

## Bond lengths for iodine impurities in III-V semiconductors derived from Mössbauer nuclear quadrupole data

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The origin of the nuclear quadrupole interactions for  $^{129}\text{I}$ , using sources of  $^{129}\text{Te}^m$  implanted in a number of III-V compound semiconductors, obtained by Mössbauer measurements, has been analyzed through electronic structure investigations based on a model for the impurity centers that has been developed in recent work on group-IV semiconductors. Our investigations support the conclusion reached in the earlier work that the impurity atom has a strong tendency to relax to a position which makes its distance to the nearest-neighbor host atoms consistent with the normal covalent-bond distance.

### INTRODUCTION

Understanding the behavior of deep impurities in semiconductors is a topic of widespread theoretical and practical interest. In a recent paper, we have presented a theoretical analysis of nuclear quadrupole interaction data on  $^{125}\text{Te}$  and  $^{129}\text{I}$  impurities in Si and Ge lattices<sup>1</sup> resulting from implantation of  $^{125}\text{Te}^m$  and  $^{129}\text{Te}^m$ . This analysis was based on a structural model for the impurity location which involved an impurity atom trapped close to a substitutional site adjacent to a nearest-neighbor vacancy<sup>2</sup> (Fig. 1). The aim of our investigation was to obtain quantitative information on the relaxation of the impurity towards the vacancy by calculating the electric field gradient (EFG) as a function of the impurity position, and comparing this with experimental results.

The calculations were performed on clusters consisting of the basic tetrad unit supplemented with a variable number of neighboring host atoms to simulate the surrounding lattice. The self-consistent charge extended Hückel method<sup>3</sup> (SCCEH) was used as the computational procedure for obtaining electronic wave functions. As a result of the investigation, a strong correlation was found between the nearest-neighbor distances in the four systems under study (TeSi, TeGe, ISi, IGe) and the sums of covalent radii for the corresponding impurity-host combination. Such a correlation can be explained by the existence of a "natural" covalent-

bond length, implying that the impurity will try to achieve its preferred bond length provided it is offered enough free space to relax. Similar conclusions have been drawn from surface extended x-ray absorption fine structure<sup>4</sup> (on Te and I) and x-ray standing-wave measurements<sup>5</sup> (on Br) adsorbed at Si surfaces.

Nuclear quadrupole interactions measured by Mössbauer spectroscopy have also been published for I impurities in several III-V compound semiconductors.<sup>6</sup> These data were obtained by implanting radioactive  $^{129}\text{Te}^m$ , which decays to the Mössbauer level of the  $^{129}\text{I}$  isotope. Although the hyperfine interactions are measured in the daughter  $^{129}\text{I}$  nucleus, they reflect the nature of the atomic environment of the atom of the implanted  $^{129}\text{Te}^m$  nucleus. The Mössbauer spectra revealed the existence of large quadrupole interactions of the  $^{129}\text{I}$  nuclei, precluding a purely substitutional<sup>7</sup> location of the implanted impurity atom. It was therefore felt desirable to apply the above-mentioned defect model,<sup>1,2,6</sup> with a near-substitutional impurity atom adjacent to a vacancy, to the III-V compounds, which are structurally equivalent to the group-IV semiconductors, and see whether similar conclusions could be drawn from a bond length calculation for the I impurity.

### PROCEDURE

We started with the assumption, also made in our earlier work<sup>1</sup> on the group-IV semiconductors, that iodine remains isoelectronic with tellurium after the nuclear  $\beta$  decay from  $^{129}\text{Te}$ . This means that the switch from tellurium to iodine does not fundamentally disrupt<sup>8</sup> the nature of the chemical bonding to the surrounding atoms, although some relaxation in the positions of the impurity and neighboring atoms can occur during a time much smaller than the lifetime of the Mössbauer level (16.8 sec). Since tellurium dopants are generally believed<sup>9</sup> to replace the column-V element, we put our iodine atom at a near-substitutional site corresponding to a column-V atom of the host lattice and adjacent to a vacancy at a column-III atom site. There is evidence for such situations from other measurements<sup>9</sup> on tellurium in III-V compounds.

Following a choice that has proven convenient for our Si

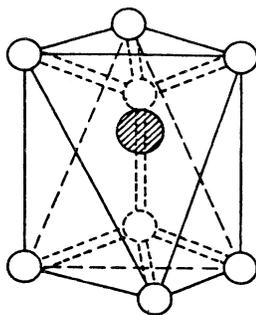


FIG. 1. Model for the location of Te and I impurities resulting from implantation of Te in diamond-type lattices.

and Ge studies, the cluster used in the calculation was a 16-atom unit consisting of the impurity, its three nearest neighbors, the nine nearest neighbors of the latter, and the three host atoms nearest to the vacancy below the impurity. We assumed trigonal bond symmetry at the impurity site, and the trigonal axis (coinciding with the  $\langle 111 \rangle$  crystal axis) was chosen as the  $Z$  axis for the EFG calculations. Although a precise determination of the asymmetry parameter is not allowed by the present Mössbauer data, this choice is consistent with the fact that the observed Mössbauer spectra are reasonably well fitted by a nearly axially symmetric nuclear quadrupole interaction.

We refer to Refs. 1 and 3 for a detailed description of the SCCEH procedure. The cluster was terminated in the same way as in our previous calculation,<sup>1</sup> by saturating each dangling bond with an extra electron attached to that particular atom. The EFG computations were performed for the impurity located at different positions along the  $Z$  axis and the iteration procedure was carried out until full charge convergence had been achieved.

## RESULTS AND DISCUSSION

We have collected the experimental and theoretical results from this work and from our earlier paper<sup>1</sup> in Table I. In order to facilitate their interpretation, we have also listed the bond length  $R_{\text{host}}$  in the undistorted lattice and the impurity-host covalent-bond length  $R_{\text{cov}}$  for each of the systems, the latter being estimated from the sum of tetrahedral covalent radii for the various elements involved.<sup>10</sup> Our results on the III-V compounds clearly confirm the strong correlation between the computed  $R$  and  $R_{\text{cov}}$ . The calculated bond lengths closely follow the sum of covalent radii for the various host-impurity combinations, with the sole exception of GaSb. The exceptional behavior of I in GaSb can, however, be understood by the fact that it is the only system where  $R_{\text{host}} > R_{\text{cov}}$ . The I impurity in GaSb, thus unlike in the rest of the host lattices, would have a trend to relax towards the nearest-neighbor host atoms rather than away from them. However, the presence of the neighboring vacancy opposes this trend, supporting instead a movement

TABLE I. Experimental field gradient ( $V_{zz}$ ) and calculated bond length ( $R$ ) for Te and I impurities resulting from implantation of Te in various diamond-type semiconductors. Bond lengths ( $R_{\text{host}}$ ) in the perfect host lattice and estimated impurity-host covalent-bond lengths ( $R_{\text{cov}}$ ) are listed for comparison.

System	$V_{zz}$ (expt) ( $10^{16}$ esu/cm <sup>3</sup> )	$R$ Å	$R_{\text{cov}}$ Å	$R_{\text{host}}$ Å
TeSi	-1.16	2.49	2.49	2.35
TeGe	-1.17	2.54	2.54	2.45
ISi	-1.28	2.41	2.45	2.35
IGe	-1.24	2.48	2.50	2.45
IGaAs	-0.70	2.57	2.54	2.45
IGaSb	-0.83	2.70	2.54	2.64
IGaP	-0.69	2.54	2.54	2.36
IInP	-0.57	2.75	2.72	2.54

of the I in the direction of the vacancy. One thus expects the bond length in GaSb to result from a compromise between these two opposite tendencies. In this respect, it would be very interesting to obtain experimental data on two remaining III-V compounds, namely, InAs and InSb. According to the proposed explanation, the general trend should be followed by I in InAs ( $R_{\text{host}} = 2.62$  Å), whereas InSb ( $R_{\text{host}} = 2.80$  Å) should constitute another exception like GaSb.

We should also like to point out that the quantitative significance of our results is largely due to the high sensitivity of the nuclear quadrupole interaction to small variations in the impurity position. As an example, a shift of 0.1 Å from the equilibrium position along the  $Z$  axis typically changes the calculated EFG by 30%. This fact illustrates the ability of nuclear hyperfine techniques to yield quantitative structural information, provided a meaningful structural model can be put forward.

The sensitiveness of the electric field gradient to variation in the position of the impurity atom also allows us to assess the confidence limit of the calculated values of  $R$ . The experimental values of the field gradients can conservatively be ascribed an uncertainty of 10%, taking into account the error ranges in the observed quadrupole coupling constants and the values of the quadrupole moments of <sup>125</sup>Te and <sup>129</sup>I used to derive the field gradients from the measured quadrupole coupling constants. From these considerations one arrives at a confidence limit of  $\pm 0.03$  Å in the calculated values of  $R$  listed in the third column of Table I.

## CONCLUSIONS

The present work on I impurities in III-V compounds provides confirmation of our previous conclusions<sup>1</sup> based on similar calculations for Te and I implanted in Si and Ge. It therefore reinforces our belief in the overall correctness of the structural model (Fig. 1) and the computational method used in our approach. It would be of interest to have Mössbauer data in systems other than the cubic fourfold-coordinated group-IV elemental and III-V compound semiconductors that we have considered in our recent investigations. In particular it would be useful to have data in the noncubic systems arsenic, and antimony, in which iodine and tellurium atoms would be in substitutional positions which are noncubic with different coordinations than in diamond-type lattices. One would then have an opportunity to test in other situations the conclusion that we have arrived at from analysis of Mössbauer data on the extensive set of group-IV elemental and III-V compound semiconductors regarding the strong tendency of the sixth- and seventh-group impurity atoms to relax to positions that restore their distances from neighboring host atoms to the normal covalent-bond distances. This conclusion is supported by recent experimental work on the locations<sup>4,5</sup> of adsorbed atoms on silicon and germanium.

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