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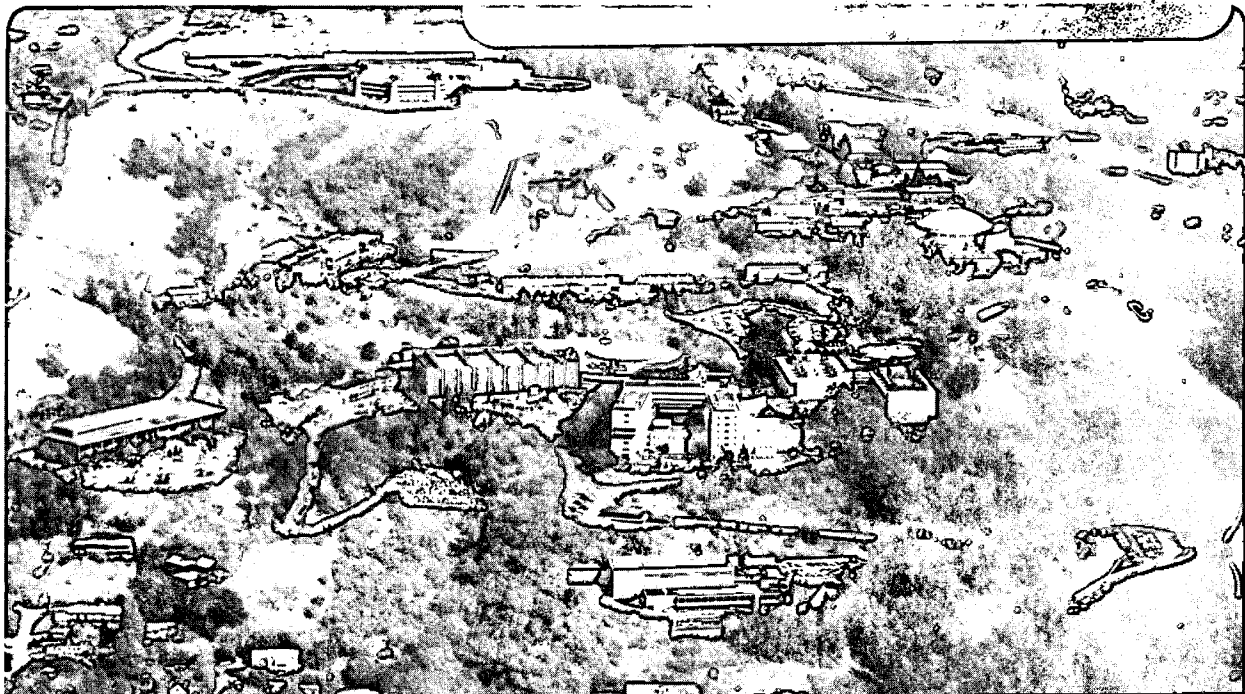
IR-SPECTROSCOPY OF IMPURITY  
COMPLEXES IN GERMANIUM

E.E. Haller

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IR-Spectroscopy of Impurity Complexes in Germanium

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Abstract

A large number of impurity complexes which create shallow levels, have been discovered in pure and doped germanium single crystals. The structure and the composition of several of these complexes have been determined using far infrared spectroscopy and information about crystal growth related residual impurities. In general, the complexes consist of a heavy substitutional impurity binding one or more light, interstitial impurities such as hydrogen or lithium. The coupling between the tunneling motion of the interstitial component and the electronic structure of the complexes can create complicated groundstate manifolds which contain stress insensitive components. Spectroscopy further shows that multivalent centers, such as double or triple acceptors, become hydrogenic complexes upon binding one or two hydrogen atoms respectively. Neutralization of shallow acceptors in silicon, which has recently attracted attention, appears to be the same phenomenon as the valancy reduction of multiple acceptors in germanium.

## I. Introduction

Far infrared spectroscopy has played a key role in the exploration of shallow levels, so called "hydrogen analoga in the solid state", in the forbidden energy gap in semiconductors. The effective mass theory (EMT) [1,2] successfully describes the shallow states in terms of a hydrogen like center in a medium with the relative dielectric constant  $\epsilon$  and an appropriately averaged effective mass  $m^*$ . The binding energy  $E$  of an electron bound to a positively charged donor core is:

$$E = - \frac{e^4 m^*}{2 \epsilon^2 \epsilon_0^2 \hbar^2} \quad (1)$$

with  $e$  = charge of the electron,  $\epsilon_0$  = permittivity of vacuum and  $\hbar$  = Planck's constant/ $2\pi$ .

With IR-spectroscopy one observes electronic dipole transitions from the ground state to one of the bound excited states. Typical photon energies required to initiate such transitions reach from  $\sim 3\text{meV}$  ( $25\text{cm}^{-1}$ ,  $400\mu\text{m}$ ) to  $\sim 300\text{meV}$  ( $2500\text{cm}^{-1}$ ,  $4\mu\text{m}$ ). An excellent review article on the "hydrogen analog in the solid state" has been published by Ramdas and Rodriguez [3].

Advances in the purification and structural perfection of semiconductor crystals, mainly silicon and germanium and more recently also gallium arsenide, have led to ever improving IR- spectra. The smaller line widths enabled the discovery of bound states with quantum numbers as large as ten. The rich experimental data [4,5] have stimulated the development of advanced theoretical treatments of shallow acceptors [6,7]. The theory for donors, less complicated because of the simpler band structure, had been developed a while ago [8].

The excellent state of affairs regarding the understanding of ground and bound excited states of shallow acceptors and

donors has been a great help in the study of impurity and defect complexes which form shallow levels. The first such complexes were discovered by Hall [9] in ultra-pure germanium which had been developed for the fabrication of gamma ray detecting p-i-n diodes [10]. In the meantime a large number of shallow level complexes have been found and characterized. It is the purpose of this review to summarize the current knowledge about these complexes.

## 2. Experimental Techniques

Spectroscopy of shallow level complexes in germanium requires photons with energies in the range  $\sim 5\text{meV}$  to  $50\text{meV}$  (i.e.,  $\nu$ :  $40\text{cm}^{-1}$  to  $400\text{cm}^{-1}$  or  $\lambda$ :  $250\mu\text{m}$  to  $25\mu\text{m}$ ). No broadly tunable, strong far-infrared sources exist in this energy range. Interferometers working with hot blackbody sources and with computers which can efficiently perform Fourier transformation of an interferogram into a spectrum, are the spectrometers of choice in this photon energy range. The older interferometers which record the interferogram point by point, are now slowly replaced with very sophisticated rapid-scan instruments which can perform on-line fast Fourier transformation and offer a great amount of operating conveniences. The standard techniques used to observe dipole transitions of bound carriers is absorption spectroscopy. At very small impurity concentrations, the absorption signals become smaller than the fluctuations in the transmitted photon stream, resulting in a signal-to-noise ratio much smaller than unity. Under these circumstances, one has to use a two step ionization technique which has been discovered by T.M. Lifshitz and F.Ya Nad' [11]. Fig.1 shows this process for a shallow hydrogenic donor. The bound donor electron is excited through the absorption of a photon of appropriate energy from the ground state to one of the bound excited states. At a temperature between  $\sim 5\text{K}$  and  $10\text{K}$  the phonon population in the germanium crystal is sufficiently large for the carrier in the excited

state to be transferred with a finite probability into the band instead of falling back into the ground state. The photo-thermally generated free carriers lead to a change in the conductivity of the germanium sample.

Application of a voltage bias generates a current which in turn is transformed into a voltage signal by a transimpedance amplifier (TIA). The schematic of a widely used circuit is shown in Fig.2. A major advantage of a TIA is that the bias is held constant across the sample with a difference amplifier. Long RC- times which one encounters with very pure, high-impedance samples are inactive because of the constant bias scheme. The critical elements of the TIA are the load resistors and the junction field effect transistor (JFET). The load resistors should be of the highest quality, preferably made of metal or metal oxide film. Cooling reduces the kTR noise of the channel. The field effect transistor can be cooled to about 100K. Upon further lowering the operating temperature, the doping atoms in the channel begin to freeze out and the device becomes very noisy and eventually it ceases to function. Metal-oxide-semiconductor (MOS) devices of the enhancement mode type do work at very low temperatures but they are still noisier at low frequencies than junction field effect transistors by many orders of magnitude. The following table shows some results of noise measurements on n-channel JFETs in the grounded gate source follower configuration [12]. The results obtained in this configuration do not directly reflect the performance in the actual TIA circuit but they offer useful guidelines for the selection of appropriate JFETs. The additional measurements of the gate leakage current further narrows down the choices.

TABLE 1: ROOM TEMPERATURE JFET VOLTAGE NOISE

<u>FET</u>	<u>VOLTAGE NOISE @ 10Hz (nV/√Hz)</u>
2N4416	21.0
2N3875	17.6
TCG132	11.4
J230	7.3
2N4867	6.4
2SK147	4.4

In the above discussion no mention was made of the contacts on the semiconductor which are required to make direct conductivity measurements. In order to operate at low temperatures the contacts must be degenerately doped. The contact fabrication process should not compromise the purity and structural perfection of the sample. This requirement practically excludes high temperature diffusion of dopant atoms for contact fabrication. Ion implantation followed by annealing at moderate temperature yields excellent ohmic contacts and does not alter the crystal quality. Low implantation voltages (20-40kV) and implant doses in the range of  $4$  to  $8 \times 10^{14} \text{cm}^{-2}$  of boron or phosphorus ions for  $p^+$ - or  $n^+$ - contacts respectively, are typically used. Boron has been shown to be electrically active without annealing [13], though treating the crystal at  $250^\circ\text{C}$  for 2 hrs removes most of the lattice damage and leads to improved contacts. Phosphorus needs to be "activated" (i.e., the phosphorus atoms have to find substitutional lattice positions) at around  $330^\circ\text{C}$ . Higher temperatures increase the probability of copper contamination. All annealing processes are performed in an inert gas atmosphere. The residual oxides can be removed with a 1% solution of HF in water. Pressing fresh, clean indium foil against the implanted annealed layers completes contact formation. Soldering or evaporation of metals may lead to strain in the crystal which in turn may result in highly undesirable line broadening.



Fourier transform spectroscopy coupled with photothermal ionization offers superb resolution and sensitivity. The technique is being adopted by an increasing number of laboratories for donor and acceptor spectroscopy studies in Si, GaAs and other compound as well as alloyed semiconductors.

### 3. Complexes containing hydrogen and electrically neutral impurities: A(H,Si), A(H,C), D(O,H)

Impurity complex studies in high-purity germanium date back to the discovery of the rapid quench acceptor and donor by R.N. Hall [9]. After quenching from temperatures around 425°C, the ultra-pure germanium samples turned p-type. Isochronal annealing leads to the by now well known p- to n-conversion and eventual return to the pre-heating condition as shown in Fig.3A. The maximum concentration of quenched-in shallow acceptors which convert through annealing to a comparable concentration of shallow donors is approximately  $1-3 \times 10^{11} \text{ cm}^{-3}$ .

An unambiguous link between the hydrogen crystal growth atmosphere and the rapid quench centers was established through the isotope shift in the ground state of the rapid quench donor and acceptor [14]. The isotope shift can be brought about through the substitution of hydrogen with deuterium. These experiments showed that hydrogen which is dissolved in the crystal, takes part directly in the formation of these rapid quench centers. Crystal growth in mixed gas (50% H<sub>2</sub> and 50% D<sub>2</sub>) further showed that only one hydrogen atom is causing the isotope shift. From this fact it was concluded with high probability that only one hydrogen atom was actually incorporated in each of these rapid quench donors and acceptors. A less direct, but still very strong link could be established between the crucible material containing the Ge melt during crystal growth and the rapid quench centers. All the crystals grown from a silica (SiO<sub>2</sub>) crucible in a hydrogen

atmosphere showed the centers after rapidly quenching. In addition it was possible to suppress the donor formation by deliberate Si doping, Fig.3B. These material correlations strongly suggest (though do not absolutely prove!) that the rapid quench acceptor contains hydrogen and silicon A(H,Si), while the donor consists of oxygen and hydrogen D(H,O). Silicon and oxygen are supplied to the melt and to the crystal through the slow reduction of the crucible by the liquid germanium and the hydrogen at temperatures close to the melting point ( $T \sim 936^\circ\text{C}$ ). The oxygen concentration, as measured by the lithium precipitation technique [15], lies around  $6-10 \times 10^{13} \text{cm}^{-3}$ . This technique makes use of the formation of stable LiO-donors which can be measured electrically. The suppression of the donor formation in crystals doped with excess silicon can be explained with the formation of strongly bound SiO complexes. Oxygen bound in such complexes is no longer available for donor formation.

Crystals grown from melts contained in bulk graphite or graphite coated crucibles contain acceptors with properties very similar to the A(H,Si) centers. Radioactive carbon labeling experiments [16] show that a carbon concentration in the  $10^{14} \text{cm}^{-3}$  to  $10^{15} \text{cm}^{-3}$  range is found in such crystals. We conclude from these observations that the shallow acceptor centers in the graphite crucible grown crystals consist of hydrogen and carbon and label them A(H,C). Comparing the maximum concentrations of A(H,Si), A(H,C), and D(H,O) with the concentrations of the constituents H, Si, C and O it becomes evident that only a very small fraction ( $\sim 10^{-3}$ ) of these neutral impurities combine to form the electrically active complexes.

IR-Fourier transform spectroscopy revealed some unusual ground state properties of these acceptor and donor complexes. The D(H,O) donor spectra do not exhibit any energy shift or splitting under uniaxial stress in all three major crystallographic directions ([111], [110] and [100]). At a well defined stress value, which is different for each of the orientations, a new

spectrum appears at lower energies. Again this lower energy spectrum does not shift or split in energy with stress. Because of this stress insensitivity these spectra are unusually sharp compared to spectra of the most important residual donor phosphorus. This experimental finding was appreciated early and is reflected in the fact that the D line series was labeled "S" for "sharp" by Secombe and Korn [17].

The effective mass theory adapted to shallow donors in Ge [8] cannot account for the experimental observations on the D(H,0) donor. The abrupt change in the ground state energy requires an extra internal degree of freedom. Falicov proposed a model in which the extra degree of freedom is provided by the tunneling motion of the interstitial hydrogen atom around the oxygen impurity [18,19].

The nuclear motion is assumed to couple to the electronic structure of the donor-complex. The idea of a light tunneling interstitial impurity goes back to an earlier model by Falicov which describes the donor D(Li,0), this center also exhibits unusual behaviour under uniaxial stress [20]. The tunneling hydrogen model can quantitatively account for all the experimentally observed properties.

Both acceptor complexes, A(H,Si) and A(H,C), also exhibit unusual ground state properties. Line intensity studies as a function of sample temperature revealed that both centers have split ground states. The two ground state components lead to two hydrogenic series of lines. The ratios of corresponding lines are proportional to a Boltzmann factor with an energy value in the exponent which is equal to the energy separation of the two line series. This fact reflects the distribution of holes between the two ground state components and directly shows that the two hydrogenic series belong to one center with a split ground state. The splittings are 1.1meV and 1.9meV for A(H,Si) and A(H,C) respectively.

Fig.4 shows one of our most highly resolved spectra. The crystal was grown in a deuterium atmosphere and the hydrogenic series of lines of the residual acceptors A1 and B as well as

the two hydrogenic series belonging to A(D,C) are visible. The lower energy lines originating from the shallower ground state component of A(D,C) are rather weak at the measurement temperature of 7.5K.

The model which quantitatively describes the properties of A(H,Si) and A(H,C) is again based on the rapid tunneling motion of the light, interstitial hydrogen atom around the substitutional Si or C impurity respectively, [19,20]. A detailed description of the dynamic tunneling effects of hydrogen in these centers is presented in an other paper in these conference proceedings [22].

Let us now briefly return to Fig.3 and summarize the various processes leading to the isochronal annealing curve in part A of the figure. The heating cycle at  $T = 425^{\circ}\text{C}$  before the rapid quench process leads to dissociation of a very small but significant fraction of  $\text{H}_2$  molecules in the Ge crystals. Upon quenching to room temperature the atomic hydrogen concentration becomes supersaturated and the hydrogen either recombines or gets trapped at impurity sites. From the experimental observation that A(H,Si) forms first, we must assume that substitutional silicon produces an extended strain well which attracts interstitial atomic hydrogen. The binding force, the nature of which is still unknown, must be small because A(H,Si) already dissociates at room temperature. Upon annealing, the hydrogen atoms which are liberated from A(H,-Si) centers become more mobile and fall into the more strongly binding but less extended strain wells around oxygen impurities, leading to the formation of the D(H,O) donors. At  $\sim 100^{\circ}\text{C}$  the donor complexes begin to dissociate as well. With increased mobility, the hydrogen atoms find each other and recombine to hydrogen molecules. We have returned to the starting point. This whole cycle can be repeated as often as one likes as long as the temperature does not exceed  $\sim 500^{\circ}\text{C}$ , when significant loss of hydrogen leads to irreversible reduction in the concentration of A(H,Si) and D(H,O). Part B of Fig.3 can be explained in the same way if one just leaves out the donor formation and dissociation. As mentioned before,

there is no free oxygen in silicon doped Ge crystals. The stress insensitivity together with the low concentration of D(H,O) offer the ideal system in which the intrinsic widths of ground and bound excited states of shallow donors can be explored. Such experiments are in progress and have yielded linewidth as low as  $\sim 5\mu\text{eV}$  [23]. Far IR-alcohol lasers which are pumped with a  $\text{CO}_2$  laser are used for these experiments. The ground-to bound excited state transitions are tuned through the discrete laser lines with a magnetic field making use of the donor Zeeman effect [24].

#### 4. Complexes containing hydrogen and the multiples acceptors Be, Zn and Cu

Copper is a rapidly diffusing impurity in germanium. It moves interstitially but also assumes substitutional positions in which it acts as a triple acceptor [25,26]. Contamination of ultra-pure Ge single crystals with Cu has been and still is one of the biggest problems for ultra-pure Ge detector technology. It is then not too surprising that copper related impurity complexes were found in the early phases of ultra pure Ge development [27]. Spectroscopy of p-type crystals containing copper and hydrogen showed at least two series of hydrogenically spaced lines belonging to centers with ground states around 17 to 18meV above the valance band top. Recent studies with  $\text{D}_2$  and  $\text{H}_2 + \text{D}_2$  atmosphere grown crystals revealed that the copper acceptor binds two hydrogen atoms [28]. Fig.5 displays spectra of  $\text{A}(\text{Cu},\text{H}_2)$ ,  $\text{A}(\text{Cu},\text{HD})$  and  $\text{A}(\text{Cu},\text{D}_2)$ . The spectra are perfectly hydrogenic which means that the bound hole which is excited with photons "sees" only one charge. This in turn means that the triply charged Cu impurity binds two positively charged protons (deuterons) which screen two of the three charges. An alternative possibility is that Cu leaves its fourfold coordinated position and assumes a two-

fold coordinated place. The two dangling Ge bonds are saturated by the hydrogen atom. Detailed studies which should lead to a quantitative model are in progress [28]. Such a model has been proposed to explain acceptor neutralization in Si [29].

The complexes which form with Be and Zn, both substitutional double acceptors, contain only one hydrogen atom each, leading to single acceptors [30,31]. The A(Be,H) centers exhibit two lines series which do not split into two equal parts under [111] stress. In full analogy to A(H,C) and A(H,Si), we assume that A(Be,H) is a tunneling center.

The properties of A(Zn,H) differ from the hitherto described tunneling hydrogen complexes. Uniaxial stress along [111] splits each line into two components with a 3:1 intensity ratio. The larger component shifts only a third as far as the smaller component. Centers oriented along [111] and distributed among all four equivalent  $\langle 111 \rangle$  orientations could account for the observed splitting. The hydrogen is assumed not to tunnel in such a configuration.

An explanation for the differences in the A(Be,H) and A(Zn,H) acceptor complexes may be found in the strength of the hole-hole interaction of the two substitutional double acceptors Be and Zn. Thewalt et al [32] have shown that this interaction increases in group II acceptors with increasing atomic number. The resulting ground state splitting in the two hole states is the smallest for Be and the highest for Hg. If we view the proton in the double acceptor-hydrogen complexes as a very heavy hole, then the heavy hole-light hole interaction would again lead to a large ground state splitting which in turn may lead to hindered tunneling of the proton or to a fixed proton position. Our hypothesis could be evaluated with studies of other double acceptor-hydrogen complexes such as Mg-H, Cd-H or Hg-H. To our knowledge no results have been published on such centers.

The role played by hydrogen in the multivalent acceptor-hydrogen complexes differs significantly from the role it assumes in the centers  $A(H, Si)$ ,  $A(H, C)$  and  $D(H, O)$  described in the preceding chapter. Whereas hydrogen is bound as  $H^-$  to the impurities of the group IV, (Si and C) and of the group VI, (O) it appears as  $H^+$  in the multivalent acceptor complexes of impurities belonging to group I and II. If we consider additional recent information gained from silicon, in which all group III acceptors have been shown to become neutral upon complex formation with hydrogen [29,33], an interesting systematic for hydrogen complex formation evolves. The periodic table of elements can be divided into two large groups. All group I, II and III elements seem to bind  $H^+$  when they occupy substitutional lattice sites while all group IV and VI impurities seem to bind  $H^-$ . Recent information on group V donor compensation in silicon [34] extends this general picture to include group V impurities as well. Compensation of group III acceptors and group V donors in germanium has not yet been demonstrated and awaits experimental verification. In a somewhat naïve picture one can summarize the role of hydrogen in germanium and silicon as follows: Hydrogen binds to many impurities and defects. Centers with excess valence electrons (donors) donate the extra electrons to one or more hydrogen atoms thereby forming  $H^-$ , while electron deficient centers use the electron of the hydrogen atom to complete their Lewis octet, leading to  $H^+$ . The impurities of group IV seem to stabilize the second electron in the hydrogen orbital, leading to  $H^-$ . This general picture, based exclusively on experimental observations, awaits a theoretical explanation.

## 5. Other complexes

Most impurity complexes which have been discovered in pure and doped germanium contain either interstitial hydrogen or

lithium. There are however a few complexes which do not contain these light impurities.

A special group of acceptor complexes is produced upon rapid quenching of pure Ge samples from temperatures close to the melting point. These centers have been studied by Kamiura et al [35], using mainly Hall effect. In collaboration with Broeckx et al, PTIS was performed on appropriate samples. Several hydrogenic series of lines were discovered and, as in the case of the tunneling hydrogen complexes, they were able to show that some centers produce two sets of hydrogenic lines, indicating split ground states. Copper has been involved as one component of the various complexes. Iron has been suggested as forming with the copper the center called  $SA_1(n)$  [36]. This identification has been questioned again in a more recent paper by Kamiura and Hashimoto [37]. More work is required to obtain a full understanding of the structure and the composition of all the SA centers.

A most unusual acceptor impurity complex, which can assume two configurations, is related to the presence of carbon and nitrogen during the crystal growth process. The same center can be created in crystals which have not been in contact with carbon or nitrogen after they have been exposed to liquid KCN salt for several hours at temperatures around 600°C. There exists strong evidence that we are observing cyanide ions in either interstitial,  $A(CN)_I$ , or substitutional,  $A(CN)_S$ , locations [38,39]. The signature of  $A(CN)_I$  is a hydrogenic set of lines,  $A_4$ , which splits under stress like all the elemental acceptors (Fig.6).  $A(CN)_I$  is the stable form of the complex above 400°C. Slow conversion to  $A(CN)_S$  takes place at temperatures below 300°C (Fig.7). This form of the complex produces two hydrogenic sets of lines  $A_3$  and  $A_5$  which are stress insensitive Fig.6. The interconversion between the two configurations of the cyanide ion related acceptor is fully reversible. Fig.8 shows the equilibrium ratio



$r = [A(CN)_S] / [A(CN)_S + A(CN)_I]$  as a function of annealing temperature. This ratio can be described with a Boltzmann distribution requiring two parameters: an activation energy  $\Delta E$  and a degeneracy factor  $g$ . A fit to the experimental data using  $r = 1 / (1 + g \exp(-\Delta E / kT))$  leads to  $\Delta E = 0.45 \text{ eV}$  and  $g = 1.6 \times 10^6$ . We obviously do not observe a simple two level system in which, at high temperatures, the two levels would be equally occupied. The very complete interconversion from one into the other configuration requires the large degeneracy factor. This experimental observation can be interpreted in terms of a large free energy ( $F$ ) reduction of the high temperature form  $A(CN)_I$  produced by a large entropy term:  $F = E - TS$ . It is this unusual equilibrium behaviour which forces one to assign the low temperature configuration to the substitutional and the high temperature configuration to the interstitial cyanide ion complex. Fig.9 and Fig.10 schematically illustrate the configurations of  $A(CN)_S$  and  $A(CN)_I$  respectively.

A complete summary of the properties of impurity complexes in pure and doped Ge has been published recently [40].

## 6. Conclusions

Far infrared spectroscopy with external disturbances such as uniaxial stress and magnetic fields, together with crystal growth related residual impurities information, has led to a rather complete picture of numerous shallow level impurity complexes in ultra-pure and doped germanium. Many of the centers which have been observed consist of a neutral substitutional impurity (Si, C, O) and a light interstitial impurity (H, Li). These centers lead to shallow acceptor and donor levels which exhibit complicated ground state manifolds. A model based on the tunneling motion of the light impurity in the vicinity of the substitutional impurity can quantitatively explain the experimental results.

The dominant role of hydrogen in the formation of these centers is not restricted to germanium. Recent work has demonstrated that hydrogen can passivate shallow acceptors [29] and donors [34] in silicon. Deep levels also have been neutralized with hydrogen.

All the experimental results seem to indicate that hydrogen has a strong tendency to bind to any imperfection in the semiconductor lattice.

Single or multiple acceptors bind one or more protons which in turn screens the negative charge of the acceptor core. Each proton screens precisely one core charge as can be seen from the perfectly hydrogenic character of the hole spectra of  $A(\text{Be},\text{H})$ ,  $A(\text{Zn},\text{H})$  and  $A(\text{Cu},\text{H}_2)$ . In the case of group IV, V, and VI impurities, the extra valence electrons seem to form bonds with hydrogen, or a negatively charged hydrogen ion is stabilized in an antibonding position of a neighbouring lattice atom [34]. In this sense, hydrogen exhibits amphoteric properties: it can neutralize both acceptors and donors. The phenomenological description of the formation of complexes leading to electrically active centers in some cases (e.g.  $A(\text{H},\text{C})$ ,  $A(\text{H},\text{Si})$ ) and to partial or full neutralization in other cases (e.g.  $A(\text{Be},\text{H})$ ,  $A(\text{Cu},\text{H}_2)$ ) so far lacks a detailed theoretical basis. It is our hope that the reviewed and on going experimental work stimulates theoretical efforts which in turn could lead to a clear understanding of the structure of and binding forces in these novel centers.

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### Figure Captions

- Fig.1 The two step ionization process which is the basis of Photothermal Ionization Spectroscopy (PTIS).
- Fig.2 Transconductance amplifier used for PTIS. In a newer version the operational amplifier OP-27 is used.
- Fig.3 Isochronal annealing curves for rapidly quenched germanium samples.  
A: crystal grown in H<sub>2</sub>- atmosphere, melt contained in silica.  
B: as A but doped with silicon, [Si] =  $3 \times 10^{17} \text{ cm}^{-3}$  in the melt.
- Fig.4 PTI spectrum of an ultra-pure, p-type Ge samples containing the acceptors B, Al and A(D,C). The narrowest lines have a full width at half height of  $\approx 17 \mu\text{eV}$ .
- Fig.5 PTI spectra of copper-hydrogen acceptor complexes.  
a) A(Cu, H<sub>2</sub>) has a complicated ground-state multiplet leading to several overlapping hydrogenic series of lines.  
b) Crystals containing equal concentrations of H and D produce three spectra assigned to A(Cu,H<sub>2</sub>), A(Cu,H,D) and A(Cu,D<sub>2</sub>).  
c) A D<sub>2</sub>- atmosphere grown crystal shows the A(Cu,D<sub>2</sub>) spectrum. Hydrogen residues lead to a very weak A(Cu, H;D) spectrum.
- Fig.6 PTI spectrum of an ultra-pure, p-type Ge crystal containing the residual acceptor Al and the cyanide ion related hydrogenic series A<sub>3</sub>, A<sub>4</sub> and A<sub>5</sub>. Uniaxial stress  $\parallel [111]$  splits the lines of Al and A<sub>4</sub> as expected from valence band top splitting. No splitting is observed for the lines of A<sub>3</sub> and A<sub>5</sub>.
- Fig.7 PTI spectra showing the lines of A<sub>3</sub> and A<sub>5</sub> in a Ge sample which was stored for several years at room temperature (lower trace). After heating to 400°C for

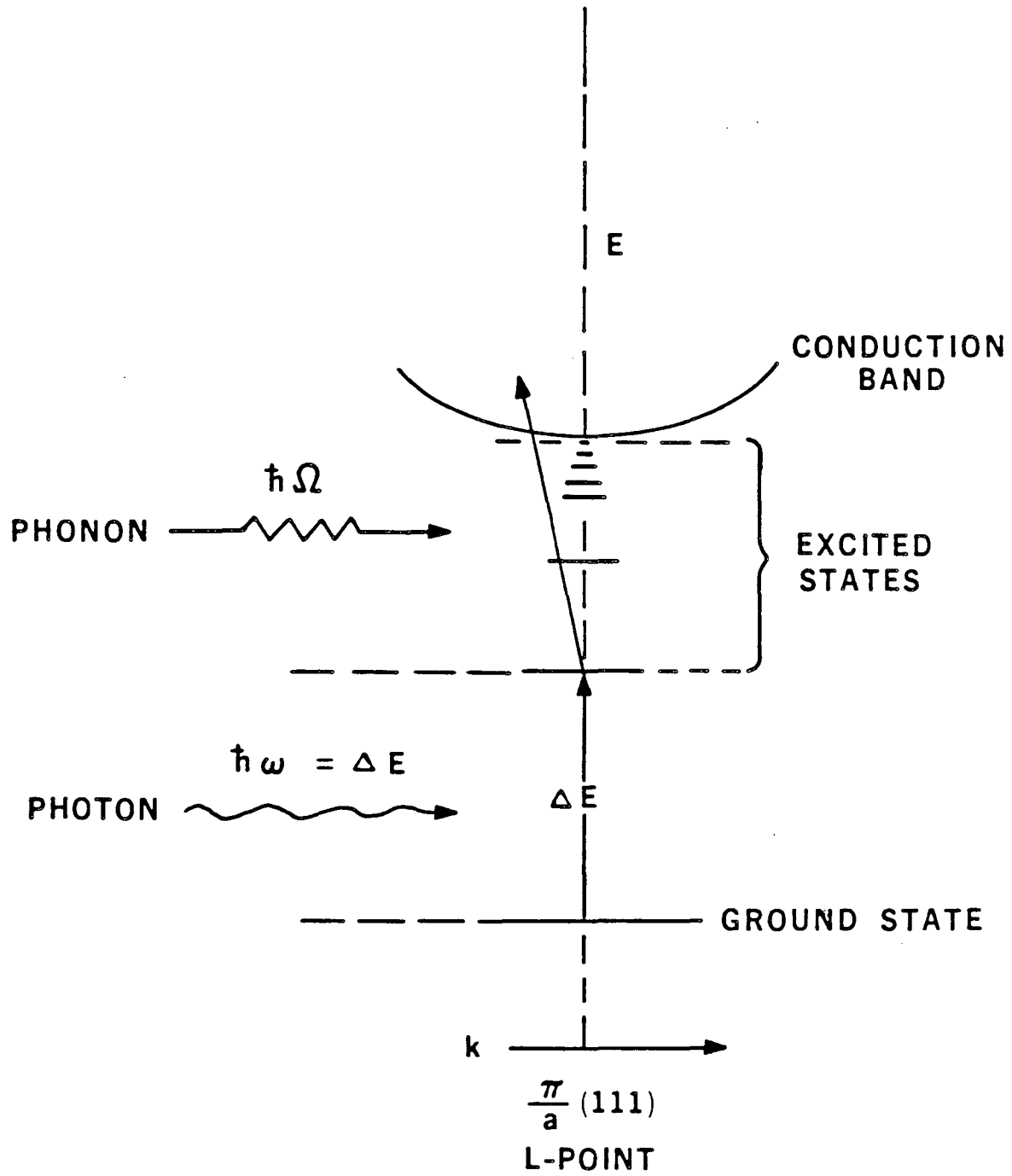
5 min. all the  $A_3$  and  $A_5$  lines have disappeared and the  $A_4$  serie is present (upper trace).

Fig.8 Equilibrium ratio as a function of temperature of corresponding lines of  $(A_3+A_5)$  to  $(A_3+A_4+A_5)$ . Full conversion between the two spectra takes place.

Fig.9 Substitutional cyanide ion:  $A(C,N)_5$  (Courtesy R.E. McMurray Jr. Ref.39)

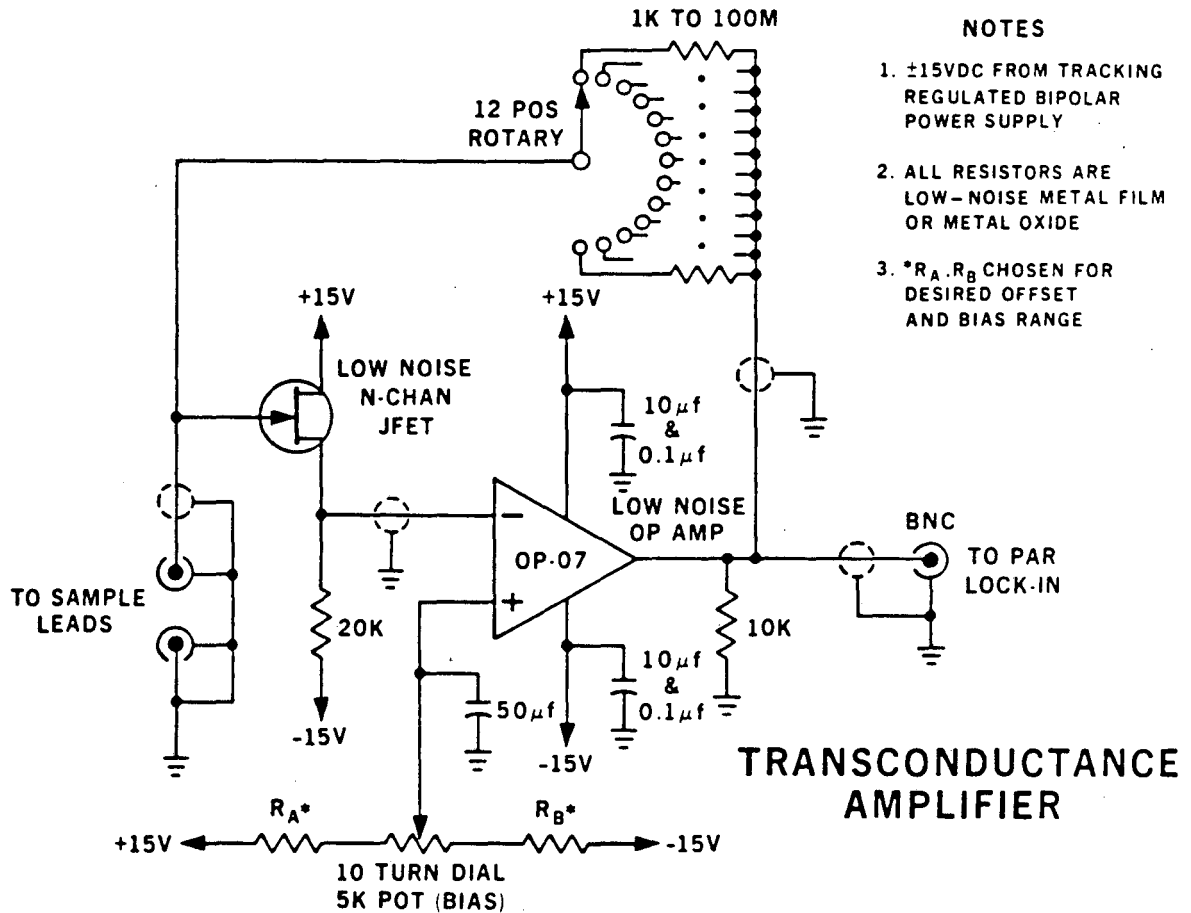
Fig.10 Interstitial cyanide ion:  $A(C,N)_I$  (Courtesy R.E. McMurray Jr. Ref.39).





XBL 7411-8629

Fig. 1.



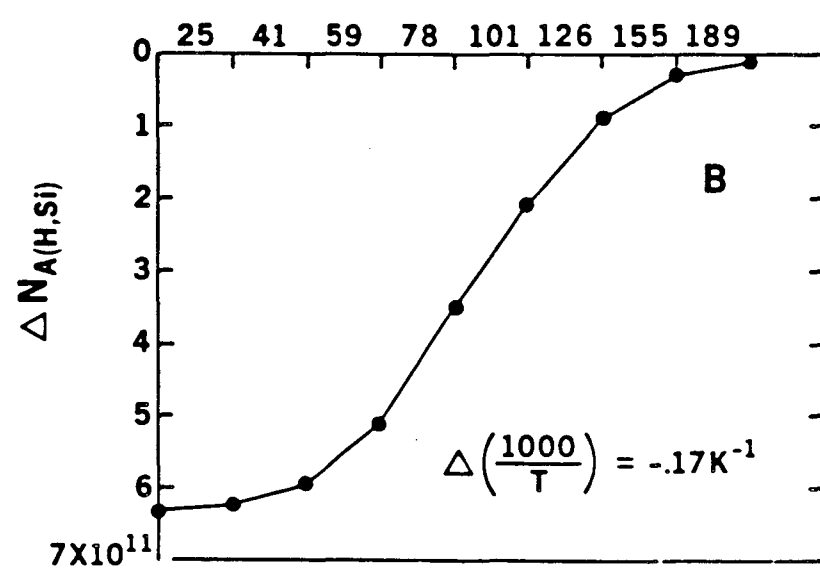
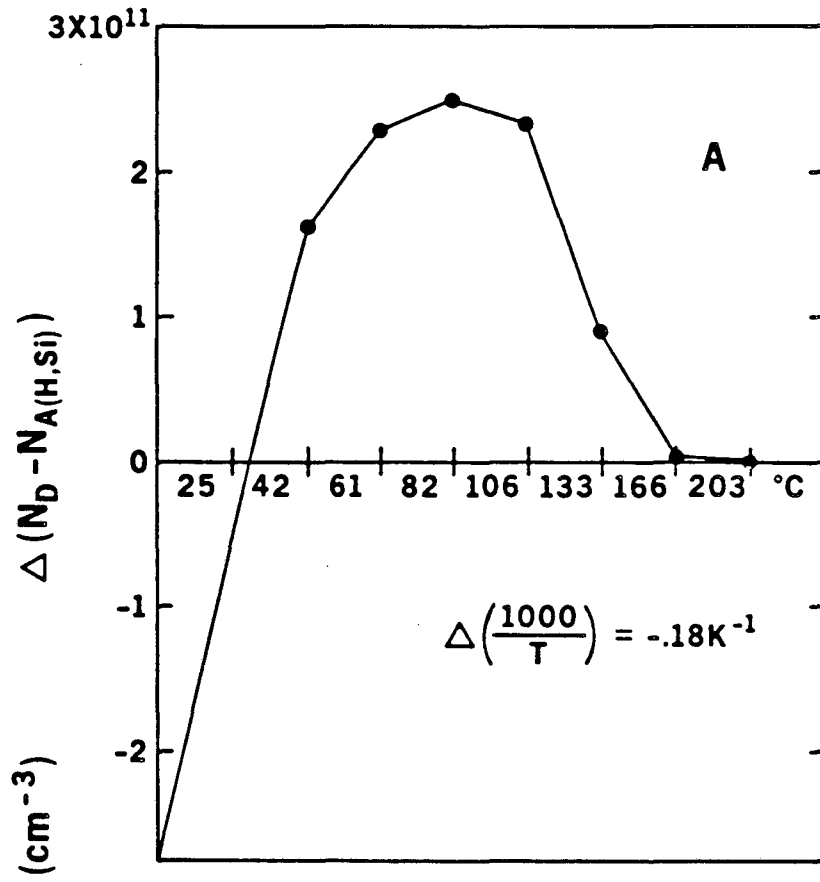
**NOTES**

1. ±15VDC FROM TRACKING REGULATED BIPOLAR POWER SUPPLY
2. ALL RESISTORS ARE LOW-NOISE METAL FILM OR METAL OXIDE
3. \* $R_A$ ,  $R_B$  CHOSEN FOR DESIRED OFFSET AND BIAS RANGE

**TRANSCONDUCTANCE AMPLIFIER**

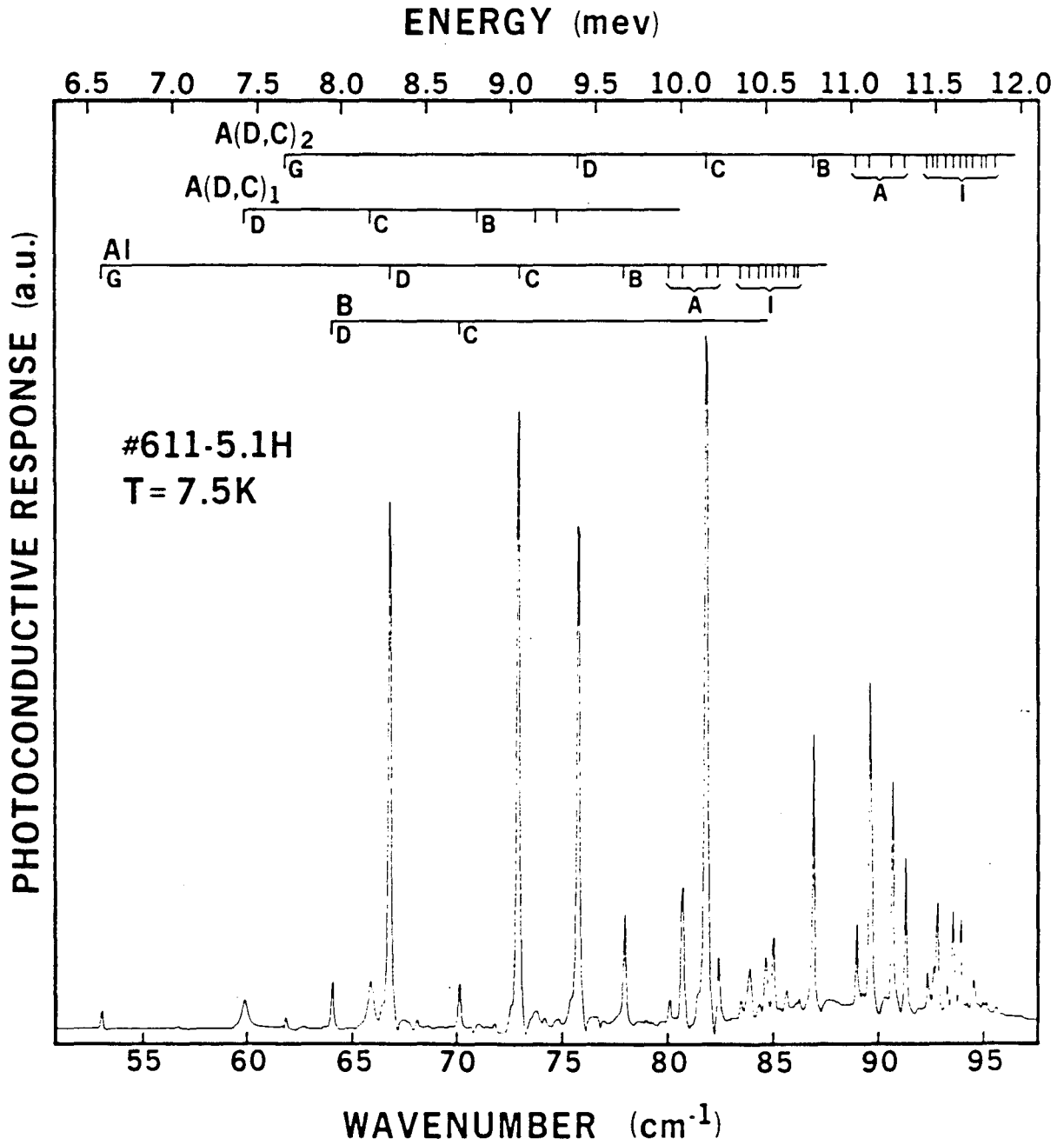
XBL 8310-12242

Fig. 2.



XBL 7911-12832

Fig. 3.



XBL 863-1160

Fig. 4.

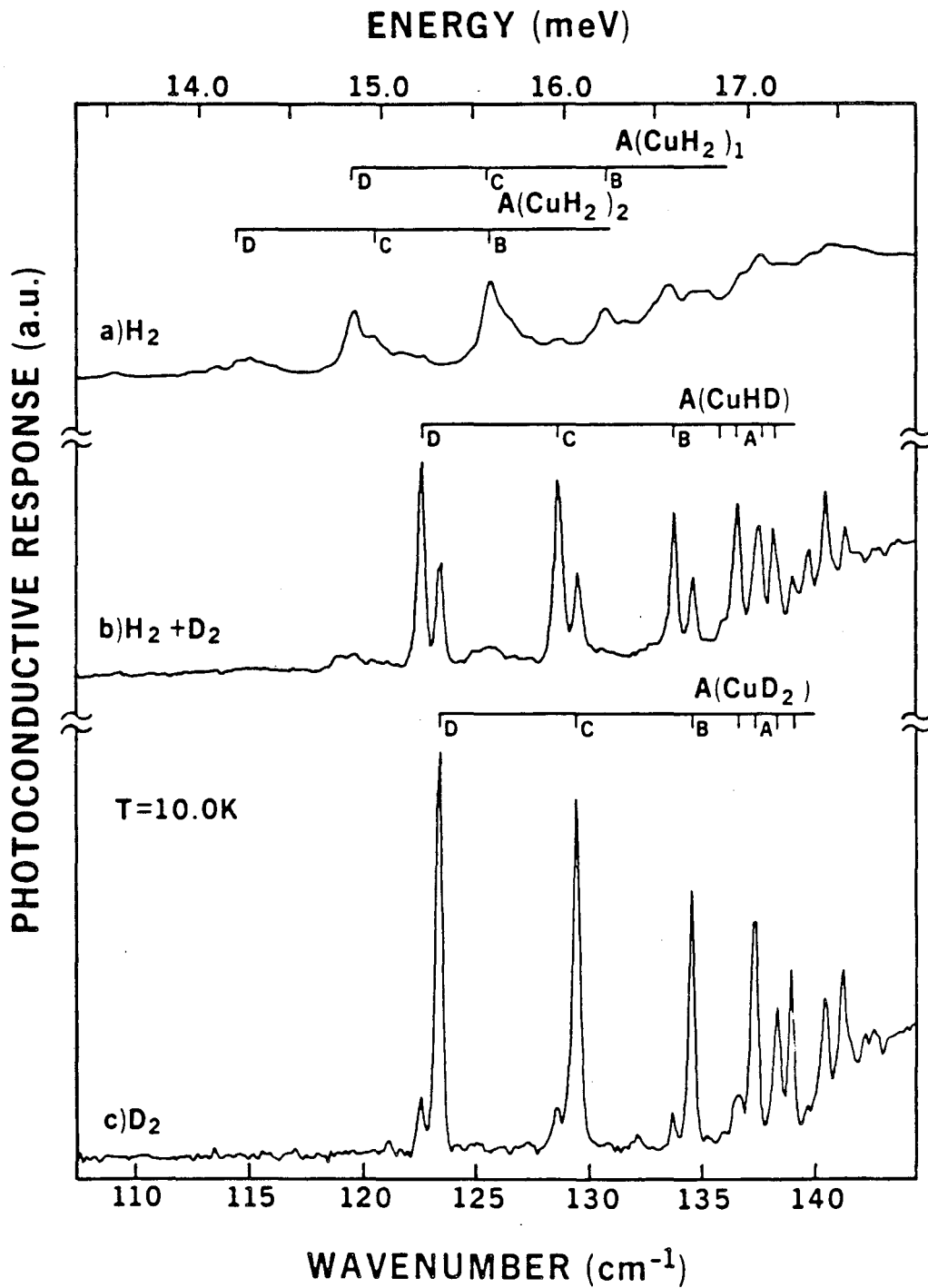
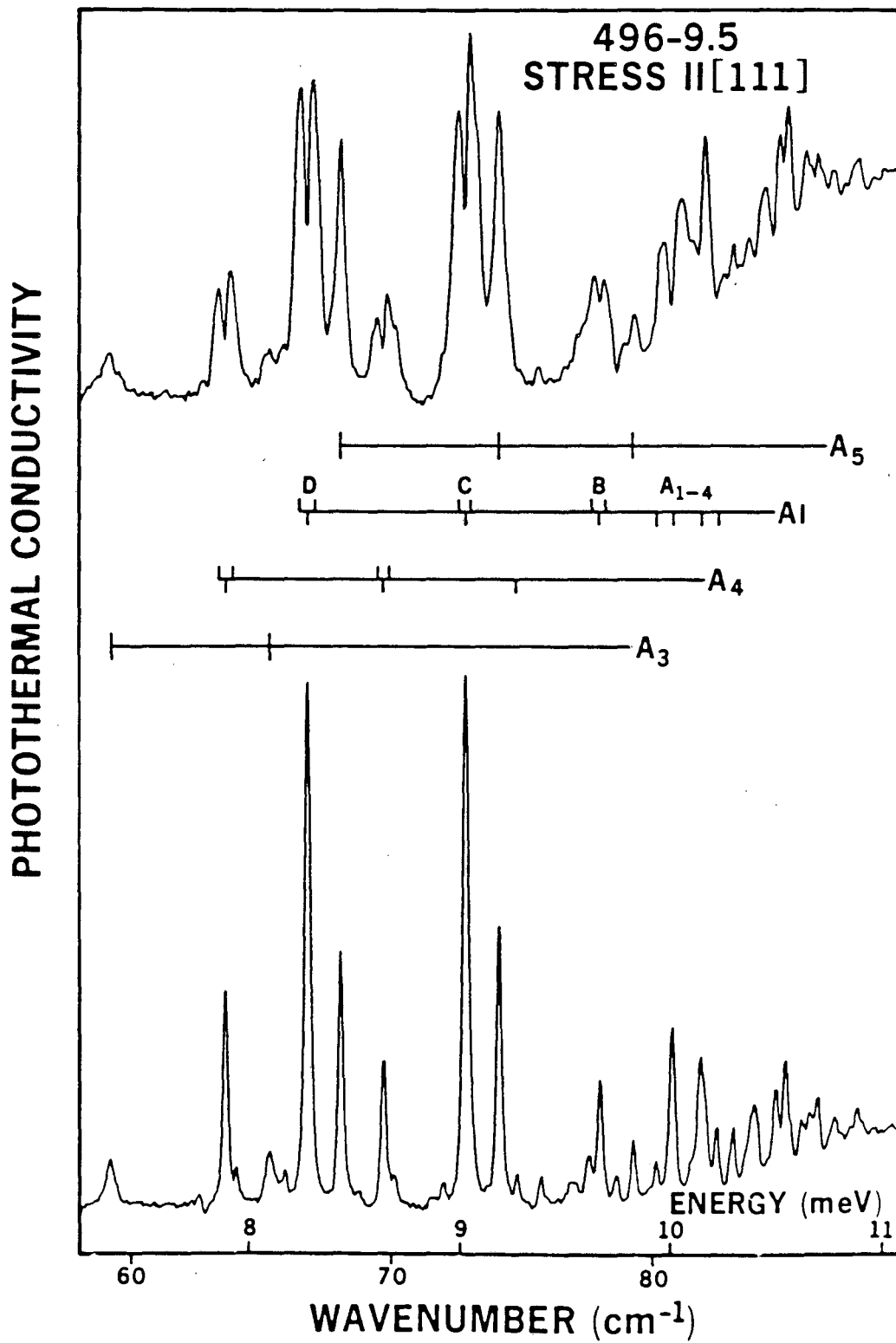


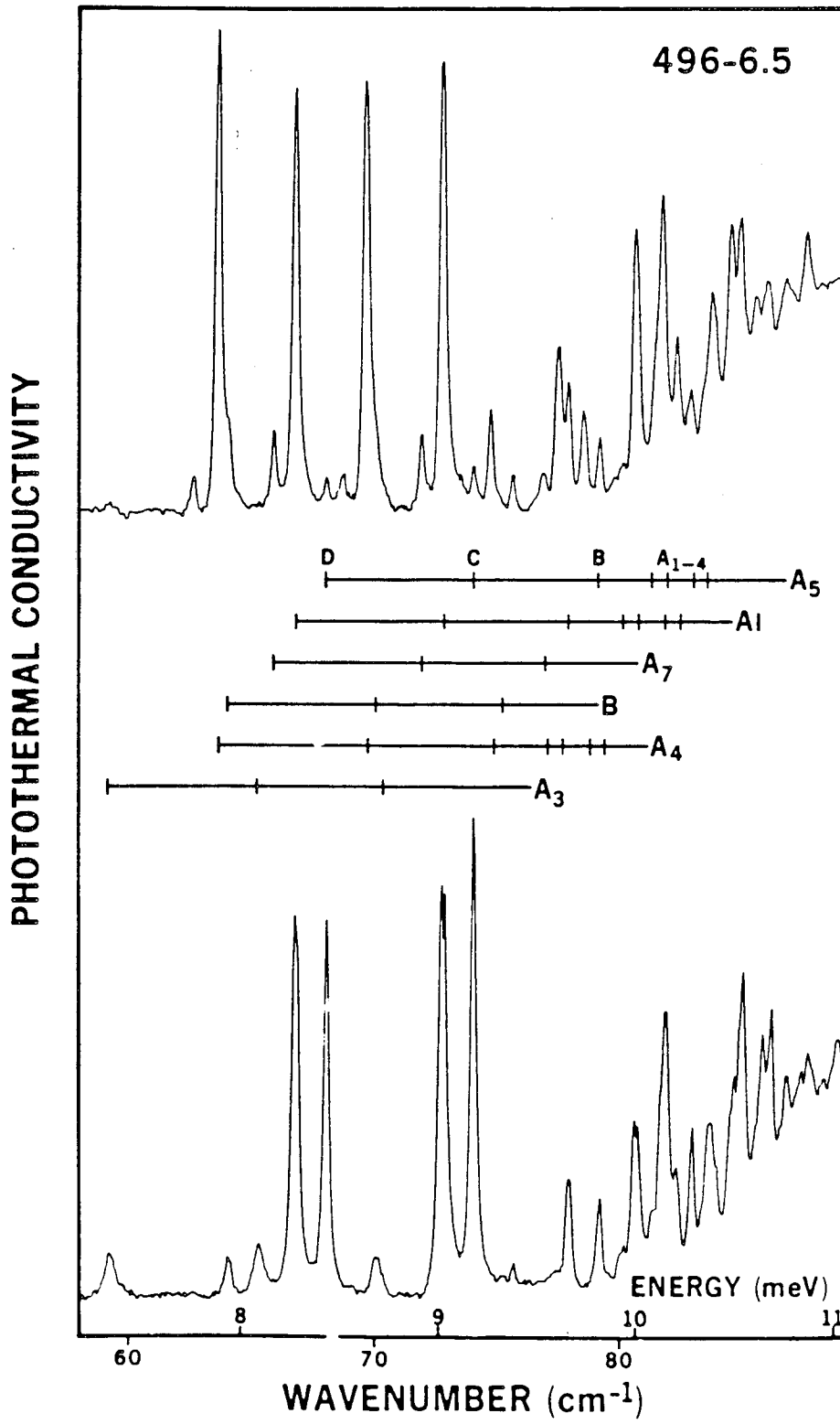
Fig. 5.

XBL 861-38



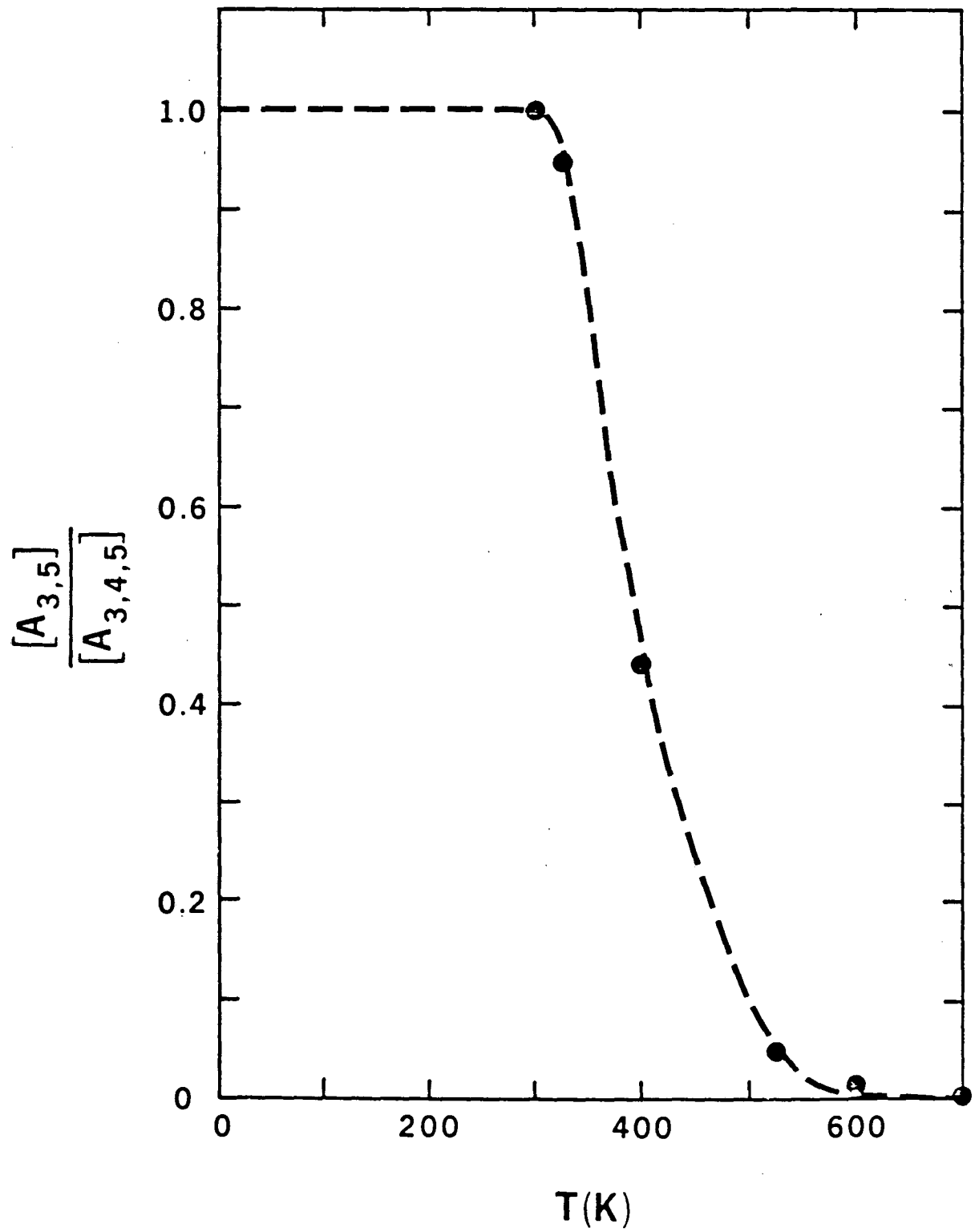
XBL 828-11320

Fig. 6.



XBL 828-11319

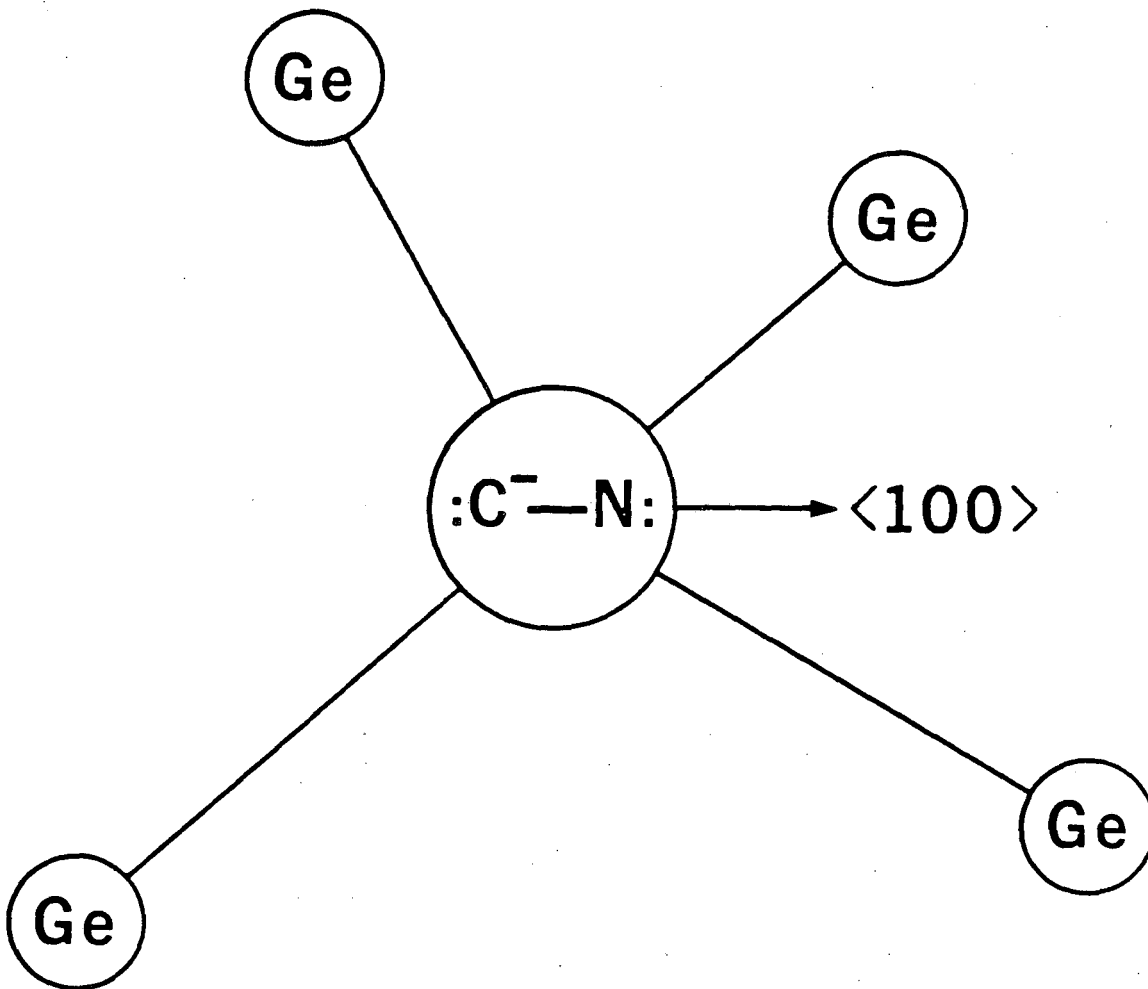
Fig. 7.



XBL 8312-4693

Fig. 8.

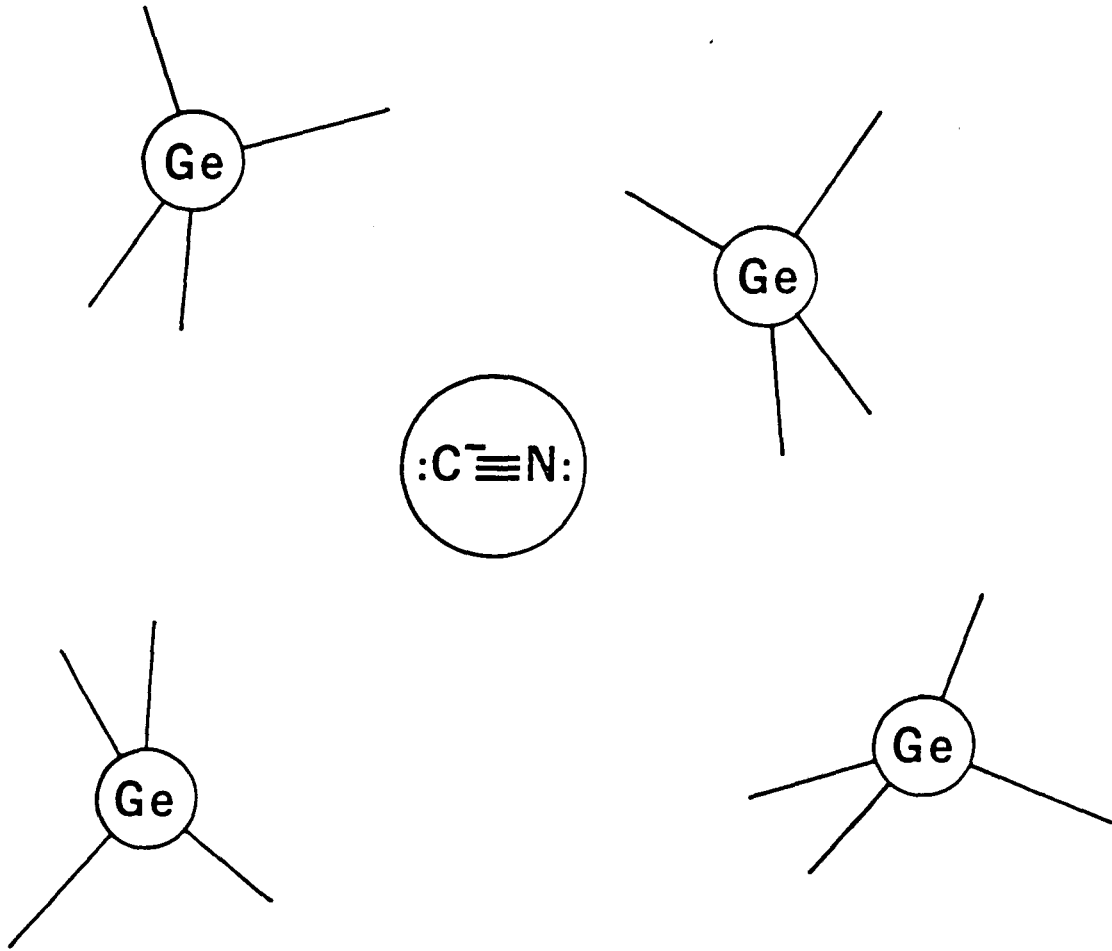




$A_{3,5} = A_S (C,N)$  SUBSTITUTIONAL  $T_d$

XBL 8310-12245

Fig. 9.



$A_4 = A_I$  (C,N) INTERSTITIAL  $T_d$

XBL 8310-12243

Fig. 10.

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