,H)₂, respectively. These spectra were recorded at 6.0 K. (From Ref. 53)
- Fig. 6. Free carrier concentration as a function of inverse temperature showing effect of annealing on compensation of shallow levels for Ge:Be. (From Refs. 48,49)
- Fig. 7. Far infrared spectra of the *D* transitions of A(H,Si)₁, A(H,Si)₂, and aluminum, under [111] uniaxial compression. In square brackets, the numbers 1 and 2 refer to A(H,Si)₁ and A(H,Si), respectively. (From Ref. 53)
- Fig. 8. Schematic total energy level diagram for the donor D(H,O) in Ge based on the tunneling hydrogen model. (From Ref. 59)
- Fig. 9. Contour plot of the energy surface for H⁺ in a (110) plane through the Si atoms. The zero of energy is chosen at *T*. The black dots represent Si atoms in

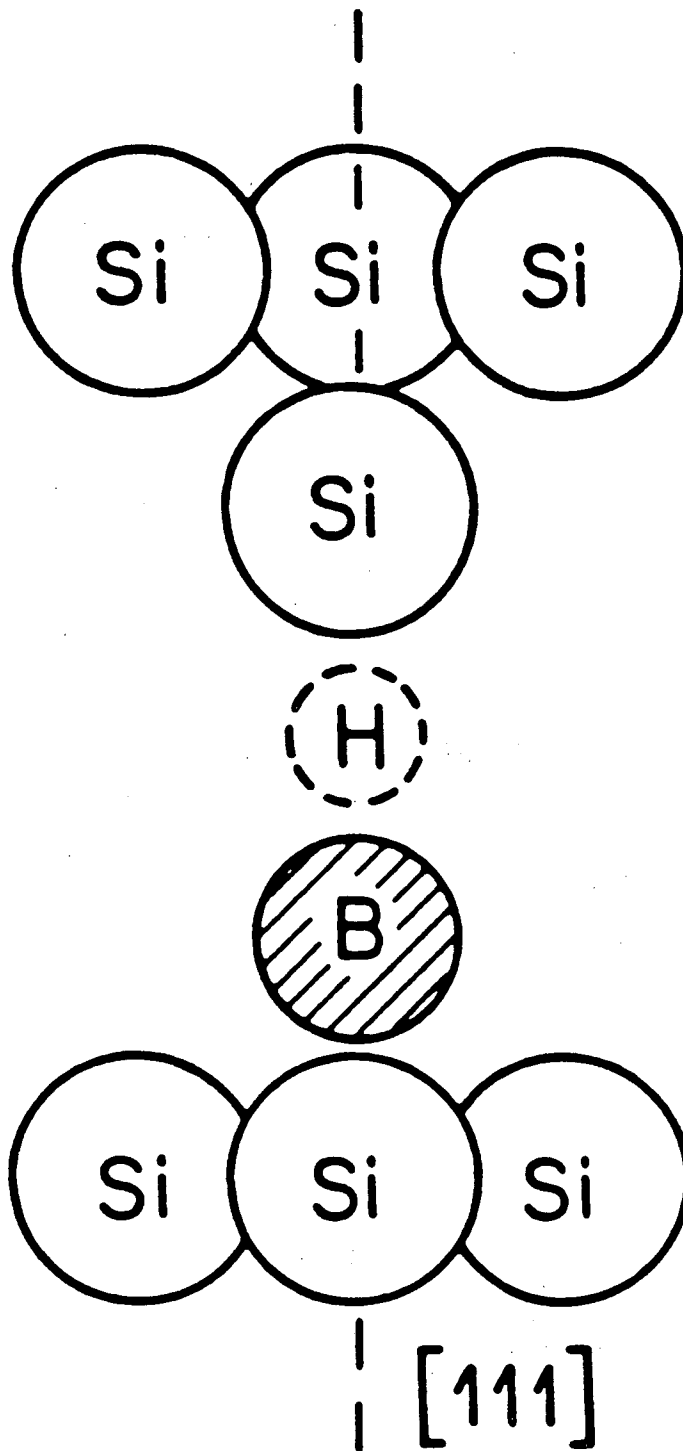
their unrelaxed positions. Relaxation is taken into account for the calculations. The contour interval is 0.1 eV. (From Ref. 72)

Fig. 10. Photothermal ionization spectra of the copper-dihydrogen acceptors that appear in samples which were grown under atmospheres of different hydrogen isotopes. (a) Pure H₂, showing the complex spectrum of A(CuH₂); (b) a 1:1 mixture of H₂ and D₂, showing A(CuH₂), A(CuHD), and A(CuD₂) in a 1:2:1 ratio; (c) nearly pure D₂, showing A(CuD₂) and a trace of A(CuHD). (From Ref. 78)

Fig. 11. The H stretching vibration band for the B-H complex measured at 10 K subsequent to a prestressing treatment with the stress orientation shown. A stress of 30 kg/mm² was applied at room temperature and maintained while the sample was cooled to 10 K. The spectra were then recorded at 0 stress. The dashed spectra shown in (a) were recorded for an unstressed sample. (From Refs. 81,82)

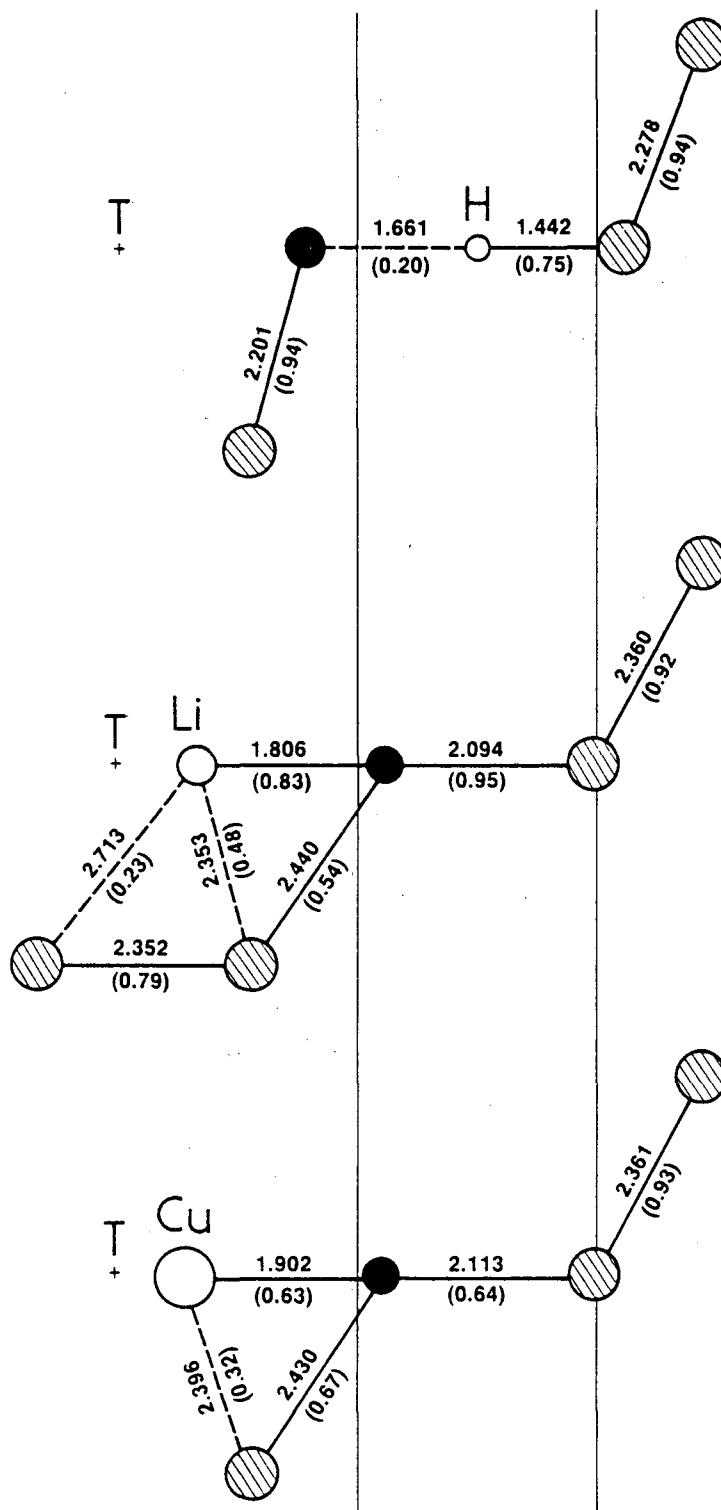
Fig. 12. Trajectory of a diffusing H⁺ at 1200 K during about 1.5 psec. The successive H⁺ positions every 6×10^{-4} psec are shown by the tiny balls. For clarity the figure shows only a small portion of the total MD cell and Si atoms, represented by the large ball, at their perfect lattice positions. The bonds connecting atom 1 to its four neighbours are explicitly indicated.

The inset shows the (110) plane formed by atoms 1,2 and 3 in the main figure. Full projected trajectories of the Si atoms belonging to this plane are reported, while the projected H⁺ trajectory is only displayed during ~ 0.2 psec corresponding to the passage through the BC position. (From Ref. 91)



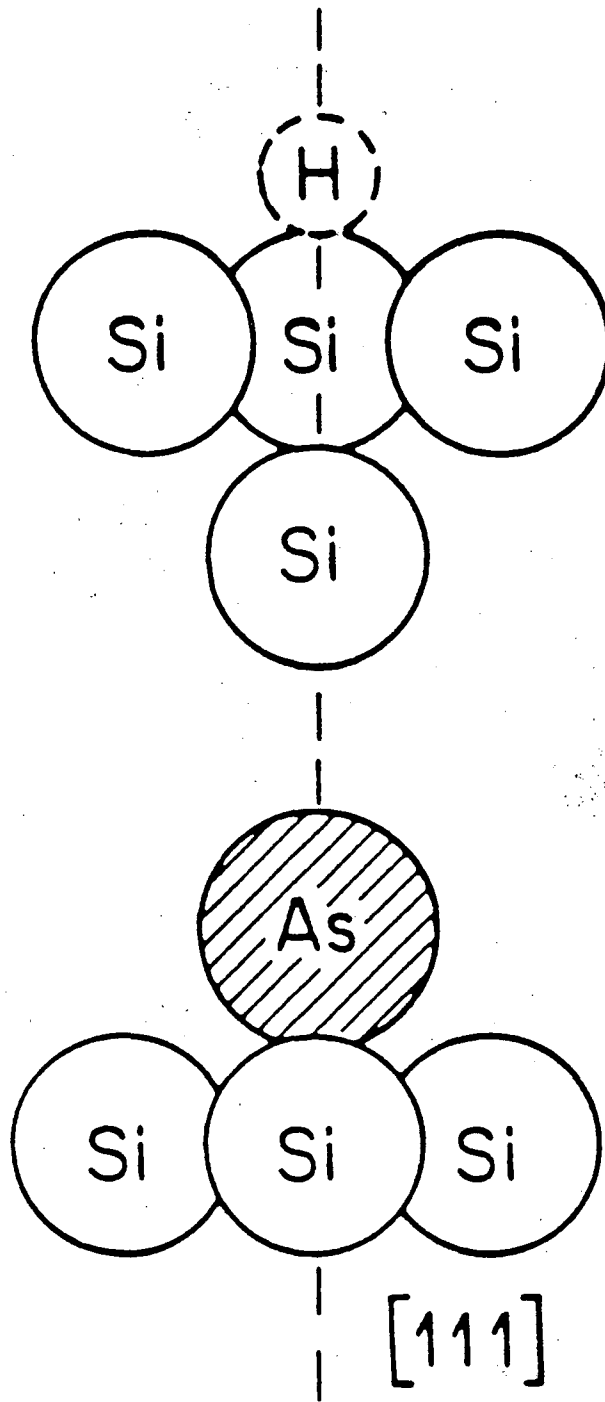
XBL 887-2664

Figure 1.



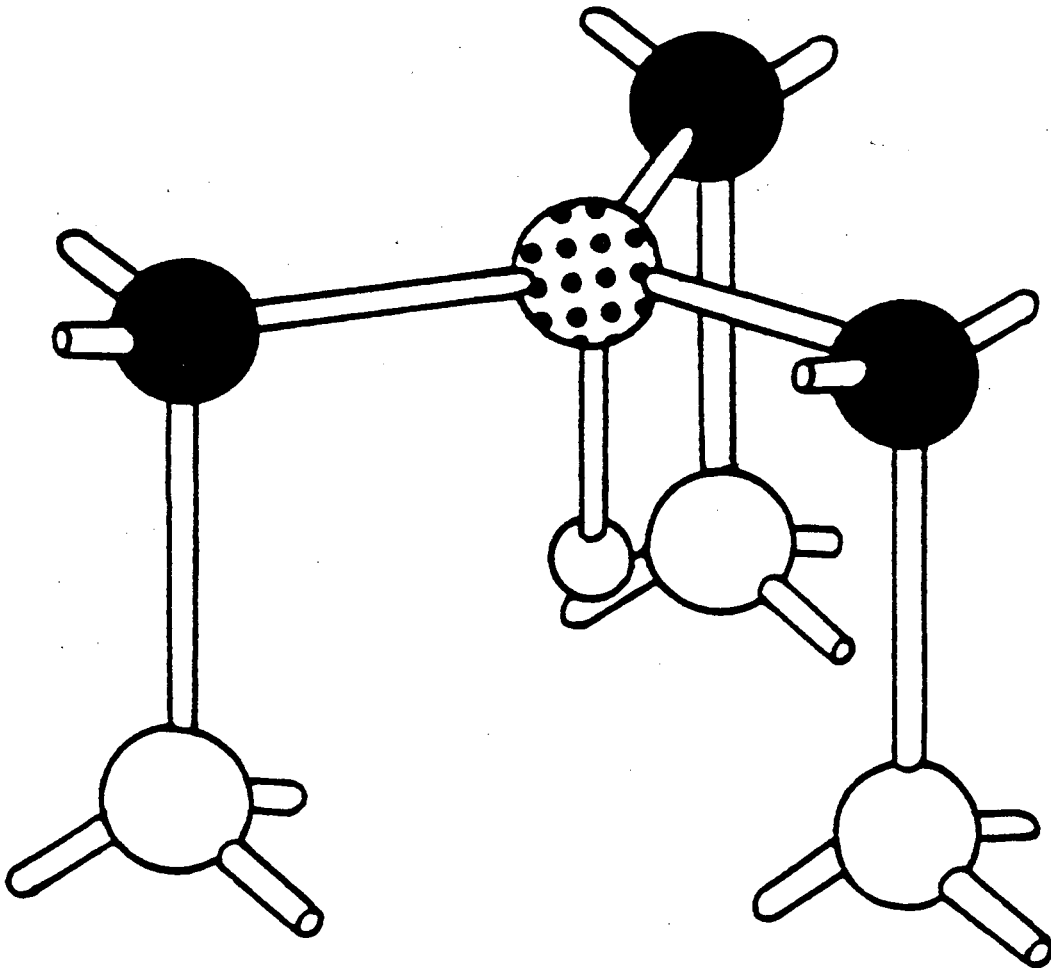
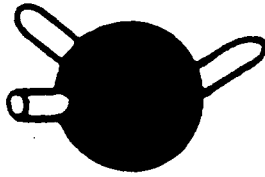
XBL 906-2261

Figure 2.



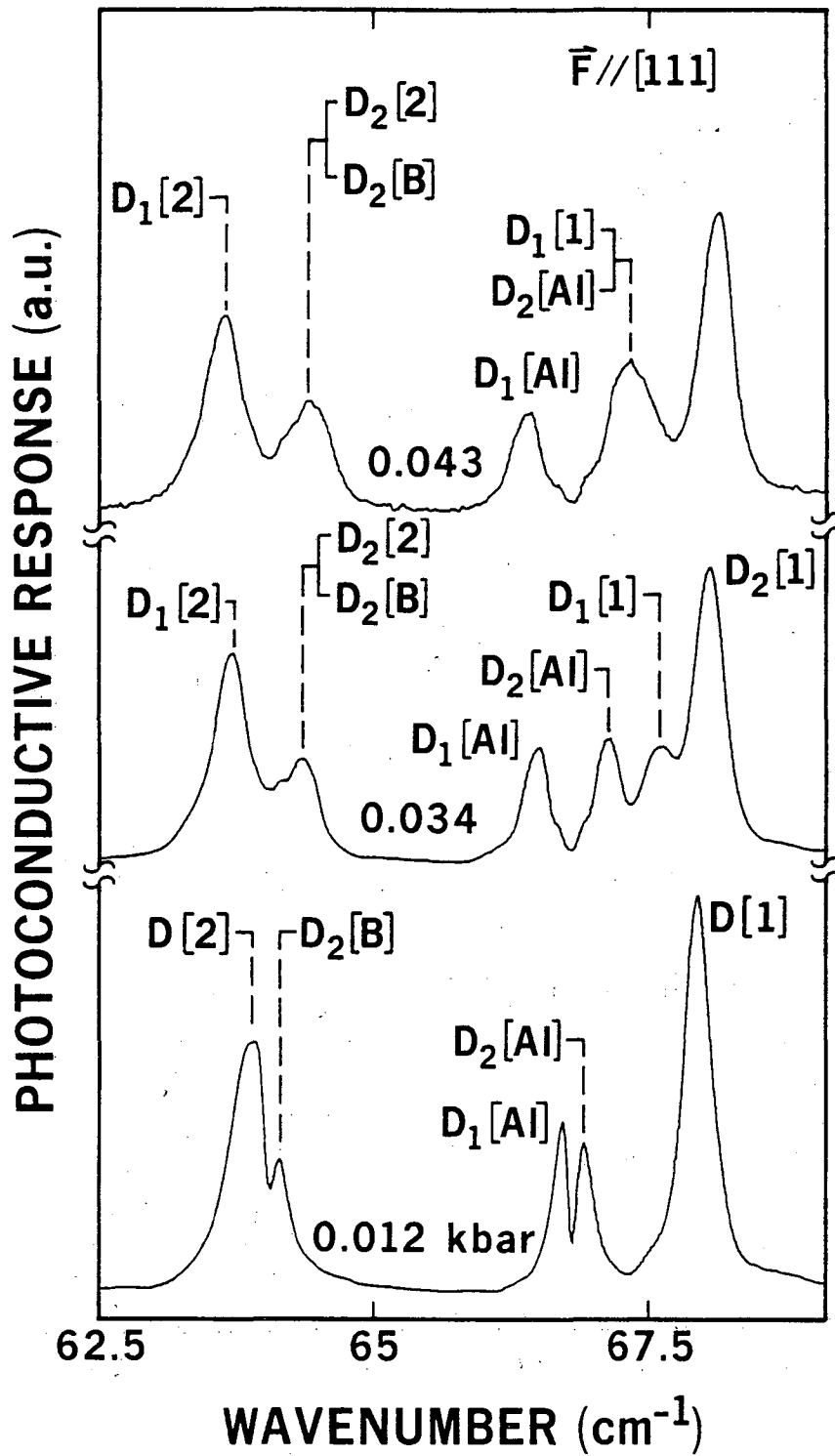
XBL 906-2260

Figure 3.



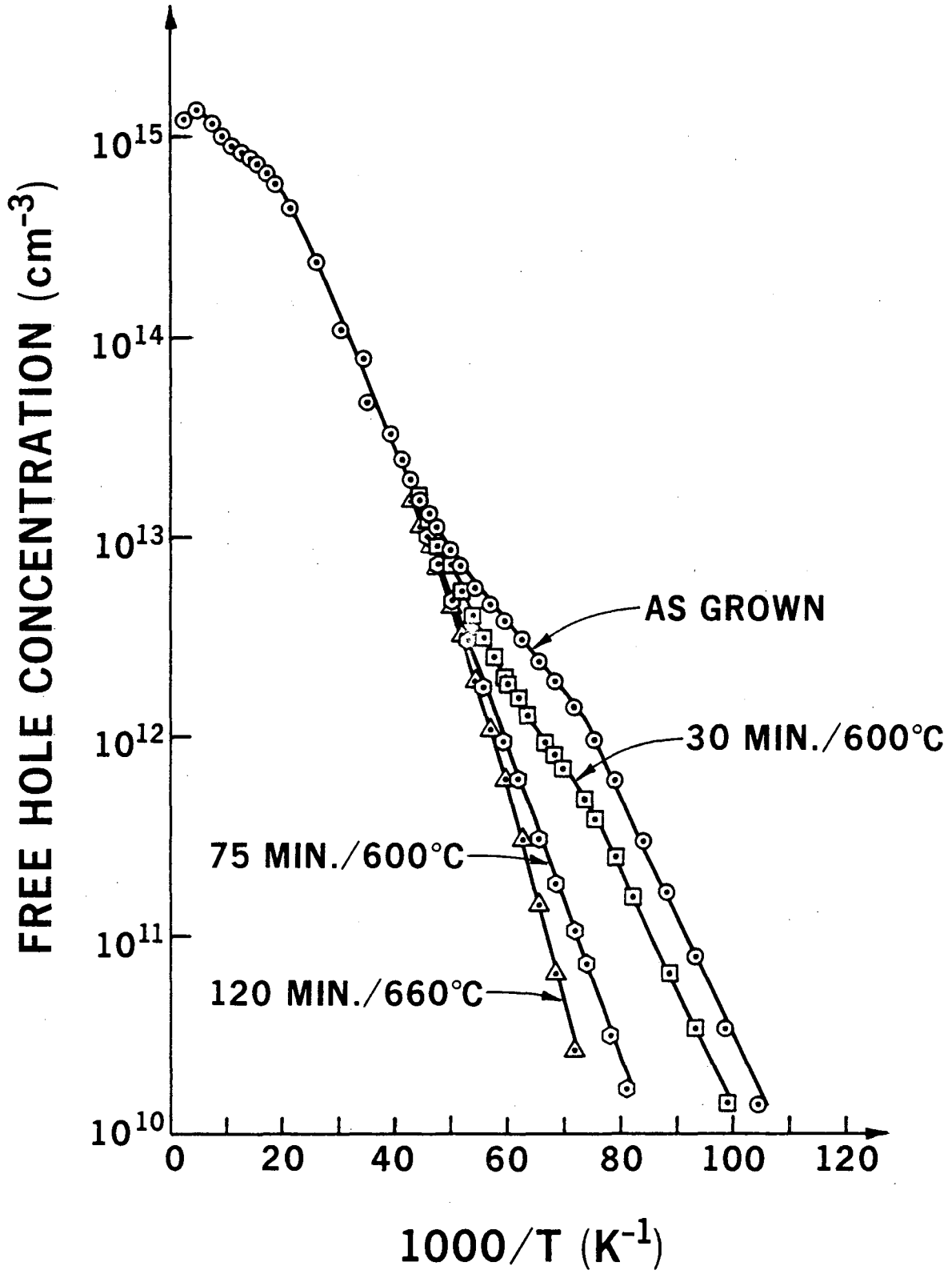
XBL 906-2258

Figure 4.



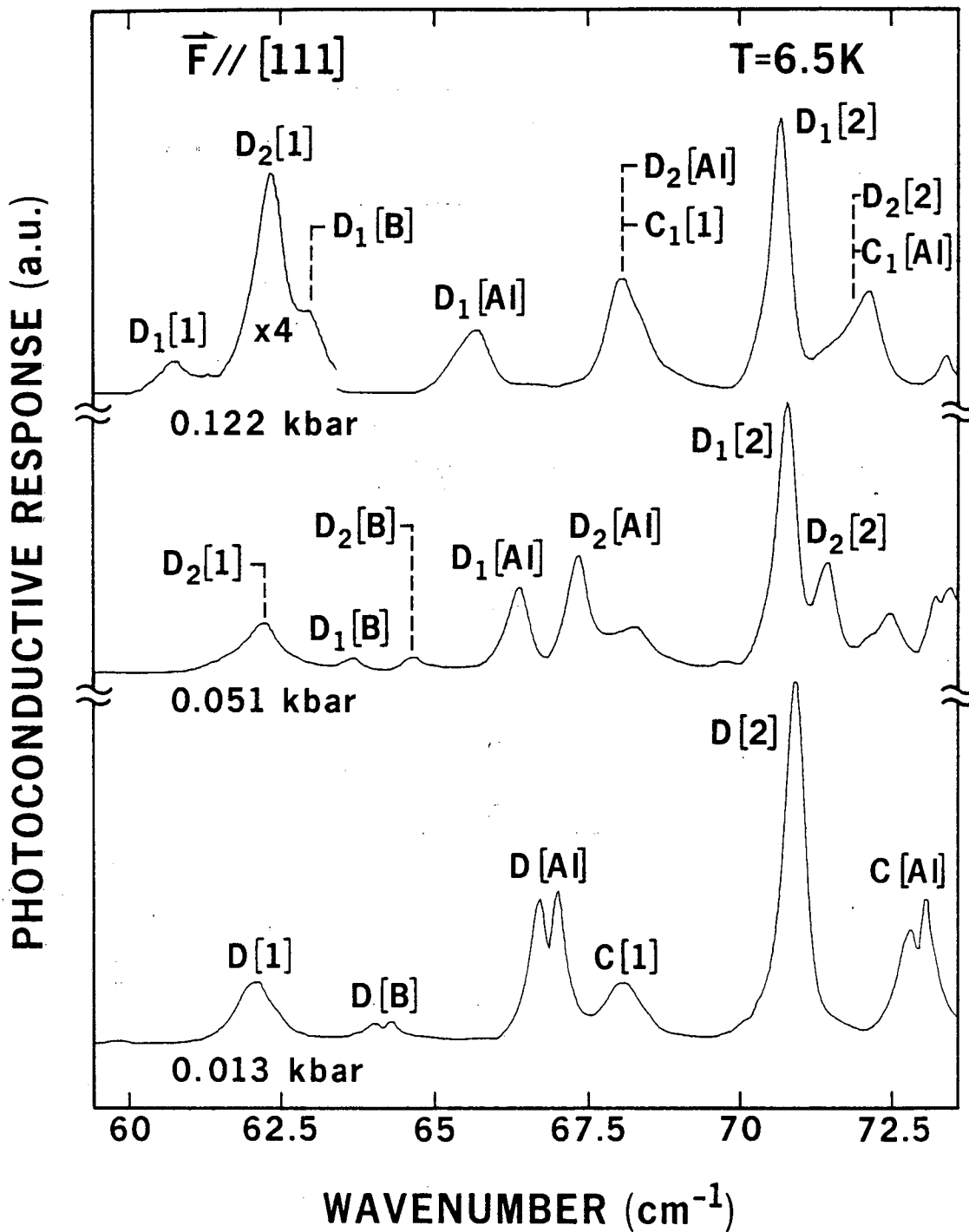
XBL 8611-4402

Figure 5.



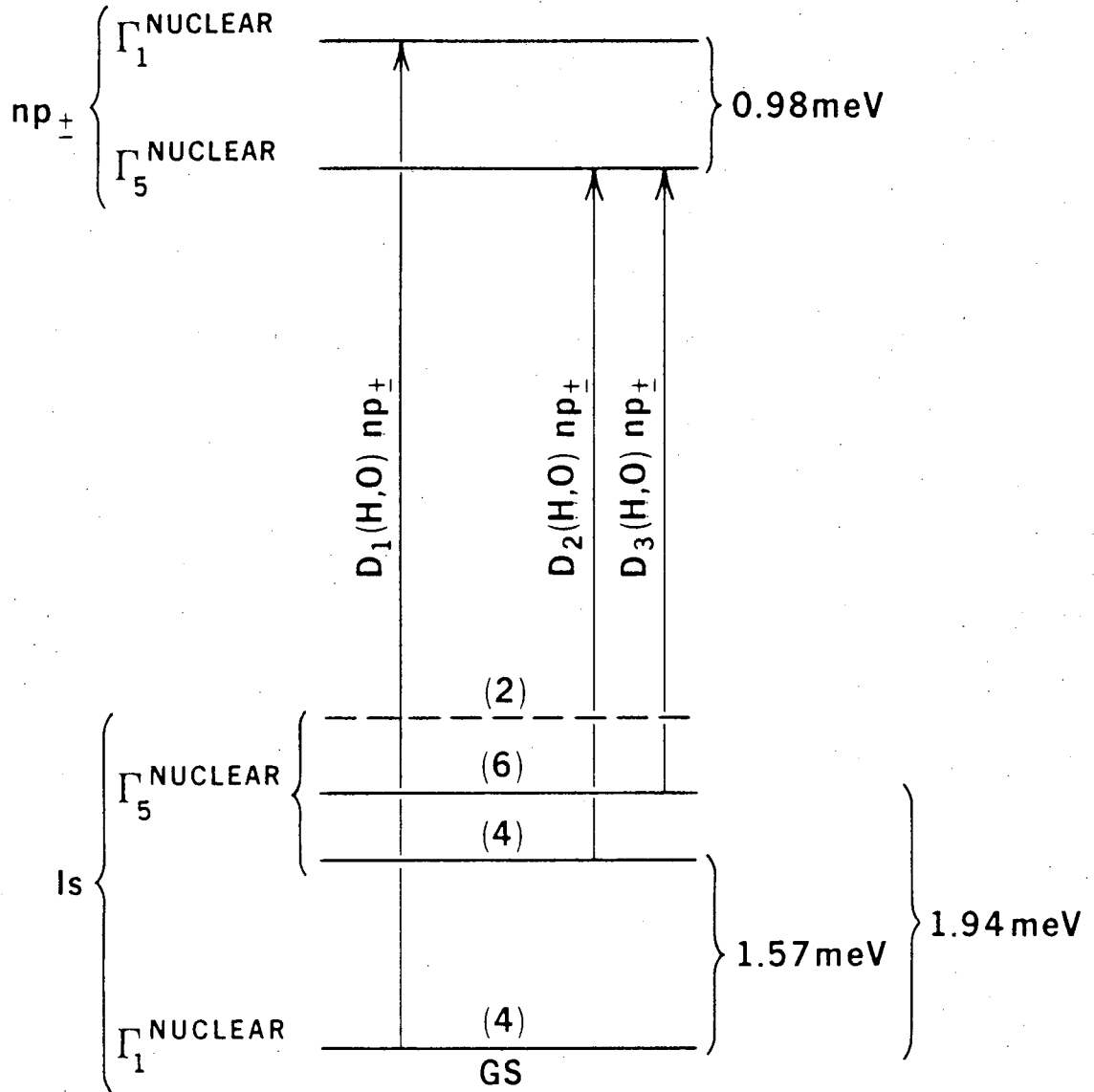
XBL 8511-4666

Figure 6.



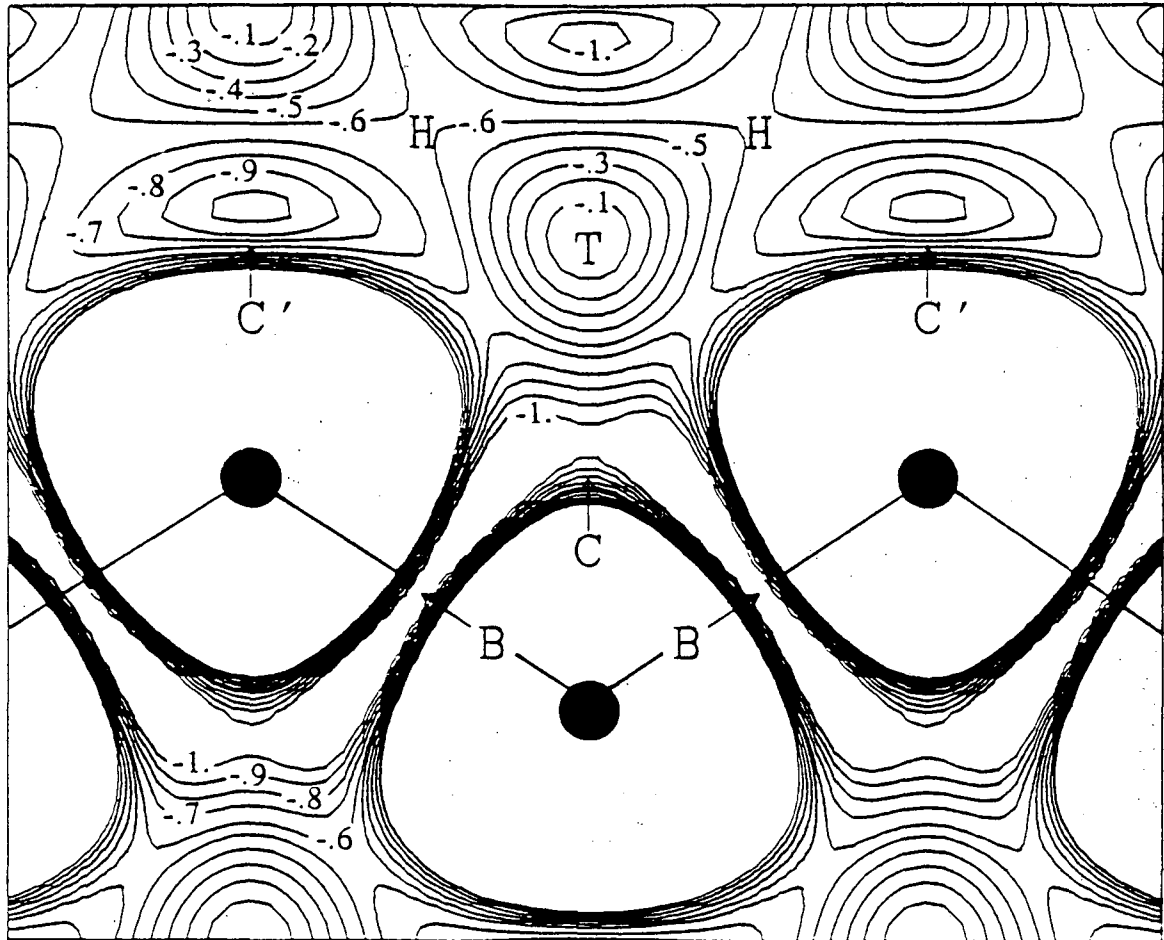
XBL 874-1719

Figure 7.



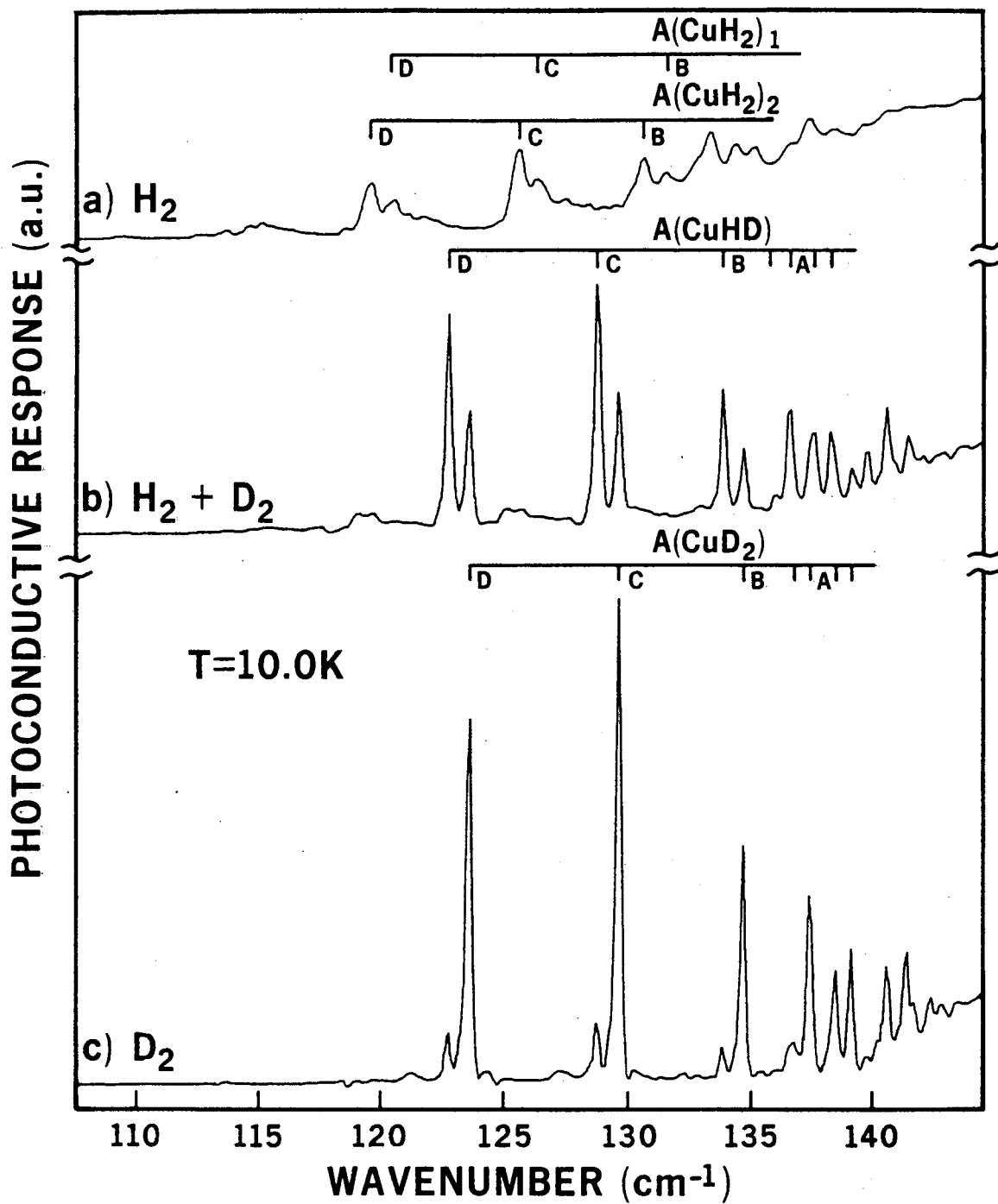
XBL 874-1501

Figure 8.



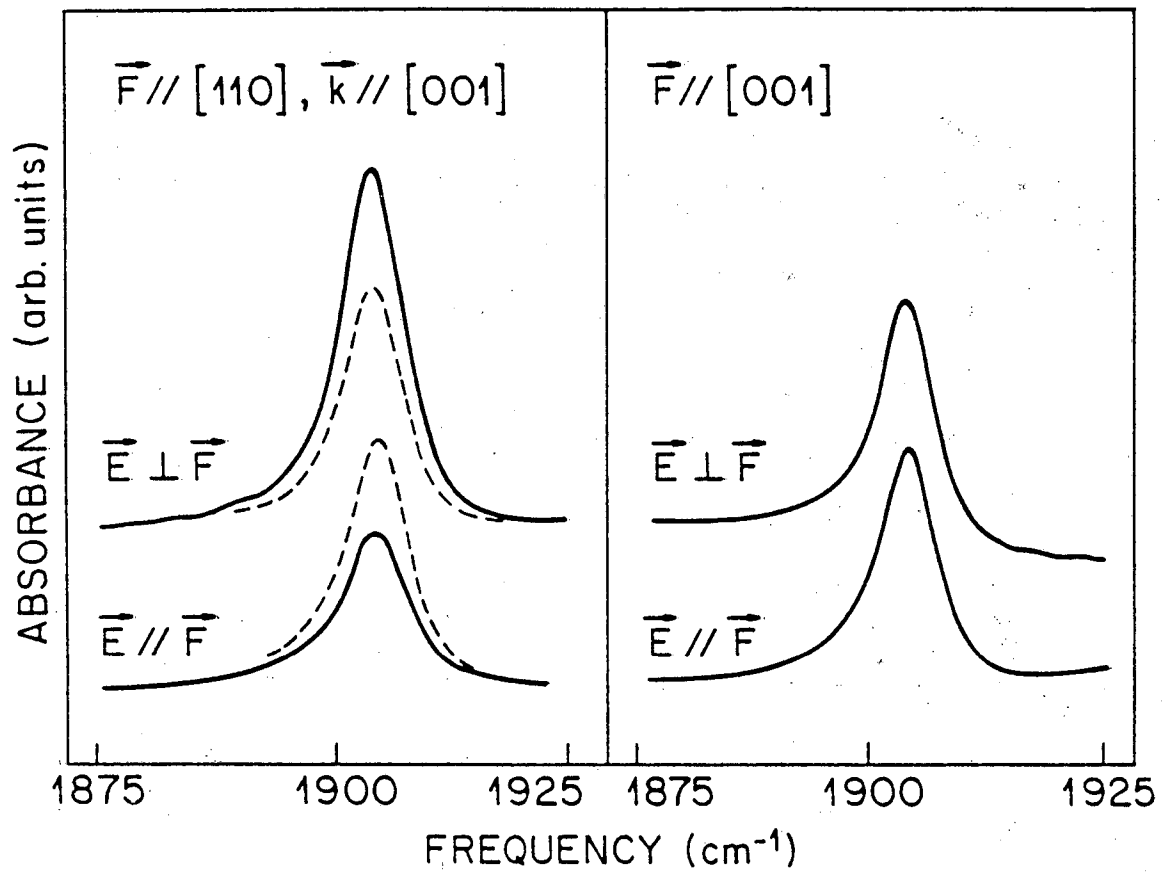
XBL 906-2257

Figure 9.



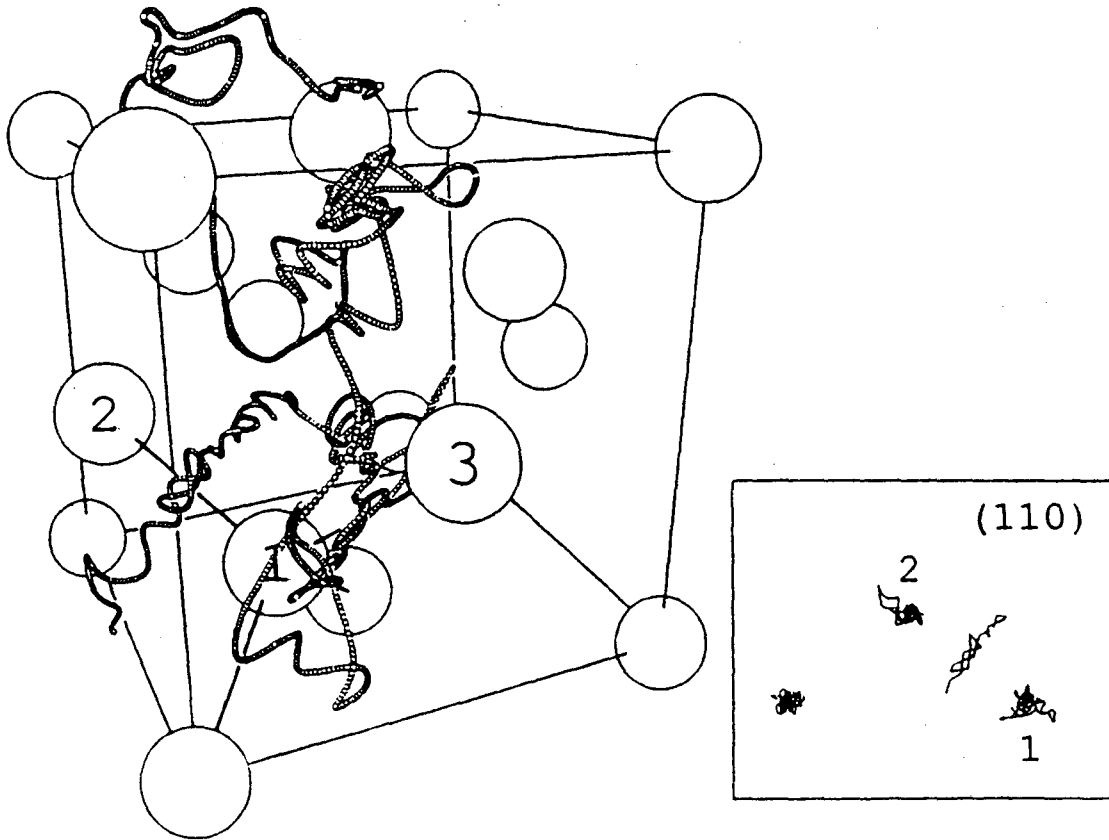
XBL 863-1157A

Figure 10.



XBL 906-2256

Figure 11.



XBL 906-2259

Figure 12.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720