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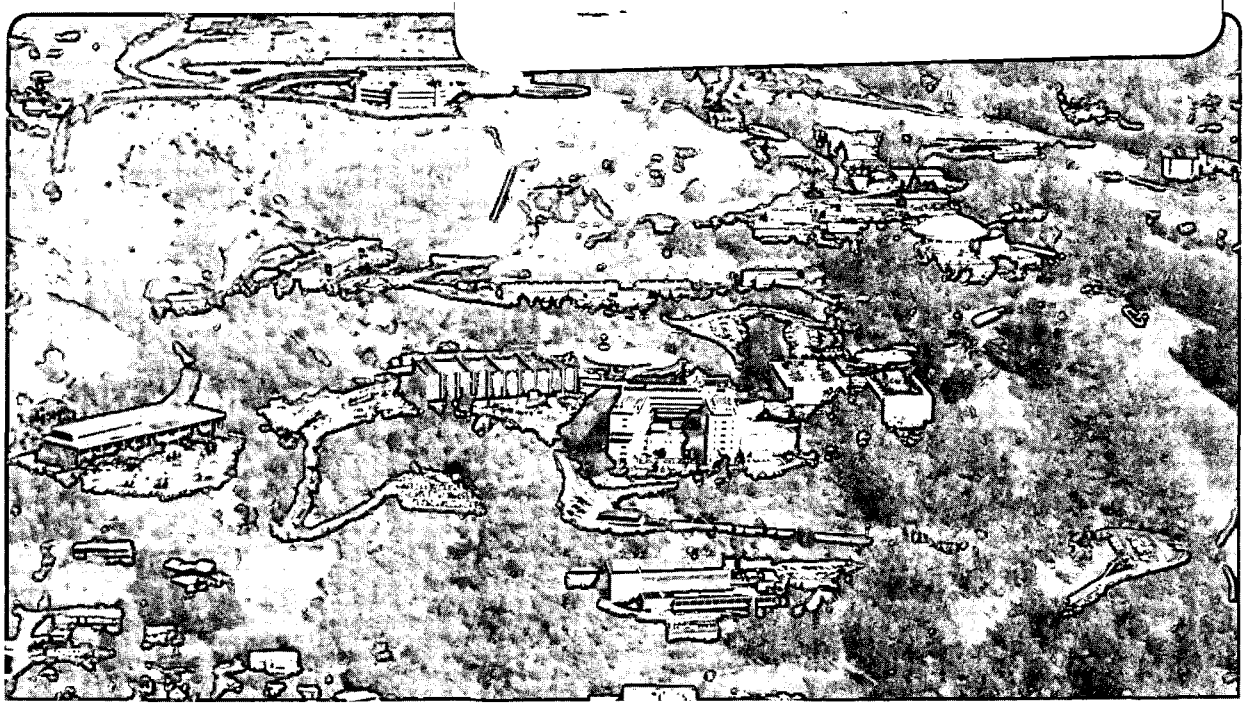

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HYDROGEN-RELATED PHENOMENA IN CRYSTALLINE GERMANIUM*

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I. Introduction

Germanium was the first crystalline semiconductor in which a number of shallow acceptor and donor complexes were discovered which were unambiguously proven to contain hydrogen. This series of discoveries began in the 1970's when several laboratories conducted research and development efforts with the aim of producing ultra-pure Ge single crystals for radiation detector applications. A net-dopant concentration (the difference between acceptor and donor concentrations (N_A - N_D) of approximately 10^{10} cm^{-3} was required for large volume (10 to 200 cm^3) fully depleted Ge p-i-n diodes which were used as charge sensitive gamma ray detectors. Such a small net-concentration can be obtained throughout large crystal volumes only if a purity level of approximately one electrically active center in 10^{12} germanium host atoms can be attained.

To date, a large number of novel acceptor and donor levels have been discovered and studied in this high-purity material. These levels are not related to the elemental impurities of the third or fifth group of the periodic table. We will begin with a brief review of all these acceptors and donors. Many of them are impurity complexes and most contain hydrogen. The neutral impurities silicon, carbon, and oxygen are "activated" by hydrogen to form the monovalent shallow acceptors A(H,Si) (Hall, 1974, 1975; Haller et al., 1980), A(H,C) (Haller et al., 1980), and the shallow donor D(H,O) (Hall, 1974, 1975; Joós et al., 1980), respectively. A similar donor D(Li,O) had been found independently in the course of oxygen studies (Haller and Falicov, 1978,1979). Contrary to the original interpretation of the optical spectra of A(H,Si) and A(H,C), Kahn et al. (1987) showed that these two acceptors consist of trigonally distorted complexes which are randomly aligned

along the four <111> axes. The donor D(H,O) exhibits an unusually sharp set of optical transition lines which led to the notation "S" in early studies (Seccombe and Korn, 1972). An isotope shift of 51 μeV in the ground state of D(H,O), upon substitution of hydrogen with deuterium, was the first direct proof of the presence of hydrogen in this center (Haller, 1978b). D(H,O) has a complicated 1s-state manifold which has been explained with the tunneling of the hydrogen ion between four equivalent real space positions along the <111> axes.

The study of the incompletely passivated multivalent acceptors beryllium, zinc, and copper in germanium has provided especially interesting physics. Crystals doped with the double acceptors beryllium and zinc with concentrations of 10^{14} cm^{-3} to 10^{15} cm^{-3} have been developed in recent years for far-infrared photoconductive detector applications (Haegel, 1985; Haegel and Haller, 1986). In hydrogen-containing Ge:Be and Ge:Zn crystals, one finds the shallow single acceptors A(Be,H) and A(Zn,H) (McMurray Jr. et al., 1987). Kahn et al. (1987) have shown that these two acceptors have trigonal symmetry like A(H,Si) and A(H,C) discussed above. In Ge:Cu crystals, which played an important role as photoconductive material in the past, one can generate $A(Cu,H_2)$ acceptors (Kahn et al., 1986; Kahn, 1986). This semi-shallow monovalent acceptor complex consists of a substitutional copper impurity which binds two interstitial hydrogen atoms.

In dislocation-free pure germanium crystals grown in a hydrogen or deuterium atmosphere, one always finds an acceptor with an energy level at E_V + 80 meV (Haller et al., 1977b). This acceptor has been assigned to a divacancy/hydrogen complex. As an effective hole trap it renders ultra-pure germanium crystals useless for radiation detector applications.

In crystals containing carbon and nitrogen, one detects the shallow acceptor complex A(C,N) (Haller et al., 1981). This unique center has a low and a high temperature configuration between which it can be interconverted reversibly (McMurray et al., 1985). The low temperature configuration has a degenerate ground state with Γ_8 symmetry while the high temperature configuration exhibits a 1s-like state which is split (Haller and McMurray, 1983).

Besides the electrically active complexes discussed above, there is indirect evidence for the existence of neutral complexes. In close analogy to the observations in silicon and several III-V materials, it appears that hydrogen passivates deep and shallow acceptors. Because of the small concentrations of these neutral centers, all attempts to detect them directly with local vibrational mode (LVM) spectroscopy or electron paramagnetic resonance (EPR) have been unsuccessful.

It is noteworthy that hydrogen activation of neutral impurities in germanium was the first evidence of electronic activity of hydrogen. All earlier attempts to detect physical or chemical effects of hydrogen in a semiconductor had failed. Several years after the discoveries in germanium, hydrogen "passivation" of shallow acceptors, i.e., the formation of a neutral complex consisting of a shallow acceptor and a hydrogen atom, was discovered in silicon (Sah et al., 1983; Pankove et al., 1983). Since then, passivation of numerous shallow and deep impurities in germanium (Haller, 1986; Haller et al., 1981), silicon (Pearton et al., 1987), and a number of compound semiconductors (Pajot, 1989) has been studied and reported (Haller, 1989). So far, hydrogen activation has been detected only in germanium. This is not necessarily an indication that activation does not occur in other semiconductors as well. One must remember that the concentrations of A(H,Si), A(H,C), and D(H,O) in germanium are very small indeed, and that the extraordinary purity of the host crystal significantly facilitated their discovery.

Electrically active, hydrogen-containing centers are particularly interesting because their electronic structure may be influenced by the atomic configuration of the impurity complex. The reduced symmetry of an impurity complex can create splittings of the ground and of the bound excited states, leading to rich electronic dipole transition spectra in the far infrared. Perhaps the most important advantage of electrically active centers is the fact that they can be studied with a wide range of sensitive techniques including variable temperature Hall effect, photoconductivity, and far infrared high resolution spectroscopy. Using photoconductivity techniques, concentrations of shallow levels as low as 10^6 cm^{-3} can be studied. The investigation of fully passivated dopants on the other hand is limited to rather insensitive methods which require defect concentrations in excess of 10^{15} cm^{-3}.

In the following sections I will give a succinct description of the properties of the various hydrogen-containing centers and the methods with which they can be generated. Because of the intimate coupling between the crystal growth parameters and the formation

of hydrogen-related centers, I will begin with a short summary of ultra-pure germanium crystal growth technology and appropriate characterization methods.

II. Ultra-Pure Germanium Crystal Growth and Characterization

1. CRYSTAL GROWTH AND RESIDUAL IMPURITIES

The limiting factors regarding the purity of bulk semiconductor single crystals grown from a melt are influenced by all the materials which form the growth chamber and its contents and, of course, the purity of the semiconductor starting material. The crystal puller parts which become hot during crystal growth and which are in direct contact with the semiconductor material determine the ultimate purity in a properly designed system. They include the crucible holding the melt, the susceptor coupling the radio frequency (RF) heating power to the crucible, and the growth atmosphere. At the melting point of germanium, 936°C, fused synthetic silica has been found, so far, to be the only acceptable crucible material for high purity growth. RF coupling is achieved through a graphite susceptor which is located inside (Hansen, 1971; Hansen and Haller, 1983) or, if protected from atmospheric oxygen, outside the growth chamber (Hall and Soltys, 1971).

From numerous trials with vacuum and gases including dry nitrogen, argon, helium, and hydrogen, only the latter has been found to lead to crystals yielding detectors with outstanding charge collection properties. The reason for the superiority of hydrogen was originally thought to be related mainly to its reducing action. More recently one favors the idea that hydrogen passivates the majority of residual deep traps which are created either by impurities or by native defects. Early studies of hydrogen permeation of single crystal germanium by Van Wieringen and Warmoltz (1956) and later by Frank and Thomas (1960) showed that hydrogen is a fast diffuser with a relatively low maximum solubility lying between 10^{14} and 10^{15} cm^{-3} near the melting point. In an elegant tritium radiotracer experiment, Hansen, et al. (1982) used a self-counting p-i-n diode to show that such concentrations of hydrogen remain trapped indeed in ultra-pure Ge when the crystal is cooled from the melting point down to room temperature.

The reduction of the silica crucible by the molten germanium generates free silicon and oxygen. In typical ultra-pure crystals, one can detect silicon concentrations [Si]

between 10^{13} and 10^{14} cm^{-3}, oxygen concentrations [0] ~ 10^{14} cm^{-3}, and, as already mentioned, hydrogen concentrations [H] ~ 5 x 10^{14} cm^{-3} (Haller et al., 1981). As isolated impurities, none of the above three elements form electrically active centers in intrinsic germanium. There exists strong evidence that the major residual shallow impurities, aluminum and phosphorus, also originate mostly in the silica crucible. From this discussion, it becomes evident that the adjective "ultra-pure" refers most appropriately to the electrically active impurities!

Even though it is the net-dopant concentration (N_A - N_D) which controls the depletion width of a pin detector diode, one understands readily why the acceptor concentration N_A as well as the donor concentration N_D must be both of the order 10^{10} cm^{-3}. Close-to-perfect compensation ($N_A \approx N_D$), a requirement when N_A and N_D are much larger than a few times 10^{10} cm^{-3}, cannot be maintained throughout large volumes of a melt-grown crystal because each impurity has its own segregation coefficient which differs slightly from the segregation coefficients of all the other impurities. This in turn leads to different impurity concentration profiles along the crystal axis and to large deviations from near-perfect compensation in most of the crystal's volume. In the well-known lithium-drifted germanium (GeLi) detectors which preceded ultra-pure germanium detectors, a net-impurity concentration as low as 10^8 cm^{-3} could be achieved automatically through the lithium ion drift process (Pell, 1960). The difficulties in keeping close-to-perfect compensation in GeLi detectors through continuous cooling has led to the complete replacement of this kind of gamma-ray detector with ultra-pure Ge detectors. It is worth mentioning that a number of additional advantages such as extremely thin ion-implanted contacts, the possibility of sectioning of the contacts into arrays, combining several detectors into one system, and the removal of radiation-induced deep level defects by thermal annealing have made ultra-pure Ge detectors much more useful than GeLi devices ever were (Haller and Goulding, 1980).

2. ULTRA-PURE GERMANIUM CHARACTERIZATION

The number of characterization techniques which are sufficiently sensitive for this material and preferably impurity species or defect structure specific is rather small. Variable temperature Hall effect measurements in the Van der Pauw (1958) configuration allow the determination of (N_A - N_D). The degree of compensation ($N_{Minority}/N_{Majority}$) is larger than 0.1 in typical ultra-pure crystals. Such values do not permit an accurate

extraction of minority impurity concentration data from Hall effect freeze-out curves (Blakemore, 1987). Ultra-pure germanium becomes extrinsic below approximately 180 K which means that all electrical measurements must be performed below this temperature if impurity data shall be obtained. Record electron and hole mobilities above a few times 10^6 cm^2/Vs have been measured in ultra-pure germanium below 10 K (Ottaviani et al., 1972), a fact which is typically overlooked by researchers working with two-dimensional electron gas structures!

Radioactive tracer experiments have yielded unique information in the study of ultra-pure germanium. A number of crystals were grown in ^{14}C-coated silica crucibles and were subsequently studied with autoradiography (Haller et al., 1982) and with self-counting and spatially-resolving radiation detectors (Luke and Haller, 1986). These measurements established a lower limit for carbon dissolved in germanium of 10^{14} cm^{-3}. They further showed that carbon is dispersed in crystals grown in a nitrogen atmosphere but forms some clusters in crystals grown in a hydrogen or deuterium atmosphere. This difference is still not understood.

Small amounts of tritium were added to the hydrogen growth atmosphere of some crystals. Radiation detectors fabricated from these crystals measure the energy distribution of the electrons created in the tritium decays inside the crystal (Hansen et al., 1982). These studies set a lower limit of the hydrogen concentration at a value between 10^{14} cm^{-3} and 10^{15} cm^{-3}.

It is important to emphasize how small the concentrations of the various impurity complexes in ultra-pure germanium are. Many of the powerful techniques including secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), ion channeling, electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and local vibrational mode (LVM) spectroscopy are simply too insensitive to be useful for the study of the novel centers. For the study of the electronic structure of acceptors (donors) present at the typical low concentrations, one uses photothermal ionization spectroscopy (PTIS) (Lifshits and Nad, 1965; Kogan and Lifshits, 1977). This low temperature technique combines electronic dipole transitions of a hole (electron) from the 1s-like ground state to a bound excited state with a phonon assisted transition from the bound excited state into the valence (conduction) band (Fig. 1). There exists an optimum temperature range for PTIS in which the phonon density is sufficiently large to ionize

bound carriers from an excited state to a band, but ionization from the ground state is still negligible. Once the hole (electron) has reached the valence (conduction) band, it increases the conductivity of the crystal. A chopped-light source and a small bias across the sample generate a photoconductive AC signal which can be easily amplified and further processed with a lock-in amplifier. Typically a far infrared Fourier transform spectrometer (Bell, 1972) is used to perform PTIS (Haller and Hansen, 1974a,b).

III. Shallow Level Complexes Containing Hydrogen

3. THE TRIGONAL ACCEPTORS A(H,SI), A(H,C), A(BE,H), AND A(ZN,H)

The members of this group of shallow acceptors share a similar structure. They consist of a substitutional impurity binding one hydrogen or deuterium atom in its vicinity. Extensive far infrared spectroscopy studies have shown that the symmetry of these complexes is trigonal (Kahn et al., 1987). This leaves essentially two choices for the location of the hydrogen atom: interstitial in one of the four anti-bonding directions, or in one of the four bonds. In silicon, the bond center location is by now experimentally (Marwick et al., 1987; Nielsen et al., 1988) and theoretically (Van de Walle et al., 1989; Denteneer et al., 1989a) established for hydrogen-passivated acceptors. There are, however, no strong physical arguments favoring the same position of hydrogen in the complexes in germanium.

The monovalent acceptors A(H,Si) and A(H,C) appear in ultra-pure germanium crystals grown from silica and graphite crucibles respectively. A(H,Si) is generated through rapid thermal quenching ($\geq$ 150°C/s) of a small sample from a temperature around 425°C (Hall, 1974; 1975). This acceptor complex dissociates already at room temperature with a time constant of minutes. Substitution of hydrogen with deuterium leads to the acceptor (A(D,Si) with a 21 μeV deeper ground state. This isotope shift is direct evidence of the presence of hydrogen in this center (Haller, 1978b). A(H,C) is present in as-grown crystals and dissociates around 200°C. The maximum concentrations of these two acceptors in standard ultra-pure germanium lie between 10^{11} and 5×10^{11} cm^{-3} depending slightly on the crystal growth conditions and the position in the grown crystal. It is important to recognize that only a very small fraction of the total concentrations of

hydrogen, silicon, or carbon participate in the formation of these electrically active complexes!

Figure 2 displays a high resolution spectrum of the deuterium-carbon-acceptor complex A(D,C) and of the residual acceptor impurities aluminum and boron. In contrast to the elemental acceptors, A(D,C) produces two hydrogenic series of lines which are shifted by 1.98 meV relative to each other. This shift is the consequence of the splitting in the 1s-state. That the two series belong to the same center was demonstrated with temperature dependent PTIS studies. The ratios of corresponding lines in the two-line series follow the same Boltzmann factor, exp(E/kT), with E = 1.98 meV. High resolution PTIS studies of this acceptor with uniaxial stress along all three major crystal orientations are fully consistent with a trigonal center randomly oriented along one of the four [111] orientations. Attempts to align all the A(H,C) complexes in a sample using a large uniaxial stress at room temperature have not been successful.

Figure 3 displays the splittings and the shifts of the D- and C-lines of aluminum and of the D-line of the $A(D,C)_2$ series with uniaxial stress in the three major orientations. Whereas the lines of the elemental acceptor split for [111] stress symmetrically into four lines about the zero stress position, the D-line of $A(D,C)_2$ separates into two components only. They exhibit a relative strength ratio of 3:1 and energy shifts of 1:3 about the zero stress position. The lines of the $A(D,C)_1$ series show the same splitting pattern but in the inverse direction.

The splitting of the C- and D-lines of the elemental acceptor aluminum is consistent with the tetrahedral symmetry T_d of this impurity in a substitutional site. The stress behavior of A(D,C), on the other hand, can be described with a trigonal acceptor whose ground state is pre-split along one of the four [111] directions. The 1s-like ground states of the acceptors A(H,Si) and A(D,Si) are pre-split by 1.07 meV. Their uniaxial stress behavior is the same as of A(H,C). It is convenient to assume that the internal splitting of the 1s-state is caused by an internal short-range stress S which affects the 1s-state but leaves the p-like bound excited states undisturbed.

The centers A(Be,H) and A(Zn,H) form in crystals grown in a hydrogen atmosphere which are doped with Be and Zn, respectively (McMurray et al., 1987). Both centers are stable to temperatures around 650° C, significantly higher than the dissociation

temperatures of (A(H,Si) and A(H,C). Assuming first order reaction kinetics, Haegel (1985) determined the prefactors ν and the dissociation energies E for both centers. She found: $\nu[A(Be,H)] = 3 \times 10^8\ s^{-1}$ and $E[A(Be,H)] = 2.1 \pm 0.6$ eV; $\nu[A(Zn,H)] = 3 \times 10^{12}\ s^{-1}$ and $E[A(Zn,H)] = 3.0 \pm 0.3$ eV. A typical set of hole freeze-out curves for a beryllium-doped germanium crystal grown in a hydrogen atmosphere is shown in Fig. 4. The concentrations of these complexes correspond approximately to 1% of the double acceptor concentrations. Both centers act under uniaxial stress like the complexes discussed above except that the small and the large components of each line move in opposite directions. This behavior can be interpreted with the opposite sign of the internal stress S which pre-splits the ground state. A somewhat simplistic interpretation of the difference in sign of this internal stress which causes the pre-splitting is based on the different roles played by hydrogen in the two kinds of centers. When partially passivating double acceptors, hydrogen acts as a positive ion, substituting for one hole. When activating neutral impurities, hydrogen binds an extra electron and acts like a negative ion. In order to express the difference between centers containing H^- and centers with H^+, we have adopted the notation (X,H) and (H,X), respectively. Figure 5 shows results of the internal stress model for A(Be,H) (a) and A(H,C) (b). The values for S have been chosen to fit the experimental splitting for zero external stress. Table 1 summarizes the 1s-state properties of the four static trigonal centers described in this section. It is interesting to note that the average value of the energy of the 1s-state in all four cases lies very close to the theoretical energy of effective mass-like acceptors (Baldereschi and Lipari, 1976).

Theoretical studies of hydrogen-containing complexes have been performed primarily for silicon (Van de Walle et al., 1989; Van de Walle et al., 1988; DeLeo and Fowler, 1985). Recently, Denteneer et al. (1989b) have performed calculations based on density-functional theory in the local density approximation for the acceptor A(H,Si) in germanium. They find a small binding energy of approximately 50 meV and large barriers between the energy minima for the location of the negatively charged hydrogen ion. The energy minima are located in the antibonding directions near the T_d sites. These theoretical results are in good agreement with major experimental findings, i.e., the low thermal stability of A(H,Si) and its static trigonal structure. Results of other calculations on the other trigonal complexes, especially A(H,C) which is similar to but much more stable than A(H,Si), would be most interesting. The large effort and the extensive computer time required for such computations, however, unfortunately impose severe selectivity.

Earlier studies of A(H,Si) at lower resolution and lower signal-to-noise ratios (Haller et al., 1980) did not reveal the small components of the uniaxial stress split lines. Based on the very small shifts of the large components, a model with tunneling hydrogen was proposed which could explain the available data. The recent improved data leave no doubt that these acceptor centers have trigonal symmetry and that they are static. In the meantime, the tunneling hydrogen model has been used successfully to describe the partially-passivated A(Be,H) centers in silicon (Muro and Sievers, 1986).

4. THE ACCEPTOR COMPLEX A(CU,H_2)

Germanium crystals which contain the substitutional triple acceptor copper (Hall and Racette, 1964), as well as hydrogen, exhibit in PTIS a series of broad lines which belong to an acceptor with a ground state at 17.81 meV above the top of the valence band (Haller et al., 1977a). PTIS studies over a range of temperatures have shown that this acceptor has a 1s-state which is split into a large number of components which are closely spaced (Kahn et al., 1987). When thermally populated, each of the components of the 1s-state manifold acts as an initial state for optical transitions of the bound hole to one of the effective mass-like excited states. This in turn explains why the lines of this center appear broad.

Partial substitution of hydrogen with deuterium or tritium leads to additional series of lines which are all sharp, indicating an unsplit 1s-ground state. In crystals containing only copper and deuterium, we observe one series of transition lines which originate from a level at 18.20 meV above the valence band. In crystals containing hydrogen and deuterium in equal concentrations, we observe not only the H- and D-related spectra but an additional spectrum of an acceptor level at E_V + 18.10 meV (Fig. 6). The existence of this third series can be explained only if we assume that each copper acceptor binds two hydrogen isotopes forming A(Cu,H_2), A(Cu,HD), and A(Cu,D_2). This explanation has been verified with crystals containing most possible combinations of H, D, and T (Kahn et al., 1986).

The difference between the 1s-ground state of A(Cu,H_2) which is split into many closely spaced components and all the other deuterium- and tritium-containing combinations has been attributed to a difference in symmetry. Uniaxial stress studies indicate that A(Cu,H_2) has full tetrahedral symmetry. This can be understood in terms of

rapid tunneling of the hydrogen which in turn explains the splitting of the ground state. In centers containing the heavier hydrogen isotopes, tunneling ceases and the ground state is no longer split. The Devonshire model (1936), which treats the energy levels of a hindered rigid rotor, qualitatively explains these observations. The model shows how the motion of a rotor changes from rotational to librational as the moment of inertia increases.

It is interesting to recall that the copper acceptor also binds lithium donors, thereby reducing its valency (Haller et al., 1977a). Centers which contain both hydrogen and lithium may have been observed but await further studies for an unambiguous identification (Haller, 1978a). Full passivation of copper by hydrogen will be reviewed in the paragraph on deep levels.

5. THE DONOR D(H,O)

Rapid thermal quenching of standard ultra-pure germanium samples from 425° C generates A(H,Si). During annealing of this acceptor complex near room temperature, a donor complex D(H,O) forms. The maximum concentration of this complex reaches a few times 10^{11} cm^{-3} (Hall, 1974; 1975). Substitution of hydrogen with deuterium leads to a ground state shift of 51 μeV, a direct proof of the presence of hydrogen in the center (Haller, 1978b).

Two experimental observations have made this donor a much debated impurity complex. First, D(H,O) produces extremely sharp lines which do not split under stress (Joós et al., 1980). This property has been used in a recent study of the fundamental line widths of donors in germanium (Navarro et al., 1988). Second, at very high stress a new set of lines appears at lower energies. Besides these two basic features, a number of additional properties of D(H,O) have been revealed. Temperature-dependent PTIS studies by Navarro, et al. (1986) have shown that the 1s-like state is split into several components (Fig. 7). The spectroscopically determined splittings between the various 1s-state components do not correspond to the energies in the Boltzmann factors determined from variable temperature PTIS studies. The differences have been explained with the nuclear tunneling induced splitting in the ground and in the bound excited p-like states. Based on the tunneling hydrogen model, Fig. 8 schematically shows the configuration of the 1s-like state and the n-th p-like state using all the available experimental information.

A dynamic model with tunneling hydrogen (Jo6s et al., 1980) and a static model (Broeckx et al., 1980; Ham, 1988) have been proposed to explain the experimental findings. Space here is far too limited to discuss all the features of the two models and their relative merits. Suffice it to state that both models can explain certain properties of this complex. At the same time, both models have some shortcomings. The static model, which is based on a trigonal complex, is clearly too limited and cannot explain all the experimental data. The dynamic model can account for all the experimental findings but some of the parameters appear "un-physical" to the supporters of the static model. In a recent magnetospectroscopic study of D(H,O) Gel'mont, et al. (1989) obtain slightly higher values for the splittings between the 1s-components than reported by Navarro, et al. (1986). This finding lends further support to the tunneling model.

IV. Hydrogen Interacting with Deep Level Centers and Dislocations

6. THE DIVACANCY-HYDROGEN COMPLEX (V_2H)

During the efforts to develop ultra-pure Ge single crystals for gamma ray detector applications, we recognized that dislocation-free crystals were effectively trapping free charge carriers (Haller et al., 1977b). Contrary to silicon single crystals which are preferably dislocation free for many applications, germanium detectors made from dislocation-free material perform extremely poorly. Variable temperature Hall effect measurements on two single crystal samples which were cut next to each other from a partially-dislocated slice reveal an acceptor level at E_V + 80 meV (Fig. 9). Only H_2- and D_2-grown crystals show this level in dislocation-free areas. Deep level transient spectroscopy (DLTS) experiments give a strong single peak signature of this level.

What makes this acceptor interesting is that its concentration can be varied reversibly over a wide range. Thermal quenching and annealing experiments showed that the acceptor must be due to a center which undergoes dissociation/recombination reactions. The following arguments led to the proposition that the acceptor level is due to a divacancy-hydrogen complex (V_2H).

Entropy at the melting point requires that a large number of point defects be present in the crystalline solid (Kittel, 1967). In germanium, these are vacancies [in silicon, it has

been shown that both silicon interstitials and vacancies are present (Seeger and Chik, 1968)]. Upon cooling, the vacancy equilibrium concentration drops rapidly and excess vacancies either condense on dislocations leading to dislocation climb or, in dislocation-free crystals, they precipitate into larger complexes. Monovacancies are very mobile and do not remain isolated at room temperature. Divacancies diffuse significantly more slowly and, together with a hydrogen atom, may be stabilized into a V_2H complex.

The reversible concentration changes can be explained with a reaction between V_2H and H. The maximum concentration of V_2H is approximately 10^{13} cm^{-3} and is low compared to the total hydrogen concentration. Based on these general arguments and experimental observations, the following reaction has been proposed:

$$V_2H \; + \; H \underset{\text{dissociation}}{\overset{\text{recombination}}{\rightleftharpoons}} V_2H_2$$

monovalent acceptor at $E_V + 80$ meV	"deep" donor	neutral complex

This reaction has been studied quantitatively in the recombination direction. The dissociation proceeds, for all practical purposes, instantaneously. Figure 10 shows the steady state concentration of V_2H as a function of temperature. This dependence is determined best by proceeding from low to high temperatures. In this way, rapid dissociation brings the sample to the new steady state quickly. Returning from high to low temperatures requires equilibration times which reach several hours at 300° C and many days at 200° C. Heating a small sample to temperatures above 400° C leads to an irreversible reduction of [V_2H]. This is due to a loss of hydrogen through diffusion out of the sample. Because one can only measure [V_2H] but not [V_2H_2] nor [H], it has been very difficult to create a complete quantitative description of the recombination/dissociation model. The evaluation of a large number of recombination curves supports this simple picture using physically reasonable parameters.

It would be desirable to obtain symmetry information on V_2H. All efforts to generate optical spectra of ground-to-bound excited state hole transitions have failed so far. Because of the low concentration of V_2H, we attempted to use PTIS. This technique

works well if the bound excited state lifetimes are long so that a phonon can interact with the bound hole and lift it into the valence band. The complete absence of any transition lines may be due to short lifetimes which could be caused by a phonon assisted return of the hole into the ground state. Uniaxial stress DLTS does not produce any splitting in the V_2H peak but generates a small shift. These results do not provide any symmetry information either. It appears that microscopic structure information on V_2H (and V_2D) may not become available unless some novel, sensitive technique can be brought to the problem.

7. HYDROGEN PASSIVATION OF DEEP LEVEL IMPURITIES AND DEFECTS

The best understood hydrogen passivated deep level impurity is the triple acceptor copper. We have discussed the effective mass-like copper-dihydrogen center $A(Cu,H_2)$ in Section 4. Using DLTS on copper- and hydrogen-containing diodes, one finds, in addition to $A(Cu,H_2)$, two distinct peaks besides the peaks generated by the well-known isolated copper levels at $E_V + 44$ meV ($Cu^{o/-}$) and $E_V + 330$ meV ($Cu^{-/--}$). Together with variable temperature Hall effect results, the two copper- and hydrogen-related levels have been located at $E_V + 80$ and $E_V + 175$ meV, respectively. It is worthwhile to note that when copper and lithium are diffused into pure germanium crystals, two deep levels at $E_V + 100$ meV and $E_V + 270$ meV are found (Haller et al., 1977b). These two levels are most likely formed by the double acceptor A(Cu,Li) while the above-mentioned levels are due to A(Cu,H). There exists no further experimental information which would make these assignments definitive.

Extending partial copper passivation from one and two hydrogen atoms to three, one expects to obtain a fully passivated (Cu,H_3) center. Strong support for the formation of such an electrically inactive center stems from hydrogenation experiments which have shown that the concentrations of all copper-related levels are reduced. Prolonged annealing in a vacuum regenerates the various levels (Pearton, 1982).

In addition, a number of other deep level impurities have been hydrogen passivated. They include nickel, cadmium, tellurium, zirconium, titanium, chromium, and cobalt (Pearton et al., 1987). Most of these studies have been qualitative, and important work remains to be done if the hydrogenation of these and most probably additional impurities such as gold, palladium, platinum and iron, is to be fully understood.

8. HYDROGEN AND DISLOCATIONS

In view of the large number of hydrogen/point defect and hydrogen/impurity interactions, it is not surprising that hydrogen would bind to dislocations as well. Two kinds of studies have reported on hydrogen/dislocation interaction: DLTS studies on ultra-pure Ge diodes and electron paramagnetic resonance (EPR) spectroscopy investigations on a variety of germanium crystals. Using DLTS, Hubbard and Haller (1980) demonstrated that the strength of a dislocation-related broad DLTS peak band was proportional to the dislocation density (Fig. 11). In the same study, it was shown that crystals grown in a hydrogen atmosphere generated broad, dislocation-related DLTS peaks at lower temperatures than crystals grown in a nitrogen atmosphere. With today's knowledge, we interpret the difference with partial passivation of the dislocation-generated levels in the bandgap. Using dislocation-rich pure germanium crystals, Pearton and Kahn (1983) showed that a dislocation-related broad band in DLTS decreased in intensity upon plasma hydrogenation. This information is consistent with full passivation of dislocation bands by hydrogen. The early DLTS studies of the effects of hydrogen on dislocation-related energy bands are qualitative in nature and do not provide microscopic information on the dislocations or the hydrogen sites. One has to remember that, as in the case of point defects and impurity complexes discussed earlier, the concentrations of dislocations and the related states in the bandgap are very small, restricting the tools for investigation to the highly sensitive techniques.

In a very detailed EPR study, Pakulis and Jeffries (1981), and Pakulis (1983) investigated a large number of ultra-pure germanium crystals which were grown in vacuum or in a hydrogen or deuterium atmosphere. Several of the samples were dislocation free. The sensitivity of EPR was greatly enhanced through the use of large cylinders of germanium. At the operating temperature of ~ 2 K, these crystals are excellent insulators and act as high Q dielectric cavities. This method had been used earlier in the study of Li-O donors (Haller and Falicov, 1978; 1979). Q-factors of up to 10^6 can be reached with such cavities. Besides the well-known shallow donor-related lines, a large number of spin resonances related to dislocations were found in optically pumped samples. In hydrogen-free crystals, these resonances showed normal absorption character. In hydrogen- and deuterium-grown crystals, however, the sign of the resonances switched. The explanation for the unusual behavior is based on the electrical detection of the spin resonances instead

of the usual magnetic detection. Pakulis and Jeffries (1981) were able to identify two sets of lines. Four broad lines were aligned along <111> while a set of 24 sharp lines were aligned along <111> with a 1.2° distortion in all six <110> orientations. Figure 12 shows the EPR derivative spectrum with H in a <100> direction. All 28 dislocation-related lines merge into a simple spectrum called "New Lines" next to the hyperfine structure of the arsenic donors. Figure 13 displays the g-values of the 24 sharp EPR lines as a function of the magnetic field orientation. The values of g range from $g_{\parallel} = 0.73$ to $g_{\perp} = 1.89$. All these lines only appeared after optical pumping but they persisted for hours after the light had been turned off. Pakulis and Jeffries (1981) explain their EPR data with dangling bonds of 60° dislocations of the shuffle set. The dangling bonds of a given dislocation point approximately along one of the [111] orientations. The small 1.2° tilt of the dangling bonds could be due to an intrinsic distortion or could be the result of a Peierls-like instability (Peierls, 1953). The mechanism of sign reversal which is unambiguously due to the presence of hydrogen in these crystals could not be explained satisfactorily.

V. Summary and Discussion

In this chapter on hydrogen-related effects, I have tried to review the interesting properties of hydrogen-related centers which have been discovered in ultra-pure and in some specially doped germanium crystals. It is obviously not only the technological importance which has been the driving force for all these studies but also the basic interest in the physics and chemistry of impurities, native defects and complex centers made up of two or more of these. In sharp contrast to the vast effort spent in recent years on hydrogen-related studies in silicon and III-V semiconductors, it was a rather small community of researchers who tried to unfold the puzzles posed by hydrogen in germanium.

The studies of hydrogen in germanium preceded the analogous studies in silicon and later III-V semiconductors by several years. They served as a useful guide in many instances. The tunneling hydrogen concept, developed first for D(Li,O), was later expanded to describe acceptors as well. The model was available for the analysis of the IR spectra of the acceptor A(Be,H) in silicon. The observation that the valency of an acceptor-like center is reduced by one for each hydrogen appears to apply not only to germanium but also to silicon and III-V semiconductors. It is very satisfying to see how the experimental

studies have stimulated the theoretical treatment of hydrogen-containing centers. The results obtained with these numerical methods no longer only describe existing data but they can predict structures and properties of defect complexes. The time and effort required by theory on a single defect appears to be very significant, however, and the experiments may remain more economical in the foreseeable future!

The restrictions on the number of usable characterization methods imposed by the very small concentrations of hydrogen-related centers in germanium have largely been compensated by the exceptionally powerful PTIS technique. Together with uniaxial stress, high resolution PTIS has provided practically all the structure-related information on hydrogen-related complexes in germanium. Making use of the special property of D(H,O), that of stress insensitivity, PTIS has generated the sharpest dipole transition lines ever recorded with a semiconductor. RBS and channeling, which led to the definitive determination of the position of hydrogen and the passivated acceptor impurity in silicon, cannot be applied to germanium. We must rely on the results of theory which tells us that hydrogen occupies an antibonding position near the T_d-site in the acceptor A(H,Si). We can safely assume that the same is true for A(H,C). For A(Be,H) and A(Zn,H), however, we may not be able to apply this result.

As is the case for silicon, we do not have any information on the microscopic structure of hydrogen-passivated deep levels. This would be most elucidating for theoretical work because it appears that energy level removal from the band gap by hydrogen is especially effective for deep level impurities. At the risk of sounding too simplistic, it appears to me that in most cases hydrogen reduces the degree of local imperfection. With the incorporation of hydrogen, the crystal appears to become more perfect. Hydrogen pushes energy levels out of the bandgap, a phenomenon quite crucial for amorphous silicon. Hydrogen has been shown experimentally as well as theoretically to play an amphoteric role, passivating both acceptors and donors. The notable exceptions are, of course, the acceptors A(H,Si) and A(H,C) as well as the donor D(H,O) in germanium. In these cases, hydrogen activates neutral impurities.

Contrary to silicon, very little work has been done in germanium regarding quantitative hydrogen diffusion or electric field drift studies. Such experiments may be complicated by the fact that ultra-pure germanium becomes intrinsic already at temperatures

near 200 K. It would be worthwhile to explore the possibility of using lightly doped germanium for such studies in order to explore Fermi level dependent effects.

A further group of interesting experiments to be done is related to the double acceptors Cd and Hg. Crystals doped with these impurities have been used for infrared detector applications and the hole binding energies of the neutral species are well known. It would be interesting to explore the electronic and the real space structure of A(Cd,H) and A(Hg,H) if they can be formed.

In conclusion, it may be stated that the variety of interactions between hydrogen and impurities or defects is much larger than anyone had imagined. Much interesting physics has been learned in the course of these experiments but a large number of puzzles remains to be solved and questions to be answered. An important one is: what is the state of isolated hydrogen in a defect- and impurity-free lattice of a semiconductor? It is surprising that the seemingly simplest question is, in fact, the most difficult one and still awaits an answer.

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TABLE I

ACCEPTOR COMPLEXES WITH TWO 1S-LIKE LEVELS[a]

Acceptor Complex	Level Designation and Binding Energy (meV)		Energy Splitting (meV)	Average Energy (meV)
	Ground State	Excited State		
A(H,Si)	$A(H,Si)_2$	$A(H,Si)_1$		
	11.66	10.59	1.07	11.13
A(H,C)	$A(H,C)_2$	$A(H,C)_1$		
	12.28	10.30	1.98	11.29
A(Be,H)	$A(Be,H)_1$	$A(Be,H)_2$		
	11.29	10.79	0.50	11.04
A(Zn,H)	A(Zn,H)	[b]		
	12.53	--------	-------	-------

[a]This 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.

[b]A second 1s-like level has not been detected, but is expected to exist; see text.

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FIGURE CAPTIONS

Fig. 1. The two-step ionization process which is the basis of PTIS.

Fig. 2. PTI spectrum of a p-type, ultra-pure Ge sample, obtained by Fourier transform spectroscopy. The sample contains the acceptors B, Al and A(D,C), in a total concentration of 6×10^{10} cm^{-3}. The most narrow lines are 0.09 cm^{-1} (= 11 μeV) wide.

Fig. 3. PTI spectra of the D- and C-transitions of Al, and the D-transition of $A(D,C)_2$, for uniaxial stress applied along a) [100], b) [110], and c) [111]. All spectra were recorded at 7.0 K.

Fig. 4. Arrhenius plot of the free hole concentration in a beryllium-doped germanium crystal grown in a hydrogen atmosphere. The shallow acceptor A(Be,H), present at a concentration of 10^{13} cm^{-3}, is shown to dissociate under thermal annealing.

Fig. 5. The piezospectroscopic behavior of the two 1s-like levels of differently oriented, trigonal shallow acceptor complexes, based on the "equivalent stress" model. (a) Trigonal distortion equivalent to a stress of +0.205 kbar (tensional). (b) Trigonal distortion equivalent to a stress of -0.810 kbar (compressional). Roman numerals denote the four possible orientations of the complexes. "Λ_4" and "$\Lambda_{5,6}$" denote the representations of C_{3v} according to which the states transform, in the absence of externally applied stress. The energy shifts are shown for externally applied compressional stress; under applied tensional stress, the behavior of (a) and (b) is reversed, as explained in the text.

Fig. 6. PTI spectra of the copper-dihydrogen acceptors that appear in samples which were grown under atmospheres of different hydrogen isotopes. (a) Pure H_2, showing the complex spectrum of $A(CuH_2)$; (b) a 1:1 mixture of H_2 and D_2, showing $A(CuH_2)$, A(CuHD), and $A(CuD_2)$ in a 1:2:1 ratio; (c) nearly pure D_2, showing $A(CuD_2)$ and a trace of A(CuHD).

Fig. 7. Photothermal conductivity of n-type ultra-pure germanium, showing some hydrogen-oxygen donor and phosphorus transitions. In (b) the subscripts 1,2,

and 3 of the D(H,O) symbol stand for transitions originating in the first, second and third shallower-lying 1s-states. In (c) P stands for phosphorus.

Fig. 8. Schematic total energy level diagram of the D(H,O) donor in Ge based on the tunneling hydrogen model (Joós et al., 1980).

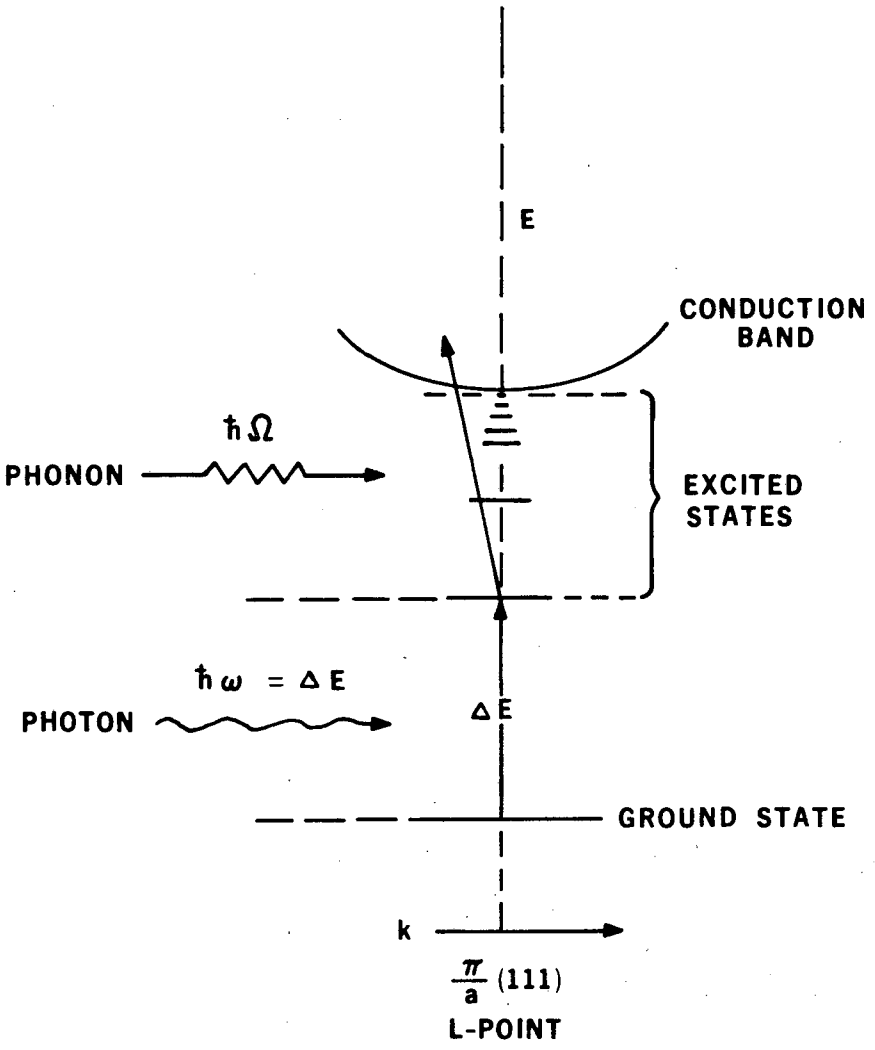
Fig. 9. Arrhenius plots of the free hole concentration p (log p versus 1000/T) in two samples cut from a partially-dislocated slice of ultra-pure germanium. The dislocation-free sample contains an acceptor with E_V + 80 meV. The shallow level net-concentration is the same in both samples.

Fig. 10. Steady state concentration of the V_2H acceptor as a function of the absolute inverse temperature for two dislocation-free samples from different crystals. The dashed vertical line indicates the temperature limit above which an irreversible loss of V_2H occurs.
The dotted line corresponds to $1.04 \times 10^{19} \exp(-0.71\ eV/kT)\ cm^{-3}$.

Fig. 11. Capacitive transient spectra of defect states associated with dislocations in ultra-pure germanium (crystal #281 grown along [100] under 1 atmosphere of H_2). The micrographs show the etch pits produced by dislocations on a (100) surface. DLTS peak b has an activation energy of E_V + 20 meV. The net-shallow acceptor concentration is $10^{10}\ cm^{-3}$.

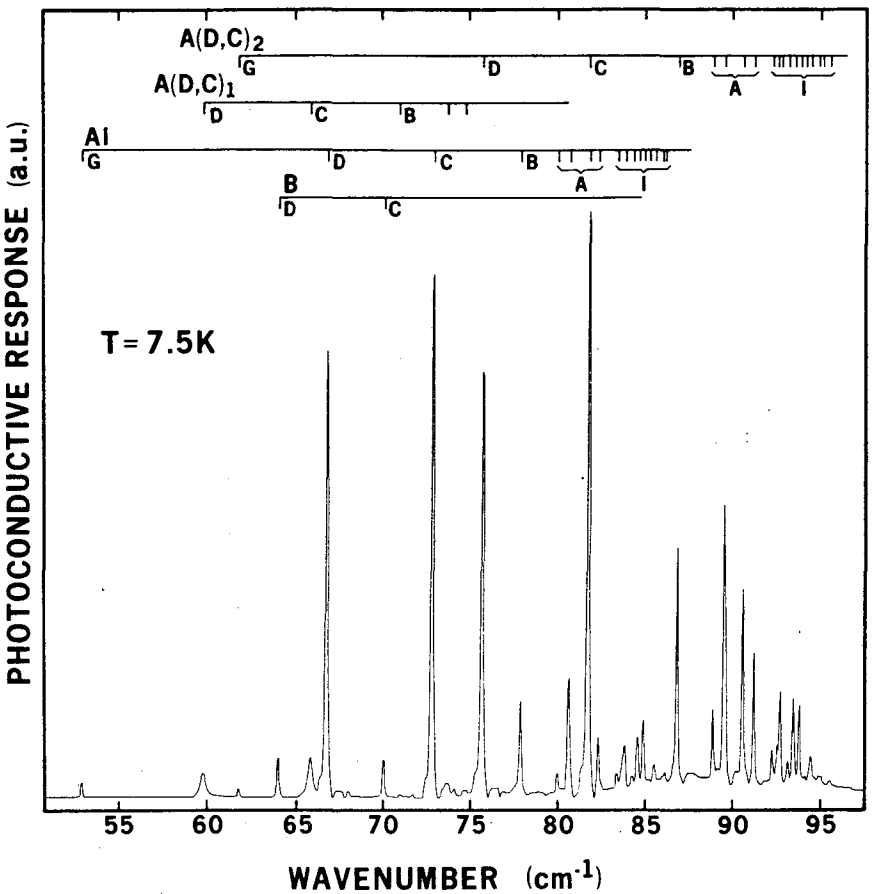
Fig. 12. Derivative curves of EPR in a highly dislocated As-doped germanium crystal grown in a H_2 atmosphere. The magnetic field is oriented along the [100] direction. T = 2 K, f = 25.16 GHz. Note the sign reversal of the new lines as compared to the As-donor hyperfine structure. Dislocation density $\approx 2 \times 10^4\ cm^{-2}$. (Courtesy: Pakulis and Jeffries, 1981).

Fig. 13. Angular dependence of the *g* tensor for the narrow new lines in a sample of germanium lightly doped with phosphorus. The magnetic field is rotated in a plane tilted ~ 3° from a (110) plane. Inset shows the continuation of the lines for low values of *g* near <110>. T = 2 K, f = 26.06 GHz, dislocation density $\approx 10^4\ cm^{-2}$. The dashed line shows a portion of one of the four broad lines. (Courtesy: Pakulis and Jeffries, 1981).



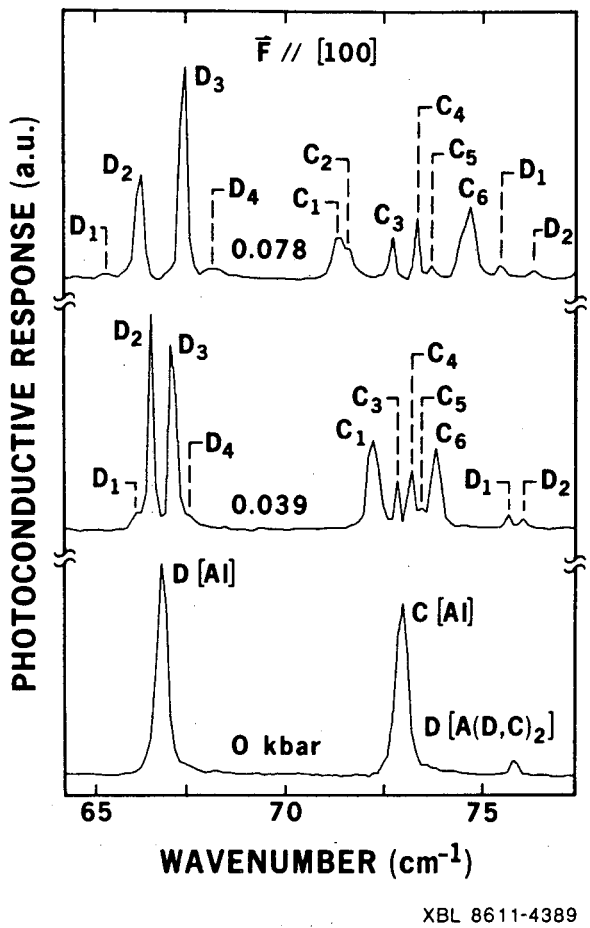
XBL 7411-8629

FIG. 1.



XBL 863-1160

FIG. 2.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D3
D2
D4
D1
C2
C1
C3
C4
C5
C6
D1
D2
0.078
D2
D3
D4
D1
C1
C3
C4
C5
C6
D1
D2
0.039
D [Al]
C [Al]
D [A(D,C)2]
0 kbar
PHOTOCONDUCTIVE RESPONSE (a.u.)
65
70
75
WAVENUMBER (cm-1)
XBL 8611-4389

FIG. 3a).

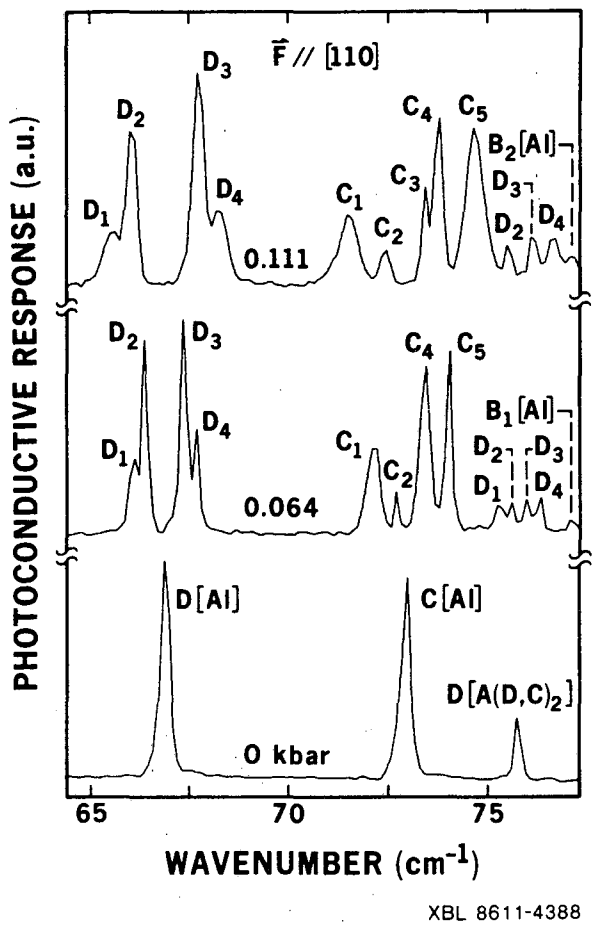

F // [110]
D1
D2
D3
D4
C1
C2
C3
C4
C5
B2[Al]
D3
D2
D4
0.111
D1
D2
D3
D4
C1
C2
C4
C5
B1[Al]
D2
D3
D1
D4
0.064
D[Al]
C[Al]
D[A(D,C)2]
0 kbar
PHOTOCONDUCTIVE RESPONSE (a.u.)
65
70
75
WAVENUMBER (cm-1)
XBL 8611-4388

Fig. 3b).

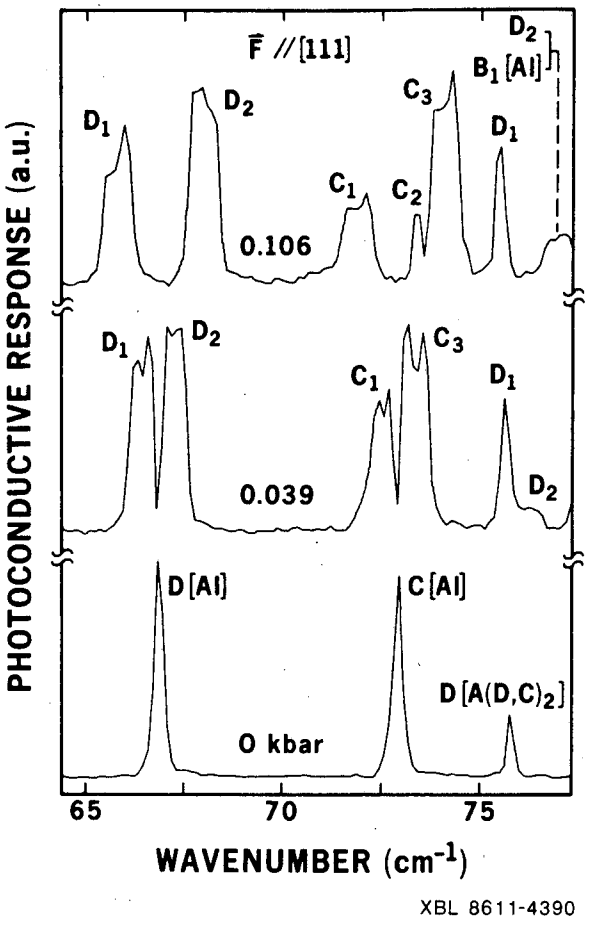
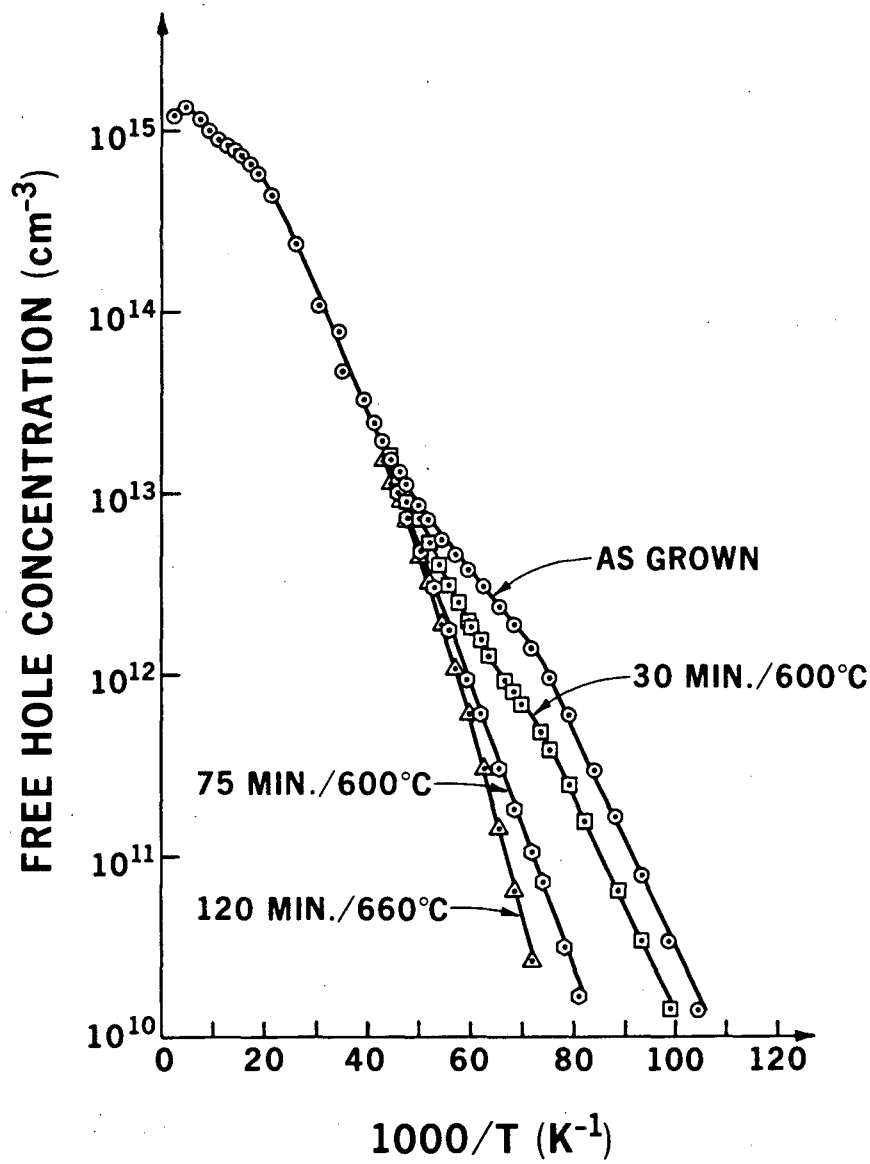
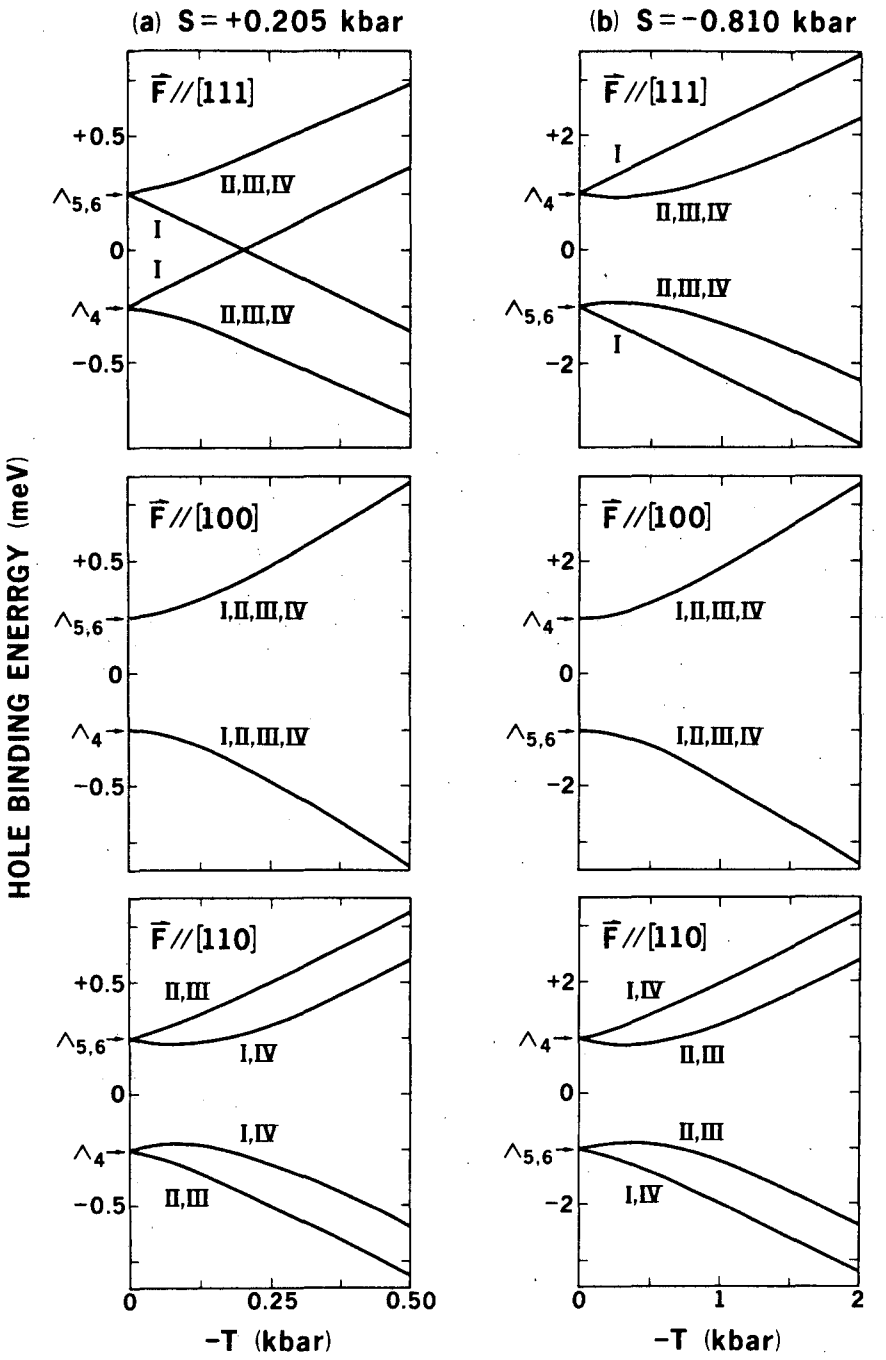

F̄ //[111]
D1
D2
C1
C2
C3
D1
D2
B1 [Al]
0.106
D1
D2
C1
C3
D1
D2
0.039
D [Al]
C [Al]
D [A(D,C)2]
O kbar
PHOTOCONDUCTIVE RESPONSE (a.u.)
65
70
75
WAVENUMBER (cm-1)
XBL 8611-4390

Fig. 3c).



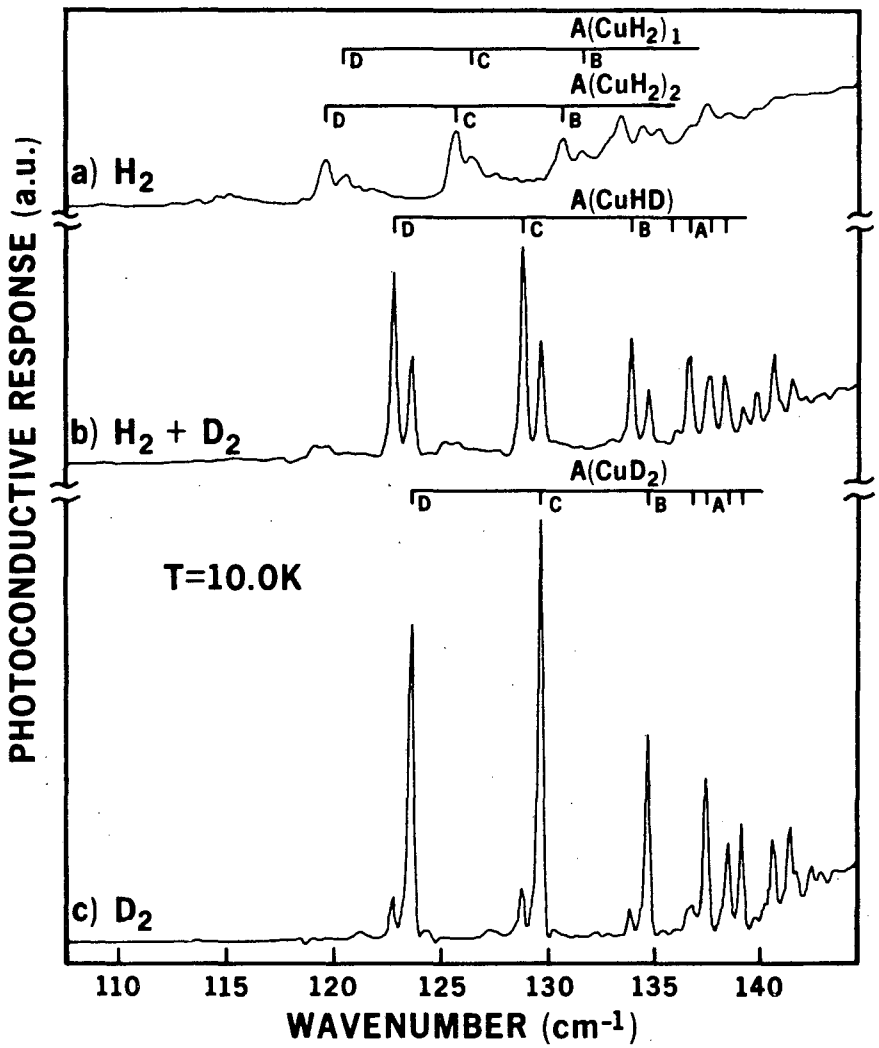
XBL 8511-4666

FIG. 4.



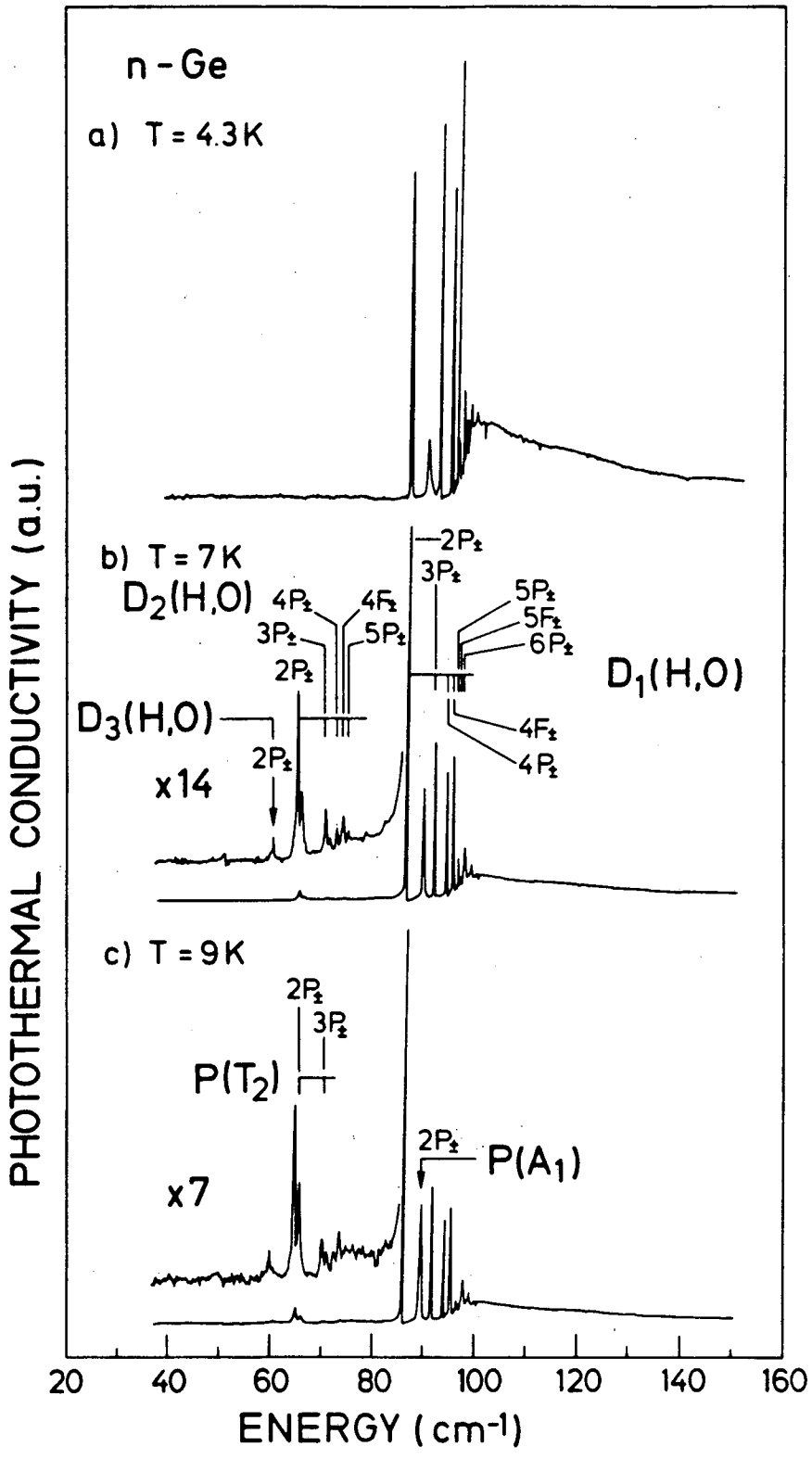
XBL 8611-4400

FIG. 5.



XBL 863-1157A

FIG. 6.



XBL 893-1013

FIG. 7.

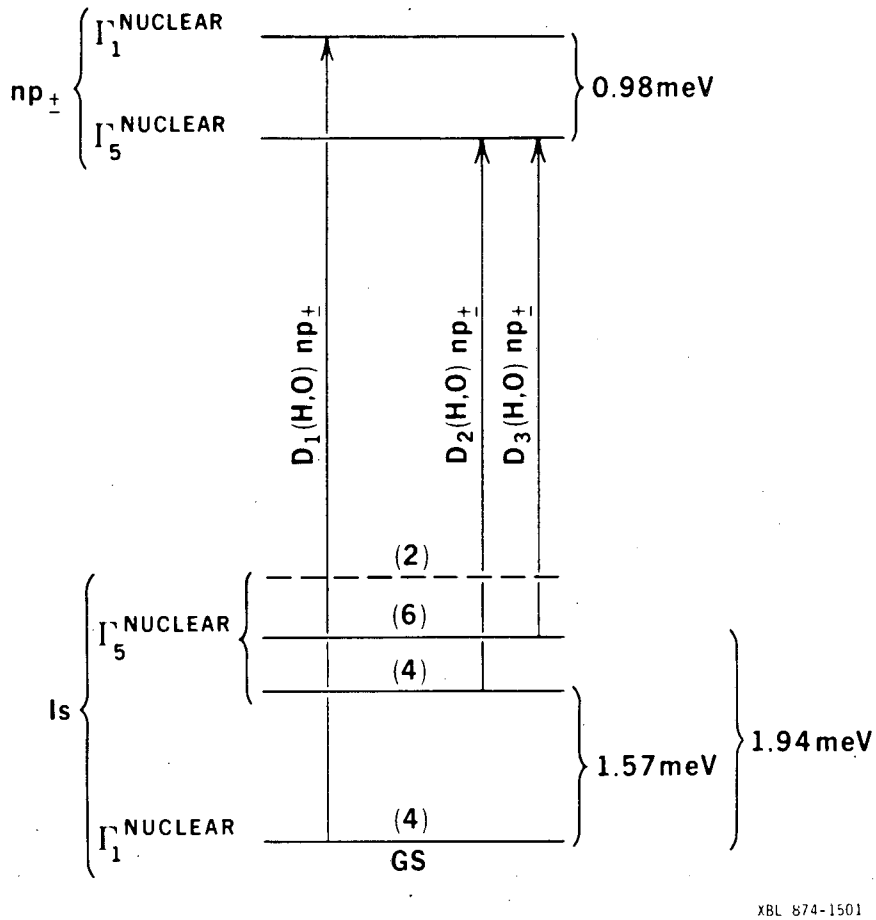

np±
Γ1 NUCLEAR
Γ5 NUCLEAR
0.98meV
D1(H,O) np±
D2(H,O) np±
D3(H,O) np±
(2)
(6)
(4)
(4)
1s
Γ5 NUCLEAR
Γ1 NUCLEAR
1.57meV
1.94meV
GS
XBL 874-1501

FIG. 8.

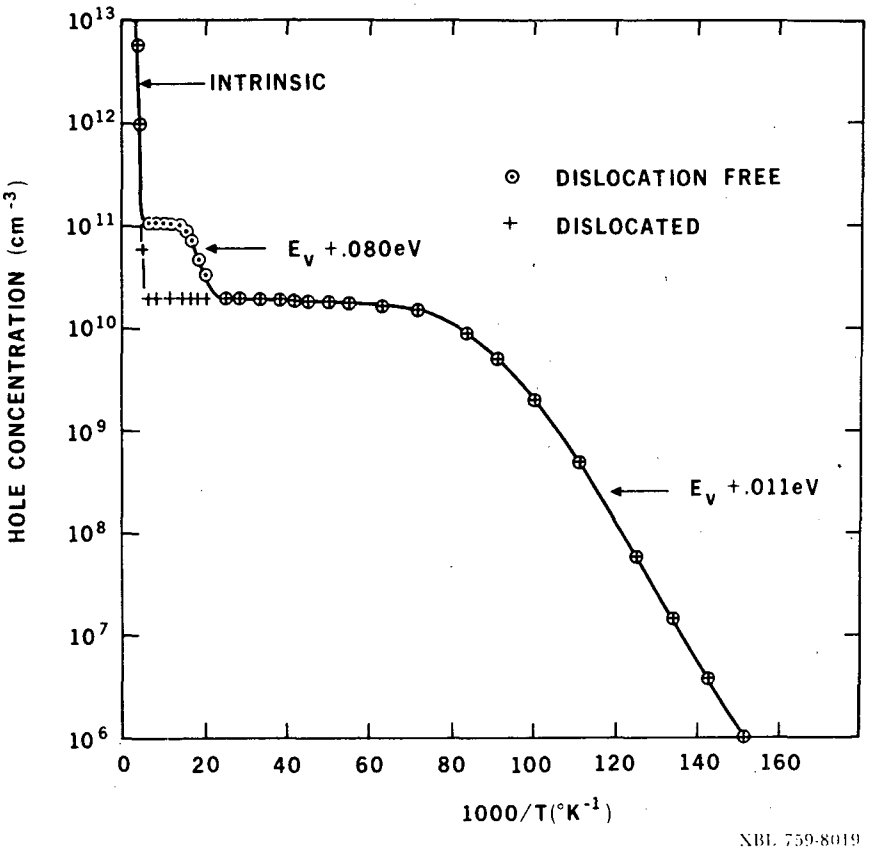

HOLE CONCENTRATION (cm^{-3})
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
INTRINSIC
DISLOCATION FREE
DISLOCATED
E_V +.080eV
E_V +.011eV
0
20
40
60
80
100
120
140
160
1000/T(°K^{-1})
XBL 759-8019

FIG. 9.

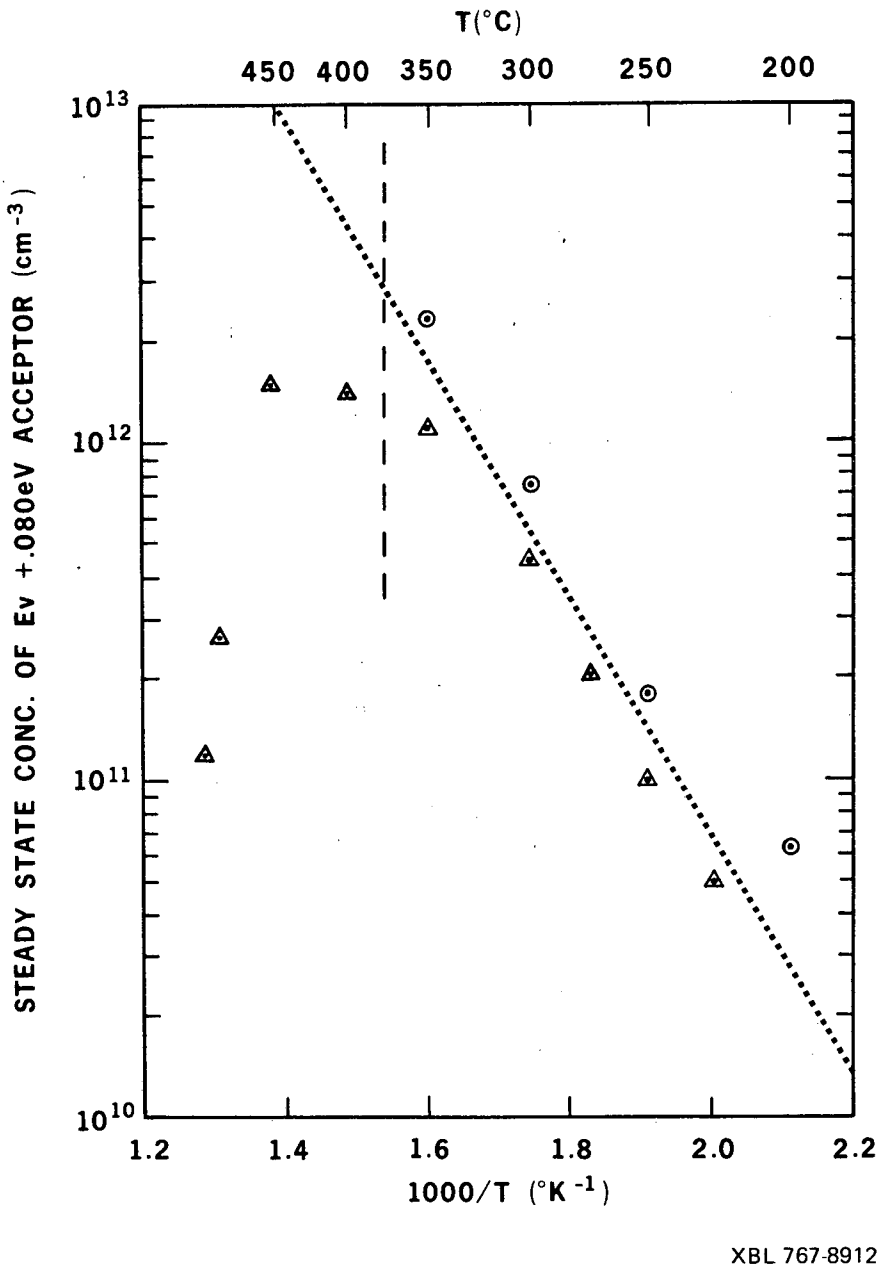
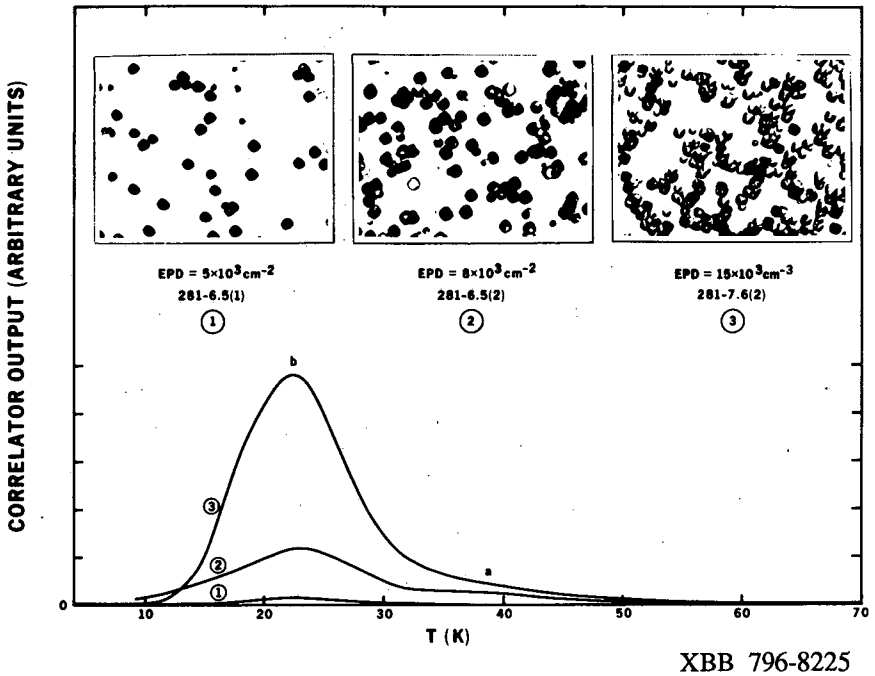
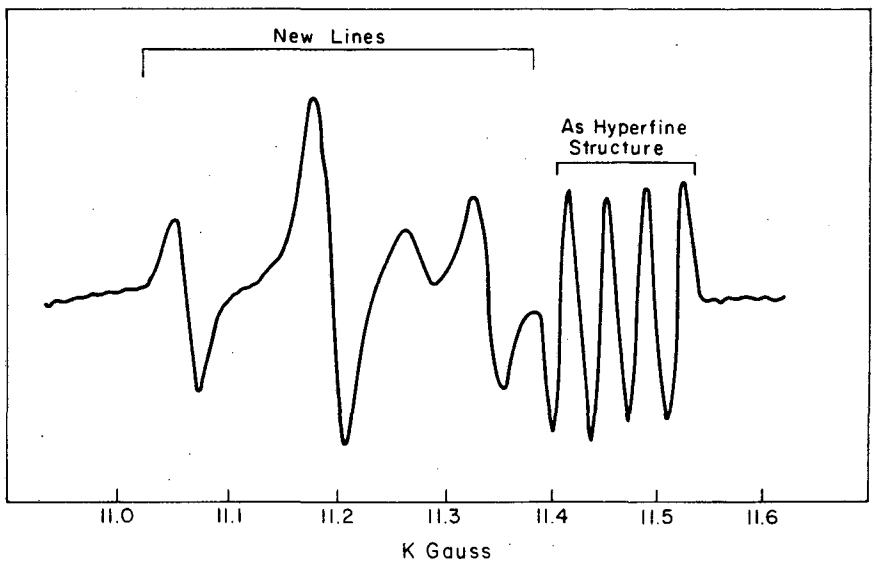

T(°C)
450 400 350 300 250 200
10^{13}
10^{12}
10^{11}
10^{10}
STEADY STATE CONC. OF Ev +.080eV ACCEPTOR (cm^{-3})
1.2 1.4 1.6 1.8 2.0 2.2
1000/T (°K^{-1})
XBL 767-8912

FIG. 10.



XBB 796-8225

FIG. 11.



XBL 811-107

FIG. 12.

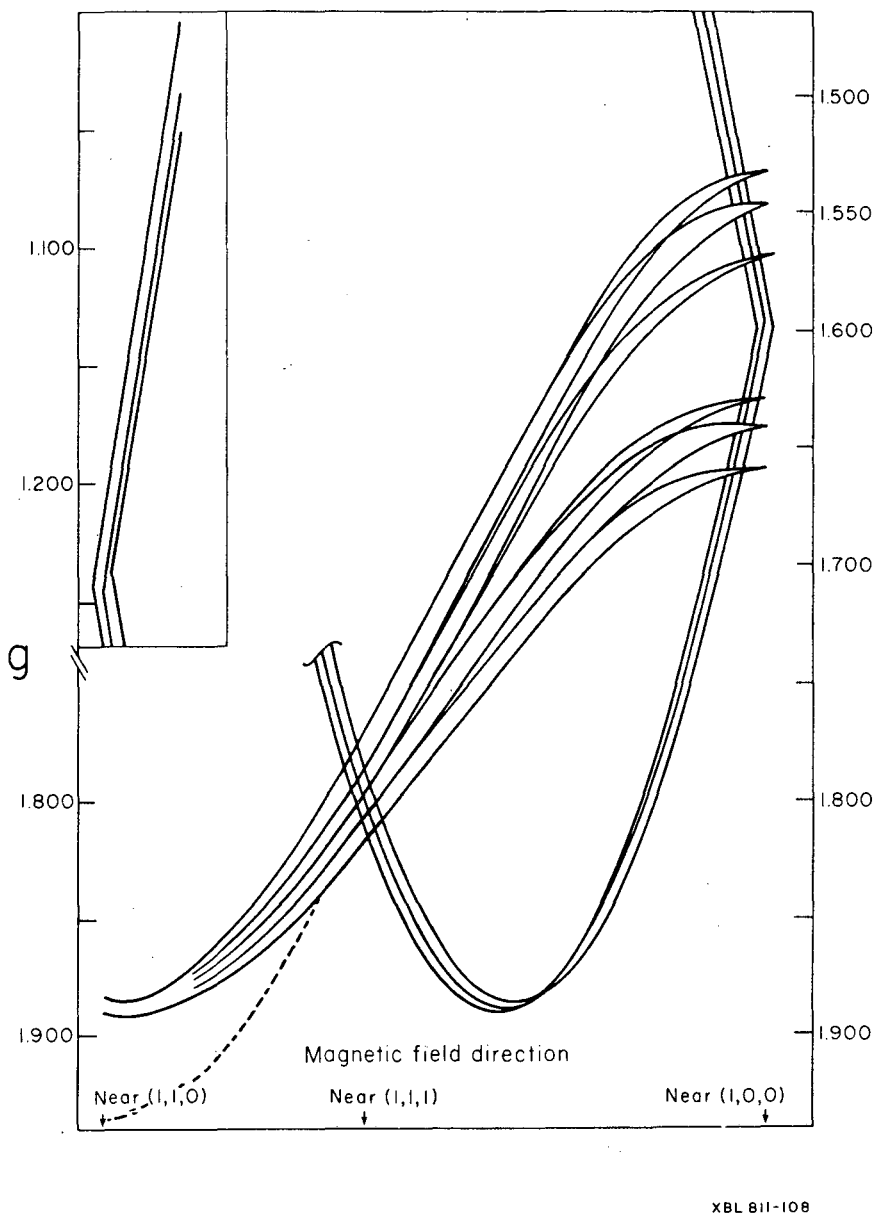

1.100
1.200
g
1.800
1.900
1.500
1.550
1.600
1.700
1.800
1.900
Magnetic field direction
Near (1,1,0)
Near (1,1,1)
Near (1,0,0)
XBL 811-108

FIG. 13.

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