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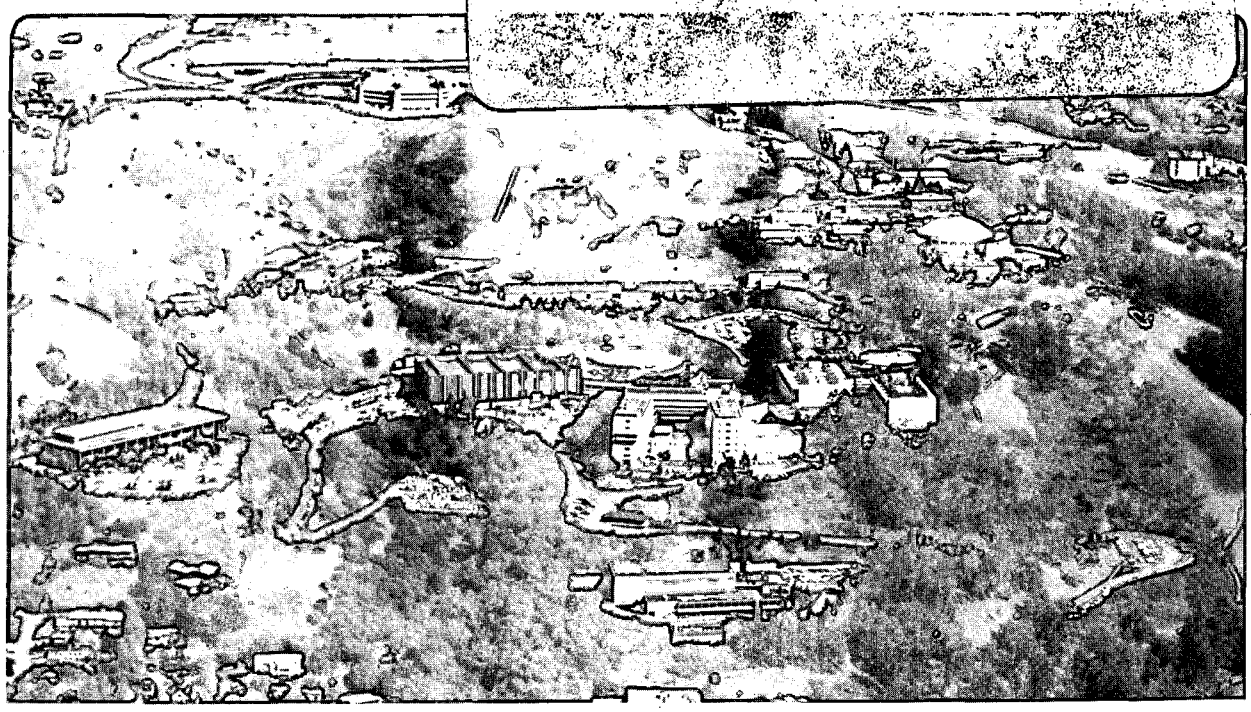

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BERYLLIUM-HYDROGEN AND ZINC-HYDROGEN SHALLOW ACCEPTOR COMPLEXES IN GERMANIUM

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New shallow acceptor complexes with hydrogenically-spaced excited states have been discovered in intentionally-doped crystals of otherwise ultra-pure germanium. The doping consists of 10^{14} cm^{-3} of group II impurities, and the crystals were grown under hydrogen atmosphere. The identification proposed in this paper is that of a hydrogen-group II impurity complex, with piezospectroscopic behavior similar to previous hydrogen-impurity complexes.

1. INTRODUCTION

Recently, several hydrogen-related shallow acceptor and donor complexes have been discovered in ultra-pure germanium single-crystals[1-4]. Of these impurity centers, the two acceptors A(H,C) and A(H,Si) and the donor D(H,O) have been explained with a model based on tunneling hydrogen[2-4]. In this model, a hydrogen atom is assumed to be trapped during rapid thermal quenching from elevated temperature in the strain field of the smaller-sized substitutional impurity atom (C, Si, or O), from which it accepts a second electron into its (1s) orbital. The double occupation of the orbital, creating a negative hydrogen ion, causes the local electronic structure of the impurity atom to behave as if the atom had been shifted one column to the left in the periodic table of elements. That is, an isoelectronic level (Group IV atom) becomes a single acceptor while a Group VI atom such as oxygen becomes a single donor. The electronic states of these impurity complexes are basically hydrogenic, except for the complication of a splitting of the normal ground state into a manifold of states due to the added internal degree of freedom of the motion of the tunneling hydrogen atom.

We have discovered two new hydrogen-related shallow acceptors, one in zinc-doped germanium and the other in beryllium-doped germanium[5]. The new impurity centers will be denoted A(Zn,H) and A(Be,H) respectively. Each of the new hydrogen-Group II atom complex centers forms a single acceptor state with hydrogenic excited state energy level spacings. They share many of the same properties of the tunneling-hydrogen complexes above, but are different in a fundamental way: the hydrogen atom does not provide an empty orbital as in the previous cases, but instead provides an extra electron.

That is to say, the addition of the hydrogen atom to the impurity element does not cause the substitutional impurity to behave like the element one column to the left in the periodic table, but rather to behave like the element one column to the right. This is reminiscent of the united atom model[6] used for calculation of the hydrogen molecule with a single electron H_2^+ in which the electronic structure is a perturbation of that of the helium ion He^+. In this case the second hydrogen atom (proton) can be thought of as being superimposed on the original nucleus (proton for H_2, but Zn or Be in the case treated in this paper) for purposes of determining the electronic structure.

The electron from the hydrogen atom is donated to the electron-deficient Group II atom, creating an overall single acceptor state in the germanium band gap. This important difference in behavior of the hydrogen in the impurity complex formation is the reason for the notational difference in the ordering of elements in the notation A(Zn,H) as opposed to A(H,C).

2. EXPERIMENTAL PROCEDURES

The impurity centers created for these studies were formed in either zinc or beryllium doped germanium single crystals grown in a hydrogen-gas ambient under ultra-pure conditions[1,7]. The doped crystals were grown from a germanium charge consisting of a high-purity zone refined polycrystalline bar and a small amount of master-alloy dopant material. Concentrations of the Group II impurities were in the range of $\leq 10^{15}$ cm^{-3}, while the residual shallow elemental acceptor concentrations were typically three orders of magnitude lower, as verified by variable-temperature Hall effect measurements. In addition, one zinc-doped crystal was grown in a nitrogen-gas ambient in order to verify the correlation of the new

shallow impurity complex formation with the presence of hydrogen in the crystal. One beryllium-doped crystal was grown in deuterium-gas ambient in an effort to search for an isotope effect on the electronic properties of the A(Be,H) center.

Samples from these specially grown crystals were cut with a diamond saw and lapped to 1900 grit surface roughness. This procedure was followed by polish-etching in a 4:1 mixture of nitric and hydrofluoric acid, followed by quenching with methanol. The electrical contacts for hole-injection and extraction at cryogenic temperatures were formed in one of two ways. For the variable temperature Hall effect samples, usually platelets of 1-2 mm thick and 7 mm x 7 mm area in the van der Pauw geometry[8], corner contacts were formed by indium solder alloy regrowth. In the case of samples for photothermal ionization spectroscopy measurements, liquid InGa eutectic was applied to two opposite faces of a 7 mm cube, and pure indium pads applied over the eutectic. In each case the contacts were found to be satisfactory down to liquid He temperatures.

Photothermal ionization spectroscopy was performed using a far-infrared Michelson interferometer with a resolution of approximately 0.125 cm^{-1} or about 16 μeV, with triangular apodization of the interferogram. Somewhat higher resolution can be obtained without apodization, but in all cases the natural linewidths of the spectral peaks were larger than the instrumental resolution. Piezo-spectroscopy was performed using a calibrated spring and lever arrangement to apply uniaxial stress to the sample through a brass plunger, with indium pads to distribute the force evenly across the surface of the sample[9].

Annealing of these samples was performed on a quartz plate in an oven at temperatures up to 1000 K. In order

to avoid copper contamination of the samples, they were first treated with a 10% aqueous solution of KCN. This solution leaves a cyanide residue on the surface of the germanium crystal which prevents copper from entering the sample[10].

3. EXPERIMENTAL DATA

Spectroscopic results for the zinc-hydrogen shallow acceptor complex are shown in Figures 1 and 2. The first figure consists of two spectra: the bottom trace is that of the as-grown crystal, in which the zinc-hydrogen line spectrum is seen at strengths larger than that of the residual aluminum acceptor; the top trace is the spectrum of the same sample after annealing for three hours at 873 K, in which only the aluminum spectrum remains. This is evidence for the presence in the as-grown sample of a new species of acceptor which can be made to disappear with thermal annealing. This new center has an ionization energy of 12.53 meV, or about two meV deeper in ground state energy than the normal elemental Group III acceptors. The center does not appear in the spectra of nitrogen-grown zinc-doped germanium, nor in any germanium crystal which is not doped with zinc. Because of the correlation with the presence of both zinc and hydrogen in the crystal, this center has been denoted as A(Zn,H). It has a hydrogenic set of excited hole states, with exactly the same energy spacings as all shallow acceptors in Ge.

The second figure shows what occurs in the line spectrum of the zinc-hydrogen acceptor center under the application of uniaxial stress along a ⟨111⟩ axis. For this stress orientation, the excited states due to p-like hydrogenic envelope functions split very little, independent of the particular central cell species. Aluminum, however, has its four-fold

ground state symmetrically split into 2 doublets, as is seen in Figure 2. For the A(Zn,H) lines, a splitting of approximately 3:1 is observed with a 1:3 shift in the energies of the split peaks. This is best seen in the B-line, for which there are no overlapping Al lines to confuse the spectrum.

Isothermal annealing studies were performed on samples containing the zinc-hydrogen shallow acceptor complex. Variable temperature Hall effect measurements were performed at each step of the anneal in order to determine the change in concentration of the shallow levels. Results of this study are presented in Figure 3. The change in shallow acceptor concentration can be seen in the change of the nature of the freeze-out curve at low temperatures. The "knee" of the curve (i.e., the region where the slope changes) indicates approximately the net concentration of shallow levels, including the A(Zn,H) complex. After sufficient annealing, one sees that the concentration of residual donors exceeds that of the shallow elemental acceptors and acceptor complexes combined. Figure 4 is a plot of A(Zn,H) concentration vs. time for two different annealing temperatures. From this data, assuming a simple exponential concentration dependence, one can extract both a dissociation energy and time constant for the zinc-hydrogen impurity complex. The temperature at which dissociation of the complex occurs is well above the temperature for out-diffusion of hydrogen from germanium. The rate-limiting step in the decrease of the center's concentration is therefore assumed to be a simple one-step dissocation process, which follows a single exponential curve and has a barrier energy of 3.0 ± 0.3 eV, with a rate prefactor of 3×10^{12} sec^{-1}.

The next three figures depict photothermal ionization spectra of the beryllium-hydrogen shallow acceptor

complex. In Figure 5, the bottom trace is that of the as-grown germanium sample, containing two new series of spectral lines, coming from initial states with ionization energies of 11.29 and 10.79 meV, and denoted as $A(Be,H)_1$ and $A(Be,H)_2$ in each of the three figures. These energies are very close to those of Ga and of B, respectively, but are due instead to a new impurity center. This can be demonstrated by the top trace, which is the spectrum of the sample after annealing for 90 minutes at 823 K. In this spectrum, the line series due to A(Be,H) is reduced by a factor of 2. This makes it clear that two new discrete line series exist that are not exactly at the same energies as the elemental acceptors.

Piezospecroscopy of the beryllium-hydrogen acceptor complex is shown in Figure 6. Uniaxial stress is applied along a random axis, causing some excited state splitting resulting in a broadening of the lines, but no split or shift of the initial states for any of the A(Be,H) transition lines, although the residual boron and aluminum do experience a ground state split.

Isothermal annealing studies were also performed for samples containing the Be-H acceptor complex, as presented in Figure 7. These were analyzed as in the previous case, giving values of an excitation energy of 2.1 ± 0.6 eV, with a rate prefactor of 3×10^{12} sec^{-1} for these complexes.

In Figure 8 a behavior is shown that was not observed in the case of the zinc-hydrogen acceptor complex. With increasing sample temperature, there is a decrease in the relative strength of the line series due to the lower-lying of the two initial states. In the lower trace, taken at T=6 K, the D-line of the 11.29 meV level is as large as that of aluminum, while in the upper trace, taken at T=8 K, the D-line is 30% lower. This demonstrates thermal population among two states of the ground state

manifold of A(Be,H).

One additional piece of experimental evidence as to the microscopic identification of the beryllium-hydrogen acceptor was also obtained. A sample from a vacuum-grown beryllium-doped crystal, which did not show the new complex, was treated with a hydrogen plasma at elevated temperature. This procedure allows free hydrogen to diffuse into the crystal. After treatment, the sample now showed the spectrum of the beryllium-hydrogen acceptor, confirming that hydrogen is indeed one of the constituents of the acceptor complex.

4. THEORETICAL MODEL

As in the cases of the tunneling-hydrogen acceptor complexes discussed in the introduction of this article, both A(Zn,H) and A(Be,H) are assumed to consist of a substitutional impurity atom with a hydrogen atom trapped and possibly orbiting in its strain field. The additional internal degree of freedom for the orbiting case again gives rise to a manifold of states created from the normal single acceptor ground state, the two lowest-lying of which are Kramers doublets rather than quartets. This model then satisfies the requirement that the ground state levels for the newly discovered Be-H acceptor complexes do not split under applied uniaxial stress.

However, in the case of the Zn-H complex, the substitutional central Zn atom is quite large, in the same row of the periodic table as the Ge host lattice, and has a full shell of 10 3-d electrons. This may preclude the possibility of a tunneling or fast-orbiting hydrogen atom, instead leading to a frozen or slow-orbiting hindered rotor configuration. On the time scale of the photo-ionization process, which can be relatively long, the nuclear configuration may not sample

a full set of four tetrahedrally equivalent orientations, but rather only one orientation. Put in a different context, the magnitude of the tunnelling matrix element between nuclear states may be small compared to the energy of the optical probe photon, so that the measured transition energy may be that of a single state rather than a mixture of states[11]. The impurity complex thus appears, on this time scale, to have a distorted non-tetrahedrally symmetric configuration. The spectrum is thus different from both the substitutional tetrahedral acceptors and the tunneling Be-H complex.

The 3:1 splitting shown in Figure 2 can be accounted for by a ⟨111⟩ oriented center, which can exist in four equivalent orientations at different impurity sites in the crystal. Such an internal orientational degeneracy can be partially lifted by a ⟨111⟩ stress axis which affects one of the orientations differently from the other three. In addition, a stress along a ⟨100⟩ direction should treat all four orientations equivalently, as has been observed experimentally. In this case there is still a splitting of the lines due to excited state splitting, which is large for acceptor states with ⟨100⟩ applied uniaxial stress[12].

The difference between the behavior of the hydrogen atom in the cases of Be and Zn can perhaps be understood in light of recent observations of large ground state splittings for isolated Zn acceptors[13]. It has been demonstrated that the ground state splitting for the two-hole state is larger for atoms lower in a given column of the periodic table, while for the one-hole state the opposite is true. If we now consider the proton H^+ as simply a very heavy hole, we may expect the zinc-hydrogen-light hole system to have a very large "splitting" of the ground state. This manifests itself as a state in which the hydrogen tunneling is

hindered or eliminated.

The important difference that occurs for the current set of acceptor complexes is that the hydrogen atom acts as a donor of an electron rather than an acceptor. This means simply that the energy levels for the 1s orbital are above rather than below the Fermi energy for occupation by either or both electrons. In contrast to this, an interstitial hydrogen atom has one orbital occupation below and one above the Fermi energy so that it remains singly occupied and is neither an acceptor nor a donor. It is possible that in the case of a hydrogen atom trapped near a Group II atom (electron deficient as a substitutional atom in the germanium lattice), it would act as a donor of its (1s) electron, while for Group IV and higher group atoms it would accept a second (1s) electron. It should be pointed out that hydrogen has been shown to neutralize boron in silicon[14], which is the equivalent of shifting that Group III acceptor one column to the right in the periodic table. This is exactly the same behavior observed for hydrogen here. The dividing line between the two behaviors of hydrogen is therefore between the Group III and Group IV columns of the periodic table.

A comparison can now be made to a less-well understood hydrogen-related acceptor complex, involving copper in germanium. The behavior of hydrogen in the presence of this Group I impurity is identical (as expected) to that with the Group II atoms, except that two hydrogen atoms must be available to donate each of their (1s) electron to the copper atom to form a single acceptor[15]. This is a likely situation in that copper is known to form single acceptor impurity complexes (ionization energies of 17-25 meV) that are correlated with the presence of both hydrogen and lithium[1]. If we consider that two electron-donors are involved in each of copper's

impurity complexes, we may now label the complexes consistently as A(Cu,H,H), A(Cu,H,Li), and A(Cu,Li,Li). This is shown to be true by mixed isotope H:D experiments. Since copper is a deep acceptor and does not follow effective mass theory, it is reasonable to expect the impurity complexes of copper to have larger than EMT binding energies as single acceptor states.

In the cases of the carbon-hydrogen, carbon-nitrogen[16], and silicon-hydrogen acceptor complexes, each contains two doublet components in its ground state electronic manifold. Although the energies of the individual components can be 1 to 2 meV different from that of EMT acceptors, it is true in each case that the average energy (center of gravity) of the two doublet states corresponds quite closely to normal elemental acceptor energies (B, Al, Ga). This is also the case for the two beryllium-hydrogen acceptor states, with average energy of 11.04 meV, very close to that of aluminum. A split ground state for A(Zn,H) has not been observed. If the same model applies for the zinc-hydrogen acceptor complex, with an energy level of 12.53 meV about 1.5 meV deeper than an average energy for single acceptors, the second doublet state would be expected at about 1.5 meV on the other side of the average, or about 9.5 meV. Such a level would then be 3 meV above the overall ground state energy and only three times this far from the valence band. Since the valence band has such a high multiplicity of available hole states, it is extremely unlikely that one could thermally populate such a state to any observable extent. However, if A(Zn,H) is a frozen rather than tunneling complex, it may not exhibit the additional split ground state component.

An effort was made to observe an isotope shift, as seen in the Cu-H complexes, in the electronic levels of A(Be,H) by forming A(Be,D). The effect

is expected to be very small since the mass of the orbiting atom only indirectly affects the electronic state energy. In the case of A(H,Si) the shift was observed to be only 20 μeV. Since the beryllium atom is lighter than silicon, the reduced mass of the diatomic system changes by 15% less when substituted with deuterium, so that the shift in energy should be smaller. There was no observable isotope shift, to a lower limit of approximately 10 μeV.

5. CONCLUSIONS

We have discovered two new impurity complexes consisting of a Group II atom and a single hydrogen atom. The concentration of these new complexes can be reduced by thermal annealing. The A(Be,H) centers exhibit stress-insensitivity, indicating a ground state symmetry which is a Kramers doublet and not the usual four-fold state of the valence band top. The A(Zn,H) centers exhibit a distorted C_{3v} symmetry, as shown by the stress splitting, and so also have a spectrum different from the usual elemental acceptor states. The ground state for the beryllium-hydrogen case, and possibly zinc-hydrogen as well, consists of a manifold of states containing at least two doublets, and possibly a number of higher-lying states which cannot be thermally populated from the overall ground state level.

The tunneling-hydrogen model for impurity complexes explains all of the observed experimental findings for the beryllium system. The only modification from the model used for previously explained impurity complexes is the fact that the hydrogen in this case contains an unoccupied rather than doubly occupied 1s orbital. With this modification and the assumption of two orbiting hydrogen atoms the model can also explain qualitatively the copper-hydrogen complex. The Zn-H

system is modelled well by a non-tunneling or frozen configuration for the H atom. Motional narrowing for this distorted system has not yet been observed.

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REFERENCES

1. E. E. Haller, W. L. Hansen, and F. S. Goulding, Advances in Physics 30, 93 (1981).
2. E. E. Haller and L. M. Falicov, Phys. Rev. Lett. 41, 1192 (1980).
3. E. E. Haller, B. Joos and L. M. Falicov, Phys. Rev. B 21, 4729 (1980).
4. B. Joos, E. E. Haller, and L. M. Falicov, Phys. Rev. B 22, 832 (1980).
5. R. E. McMurray, Jr., N. M. Haegel, J. M. Kahn, and E. E. Haller, Solid St. Comm. 53, 1137 (1984).
6. W.A. Harrison, "Electronic Structure and the Properties of Solids", p.20 (Freeman, San Fransisco, 1980).
7. J. Czochralski, Z. Phys. Chemie 92, 219 (1918).
8. L. J. Van der Pauw, Philips Res. Rev. 13, 1 (1958).
9. A. G. Kasanski, P. L. Richards, and E. E. Haller, Solid St. Comm. 24, 603 (1979).
10. A. O. Evwayare, R. N. Hall, and T. J. Soltys, IEEE Trans. Nucl. Sci., 26, 271 (1979).
11. C. E. T. Goncalves da Silva and L. M. Falicov, Phys. Rev. B 13, 3948 (1976).
12. A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. 44, 1297 (1981).
13. M. L. W. Thewalt, B. P. Clayman, and D. Labrie, Phys. Rev. B 32, 2663 (1985).
14. J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and P. O. Wance, Phys. Rev. Lett. 51, 2224 (1983).
15. J. M. Kahn and E. E. Haller, submitted to Bull. Am. Phys. Soc., March Meeting (1986).
16. E. E. Haller and R. E. McMurray, Jr., Proc. of 12th Intl. Conf. on Defects in Semiconductors, Physica 116B, 349 (1983).

Figure Captions

Figure 1. Lower: Photothermal ionization spectrum at T=6 K of as-grown zinc-doped Ge sample, grown in H_2-gas ambient, showing A(Zn,H) and Al spectra.
Upper: Spectrum of annealed sample. Note the absence of A(Zn,H) after 3 hrs at 660° C.

Figure 2. Lowest: Unstressed spectrum, as in Figure 1. Upper two: Sample under uniaxial compression along the ⟨111⟩ axis shows normal 1:1 splitting of Al lines, but 3:1 splitting of A(Zn,H) lines.

Figure 3. Variable-temperature Hall effect data, given as an Arrhenius plot, showing the decrease in concentration of A(Zn,H) with annealing time at a temperature of 660° C. Note that the remaining shallow levels are totally compensated after a 3 hr. anneal.

Figure 4. Plots of log of A(Zn,H) concentration vs. annealing time for two different temperatures, showing first-order exponential decrease due to dissociation of the acceptor complex.

Figure 5. Lower: Photothermal ionization spectrum at T=6 K of as-grown beryllium-doped Ge sample, grown in H_2-gas ambient, showing the two sets of A(Be,H) spectra plus Al and B spectra.
Upper: Spectrum of annealed sample showing reduction of A(Be,H) by a factor of 2 after 90 min at 550° C.

Figure 6. Lowest: Unstressed spectrum, as in Figure 5. Upper three: Sample under increasing uniaxial compression along a random axis shows splitting of Al and B lines but not those of A(Be,H).

Figure 7. Variable-temperature Hall effect data, given as an Arrhenius plot, showing the decrease in concentration of A(Be,H) with annealing time at a temperature of 600° C. Note that the remaining shallow levels are totally compensated after a 2 hr anneal.

Figure 8. Lower: Photothermal ionization spectrum at T=6 K, as in Figure 5. Upper: Photothermal ionization spectrum at T=8 K, showing decrease in relative strength of A(Be,H)$_1$ (11.29 meV ground state) spectrum by 30% from thermal population of the second doublet level in the ground state manifold.

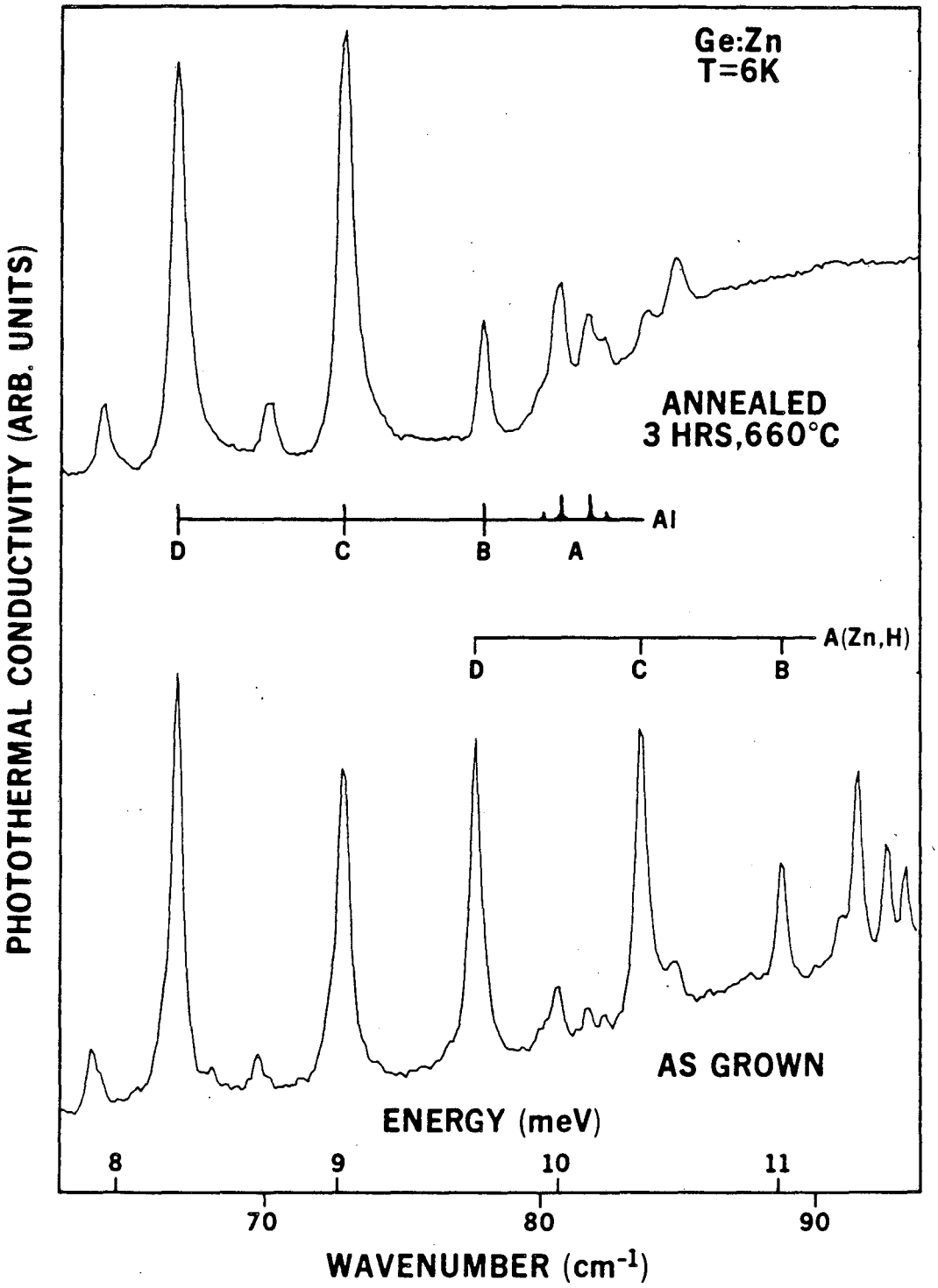

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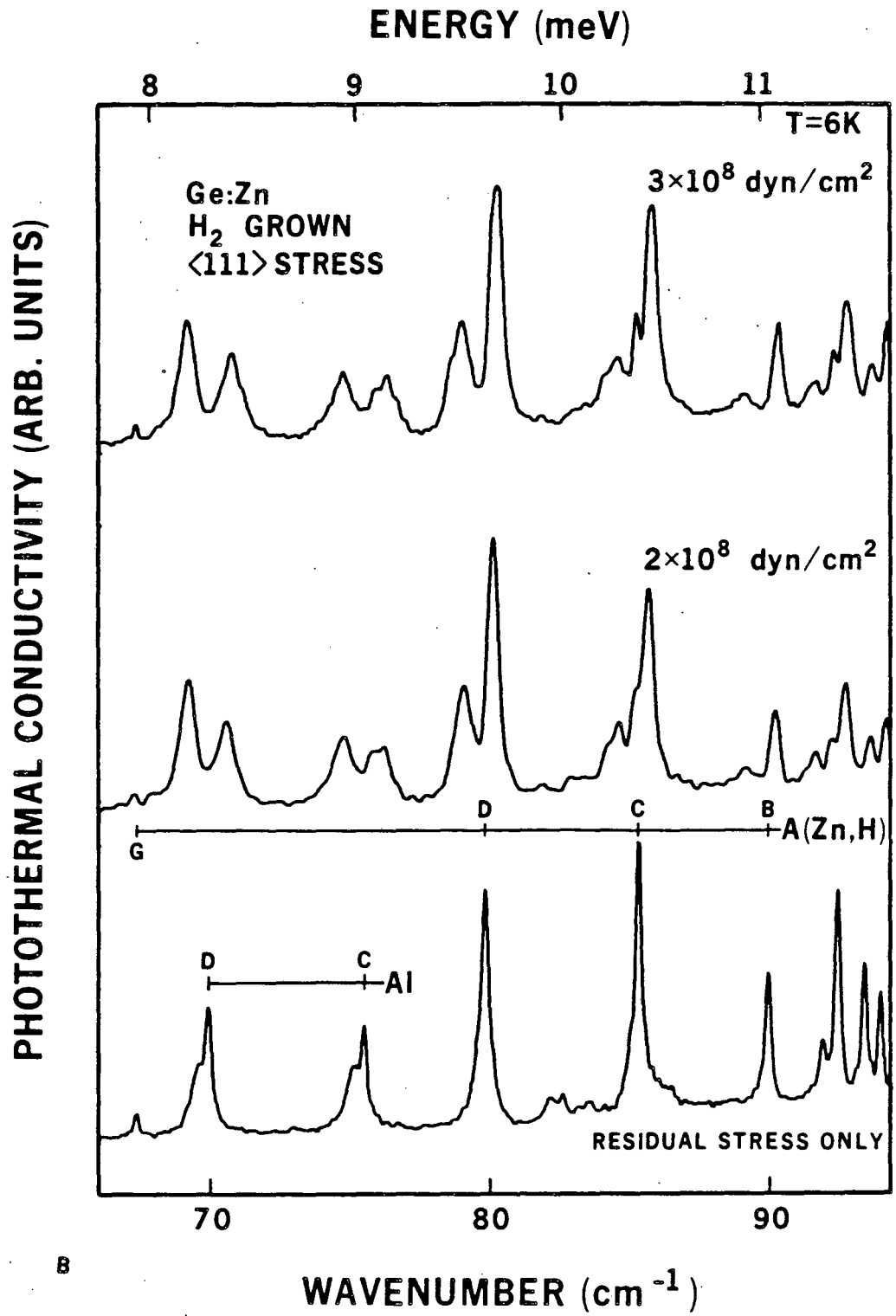
Fig. 1.



B

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Fig. 2.

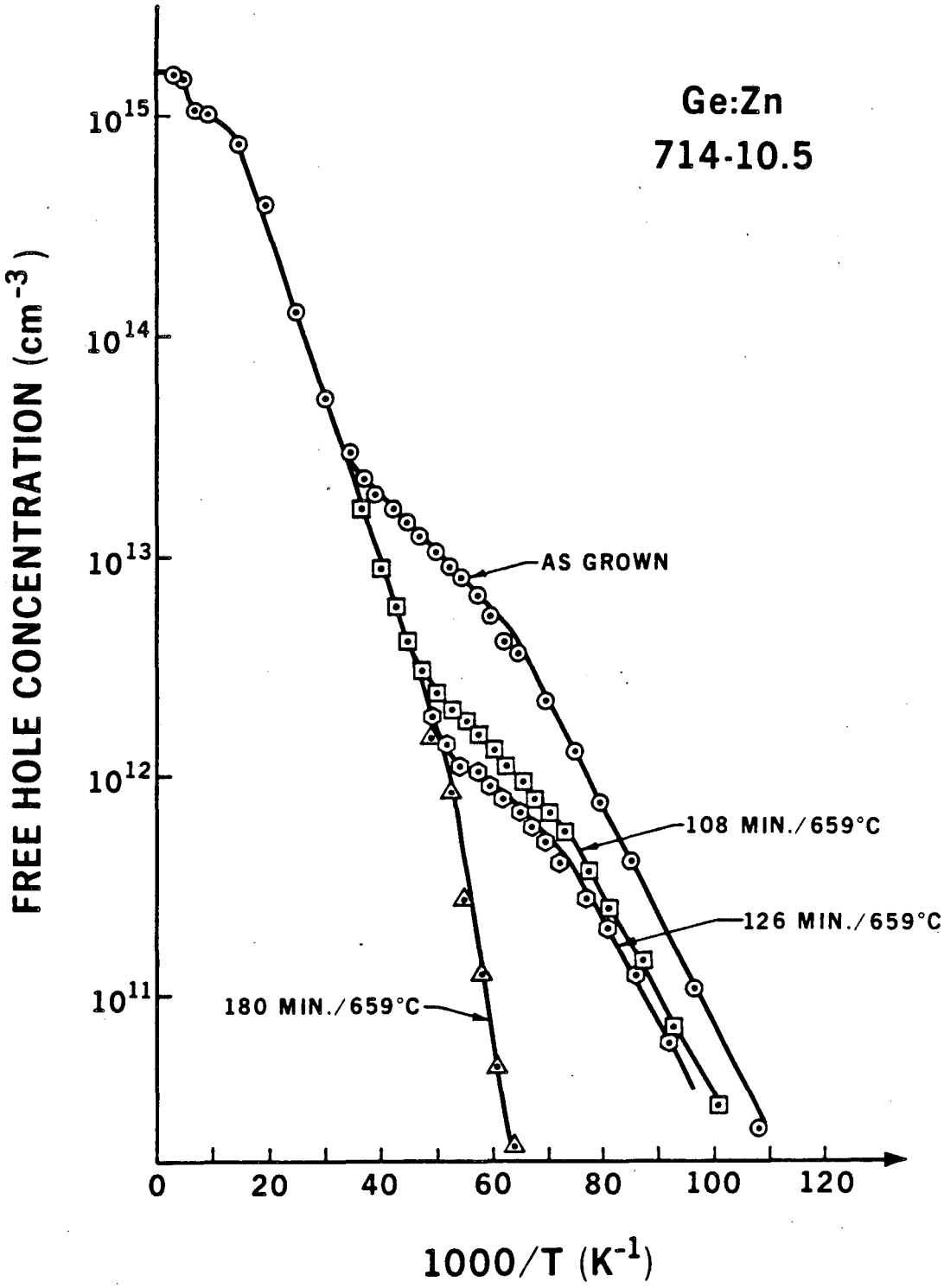

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Fig. 3.

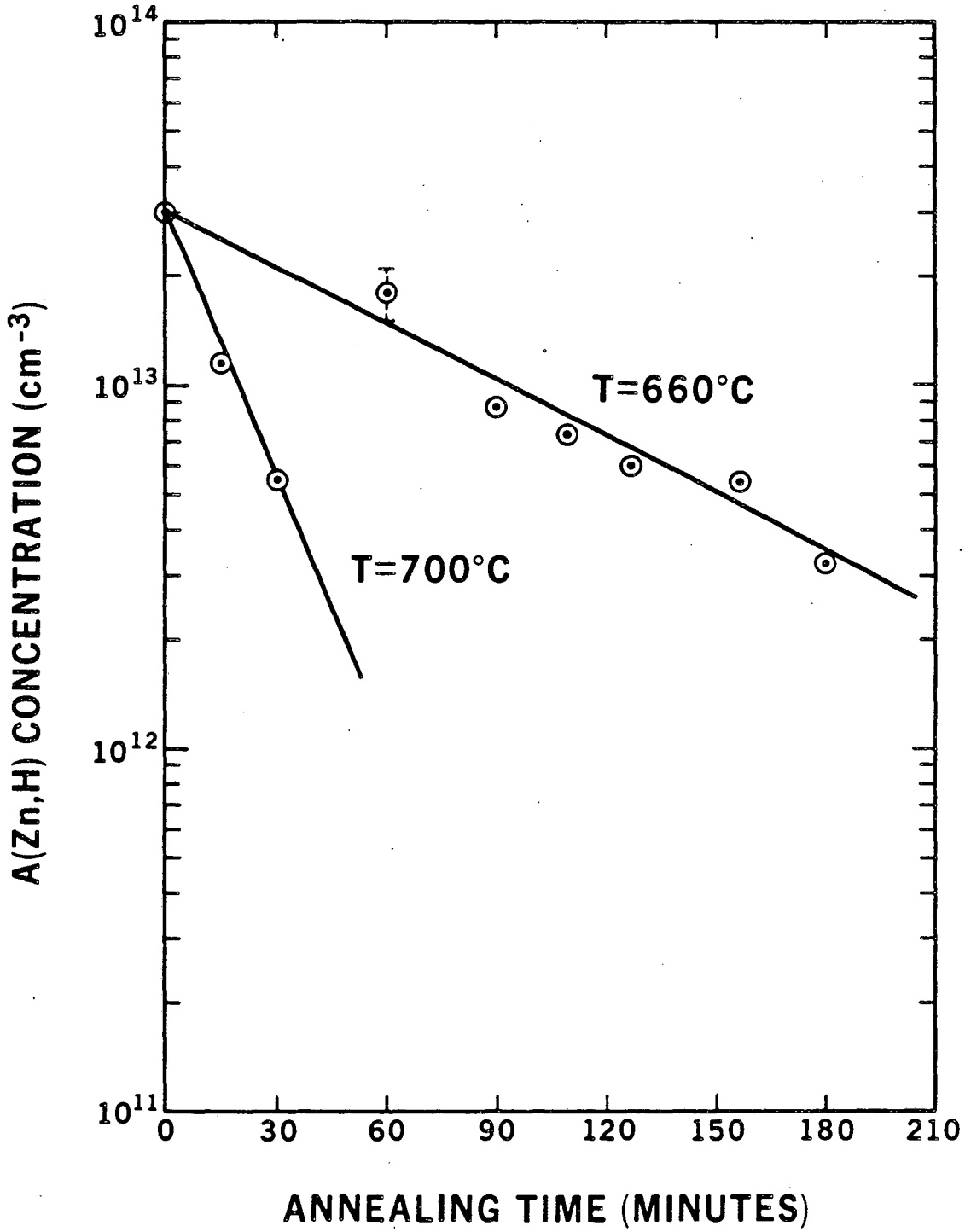

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Fig. 4.

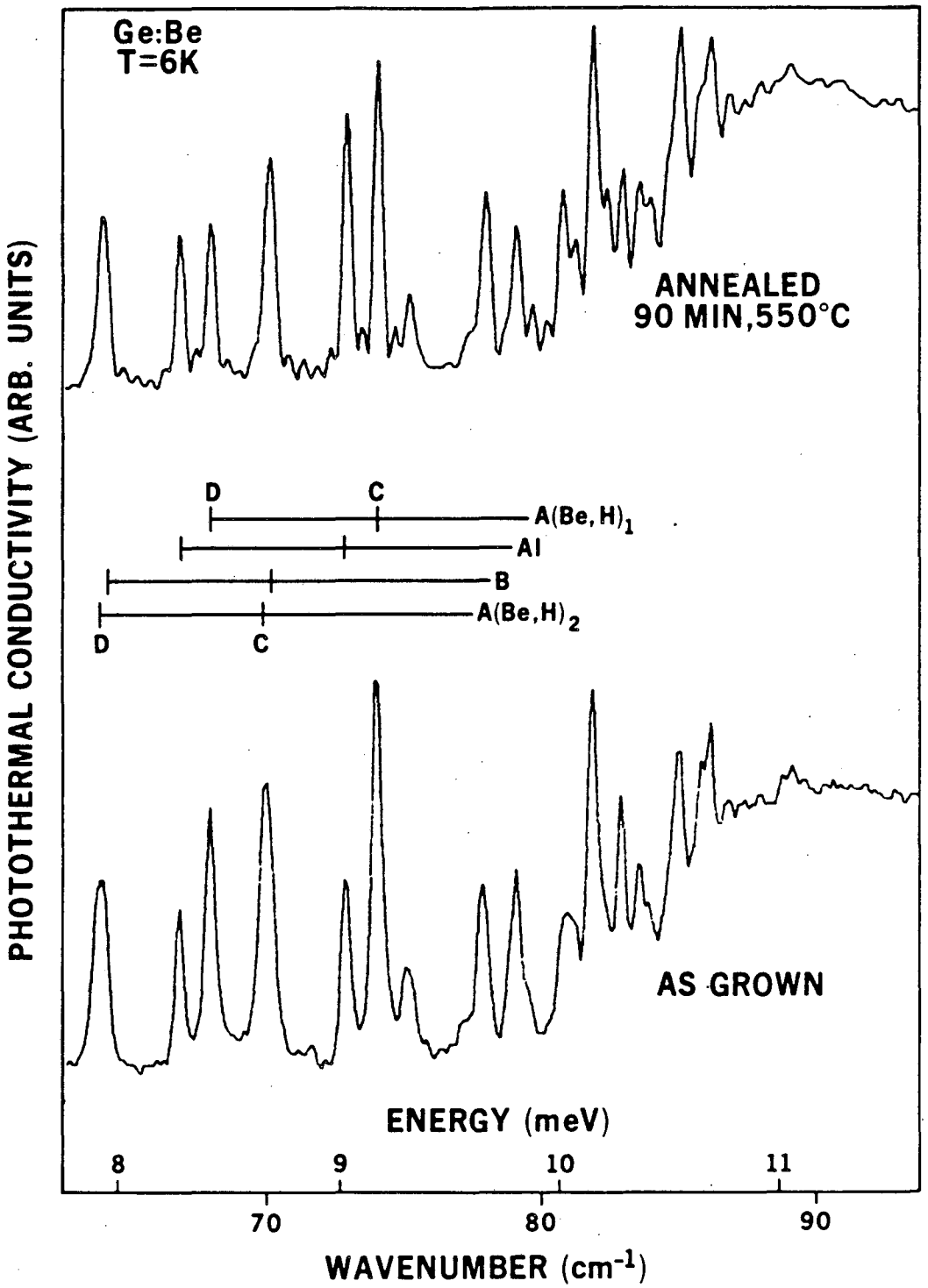

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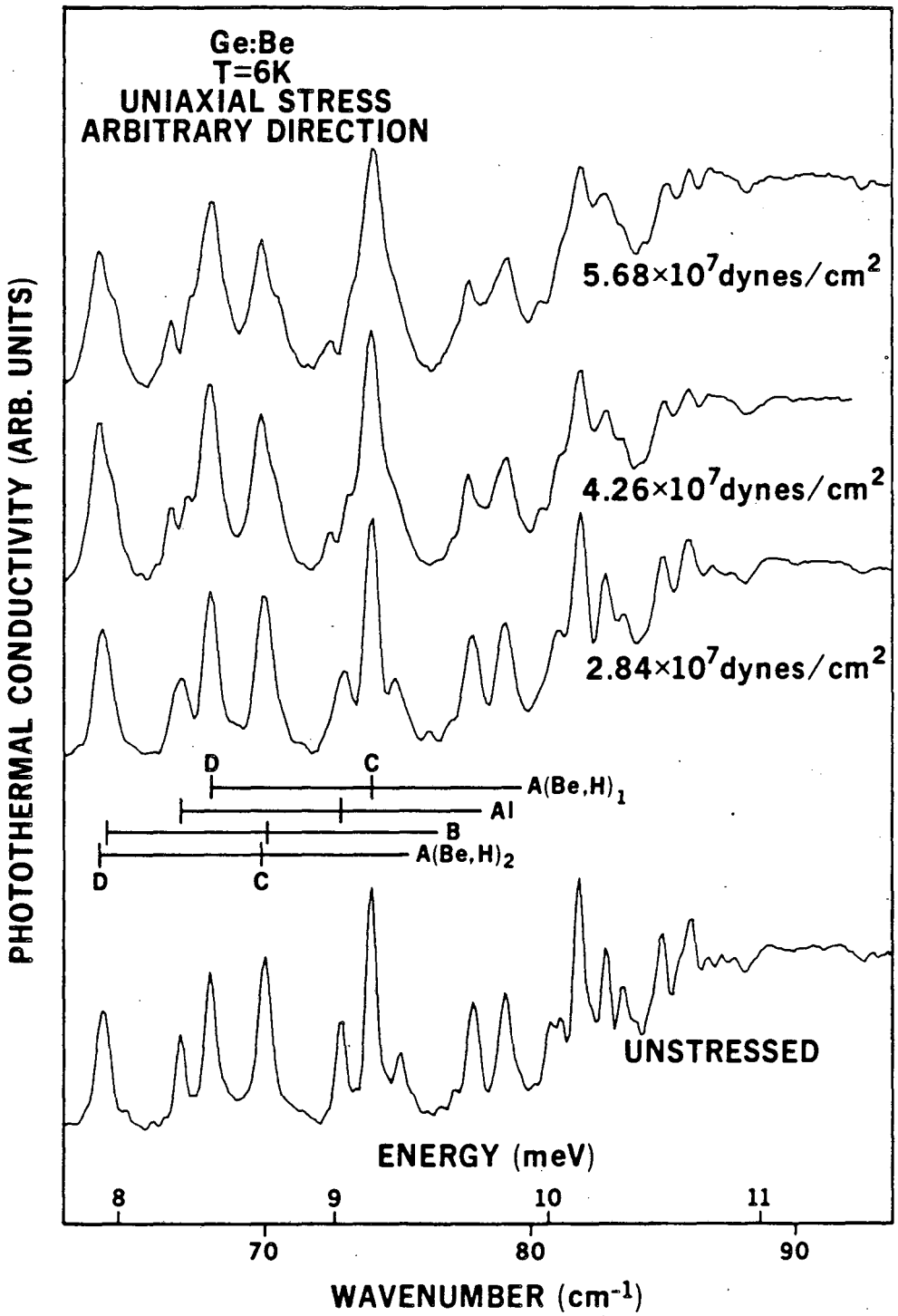
Fig. 5.



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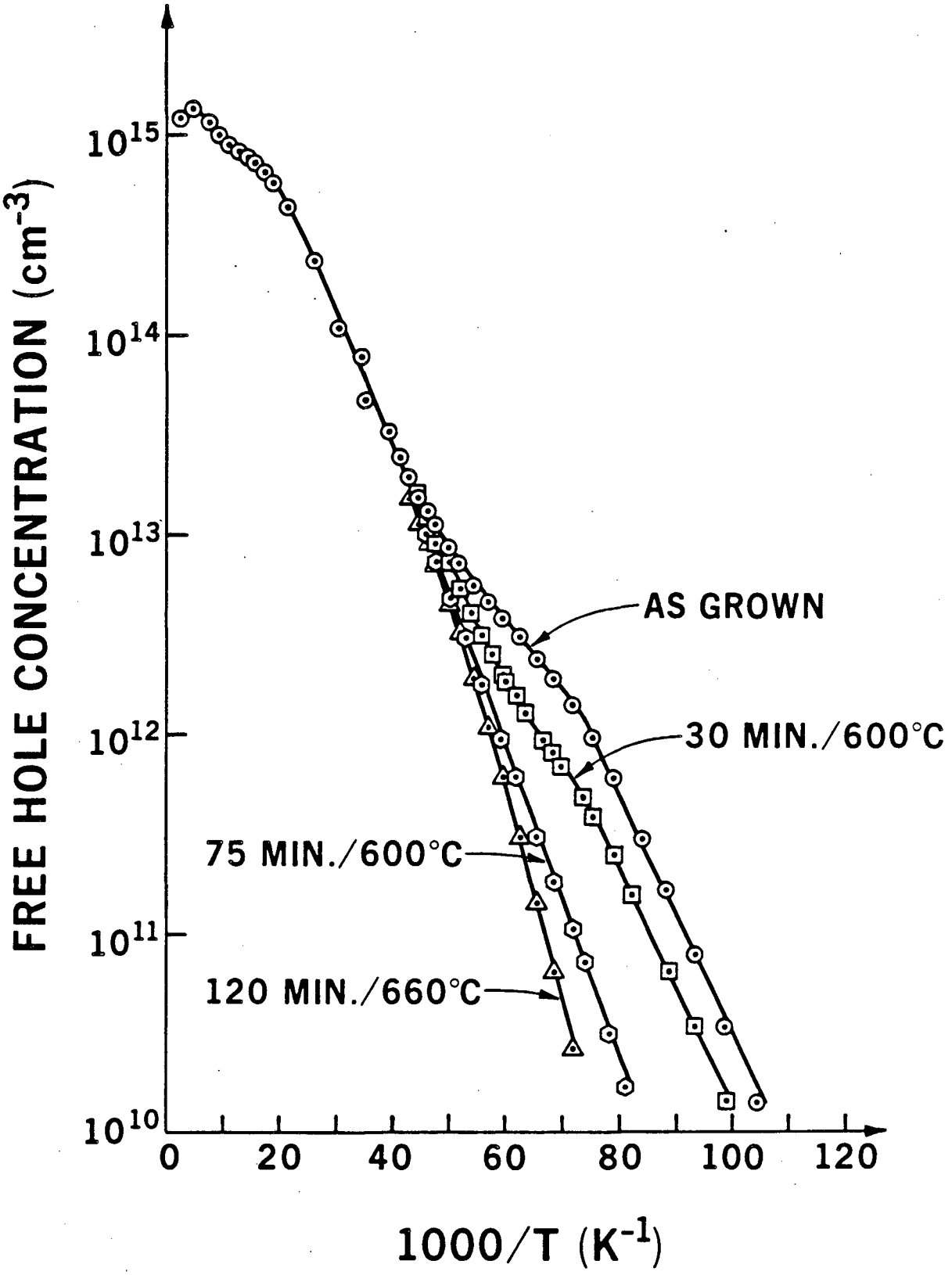

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Fig. 7.

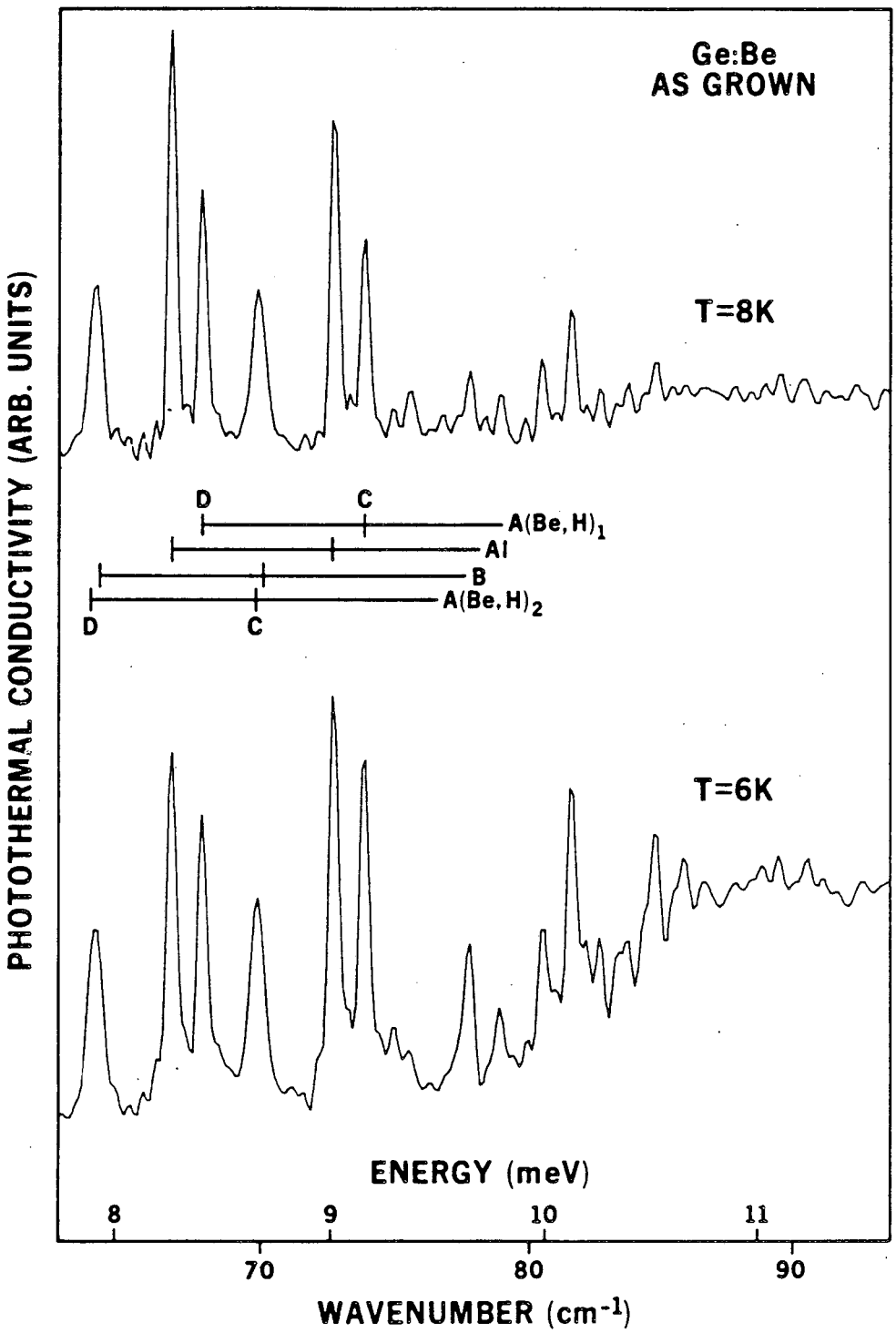

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Fig. 8.

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