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12 August 1993

Major Gernot Pomrenke
AFOSR
Building 410
Bolling Air Force Base
Washington, DC 20332-6448

Dear Major Pomrenke:

This is my final technical report covering progress from May 15, 1990 through May 14, 1993 on grant AFOSR 90-0276 as requested.

Our ab-initio quantum mechanical calculations on grain boundaries have progressed beautifully. We have succeeded in obtaining some very interesting and new results for both clean and doped grain boundary systems. In particular we find the following.

Clean Grain Boundaries

For the clean Ge$\sum 5$ (310) tilt boundary the ideal atomic configuration is as shown at the top of Fig. 1. Here we are looking along the [130] axis. The (310) grain boundary plane is perpendicular to the plane of the figure and passes through the atoms represented by unfilled circles. The horizontal direction is [001]. On either

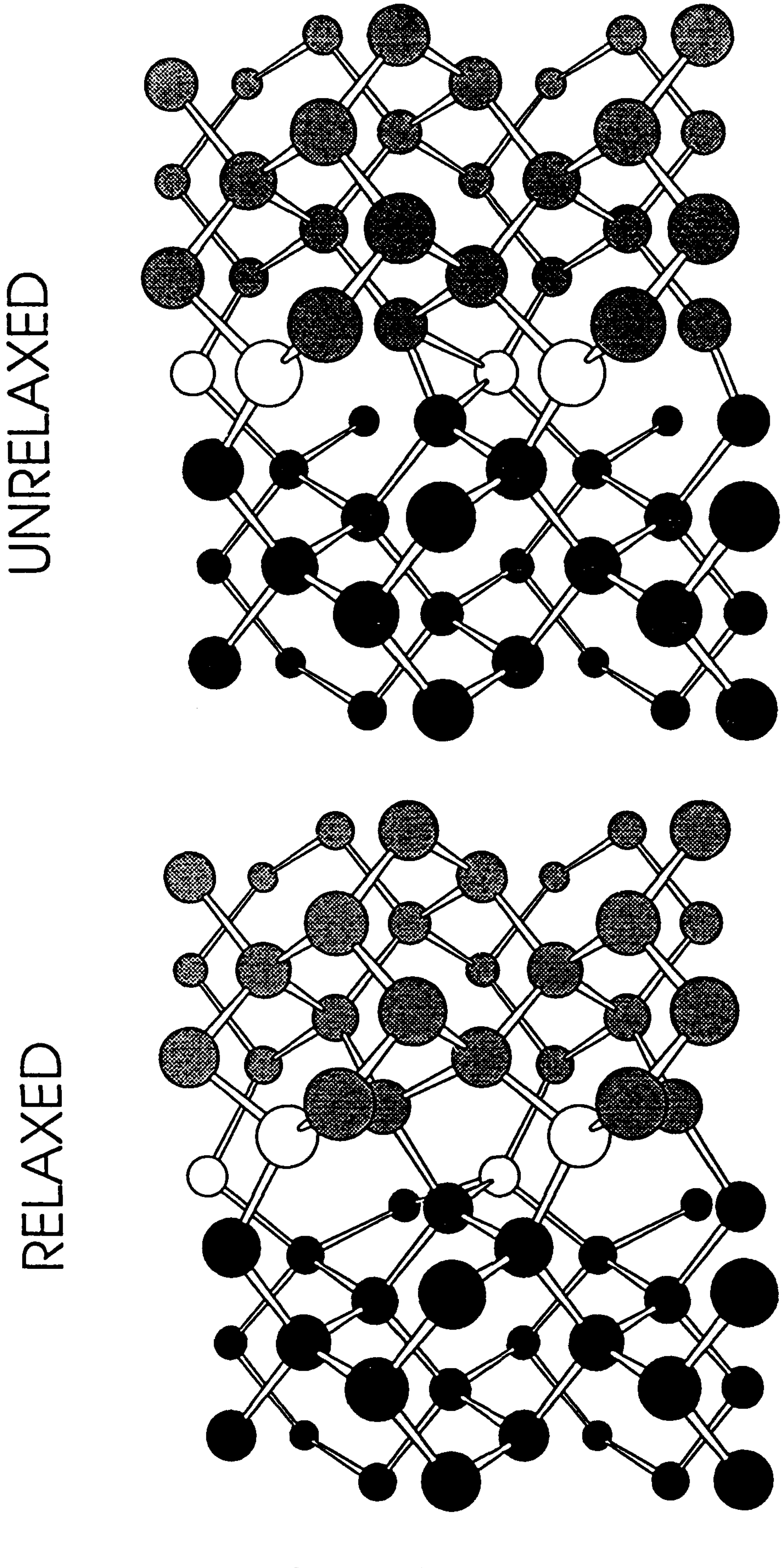

Fig. 1

side of the boundary plane we see atoms from the two grains, filled circles on the bottom and shadowed circles on the top. Note that the atoms with unfilled circles (which are in the immediate vicinity of the grain boundary) form strange-looking bonds with neighboring atoms. One can even see a three-fold ring of bonds right at the interface. This, however, is the ideal, unrelaxed, geometry. To determine the true positions of the atoms we must calculate the total energy of this system and minimize it with respect to atomic displacements. To accomplish this goal we employ an ab-initio local density functional formalism in which the only input is the atomic number of Ge and the grain boundary orientation. In particular, we use an improved Car- Parrinelo molecular dynamics algorithm and local Starkloff-Joannopoulos pseudopotentials. The calculations are executed in a supercell approximation with two grain boundaries and 68 atoms per supercell. We use a 16 Rydberg planewave energy cutoff (which corresponds to about 10,000 planewaves per cell) and 3 special k-points for performing the Brillouin zone averages. Once the atoms are allowed to move, the fully relaxed positions are determined when the forces on the atoms have been reduced to 0.1 eV/A.

The relaxed geometry obtained in this fashion is shown at the bottom of Fig. 1. Now all the atoms are four-fold coordinated and the bonding is close to being tetrahedral. The new structure, however, has five-, six-, and seven-fold rings of bond present while in the bulk we only find six-fold rings of bonds. The deviations from the bulk bond length are less than about 3% and the deviations from the perfect tetrahedral bond angle less than 19°. The atomic positions obtained in this geometry are in excellent agreement (within 0.01A) with experimental measurements. From these calculations we predict the energy associated with the grain boundary to be 16 meV/A^2 (0.26 J/m^2). Our calculations also predict that the clean boundary has an empty and very localized grain boundary state that could trap injected electrons! This state lies just below the conduction band edge.

An Arsenic Impurity on the Grain Boundary

The electronic charge density associated with this bona-fide grain-boundary state is shown in Fig. 2 as a solid line. This is the charge density projected onto a direction perpendicular to the plane of the grain boundary. This is a fairly well-localized state with a width of about 3.8 A. Since this state is empty in the absence of impurities, one might expect donor electrons from an impurity such as As to get

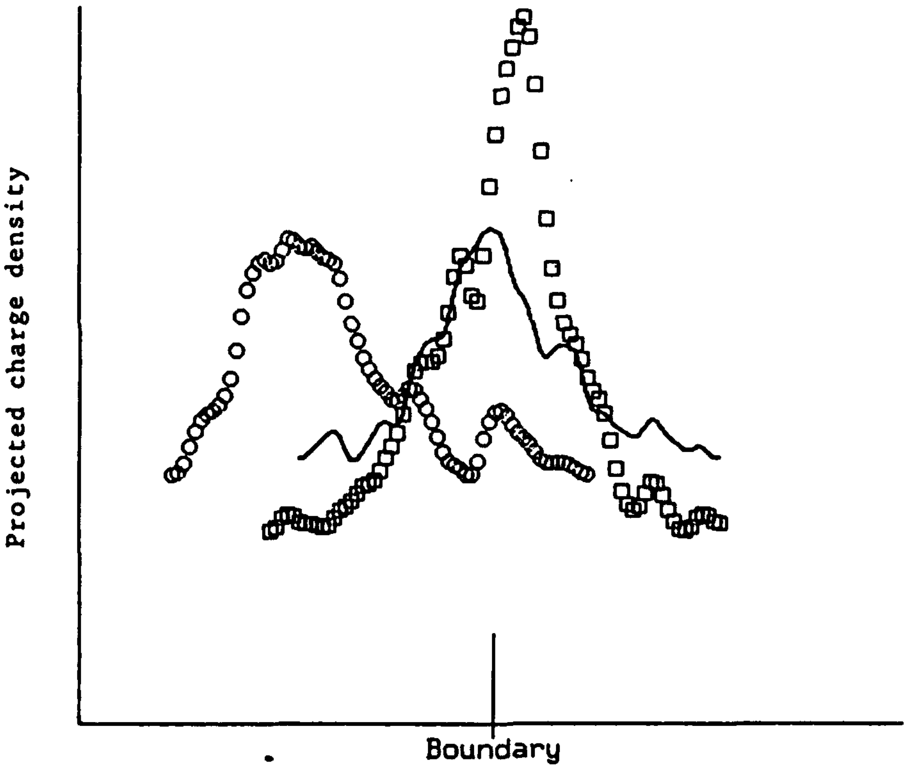

Fig. 2 Boundary electronic state for different impurity states.

Line: undoped
Circles: As substituted away from grain boundary
Squares: As substituted in grain boundary

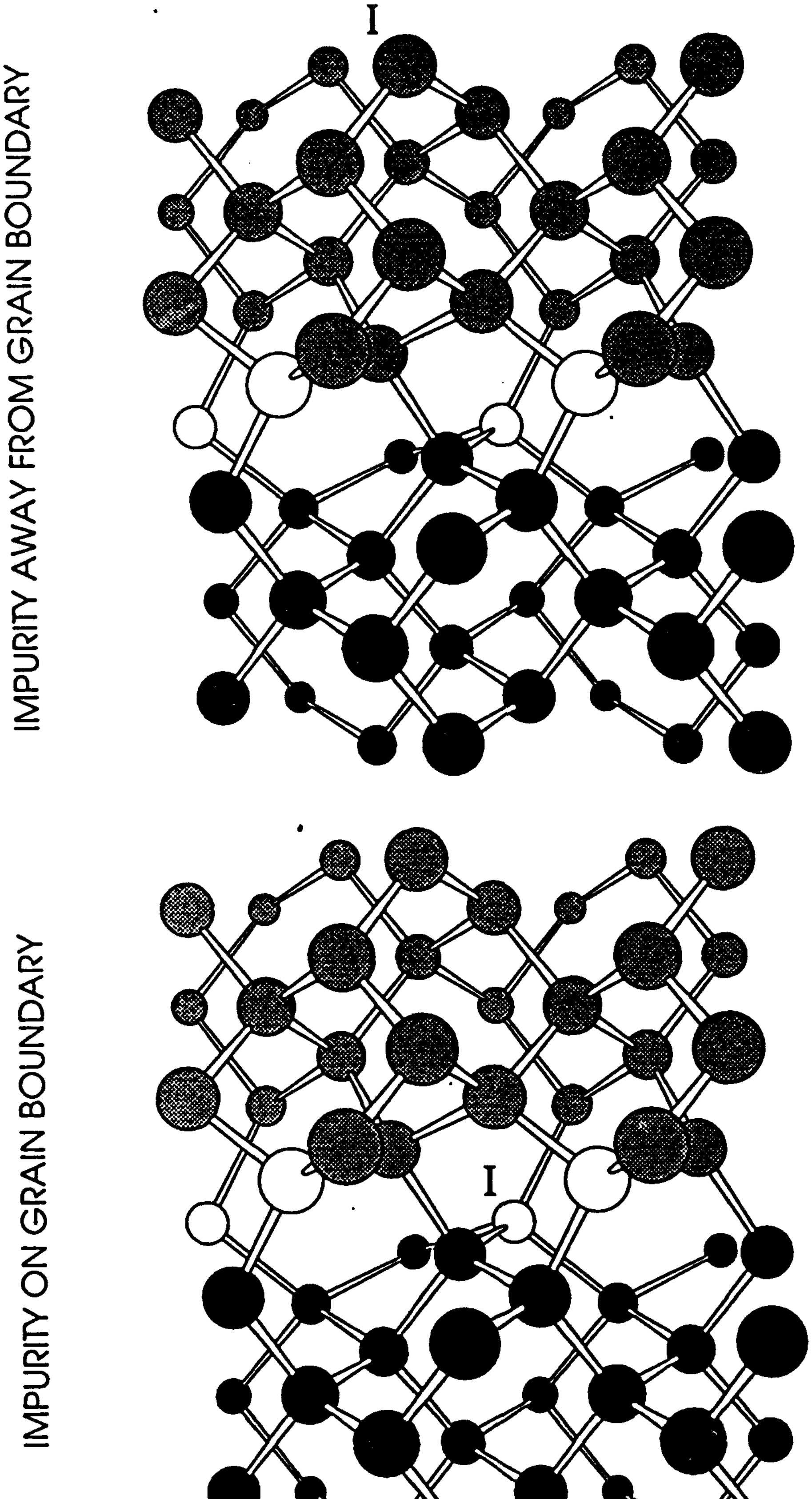
IMPURITY AWAY FROM GRAIN BOUNDARY
I
IMPURITY ON GRAIN BOUNDARY
I

Fig. 3

partially trapped at the grain boundary interface. To test this hypothesis we performed ab-initio total energy calculations for this grain boundary with As atoms on and away from the grain boundary interface. The results of the charge density calculations for this trapped state are shown in Fig. 2 as open circles and open squares. Note that the trapping is greater when the impurity is closer to the grain boundary interface.

We have also performed calculations of the energetics of an As impurity on and away-from the grain boundary region. The positions chosen for the substitutional As impurity are shown in Fig. 3. Here the symbol, I, denotes the position of an As Atom. We find that an As impurity definitely prefers to exist *on* the grain boundary rather than in the "bulk" of Ge. Our calculations thus predict that the presence of the grain boundary provides an effective *attractive* force on As impurities which would eventually lead to the impurities segregating to the boundary. We predict that the "binding energy" of As impurities to the grain boundary is 0.18 eV.

Finally, we have performed an analysis to determine the origin of this binding. We find that if we "freeze" the Ge lattice and simply substitute As on and away from the grain broundary, that the energy "on" the grain boundaryis lower by 0.21 eV. This is due primarily because of the trapped electron state! When the atoms are now allowed to relax, the As atom in the bulk actually can relax more than the As atom on the grain boundary by about 0.03 eV. This gives rise to a net binding energy of 0.18 eV.

New Method for ab-initio total energy calculations:

In a milestone paper of the last decade Car and Parrinello introduced a novel technique for performing ab-initio density functional pseudopotential total energy calculations. The technique involved use of a fictitious molecular dynamics approach to relax both the ionic and electronic coordinates. However, with growing interest in larger and more complex systems, it has been shown that this method becomes intractable as the longest lengthscale in the system increases. Recently, the conjugate gradient procedures of Teter et al. and Gillan have been shown *not* to exhibit this instability. But they are relatively much more costly and consequently intractable for performing dynamical simulations. Very recently, we have succeeded in developing a new method that is an extension of the conjugate gradient approach that is very efficient and tractable both at long lengthscales and for dynamical simulations. There are two basic ingredients to the new method. The first introduces alternative initial conditions for the efficient refinement of the wavefunction at each time step and the second introduces a prescription for the analytic continuation of traditional total energy functionals into the space of non-orthonormal single particle orbitals. The benefit of this approach is significant as shown in Fig. 4. Here we present the results of a test calculation on a supercell of Si whose one dimension is over 50Å long! What is shown is the average CPU consumption (expressed in terms of the number of hours required to simulate one picosecond on a Cray-YMP supercomputer) as a function of iteration number for several schemes for relaxing the wavefunctions using a traditional energy functional (dashed lines) and our new analytically continued functional (solid lines). Clearly, the gain is significant.

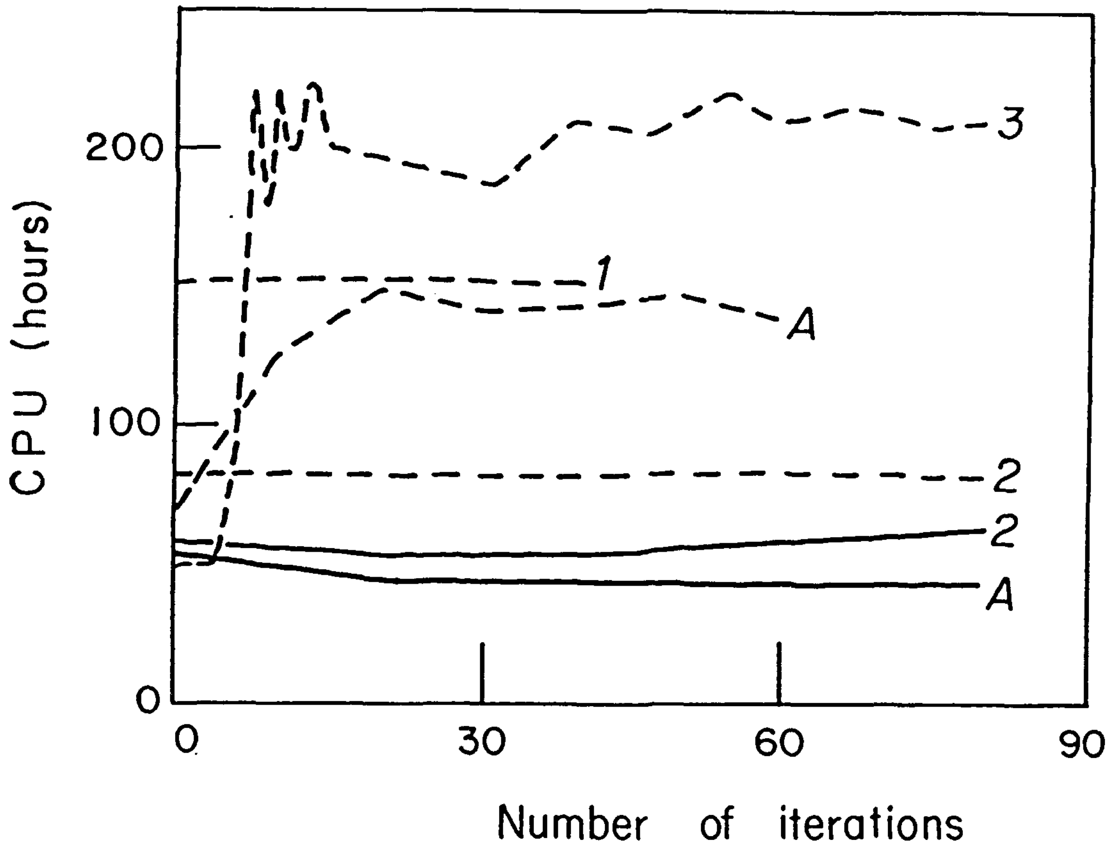

Fig. 4

In order to test the accuracy of this new technique, we followed the dynamical evolution of this very long supercell of Si at room temperature for 3 picoseconds. We then calculated the velocity autocorrelation function from which we deduced the phonon modes and frequencies. The results are shown in Fig. 5. Clearly , the agreement between theory and experiment is excellent.

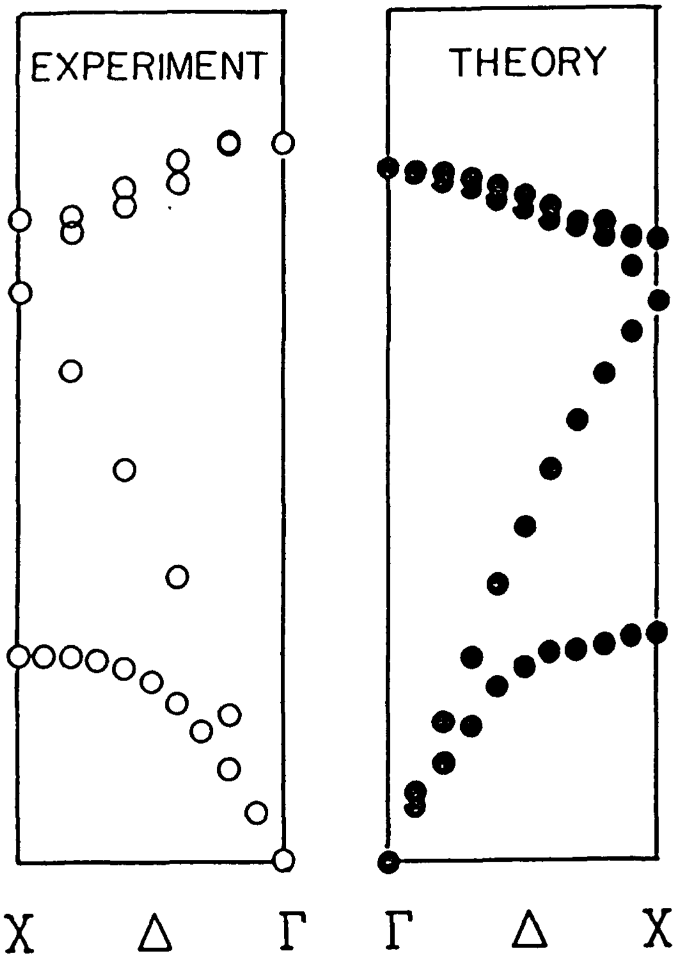

Fig. 5

Dopant segregation at grain boundaries:

In our last progress report we described our success in modelling accurately the grain boundary structure of $\sum 5$ (310) tilt in Ge and our prediction that neutral As will segregate to this boundary. This attraction was explained in terms of the filling of an empty interface state localized at the grain boundary of the undoped system.

Since then we have extended our calculations (some fof the most recent ones using the new method described above) to include As^+ and Ga impurities. These impurities were placed at various substitutional sites as shown in Fig. 6. Here "bk" corresponds to bulk, "i" to intermediate, and "gb" to grain boundary. With the impurities at these locations we first calculate the total energy of the system with all atomic positions held fixed at their equilibrium values in the undoped state and then allow the positions of the impurities and all surrounding atoms out to third nearest neighbors to relax. This approach helps to separate lattice relaxation from electronic effects by determining the relaxation energy as the lattice responds to the impurity, a measure of the elastic energy associated with the incorporation of the impurity into the lattice. The results are shown in Fig. 7. The horizontal lines represent the energy of the system with the surrounding lattice held fixed (arrow tails) and with the surrounding lattice allowed to relax (arrow heads). Let us concentrate first on the results for neutral As. We note that although lattice relaxation is a significant energy, the *differences* between the elastic energies of the three substitutional sites are relatively small compared to the final interaction with

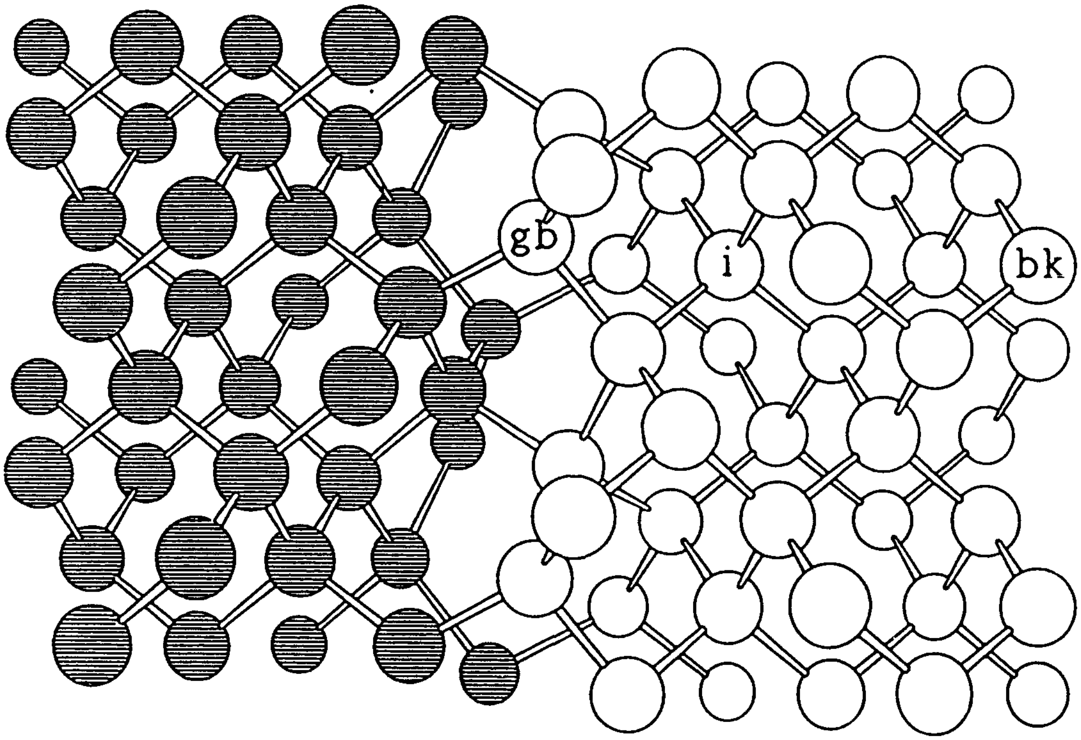

Fig. 6

the boundary. Thus lattice effects do not contribute significantly to the boundary-dopant interaction which therefore must be dominated by electronic effects. Note that despite the lack of blatant electronic defects, -like dangling bonds or over-coordinated sites to interact with the As dopant, we still find an appreciable tendency for As to segregate to the boundary. This segregration is due to a natural competition in the dopant-boundary system as both the donor and the interface state compete for the donated electron. Placing the impurity on the boundary relieves this competition simply and minimizes the energy of the system. To confirm that this competition is indeed responsible for the binding, we have removed the donor electron and studied the possible segregation of As^+. As expected (see Fig. 7), the interaction with the boundary is dramatically reduced.

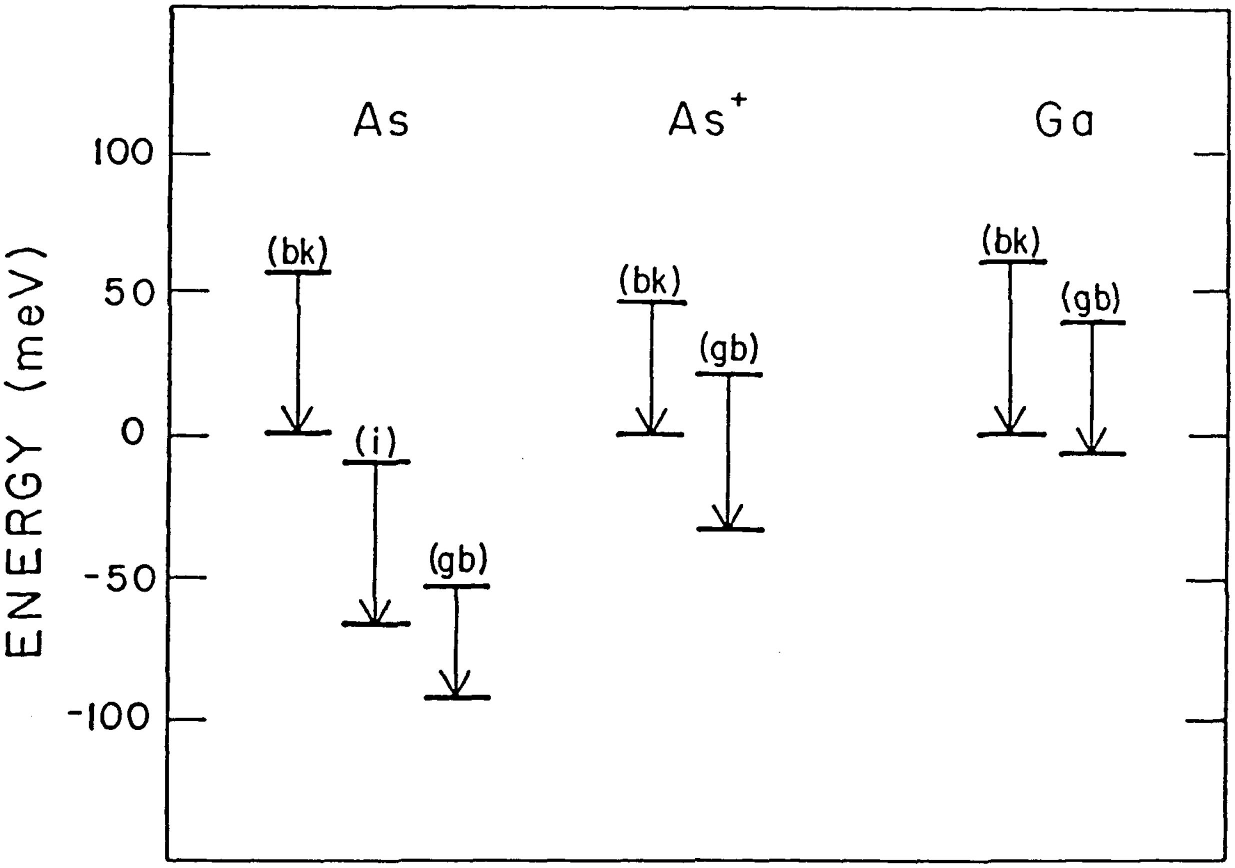

Fig. 7

Finally, we turn to possible segregation of a p-type dopant, Ga. Again, as shown in Fig.7, the lattice relaxation around the impurity is a significant source of energy but one that remains insensitive to the location of the dopant. Moreover, because of the lack of boundary hole states, there is now no competition for the donated carrrier and very little net interaction with the boundary. This then leads us to the very interesting prediction that n-type dopants should segregate to the $\sum 5$ (310) boundary, whereas p-type dopants should not.

Generalization to other classes of Grain Boundaries

Though we have studied just one particular grain boundary, the behavior of our boundary is representative in many aspects of the behavior of the ensemble of boundaries found in polycrystalline samples, and a very general picture emerges from our study. Tetrahedrally rebonded grain boundaries not only are low in energy, they also reconstruct reliably without falling into false local minima. Further, the *ab initio* calculation show that tetrahedrally reconstructed boundaries respond to long-length scale excitations, such as elastic effects around an impurity, very much in the same way as does the bulk, so that these excitations are relatively blind to the presence of the boundary. More locally sensitive excitations such as electrons, on the other hand, sense the subtle topological differences (e.g., 5- and 7-fold rings) between the bulk and boundary and may bind to the boundary in bona fide interface states, even in boundaries without dangling bonds.

These general features of undoped tetrahedral boundaries have very specific implications about their ability to bind different dopants. Mechanical effects in the incorporation impurities do not contribute significantly to the impurity-boundary interaction, leaving electronic phenomena alone to drive segregation. Without dangling bonds, the one electronic feature which may distinguish the bondary from the bulk is the presence of localized states which may compete for the carriers donated by impurities. The local application of the HSAB principle gives a unified description of the effect of such states on segregation. The predictions of this principle agree perfectly both with the results of direct total energy calculations and with the explicit analysis of the interactions among the electronic states in these systems. Because the application of the local HSAB principle depends only on knowledge of the electronic structure of the isolated reactants (interface and impurity), this general principle may be applied in conditions where a total energy calculation of the combined system is very expansive or impossible, leading to significant savings in computational effort.

This general picture not only is in complete agreement with the explicit *ab initio* results that the $\Sigma = 5$ (310) tilt boundary binds arsenic but not As^+ or gallium, it also predicts that this boundary *generally* binds n-type dopants. Furthermore, we see that if we were to divide all of the tetrahedrally reconstructed grain boundaries into classes based on segregation behavior, we would find just four simple classes: those boundaries which attract n-type but no p-type impurities, p-type but not n-type, both groups, or neither, depending on whether the particular boundary localized either electrons but not holes, holes but not electrons, both types of carrier, or neither, respectively. This expectation is borne out in germanium, where the boundaries, almot without exception, both trap electrons but not holes and attract n-type but not p-type impurities. Although the presence of imperfect reconstructions with dangling bonds *is* indicated in the experimental boundaries by the experimental trap states being so deep into the gap and the dopant-boundary energies being so large, the basic reasoning behing applying the HSAB principle remains intact. We should still expect the observed correlation between carrier trapping (related to the softness of the boundary) and segregation of shallow (soft) donors.

Finally, our arguments about tetrahedrally coordinated grain boundaries make no reference to the dimensionality of the defect, so that dislocations or local defects which find tetrahedral rebondings should also exhbit the same behaviors. They also may have localized softness, $s^-(r)$ or $s^+(r)$, and so attract n-type or p-type dopants, respectively, through the same mechanisms operating in the grain boundary of this study.

Our work in this proposal has led to the following manuscripts and invited papers.

Manuscripts

1. E. Tarnow, T. Arias, P. Bristowe, P. Dallot, G. Francis, J. Joannopoulos and M. Payne, "The Relationship Between the Microscopic Properties of Semiconducting Grain Boundaries and their Orientation," Proc. Mat. Res. Soc. Spring (1990).

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4. T. Arias, M. Payne and J.D. Joannopoulos, "Ab-initio Molecular Dynamics Techniques Extended to Large Length Scale Systems, Phys. Rev. B **45**, 1538 (1992)

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6. M. Payne, G. Francis, M. Needels, E. Tarnow, P. Dallot, P. Bristowe and J.D. Joannopoulos, "Ab-Initio Investigations of Surfaces and Grain Boundaries in Germanium", *Ordering at Surfaces and Interfaces,* Springer Verlag, p. 169 (1992).

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9. T. Arias and J.D. Joannopoulos, "Ab-initio Prediction of Dopant Segregation at Grain Boundaries", Phys. Rev. Let. **69**, 3330 (1992).

10. A. Dal Pino,M. Galvan, T. Arias and J.D. Joannopoulos, "Chemical Softness and Impurity Segregation at Grain Boundaries", J. Chem. Phys. **98**, 1606 (1993).

11. T. Arias and J.D. Joannopoulos, "The View of Grain Boundaries from the Computational Leading Edge", Electrochem.Soc., in press, (1993).

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1. M. Payne (J. Joannopoulos), 20th Inst. Conf. Phys. Semi. Thessaloniki, Greece (1990).

2. M. Payne (J. Joannopoulos), 3rd NEC Sym. Fund. App. New. Mat. Phys., Hakone, Japan (1990).

3. J. Joannopoulos, "Phys. Computing 1991," March Bull. APS (1991).

4. T. Arias (J. Joannopoulos, M. Payne), Total Energy Workshop, Trieste, Italy (1991).
5. K. Cho (J.D. Joannopoulos), Molecular Dynamics Workshop, Telluride (1991).
6. J.D. Joannopoulos, (T. Arias) Workshop on Epitaxy, Interfaces and Defects, Pittsburgh (1991).
7. T. Arias (J.D. Joannopoulos), Europ. Res. Conf. on El. Struct. of Solids, Cambridge (1992).
8. T. Arias (J.D. Joannopoulos), Mat. Res. Soc., San Francisco (1993)
9. T. Arias (K. Cho, P. Lam, J.D. Joannopoulos), Workshop on Electronic Structure Algorithms, Penn State (1993).

I hope this is sufficient. If you have any further questions please do not hesitate to contact me.

Sincerely,

J.D. Joannopoulos
Professor of Physics

JDJ:ia