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X-ray and Mössbauer spectroscopy studies of the silicon-antimony and bismuth-antimony alloys

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X-RAY AND MOSSBAUER SPECTROSCOPY STUDIES OF THE 
SILICON-ANTIMONY AND BISMUTH-ANTIMONY ALLOYS 

by 

JAMES RALPH TEAGUE, 1946- 

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Advisor 

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ABSTRACT

X-ray and Mossbauer spectroscopy were used to investigate two antimony alloys, Bi-Sb and Si-Sb, showing semiconductor-semimetallic transitions or vice versa, depending on the antimony concentration in the host lattice. Resistivity and density measurements were found to be helpful in the analysis of the results.

X-ray studies for dislocation-free antimony-doped silicon showed that the lattice constant of the alloy increased as the antimony concentration increased from $10^{18}$ to $10^{19}$ Sb atoms/cc. Rather good agreement was found between theoretical and experimental changes in lattice constant for dislocation-free silicon. Mossbauer studies showed that the isomer shift decreased linearly with increasing antimony concentration, which implies that the s-electron density at the antimony nucleus increases linearly with increasing antimony concentration. The relation between isomer shift and lattice constants is linear. Hence it is believed that the electrons in p-orbits are moving away from the nucleus as the antimony concentration increases, and there is an increase in the measurable s-electron density at the nucleus. The resistivity measurements showed that a semiconductor-semimetallic transition occurs between 2.8 and $4.5 \times 10^{18}$ Sb atoms/cc.

X-ray studies of the Bi-Sb alloys showed similar results as previously reported for most of the compositional range. The lattice constants were found to decrease linearly with
increasing antimony concentration, except for large antimony concentrations, where the $c_0$ lattice constant deviated from a linear relation. The Mossbauer studies showed that the isomer shift became more negative in the semiconducting region of the Bi-Sb phase diagram (5 to 45-55 atomic percent antimony) as contrasted to the region where the alloy is a semimetal (0 to 5 and 45-55 to 100 atomic percent antimony). The isomer shift change is believed to be due to the shielding by the conduction electrons of the s-valence electrons, as is indicated by the band structure of the Bi-Sb alloys. The linewidth, FWHM, was found to be a minimum in the semiconductor compositional range. This could be the result of the antimony atoms being in a more symmetrical environment in this semiconductor range of antimony concentrations as opposed to the semimetallic regions. However, a more plausible explanation is that the linewidth behavior is due to deformations of the lattice caused by the interaction between the conduction electrons and the s-electron core of the atoms. The semimetal regions are expected to have a stronger lattice deformation which could perhaps cause the measured linewidth to broaden (because of unresolved quadrupole splitting) as contrasted to the weaker lattice deformation and measured narrower linewidths of the semiconductor region of the Bi-Sb alloy system.
ACKNOWLEDGMENT

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This dissertation is dedicated to Jeffrey David Teague.
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I. INTRODUCTION

The object of this work was to use Mossbauer spectroscopy for the study of materials which change from semiconducting to metallic over a given compositional range. The Mossbauer isotope used was $\text{Sb}^{121}$, and two systems chosen for investigation were antimony-doped silicon and bismuth-antimony alloys.

According to current theories concerning moderately and heavily-doped semiconductors, the intrinsic energy bands in these materials are shifted by only a small amount but are otherwise unaffected. An impurity band is formed for moderate doping, however, and this band overlaps the intrinsic band for heavy doping. The techniques which have been used to investigate the band structures of lightly-doped semiconductor crystals either cannot be used at all or become considerably more difficult when the impurity concentration is high. Significant data have involved measurements of several transport and galvanomagnetic effects which have been explained in terms of the impurity band or density of states model.

It was suggested that the Mossbauer effect might be an appropriate probe for investigating the behavior of high concentrations of antimony atoms in the silicon lattice. A specific thickness ($\text{g/cm}^2$) of the given Mossbauer nucleus is required for resonant absorption to be detected (for antimony it is $7.6 \times 10^{18}$ atoms/cm$^2$). Studies of antimony-
doped silicon can be done for heavily-doped semiconductors of concentrations greater than about $10^{18}$ atoms/cc. In this concentration range the material undergoes a semiconductor-metallic transition. At first it was also hoped that the Mossbauer effect could be used to investigate the impurity surface states of antimony-doped silicon. However, it was later shown that the sensitivity needed for detection of surface states was not attainable.

Bismuth-antimony alloys exhibit the behavior of changing from semimetallic to semiconductor and back to semimetallic as the concentration of antimony is increased. The alloys of bismuth-antimony have a solid solubility range from 0-100 atomic percent antimony.

The object of these Mossbauer studies is to investigate the nuclear s-electron density behavior (measured by the isomer shift) in transitions from semiconductor to metallic and vice versa with varying antimony concentration. X-ray diffraction, resistivity and density measurements also proved to be invaluable aids in these studies.

The literature survey discusses the basics of the Mossbauer effect, moderately and heavily-doped semiconductors, bismuth-antimony alloys and Mossbauer studies in antimony compounds. The experimental section discusses the parameters obtained in Mossbauer effect measurements, apparatus needed to perform these studies and preparation of the materials. The results are presented and discussed with conclusions in the final section.
II. LITERATURE SURVEY

A. The Mossbauer Effect

In 1958, R. L. Mossbauer\(^1\),\(^2\) reported that the resonant absorption in the Ir\(^{191}\) 129 keV line increased as the temperature was decreased from 370°K to 90°K. This result was in complete contradiction to previous theoretical expectations. Mossbauer's explanation was based on the reported results of Lamb\(^3\) for neutron capture in crystals. He applied Lamb's theory to the problem of resonance absorption of gamma radiation, which showed that under the conditions chosen, there existed a high probability of nuclear transitions with no simultaneous change of the lattice state. In these transitions no recoil energy is transferred to the lattice in the form of internal energy.\(^4\)

Lipkin\(^5\), who clarified the phenomena involved in the Mossbauer effect, calculated the probability, \(P(n_i,n_i)\), for the lattice to remain in its initial state after the emission of the gamma ray, the latter, therefore, representing the full energy of the nuclear transition. He assumed that the gamma ray may interact with the crystal, a quantized vibrational system, with or without the production of a phonon and he found that the probability for the emission of a gamma ray without a change in the vibrational state of the lattice is large. For such a transition, the lattice as a whole absorbs the recoil momentum, and the recoil
energy loss is negligibly small. The probability of such a transfer is given by:

\[ P(n_f, n_i) = \left| \langle n_f | \exp(-i\vec{k} \cdot \vec{x}) | n_i \rangle \right|^2 \]  

(1)

where \( \vec{k} \) is the wave vector for the gamma ray, \( n_f \) and \( n_i \) are final and initial states, respectively, and \( \vec{x} \) is the displacement of the atom. This expression was evaluated to give the Lamb-Mossbauer fraction, \( f \), equivalent to the Debye-Waller factor, commonly known from coherent scattering of x-rays:

\[ f = e^{-2W} \]  

(2)

where \( e^{-2W} \) is the Debye-Waller factor,

\[ W = 2\pi^2 <x^2>/\lambda^2 \]  

(3)

and \( <x^2> \) is the mean square displacement of the radiating atom taken along the propagation direction of the photon with wavelength \( \lambda \). Using the Debye model\(^6-\)\(^9\) it was shown that

\[ W = (3E_R/k\Theta)[1/4 + (T/\Theta)^2 \int_0^{\Theta/T} (x/e^x-1)dx] \]  

(4)

which gives for \( T \ll \Theta \) a recoilless fraction,

\[ f = \exp\left[ -3E_R/2k\Theta \left\{ 1 + (2\pi^2/3)(T/\Theta)^2 \right\} \right] \]  

(5)

where \( k \) is Boltzmann's constant,

\( \Theta \) is the Debye temperature of the absorber,

\( T \) is the experimental temperature and

\( E_R \) is the free-atom recoil energy, and is equal to

\( (E_y^2/2M_c^2) \)
where \( E_\gamma \) is the emitted gamma ray energy, \( Mc^2 \) is the rest energy of the emitting nucleus. For low temperatures, \( f \) depends only on the ratio of the free-atom recoil energy to the Debye temperature. That is:

\[
f = \exp\left\{\frac{-3E_R}{2k\Theta}\right\} = \exp\left\{\frac{3E_\gamma}{4Mc^2k\Theta}\right\}
\]

(6)

This relation shows that the fraction of recoilless events increases as \( \Theta \) increases. In the Mossbauer experiment, the Debye-Waller factors of the source and the absorber jointly determine the magnitude of the observable effect.

The Debye model, which is the most useful and practical model, applies only to homogeneous lattices in which the Mossbauer active atom is usually an impurity. Lipkin\(^1\) and Visscher\(^1\) have shown that an impurity atom behaves as though the host lattice atoms have the same mass as the impurity, provided that the binding forces between the host lattice and the impurity and between the host lattice atoms themselves are the same. One can define an effective Debye temperature for the Mossbauer effect at zero temperature, \( \Theta_{ME} \), in terms of the Debye temperature of the host lattice, \( \Theta_H \), as:

\[
\Theta_{ME} = \Theta_H \left(\frac{M_{ME}}{M_H}\right)^{\frac{1}{2}}
\]

(7)

where \( M_{ME} \) is the atomic weight of the Mossbauer impurity, \( M_H \) is the atomic weight of a host atom.

Historically, the linewidth measurement of the resonance was one of the first accomplishments reported by Mossbauer\(^1\).
One can use the Heisensberg uncertainty principle to calculate the natural linewidth, which is¹⁰:

\[ \Gamma = \frac{\hbar}{\tau} \]  (8)

where \( \Gamma \) is the full linewidth at half maximum, \( \hbar \) is Planck's constant, \( h \), divided by \( 2\pi \), \( \tau \) is the mean life of the excited state of the nucleus.

The mean life, \( \tau \), is related to the half-life, \( \tau_{1/2} \), by the relation:

\[ \tau_{1/2} = \tau \ln 2 \]  (9)

Therefore, the linewidth is related to the half-life by the relation:

\[ \Gamma = 0.693 \frac{\hbar}{\tau_{1/2}} \]  (10)

The theoretical linewidths have been shown to be in good agreement with observed linewidths.

One defines the energy resolving power, \( E/\delta E \), by the ratio of the energy, \( E_\gamma \), of the nuclear transition to the natural linewidth, \( \Gamma \), of the resonant line:

\[ E/\delta E = E_\gamma / \Gamma \]  (11)

For a gamma ray of energy 100 keV and a nuclear lifetime of \( 10^{-7} \) sec, the energy of the gamma ray is resolved to within one part in \( 10^{13} \).

The cross section for the absorption of the gamma ray by the resonant isotope is given by the relation:¹⁰

\[ \sigma_o = \frac{\lambda^2}{2\pi} \frac{(1 + 2I_E)(1 + 2I_G)(1/1 + \alpha)}{(1 + I_E)(1 + I_G)} \]  (12)

where \( I_E \) and \( I_G \) are the nuclear spins of the excited state and the ground state, respectively, and, \( \alpha \) is the internal
conversion coefficient of the gamma transition.

The width of the level is given entirely by decay processes. In nuclei the two competing modes are gamma-ray emission and internal conversion. The relation between the two is given as:

\[ \Gamma_\gamma / \Gamma = 1 / (1 + \alpha) \]  

(13)

where \( \Gamma_\gamma \) is the linewidth for gamma ray absorption, and \( \Gamma \) is the total width of the absorption line. For resonance absorption, the total cross section (12), multiplied by the recoilless fraction, \( f \), and the Lorentzian line shaped function given by the Breit-Wigner formula, gives the effective cross section in a Mossbauer experiment: 6, 8

\[ \sigma_{\text{ME}}(E) = f \sigma_0 \left[ 1 + 4((E - E_\gamma)(\Gamma_\gamma + \Gamma_A))^2 \right]^{-1} \]  

(14)

where \( E_\gamma \) is the nuclear transition energy, and \( \Gamma_\gamma \) and \( \Gamma_A \) are the linewidths of the source and absorber respectively.

B. Heavily-Doped Semiconductors

A semiconductor is a material in which at thermal equilibrium some charge carriers are mobile. An ideal semiconductor would become an insulator at absolute zero. Characteristic semiconductor properties are usually a result of impurities, lattice defects and thermal agitation.

By means of doping, semiconductors can be made to exhibit extrinsic conductivity over a reasonably wide temperature range. Doping, in the lattice of a group IV semiconductor, may be achieved by substituting certain atoms of valence +3 or +5. These substitutional atoms are called acceptors and
donors, and the semiconductors are called p-type and n-type respectively, the majority carriers being holes and electrons, respectively.  

1. Resistivity and Mobility Measurements

Pearson et al. reported that the ionization energy decreased as the acceptor concentration increased in silicon and vanished when the impurity concentration exceeded $5 \times 10^{18}$/cc. The ionization energy of donors was reported to be lower than that of acceptors, which was attributed to the fact that the conduction electrons have a smaller effective mass than the holes. They found that for large impurity concentrations, the resistivity, $\rho$, and Hall coefficient, $R_H$, were independent of temperature, while the mobility passed through a maximum value at low temperatures which depended on impurity concentration. Later, Hung et al. reported similar results for highly-doped germanium samples. The activation energy was found to decrease as impurity concentration increased. Hung explained the previous results by assuming the formation of an impurity band at high concentrations, due to the interaction between the impurity states. This implied that an electron could move from one impurity state to another, causing conduction in the impurity band. Hung believed that impurity band conduction would be important at low temperatures but could be neglected at high temperatures.

In 1953, James et al. introduced the concept of overlapping of the impurity wave functions causing the formation
of an impurity band. The broadening of the impurity level into a band implies the delocalization of impurity states. Hung et.al.\textsuperscript{19} proposed a model representing the impurity states as narrow bands. Their theoretical calculations were in good agreement with their experimental results.

Morin, et.al.\textsuperscript{20} found similar results to those previously mentioned, using single crystals of silicon highly doped with arsenic and boron. They reported Fermi degeneracy as occurring at an impurity concentration in silicon between $10^{18}$ and $10^{19}$/cc. Yamunouchi, et.al.\textsuperscript{21} reported that phosphorus-doped silicon was clearly metallic in behavior at an impurity concentration of $4 \times 10^{18}$/cc. Swartz\textsuperscript{22} investigated heavily-doped n-type and p-type silicon samples and reported that they exhibited impurity conduction. He did Hall effect measurements between 15 and 300°K and resistivity measurements between 3 and 30°K on 15 heavily doped samples. He found that impurity conduction is of two types: non-band conduction for impurity concentrations less than $10^{18}$/cc, characterized by exponentially temperature-dependent resistivity, and impurity band conduction for concentrations of $10^{18}$/cc or greater, which have moderately temperature dependent resistivity. He further proposed that the activation energy for impurity conduction may increase with carrier ionization energy, and the impurity atoms having more tightly bound electrons with radically smaller wave functions will exhibit a higher resistivity for equal impurity concentrations. Chapman et.al.\textsuperscript{23} reported
a maximum in the $\rho$ vs. $T$ curve for heavily-doped n-type or p-type silicon at or near the degeneracy temperature, the effect being more pronounced in the least heavily-doped samples and gradually fading out with increasing impurity concentration. The maxima could be caused by a resonance in scattering by impurities. Sclar\textsuperscript{24} has done partial wave analyses of scattering by attractive impurity ions in moderately-doped (statistically nondegenerate) semiconductors. Also the studies by Domenicali\textsuperscript{25} of impurity scattering in metals have indicated the possibility of resonance in scattering. Another interesting feature from the results of Chapman et.al.\textsuperscript{23} was the difference in resistivity between n-type and p-type heavily-doped silicon at 4.2°K.

Fritzsche\textsuperscript{26} has reported observations of the anomalous behavior of highly-doped n-type and p-type single crystals of germanium. This was also previously reported by Hung and Gliessman\textsuperscript{16}. Furukawa\textsuperscript{27} observed a difference in mobility between arsenic- and antimony-doped germanium at room temperature. He proposed that this is related to the difference in ionization energy and concluded that the interaction between electrons and ionized impurities should be treated as a short range force, due to the fairly large screening effect. As a result the nature of the impurity core directly influences the impurity scattering.

Debye et.al.\textsuperscript{28} found that the Hall mobility, $\mu_H$, varies little with temperature for n-type and p-type silicon at impurity concentrations of $10^{19}$/cc, and for n-type and p-type germanium at concentrations of $10^{18}$/cc. This
agrees quite well with Conwell's values for the overlap of the impurity wave functions and impurity-conduction band overlap given in Table I.

2. ESR Studies

Fletcher et al. reported ESR results for n-type silicon which showed that the hyperfine splitting disappeared when donor concentrations exceeded $10^{18}$/cc. Observation of the hyperfine lines requires that the electrons be fairly well localized about the donors and not moving too rapidly from one donor to another. One therefore expects the highest concentration at which hyperfine splitting is observed to be approximately equal to the concentration at which impurity wave functions overlap. Hedgcock et al. observed only one ESR absorption line at liquid helium temperature for a phosphorus concentration of $1.38 \times 10^{19}$/cc in silicon. This was explained as due solely to free charge carriers. Kodera reported ESR measurements as indicating impurity band conduction occurring at phosphorus concentrations of $3.9 \times 10^{18}$/cc in silicon. His results confirmed that the ESR measurements are related to electrical conductivity. He suggested that impurity band electrons are trapped in the neighborhood of a few impurity atoms and cannot move as freely as those in the conduction band. Kodera reported that only single absorption lines occurred in his ESR spectra of Si samples having phosphorus concentrations of $1.52 \times 10^{18}$/cc and greater. The linewidth was minimal at a phosphorus concentration of $3 \times 10^{18}$/cc. He
TABLE I

ESTIMATED IMPURITY CONCENTRATIONS FOR "FORMATION OF AN IMPURITY BAND", AND FOR ITS OVERLAP WITH THE CONDUCTION BAND*

<table>
<thead>
<tr>
<th>Semiconductor Type</th>
<th>Hydrogenic Approx. ($m^*/m_0$)</th>
<th>$N_I$ for Overlap (cm$^{-3}$)</th>
<th>$N_I$ for &quot;Band Formation&quot; (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Ge</td>
<td>0.13</td>
<td>$&gt;9 \times 10^{17}$</td>
<td>$&gt;1 \times 10^{16}$</td>
</tr>
<tr>
<td>p-Ge</td>
<td>0.2</td>
<td>$&lt;3 \times 10^{18}$</td>
<td>$&lt;5 \times 10^{16}$</td>
</tr>
<tr>
<td>n-Si</td>
<td>0.27</td>
<td>$&gt;2 \times 10^{19}$</td>
<td>$&gt;1 \times 10^{18}$</td>
</tr>
<tr>
<td>p-Si</td>
<td>0.5</td>
<td>$&lt;1 \times 10^{20}$</td>
<td>$&lt;1 \times 10^{18}$</td>
</tr>
</tbody>
</table>

* From Conwell$^{29}$
proposed a model in which the observed central line originates from the free electron in an impurity cluster, and in which there are two types of electron motion: rapid motion in a cluster, and slow transitions between the clusters. The size and quantity of clusters would increase as the donor concentration increased, resulting in a metallic band at higher concentrations. Morigaki et.al. also considered the origin of the single resonance line observed in ESR spectra in terms of the cluster-like state of donor impurities in the high concentration region.

3. Optical Studies

Newmann reported from infrared photoabsorption experiments on p-type silicon that the energy spectrum of the excited states of the acceptor atoms broadened and merged with the valence band as the impurity concentration increased.

4. Lattice Parameters

Pearson et.al. have done lattice parameter measurements for silicon samples doped with boron and phosphorus at concentrations between 0.0 and 1.0 weight percent. Their results showed that both impurities cause the silicon lattice to contract and that boron has the greater effect. Since the atomic radius of boron is less than that of phosphorus, (both are less than that of silicon), Vegard's law predicts this behavior if the impurity enters the lattice substitutionally. Horn has confirmed the results of Pearson et.al., that boron enters the silicon lattice substitutionally up to concentrations of 0.3 atomic percent. The lattice parameter measurements made by Horn were
done using single crystals. His results showed a larger lattice contraction as compared with the measurements of Bardeen and Pearson\textsuperscript{15}. Bublik et.al.\textsuperscript{41} have reported precision lattice constant measurements of heavily doped germanium and silicon. Their results are shown in Table II, from which one can see a rather close correspondence between the change in lattice constant for some impurities, as compared to the calculated change in lattice constant using the tetrahedral radii values given in Table III. The discrepancies were proposed to be due to vacant lattice points, migration to intermediate lattice points in the form of un-ionized atoms, complexes at the lattice points or inhomogeneity in concentration. Annealing the antimony and arsenic doped germanium samples at 350°C resulted in a decrease in the concentration of carriers. Barsukov et.al.\textsuperscript{43} have reported that the lattice parameter of arsenic-doped germanium increased when the arsenic concentration reached $10^{19}$/cc. This was attributed to the formation of precipitates during decomposition of the substitutional solid solution.

Milvidskii et.al.\textsuperscript{44} have found that dislocations disappear in semiconductors at donor concentrations of approximately $10^{17}$/cc. On approaching the solubility limit however, the dislocations reappeared. It was believed that large amounts of antimony in the crystal would generate additional vacancies, due to their large tetrahedral radii. Milvidskii et.al.\textsuperscript{45} reported that, at large donor concentr-
### TABLE II

**CALCULATED AND MEASURED VALUES OF LATTICE CONSTANTS OF SILICON AND GERMANIUM DOPED WITH VARIOUS DOPANTS***

<table>
<thead>
<tr>
<th>Material</th>
<th>(nx10^{19}/\text{cm}^3)</th>
<th>(a, \text{Å})**</th>
<th>(a_{\text{exp}}(10^{-5}\text{Å}))</th>
<th>(a_{\text{calc}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-</td>
<td>5.43070</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si-B</td>
<td>0.5</td>
<td>5.43049</td>
<td>-21</td>
<td>-17</td>
</tr>
<tr>
<td>Si-Sb</td>
<td>1</td>
<td>5.43085</td>
<td>+15</td>
<td>+16</td>
</tr>
<tr>
<td>Si-P</td>
<td>0.8</td>
<td>5.43049</td>
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<td>-6</td>
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<td>Si-P</td>
<td>3.4</td>
<td>5.43033</td>
<td>-37</td>
<td>-20</td>
</tr>
<tr>
<td>Si-As</td>
<td>3.2</td>
<td>5.43063</td>
<td>-7</td>
<td>0</td>
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<td>Si-As</td>
<td>4</td>
<td>5.43021</td>
<td>-49</td>
<td>0</td>
</tr>
<tr>
<td>Ge</td>
<td>-</td>
<td>5.65757</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ge-Sb</td>
<td>0.67</td>
<td>5.65796</td>
<td>+41</td>
<td>0</td>
</tr>
<tr>
<td>Ge-Sb***</td>
<td>0.26</td>
<td>5.65796</td>
<td>0</td>
<td>+3</td>
</tr>
<tr>
<td>Ge-As</td>
<td>4.8</td>
<td>5.65757</td>
<td>+8</td>
<td>-28</td>
</tr>
<tr>
<td>Ge-As***</td>
<td>3.7</td>
<td>5.65790</td>
<td>+27</td>
<td>-21</td>
</tr>
</tbody>
</table>

*From Bublik et.al.*

**Without correction for refraction

***Annealed at 350°C for 20 hours
### TABLE III

VALUES OF TETRAHEDRAL RADII OF ATOMS USED TO OBTAIN THE CALCULATED LATTICE PERIODS*

<table>
<thead>
<tr>
<th>Element</th>
<th>Coordination Number 12</th>
<th>Coordination Number 4</th>
<th>$r_{\text{actual}}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{\AA}$</td>
<td>$\text{\AA}$</td>
<td>$\text{\AA}$</td>
</tr>
<tr>
<td>Si</td>
<td>1.34</td>
<td>1.176</td>
<td>1.176</td>
</tr>
<tr>
<td>Ge</td>
<td>1.39</td>
<td>1.225</td>
<td>1.225</td>
</tr>
<tr>
<td>Sb</td>
<td>1.61</td>
<td>1.42</td>
<td>1.35</td>
</tr>
<tr>
<td>As</td>
<td>1.48</td>
<td>1.30</td>
<td>1.17</td>
</tr>
<tr>
<td>P</td>
<td>1.30</td>
<td>1.145</td>
<td>1.10</td>
</tr>
<tr>
<td>B</td>
<td>0.91</td>
<td>0.80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

*From Bublik et.al.\textsuperscript{41}

**$r_{\text{actual}}$ is the actual tetrahedral covalent radius according to Palatnik et.al.\textsuperscript{41}
rations, part of the impurity does not display donor properties. It has also been reported that formation of complexes, precipitation of a second phase, formation of impurity atmospheres at dislocations, and impurity substructures have been observed. Kodera found that antimony-doped silicon becomes polycrystalline when the antimony concentration exceeds \(2.9 \times 10^{19}/\text{cc}\). Precipitates observed in silicon heavily-doped with antimony were identified as antimony.

5. Debye Temperature

Beilin et al. have found an expression for the zero Debye temperature (Debye temperature at 0°K) for various heavily doped semiconductors:

\[ \Theta_D^0 = 1146.8(s\rho/\text{Al})^{1/3} \]  

(15)

where \(s\) is the number of atoms of different kind in one unit cell,

\(\rho\) is the density of the crystal,

\(A\) is the atomic weight,

\(I\) is the sum of the reciprocals of the phase velocities cubed of elastic waves over all directions in the crystal.

6. Theoretical Models

Mott has shown for donor and acceptor impurities in semiconductors that as the impurity concentration is increased, free carriers (metallic behavior) will not appear until a critical impurity concentration has been reached, at which screening by the electrons of nearby atoms prevents binding by electron-hole pairs. That is, the
activation energy for carrier production falls to zero, and
a metallic behavior system is formed. He expressed the
Thomas-Fermi screening length, $\lambda$, as:

$$\lambda = \left(\frac{\hbar}{2e}\right)\left(m^*N^{1/3}/\varepsilon\right)^{-1/2}$$  \hspace{1cm} (16)

where $m^*$ is the effective mass of the electron,
$e$ is the electric charge,
$\hbar$ is Planck's constant divided by $2\pi$
$\varepsilon$ is the dielectric constant of the material,
$N$ is the electron density.

Setting the expression for $\lambda$ equal to the usual
expression for $a^*$ (first Bohr orbit for the impurity elec­
tron) gives:

$$\left(\frac{\hbar}{2e}\right)\left(m^*N^{1/3}/e\right)^{-1/2} = \left(\frac{\varepsilon h^2}{me^2}\right) = a^*. \hspace{1cm} (17)$$

Hence $N^{-1/3} \approx 4a^*$. Mott then developed an approximation for
the critical concentration for semiconductor-to-metallic
transition, $n_c$:

$$n_c = (0.25/a^*)^3. \hspace{1cm} (18)$$

Baltensperger\textsuperscript{54} has shown that as the distance between
impurities, $r_s$, expressed as

$$r_s = (3/4\pi N)^{1/3} \hspace{1cm} (19)$$
decreased, the wave functions of successively lower excited
states (satisfying the effective mass equation from the
simple model of the band structure derived by Kohn et.al.\textsuperscript{55})
overlap and form bands. The impurity band appears when the
separation between impurities is

$$r_s = 5\varepsilon a_H(m_o/m^*) = 5a^*. \hspace{1cm} (20)$$
As the impurity concentration increases still further, separation between the impurity and intrinsic bands vanish at

\[
\epsilon_s \approx \epsilon a_H (m_0/m^*) = a^* \tag{21}
\]

where \(a_H\) is the Bohr orbit for the hydrogen atom.

Matsubara et al. \(^{56}\) did a theoretical calculation for the donor concentration at which the Fermi level should pass into the conduction band of the host lattice, which gave the concentration, \(n_{cb}\), as:

\[
ncb = (1/4\pi)a^*^{-3} \tag{22}
\]

where \(a^*=(e^2/2\epsilon) E_0\) and \(E_0\) is the experimental ionization energy. The Mott critical concentration, \(n_c\), is then related to the Fermi degeneracy concentration, \(n_{cb}\), by:

\[
n_{cb} = (16/\pi)n_c \tag{23}
\]

Alexander et al. \(^{57}\) discussed: (1) the donor concentration above the critical concentration, \(n_c\), where the electrons are delocalized, (2) the donor concentration where the Fermi level of the electron system passes into the conduction band of the host crystal, \(n_{cb}\), and (3) the donor concentration where the electrons exist in a continuum of energy states (impurity band), \(n_{cb} > n_d > n_c\). They reported for phosphorus-doped silicon that \(n_c\) was equal to \(3 \times 10^{18}/\text{cc}\) and \(n_{cb}\) exceeded \(2 \times 10^{19}/\text{cc}\). Thus an impurity band would be found in the donor region: \(3 \times 10^{18}/\text{cc} < n_d < 2 \times 10^{19}/\text{cc}\). A summary of the characteristic critical impurity concentrations, \(n_c\) and \(n_{cb}\), in group IV semiconductors is given in
Holcomb et al.\textsuperscript{58} have reported the results of a Monte Carlo percolation calculation in highly-doped semiconductors, considering the impurities as located at random in the lattice sites. The results of their calculations for various cluster sizes for different donor concentrations, show that larger clusters are more probable for moderately-doped materials, (5x10\textsuperscript{17} to 3x10\textsuperscript{18} impurity atoms/cc). Above these concentrations, clusters of various sizes are equally probable.

At low impurity concentrations the hydrogen-like impurities are effectively isolated from each other, so overlapping of the electron wave functions of adjacent impurities is negligible. However, these isolated shallow donors display discrete donor levels in the forbidden band.\textsuperscript{59,60}

With increasing donor impurity concentration, the hydrogen-like wave functions of adjacent donor excess electrons begin to overlap, causing the discrete donor energy level to broaden into an impurity band in the gap between the intrinsic valence and conduction bands.\textsuperscript{61,62} The electron energy level broadens symmetrically above and below its original position, causing the values of $E_d$ and $E_a$ to decrease as shown in Figures 1 and 2.\textsuperscript{63} The impurity concentration at which the impurity band formation becomes noticeable depends on the nature of the impurity, and can be calculated only within the framework of some specific model. Bonch-Bruyevich\textsuperscript{64} showed an energy spectrum indicating an impurity band for what he considered a moderately-doped
<table>
<thead>
<tr>
<th>Material</th>
<th>Empirical Value of x</th>
<th>((n_c)_{\text{exp}}) (all given in cm(^{-3}))</th>
<th>((n_{cb})_{\text{exp}})</th>
<th>((n_c)_{\text{MT}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-P</td>
<td>0.20</td>
<td>(3 \times 10^{18})</td>
<td>(2 \times 10^{19})</td>
<td>(3.2 \times 10^{19})</td>
</tr>
<tr>
<td>Si-As</td>
<td></td>
<td>(5 \times 10^{18})</td>
<td></td>
<td>(4.0 \times 10^{19})</td>
</tr>
<tr>
<td>Ge-Sb</td>
<td>0.21</td>
<td>(0.95 \times 10^{17})</td>
<td>(1 \times 10^{18})</td>
<td>(7.2 \times 10^{17})</td>
</tr>
<tr>
<td>Ge-As</td>
<td>0.25</td>
<td>(3.5 \times 10^{17})</td>
<td></td>
<td>(1.7 \times 10^{18})</td>
</tr>
<tr>
<td>Ge-P</td>
<td>0.23</td>
<td>(2.5 \times 10^{17})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ x_{\text{mott}} = 0.25 \quad n_c = (x/a^*)^3 \]

*From Alexander et al.\(^{57}\)
Figure 1. Dependence of the ionization energies of donors and acceptors in silicon on their concentrations

(From Fistul$^{63}$)
Figure 2. Dependence of the ionization energy of donors in germanium on their concentration

(From Fistul\textsuperscript{63})
semiconductor (Figure 3).

The width of the impurity band increases as the dopant concentration increases, due to increasing overlap of the wave functions. As the donor concentration increases, the attraction of donor electrons to donor atoms decreases because of the increased screening by the increased number of free charge carriers, causing the impurity energy band to broaden and eventually overlap with the conduction band. The merging of the impurity and intrinsic bands occurs when the screening radius, \( r_0 \), becomes equal to the first Bohr orbit for a given impurity in the crystal, \( a^* = \frac{\epsilon h^2}{me^2} \).

The earliest concept of a heavily-doped semiconductor assumed that the impurity band would consist of an approximately Gaussian distribution of states centered at the original energy level, so that the conduction band would resemble the band of the pure crystalline lattice, except for the hump in the density of states extending deep into the energy gap. Brody modified Baltensperger's theory to allow for randomly distributed impurities throughout the host crystal lattice. In Figure 4, his results are compared to Baltensperger's model, which assumed a regular arrangement of impurities.

Bonch-Bruevich has shown that as a result of the interaction of charge carriers with many impurity atoms located close to one another, \( na^*^3 \gg 1 \), the intrinsic bands are shifted downward in energy, but are not changed in shape.
Figure 3a. Energy spectrum of lightly-doped semiconductor assuming that each impurity give rise to only one discrete level.
(From Bonch-Bruyevich)

Figure 3b. Energy spectrum for moderately-doped semiconductor showing the impurity band.

Figure 3c. Energy spectrum for heavily-doped semiconductors showing the merging of the impurity band with the conduction band.
Figure 4. Energy dependence of the density of states for overlapping impurity and conduction bands. (1) Baltensperger model and (2) Brody's Modified Baltensperger Model, both calculated on the assumption that $N=2 \times 10^{19}$ impurity atoms/cc.

(From Fistul$^6$)
for heavily-doped semiconductors. Pankove\textsuperscript{62} has observed that high concentrations of arsenic reduce the energy gap in germanium by an amount of the order of the penetration of the Fermi level into the conduction band. The expression for the density of states is given by:\textsuperscript{68,70}

\[ \rho(E) \approx \exp\left[ -\left( \frac{|E|}{E_0}\right) \ln\left( \frac{|E|}{E_0}\right) \right] \quad (24) \]

where $E$ is the energy measured downward into the forbidden band, and

\[ E_0 \approx \frac{(2me^4/e^2\hbar^2)(na^3)^{1/6}}{} \quad (25) \]

Hence the density of states decreases very rapidly in the forbidden gap and is appreciable only near the bottom of the conduction band, for donor impurities. A density of states tail is formed in either n-type or p-type, heavily-doped semiconductors. These states in the forbidden band represent impurity bands, or more precisely, impurity bands modified by the screening of the free charge carriers.\textsuperscript{64}

These two theoretical models can be considered complementary. The first is an impurity band model for moderately-doped semiconductors, where impurity banding has just begun to occur for high concentration, and the second is the density of states tail model for extremely heavily-doped materials.\textsuperscript{61}

C. Bismuth-Antimony Alloys

Bismuth and antimony crystallize with the same lattice structure, as do all of the alloys composed of bismuth and antimony,\textsuperscript{71} which is hexagonal.
1. Electrical Properties

Smith\textsuperscript{72} observed that no compound of bismuth or antimony is formed in the Bi-Sb alloys, but that each property studied (resistivity, Hall coefficient, thermoelectric force and Nernst effect) showed a well defined maximum or minimum at an alloy concentration of 10 atomic percent antimony. For an alloy containing 70 atomic percent antimony, the Hall coefficient, $R_H$, is nearly zero, while, for concentrations above and below this, it increases toward that of antimony and bismuth respectively.

Utilizing the de Haas-van Alphen\textsuperscript{73} results on Bi-Sb alloys, Heine\textsuperscript{74} predicted a semimetal to semiconductor transition at about 4 atomic percent antimony, and typical semiconductor properties for higher concentrations.

Tanuma\textsuperscript{75} found anomalous electrical properties which could be explained by the assumption that the Bi-Sb alloys of intermediate composition become intrinsic semiconductors. He reported that alloys containing more than 4 atomic percent antimony appear to be semiconductors, and suggested that the semiconduction range of the alloys extends from 4 to about 50 atomic percent antimony. His results showed intermediate compositions having high resistivities, which peaks at around 10-20 atomic percent antimony. This is probably due to the depletion of carriers in the alloys. Jain\textsuperscript{76} confirmed Tanuma's conclusion, but reported that, below 100°K, the semiconducting region extends from 5 to 40 atomic percent antimony. He found that, below 5 atomic percent and above
40 atomic percent antimony, the alloys are semimetallic. Figure 5 shows the overlap energy and the energy gap plotted against atomic percentage of antimony. At approximately 12 atomic percent antimony, the energy gap is maximum. At 4.2°K a pronounced maximum in the measured resistivity, plotted against atomic percent antimony, occurs at the same concentration at which the maximum activation energy is reached. The results were explained in terms of the effect of antimony displacing heavy mass bands relative to light mass bands, a model proposed by Blount and Cohen\textsuperscript{76}, (see Figure 6).

Smith and Wolf\textsuperscript{77} reported variations of resistivity with temperature for single crystals of Bi-Sb alloys similar to Jain's\textsuperscript{76} data. They claimed that for Bi\textsubscript{95}Sb\textsubscript{5} that the Fermi energy with respect to the conduction band edge is practically zero, but in the Bi\textsubscript{88}Sb\textsubscript{12} alloy the Fermi energy level lies within the energy gap. Smith\textsuperscript{78} also found that the electron effective masses are smaller by about a factor of two, and the hole masses are essentially unchanged, for the Bi\textsubscript{95}Sb\textsubscript{5} alloy, as compared to pure bismuth. The energy gap was assumed to be the same for both materials but the Fermi energy was 7meV for Bi\textsubscript{95}Sb\textsubscript{5} as compared to 25meV for pure bismuth.

Brown and Silverman\textsuperscript{79, 80} reported the energy gap for single crystal Bi\textsubscript{85}Sb\textsubscript{15} alloy as 24±3meV, a significantly higher value than the previously measured maximum gap of 14meV\textsuperscript{76} for the alloy system. They have concluded that the
Figure 5. Activation energy $E_g$ vs. atomic percent of antimony

(From Jain'76)
Figure 6. E vs. k diagrams for bismuth and bismuth-antimony alloys. \( C_L \) and \( V_L \) represent light mass bands, each having six extrema in k-space. \( V_H \) is the heavy mass band having two extrema.

(Model proposed by Blount and Cohen\textsuperscript{76})
semiconductor model proposed by Jain\textsuperscript{76} for Bi-Sb alloys containing between approximately 10 and 30 atomic percent antimony may be qualitatively correct. Aono\textsuperscript{81} has reported that the energy gap changed from $-3 \times 10^{-3}$ eV to $2 \times 10^{-2}$ eV between 3 and 12 atomic percent antimony. He found that at 6 atomic percent antimony there was a semimetal to semiconductor transition.

Ivanov and Popov\textsuperscript{82} show that a forbidden zone is formed at temperatures below 173°C in single crystal Bi-Sb alloys containing more than 5 atomic percent antimony. The forbidden gap attained its maximum value when the concentration of antimony was 7 to 8 atomic percent. Ivanov and Popov\textsuperscript{83} also suggested that the Hall coefficient measured in polycrystalline samples was much smaller than that found for single crystals.

Tanuma\textsuperscript{84} has shown that the thermoelectric power behaves as in intrinsic semiconductors for antimony concentrations of 4 to 16 atomic percent. The absolute magnitude of the thermoelectric power is large in the semiconductor range of antimony concentration. The sign is reversed at about 70-80 atomic percent antimony, which agrees with the sign reversal of the Hall coefficient at 73 atomic percent antimony.\textsuperscript{84} The carrier concentration\textsuperscript{85} is found to be a minimum at around 15 atomic percent antimony.

Kao et al.\textsuperscript{86} observed that in dilute Bi-Sb alloys the measured electron cyclotron resonant mass, $m^*$, decreased monotonically with increasing antimony concentration. Theore-
tical and experimental studies\textsuperscript{87-89} have shown that the conduction band in bismuth is nonparabolic. According to this model, the cyclotron masses should change when the Fermi energy is decreased by alloying with antimony.

Brandt and Shchekochikhina\textsuperscript{90} found that the Fermi energy decreased with increasing antimony concentration, owing to the decreased overlap of the conduction and valence bands. Kao et al.\textsuperscript{86} report that, at an antimony concentration of approximately 4.3 atomic percent, the overlapping of the conduction and valence bands disappeared. Tichovolisky and Mavroides\textsuperscript{91} found in magnetoreflection studies that the energy gap decreased with increasing antimony concentration and became zero at a concentration of approximately 4 atomic percent antimony. The experimental data suggested that the semimetal to semiconductor transition occurs between 5 to 8 atomic percent antimony.

Grabov et al.\textsuperscript{92} reported resistivity studies at 77°K using high-quality single crystals of Bi-Sb alloys, which indicated that the semiconductor region lies between 7 and 20 atomic percent antimony. The range of antimony concentrations displaying semiconductor characteristics narrowed with increasing temperature, and vanished at approximately 180-190°K. Brandt\textsuperscript{90} found that the resistivity was similar in behavior to a semiconductor down to very low temperatures, if the antimony concentration exceeded 8 atomic percent.

Brandt and Ponomarev\textsuperscript{93} showed that single crystals of Bi-Sb alloys, containing less than 5 atomic percent antimony,
change under pressure from the semimetal to semiconductor phase; the energy gap of the material increased with increasing pressure. Brandt et al.\textsuperscript{94} reported that when pressure was applied to Bi-Sb alloys of antimony concentrations greater than 5 atomic percent, the alloy was transformed into a new state, which they called "quasimetallic", characterized by anomalously small values of the energy gap and of the effective carrier masses.

2. Lattice Constants

Ehret and Ahramson\textsuperscript{95} and Bowen and Morris-Jones\textsuperscript{96} concluded from their lattice constant measurements that Vegard's law is obeyed by the Bi-Sb alloys. However, Jain\textsuperscript{76} observed deviations at low concentrations of antimony from Vegard's law. The deviations were most pronounced in the concentration range in which the alloys change from semimetallic to semiconducting behavior. Cucka and Barrett\textsuperscript{97} reported that the lattice constants for the Bi-Sb alloys varied linearly with antimony concentration in the range from 0 to 30 atomic percent. The abrupt deviations of the lattice constants below 8 atomic percent reported by Jain\textsuperscript{76} were not found by Cucka and Barrett\textsuperscript{97}. The atomic positional parameter, \( z \), in the Bi-Sb alloys remained approximately constant to 12 atomic percent antimony, and then increased as the antimony content increased.

Brandt and Shchekochikhina\textsuperscript{90} assumed that the changes in the energy spectrum of bismuth due to antimony impurities, in the region of small concentrations (0-1 weight percent
antimony), were connected in a fundamental way with changes in the lattice constants of bismuth.

3. Theory

The band structure of Bi-Sb alloys was first considered by Mase.\textsuperscript{98,99} Noting that the lattice constants of bismuth and antimony are almost equal, he suggested that the difference in the band structure of these two semimetals should arise primarily from the difference in the spin-orbit energy, $\lambda_{\text{S-O}}$, and on this basis he predicted a semimetal-semiconductor transition. He restricted the semiconducting region to a narrow range of antimony concentrations and stated that the energy gap should be very small. He claimed that further alloying of antimony in the Bi-Sb alloy system would result again in a semimetallic state, as antimony is a semimetal.

Hall and Koenig\textsuperscript{100} considered the nearly free electron model of Jones\textsuperscript{101,102} and Harrison\textsuperscript{103}, which suggested that a linear variation of the spatial potential upon alloying bismuth with antimony is sufficient to account for the changes (semimetallic to semiconductor transition of the alloy system) observed in the transport properties of the alloy system.

Hall and Koenig\textsuperscript{100} and Cohen et.al.\textsuperscript{104} suggested that the energy gap in bismuth and its alloys may be associated with the displacement of the sublattices, while the overlap of the hole and electron bands may be associated with the rhombohedral distortion and spin-orbit interaction.
Brandt et.al.\textsuperscript{105} calculated the Fermi energy and electron concentration using a nonquadratic dispersion law.\textsuperscript{106} They reported, from the results of their data and theoretical considerations, that the overlap between the conduction and valence bands decreases in proportion to the antimony concentration in the Bi-Sb alloys. At an antimony concentration of 5 atomic percent the overlap disappeared.

D. The Mossbauer Effect in Antimony Compounds

A brief history of the experiments on the Mossbauer effect in Sb\textsuperscript{121} compounds will be given before examining the specific parameters that can be measured. In fact, very few Mossbauer studies have been done on the Sb\textsuperscript{121} nuclei as compared to Fe\textsuperscript{57} and Sn\textsuperscript{119}.

Nelson et.al.\textsuperscript{107} reported in 1950 that the long-lived isomer of Sn\textsuperscript{121} decays by beta emission to a low-lying excited state, approximately 10 keV, of Sb\textsuperscript{121}. Ruby\textsuperscript{108} indicated that he, as well as others, made attempts to detect this 10 keV gamma ray but failed because he used a detector that would not detect radiation of higher energy. Auble et.al.\textsuperscript{109} and Chu et.al.\textsuperscript{110} reported in 1964 the decay of Te\textsuperscript{121} isomers to Sb\textsuperscript{121} lies at 37 to 38 keV. The half life of the excited state (37.2 keV level) in Sb\textsuperscript{121} was found to be 3.5 nsec.

After these findings, Snyder and Beard\textsuperscript{111} prepared a source for the 37.2 keV gamma rays of Sb\textsuperscript{121} and observed a resonance absorption effect in antimony and antimony oxide absorbers. Ruby\textsuperscript{108} and Ruby et.al.\textsuperscript{112,113} then reported
observing the resonance absorption lines in various antimony compounds. They found that the Mossbauer absorption was readily measurable and large compared to that in Sn\textsuperscript{119}, but with poorer spectral resolution. They also realized that several pairs of compounds which contain tin and antimony are isoelectronic with each other. The interpretations given in the highly investigated Sn\textsuperscript{119} nucleus could then be readily extended to Sb\textsuperscript{121}.

The first excited state of Sb\textsuperscript{121} has a nuclear spin, I, of 7/2, a half life of 3.5 nsec, and emits a gamma ray of energy 37.2 keV in decaying to the ground state (I=5/2). Ruby\textsuperscript{108} reported that the internal conversion coefficient, α, is equal to 9.3±0.4. This was in agreement with the conclusion of Brukhnov et.al.\textsuperscript{114} that α is approximately ten.

Chemists have used the Mossbauer effect of Sb\textsuperscript{121} in studying the ionic characteristics of antimony compounds. Kothekar et.al.\textsuperscript{115} and Bowen et.al.\textsuperscript{116} have reported Mossbauer investigations in trivalent antimony halides. They showed that as the electronegativity of the ligand increased, which implied that the ionic character of the bond increased, electrons were withdrawn from antimony, resulting in a decrease in the s-electron density at the antimony nucleus. This change in s-electron density at the antimony nucleus was detected by Mossbauer spectroscopy and confirmed the changing ionic character of the compound. Brukhanov et.al.\textsuperscript{114} reported a linear relationship between the s-electron density at the antimony nucleus and the electronegativity of the
antimony-ligand, for six-coordination antimony compounds. Long et.al.\textsuperscript{117} have investigated organoantimony compounds (the Ph\textsubscript{4}SbX and Ph\textsubscript{3}SbX\textsubscript{2}, triphenylantimony dihalides, series where Ph is phenyl and X is a negative ion such as F, Br, N\textsubscript{O}\textsubscript{3}, etc.) and found that the results were consistent with the known variations in electronegativity of the X groups. They also showed that the Mossbauer parameters were determined much more precisely at lower temperatures (4.2\degree K as compared to 78\degree K) due to the distinct increase in the resonant absorption, which was a 26-45\% effect at 4.2\degree K as compared to 1-3\% at 78\degree K. Gakasyan and Shpinel\textsuperscript{118} reported Mossbauer studies in antimony-organic compounds of types Ar\textsubscript{3}SbX\textsubscript{2}, Ar\textsubscript{4}SbX and Ar\textsubscript{3}Sb (where Ar=C\textsubscript{6}H\textsubscript{5},CH\textsubscript{3}OC\textsubscript{6}H\textsubscript{4}, ClC\textsubscript{6}H\textsubscript{4} and X=F, Cl, Br, BF\textsubscript{4}), the results of which were interpreted using hybrid orbital concepts. The resonant absorption spectra were reported to be broad single lines with appreciable asymmetry.

Long et.al.\textsuperscript{119} have shown in their studies of antimony oxides that the Mossbauer spectrum for α-Sb\textsubscript{2}O\textsubscript{4} indicated that antimony does not exist in the oxidation state Sb(IV) but in two oxidation states, Sb(III) and Sb(V), with equal concentrations. Their results confirmed the conclusion given by Skapski and Rogers\textsuperscript{120}, who did x-ray analysis of this compound and found no indication of an Sb(IV) oxidation state. Birchall and Della Valle\textsuperscript{121} investigated some antimony chalcogenides and oxides and reported that Mossbauer investigations showed no evidence for the existence of the
compound $\text{Sb}_2\text{S}_5$.

Dokuzoguz et al.\textsuperscript{122} reported Mossbauer investigations of Sb$^{121}$ in the III-V semiconductors (InSb, GaSb and AlSb). The results indicated that electron transfer occurs from group V to group III atoms to a greater extent in AlSb than in GaSb, with InSb having the least transfer. However, Pruitt et al.\textsuperscript{123}, in studies of the same compounds (InSb, GaSb and AlSb), noted that the decrease in s-electron density could be due to either a decrease in the population of s-electrons or an increase in p-electron shielding, or perhaps both effects occurring simultaneously. They showed by molecular orbital calculations that the s-electron population was relatively constant, as has been reported for alkali iodides\textsuperscript{124} and tin compounds\textsuperscript{125}. It was concluded that in the group-III antimonides the number of p-electrons increased from InSb to GaSb to AlSb, creating an observable decrease in the s-electron density at the antimony nucleus due to reduced shielding by p-electrons. AlSb was found to be more ionic than InSb, this order of ionicity being in agreement with that calculated from electronegativity differences. A monotonic variation with composition of the s-electron density at the antimony nucleus was found in the ternary alloys (InSb-GaSb), which is similar to the experimentally observed linear variation of lattice constant with composition.\textsuperscript{126}

Dokuzoguz et al.\textsuperscript{127} found that the s-electron density at the antimony nucleus decreases as the atomic percentage
of nickel increases in a series of compositions of the Ni-Ge-Sb and Ni-Sn-Sb ternaries. The s-electron density at the tin nucleus showed similar behavior, decreasing in the Ni-Sn-Sb ternary system as the nickel content increased. The changes in s-electron density were consistent with partial transfer of valence electrons from the non-transition metals to nickel. Similar behavior was reported by Ibraimov and Kuz'min\textsuperscript{128} and Harris and Cordey-Hayes\textsuperscript{129} for Pd-Sn alloys, and by Kanekar et.al.\textsuperscript{130} for alloys for Pt-Sn, for which the results were interpreted in terms of electron transfer.

Montgomery and Ruby\textsuperscript{131} showed that, in Pd-Sb alloys, the s-electron density at the antimony nucleus increased with increasing antimony concentration, and the line width of the resonant line appeared to increase with increasing antimony concentration in palladium. These results were compatible with a model in which the solute atoms were almost perfectly screened by conduction electrons. A charge transfer model was also possible, but Montgomery and Ruby suggest that the general weight of evidence is opposed to it.

Ruby et.al.\textsuperscript{132} studied the tin-rich and antimony-rich Sb-Sn alloys over the complete range of solid solubility and found a variation of s-electron density with concentration. The s-electron density at the antimony nucleus when it was surrounded entirely by antimony atoms was about the same as when it was surrounded entirely by tin atoms, and the same was true for the tin nucleus. This is a much weaker behavior
in comparison to the changes observed in nonconducting compounds of tin and antimony, for which relatively large variations in isomer shift have been found. Their results indicated that each atom in the alloy was strongly screened. This behavior of the s-electron density showed that changes must occur principally in the occupation of p (or higher angular momentum) states, a conclusion consistent with the results of Verken et al.\textsuperscript{133} for Sn\textsuperscript{119} nuclei. Rigney and Flynn\textsuperscript{134} attributed the magnitude and variation of the Knight shift for antimony in Sb-Sn liquid solutions to s-structure saturation and p-wave scattering only.

The Mossbauer effect has been used to measure magnetic fields at the antimony nucleus in the following materials: NiMnSb\textsuperscript{135}, MnSb\textsuperscript{136}, solid solutions of antimony in iron and nickel\textsuperscript{137} and the iron spinels Ni\textsubscript{1-2x}Fe\textsubscript{2-3x}Sb\textsubscript{x}O\textsubscript{4}.\textsuperscript{138} The resolution of hyperfine splitting was reported as difficult, but good agreement was achieved between experimental and calculated values for the magnetic moments of the ground and excited states of Sb\textsuperscript{121}.

As can be seen, most of the Sb\textsuperscript{121} Mossbauer studies have been done outside the field of solid state physics. There are, however, a vast number of materials that can be prepared and studied using this relatively new Mossbauer nucleus. The difficulties involved with these studies are that low temperatures and long periods of observation may both be necessary. Perhaps these difficulties have influenced the amount of research that has been completed with solids
containing antimony.

The useful parameters obtained from the Mossbauer effect will be discussed in the experimental section. Those parameters of interest in these studies are isomer shift, electric quadrupole splitting and linewidth. The discussion of other experimental techniques and tools used to complete these investigations are also in the following experimental section.
III. EXPERIMENTAL METHODS

A. Mossbauer Effect Measurements

There are several ways by which electrons in a solid interact with the nuclei to perturb the nuclear energy levels. Of these only the nuclear electric monopole and nuclear electric quadrupole interactions will be considered in these investigations.

1. The Isomer Shift, \( \delta \)

If the source and absorber nuclei in a Mossbauer experiment are in different chemical environments, there will in general be a difference between their electric monopole interactions, due to differences in the net s-electron density at the nucleus. This gives rise to an isomer shift (energy shift) in the centroid of the Mossbauer spectrum. The expression generally given for the isomer shift is:

\[
\delta = (2\pi/5)Z e^2 R^2 (\delta R/R)[|\psi_a(0)|^2 - |\psi_s(0)|^2] 
\]

where

- \( Z \) is the atomic number,
- \( e \) is the electronic charge,
- \( \delta R = (R_{\text{ex}} - R_{\text{gd}}) \) is the difference in the excited state \( (R_{\text{ex}}) \) and the ground state nuclear radii, \( (R_{\text{gd}}) \)
- \( R \) is the average of the ground state and excited state nuclear radii,
- \( \psi_a \) is the s-electron wave function for the absorber,
- \( \psi_s \) is the s-electron wave function for the source.
However this is a non-relativistic approximation for the isomer shift value, which is fairly accurate for very light elements. For heavy elements, relativistic corrections must be made, and the equation becomes\textsuperscript{139}:

\[
\delta = \left(\frac{4\pi}{5}\right) Ze^2 R^2 (\delta R/R) (c/E_\gamma) S'(Z) \\
\left[|\psi_a(0)|^2 - |\psi_s(0)|^2\right]
\]

where \(c\) is the velocity of light,
\(E_\gamma\) is the emitted gamma ray energy,
\(S'(Z)\) is a dimensionless factor to account for distortion of the electron wave functions by the nucleus and for their nonrelativistic value.

Shirley\textsuperscript{139} has calculated and tabulated the values for \(S'(Z)\). For antimony (\(Z=51\)) he found \(S'(Z)=2.38\). Since the isomer shift depends on the product of an electronic factor and a nuclear factor, electron densities can be measured if the nuclear factor for a particular gamma ray transition has been determined.

Values for the nuclear parameter, \(\delta R/R\), have been calculated and reported to be (listed here chronologically):
\((-8.5\pm3)\times10^{-4}\)\textsuperscript{113}, \((-9.5\pm3)\times10^{-4}\)\textsuperscript{115}, \((-7.3\pm0.8)\times10^{-4}\)\textsuperscript{140} and \((-6.7\pm3)\times10^{-4}\)\textsuperscript{123}. Only the sign of \(\delta R/R\) is vital to the ionicity order, and not its absolute value.

Since the isomer shift actually measures the s-electron density at the nucleus, a WWJ plot\textsuperscript{141} (a correlation plot of observed isomer shift values for some ionic compounds with the Hartee-Fock wave functions for the valence electron contributions due to ionicity, as first shown by Walker,
Wertheim and Jaccarino) of the total s-electron density, as a function of the 5s-electron character for various configurations of 5p-electrons, has been constructed by Ruby et.al.\textsuperscript{13} (Figure 7). It clearly shows how the total s-electron density, $|\psi(0)|^2/a_0^3$, at the nucleus varies with the addition of s and p electrons. The addition of p-electrons decreases the total s-electron density, due to shielding effects. Table V gives the total electron densities for various electron configurations of 5s and 5p character.

2. Electric Quadrupole Coupling

The electric quadrupole splitting is the result of interactions between the crystal's electric field gradient (EFG) at the nucleus, produced by all charges exterior to the nucleus, with the nuclear electric quadrupole moment of the atom undergoing a recoilless transition. A degeneracy may be partially removed through this interaction, with the splitting of the nuclear energy levels by the amount:

$$E_Q = \frac{eqQ}{4I(2I-1)[3m_I^2-I(I+1)][1+n^2/3]^{1/2}}$$

where $e$ is the electronic charge,

- $eq$ is the major term of the diagonalized electric gradient, $V_{zz}$,
- $Q$ is the nuclear quadrupole moment,
- $(Q_{ij} = \int \rho(r)x_i x_j r^+)$,
- $I$ is the nuclear spin quantum number,
- $m_I$, ($m_I = I, I-1, \ldots, -I$), is the magnetic quantum number,
Figure 7. Antimony isometric shifts vs. electronic configuration, $5s^m5p^n$.
(From Ruby et al. $^{113}$)
<table>
<thead>
<tr>
<th>Electron Configuration</th>
<th>((\psi(0)^2/a_0^3) - k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s(^2)5p(^3)</td>
<td>27.72(^a)</td>
</tr>
<tr>
<td>5s(^2)5p(^2)</td>
<td>36.22(^a)</td>
</tr>
<tr>
<td>5s(^2)5p(^1)</td>
<td>40.55(^a)</td>
</tr>
<tr>
<td>5s(^2)5p(^0)</td>
<td>44.55(^a)</td>
</tr>
<tr>
<td>5s(^1)5p(^3)</td>
<td>18.28(^a)</td>
</tr>
<tr>
<td>5s(^1)5p(^2)</td>
<td>19.97(^a)</td>
</tr>
<tr>
<td>5s(^1)5p(^1)</td>
<td>22.10(^a)</td>
</tr>
<tr>
<td>5s(^1)5p(^0)</td>
<td>24.59(^a)</td>
</tr>
<tr>
<td>5s(^0)5p(^0)</td>
<td>00.00(^a)</td>
</tr>
<tr>
<td>5s(^0)5p(^1)</td>
<td>-00.57(^b),(^c)</td>
</tr>
<tr>
<td>5s(^0)5p(^2)</td>
<td>-00.91(^b),(^c)</td>
</tr>
<tr>
<td>5s(^0)5p(^3)</td>
<td>-01.04(^b),(^c)</td>
</tr>
</tbody>
</table>

\(k\) is the contribution of the core electrons (Kr\(^{4d^{10}}\)) which is given as 93291

\(^a\)From Ruby et al.\(^{113}\)

\(^b\)From Pruitt et al.\(^{123}\)

\(^c\)Determined by extrapolation\(^{123}\)
\( \eta \) is the asymmetry parameter of the electric field gradient, \((V_{xx} - V_{yy})/V_{zz}\).

The EFG is the second derivative tensor of the electric potential or the gradient of the electric field vector. It exists whenever the symmetry of the surrounding charge distribution is lower than cubic, and when reduced to diagonal form in the proper coordinate system it is generally specified by two independent parameters, \( \eta \) and \( \varepsilon \). It is diagonalized by a suitable choice of axes and arranged so that the dominant term is the \( V_{zz} \) term. From the above equation for antimony, with \( I=7/2 \) and \( 5/2 \) for the excited and ground states respectively, we see that both states can be split by this interaction permitting eight lines to be observed in a spectrum if the sample has less than cubic symmetry. The energy level diagram is given in Figure 8. Sternheimer\(^{142} \) has considered the contribution from the electrons of Mossbauer atoms to their surrounding electric field gradient and developed an antishielding factor, \((1 - \gamma_{\infty})\), for the enhancement of the field gradient at the nucleus due to the distant charges, \( q' \), expressed as:

\[
q = q' (1 - \gamma_{\infty}).
\] (29)

Ruby\(^{108} \) has indicated that it is difficult to resolve the eight-line quadrupole pattern of antimony and has suggested that accurate measurements of the quadrupole coupling using the Mossbauer effect in Sb\(^{121} \) will not be easy. However, Ruby et.al.\(^{112} \) have reported that the value of the excited state quadrupole moment, \( Q(7/2) \), is
Figure 8. Nuclear hyperfine interactions for antimony 121
-0.75±0.09 barns, using the optically determined value of Q(5/2), equal to -0.54±0.07 barns. In order to deduce this value they measured R, where R=Q(7/2)/Q(5/2), the ratio of the first excited state quadrupole moment to that of the ground state of Sb\textsuperscript{121} and obtained 1.36±.02. The value of R has also been determined by Long et.al.\textsuperscript{149} to be 1.32±.02. Stevens and Ruby\textsuperscript{143} have since improved the accuracy of the value by using organic antimony compounds, which have larger electric field gradients, and report a value of 1.34±.01. Later Ruby et.al.\textsuperscript{113} reported the value of Q(5/2) to be -0.26 barns, which is larger than the previously mentioned value. They claim however agreement with the weighted average of the widely scattered results of other experiments.

Knowing the quadrupole moments for the first excited and ground state of Sb\textsuperscript{121}, one has the means of determining the EFG at the nucleus, if a quadrupole coupling is observed in the Mossbauer spectrum.

3. The Magnetic Hyperfine Interaction

While this effect is not present in the author's studies there have been Mossbauer studies done on magnetic environments involving antimony. These include MnSb\textsuperscript{136}, NiMnSb\textsuperscript{135}, solid solutions of antimony in iron and nickel\textsuperscript{137}, and iron spinels \( \text{Ni}_{1-2x}\text{Fe}_{2-3x}\text{Sb}_0.8\text{S}_4 \)\textsuperscript{138}. The interaction is between the electron spin and the nuclear spin, I. The degeneracy of the energy levels is completely removed by splitting of the levels according to the equation:
where $g$ is the gyromagnetic ratio of the nucleus, $\mu_N$ is the nuclear magneton, $H$ is the magnetic field at the nucleus and $m_I$ is the nuclear magnetic quantum number.

The allowed transitions are given by the magnetic dipole selection rule:

$$\Delta m_I = 0, \pm 1.$$  \hspace{1cm} (31)

In the case of antimony the transitions are between states for which $I=7/2$ and $5/2$. This means that there are 8 levels in the excited state which can decay to 6 levels in the ground state, a possible 18 transitions, and a fully resolved Mossbauer spectrum would display 18 resonant absorption lines.

4. The Linewidth

The observed linewidth is due to the overlap of both the source and absorber linewidths. The linewidth of either the source or absorber may be broadened due to inhomogeneous hyperfine interactions, fluctuations and electronic relaxation time. Unresolved quadrupole coupling may be the most important source of linewidth broadening in this study. The fluctuations and relaxations occur near phase transitions and are not of importance in these experiments. Other sources\textsuperscript{143} of broadening are of little fundamental significance as they are due to faults in experimental techniques and data processing which can be avoided. One finds, for the 3.5 nsec half life of Sb$^{121}$, that the minimum width is
is $2I=2.1$ mm/sec. Some broadening is expected from the above causes which implies that the measured linewidth will always be greater.

5. The Source

The source is selected on the basis of its activity, clean spectrum, and lack of hyperfine interactions and line broadening effects. The Sb$^{121}$ source uses a natural decay scheme involving the parent Sn$^{121}$, as shown in Figure 9. In the preparation of sources, a given tin compound is enriched with Sn$^{120}$, and then irradiated in a slow neutron flux causing the production of the Sn$^{121m}$ isomer state. This has a long half life (76.3 years), and as a result the source strengths are somewhat weak. Also, since Sn$^{120}$ at its highest enrichment contains some Sn$^{119}$, some Sn$^{119m}$ is also created during bombardment. As a result, a source for both tin and antimony experiments is produced. $^{108}$ The first sources were $\beta$-Sn(Sb$^{121}$) which had a full width at half maximum, FWHM, of 2.6 mm/sec. The broadening was accounted for by the noncubic nature of $\beta$-Sn. In addition, $\beta$-Sn has a low Debye temperature and the recoilless fraction, $f$, is small. CaSnO$_3$(Sb$^{121}$) sources have also been made, and the FWHM has been reported to be approximately 2.6 mm/sec, but $f$ is greatly increased, ($f=20\%$ at $300^\circ$K and $f=60\%$ at $78^\circ$K). Ruby$^{108}$ reports that the observed effect with the CaSnO$_3$(Sb$^{121}$) source at $78^\circ$K is larger than with the $\beta$-Sn(Sb$^{121}$) source at $4.2^\circ$K. Sources have also been made from SnO$_2$(Sb$^{121}$), which have about the same recoilless
51Sb\textsuperscript{121}(37.2 keV)

$^{11/2^-}\text{Sn}\textsuperscript{121m} 76.3\gamma 0.008$

$^{3/2^+}\text{Sn}\textsuperscript{121} 25.53h 0$

$\beta^- 100\%$

$7/2^+ 3.5 \text{nsec}$

$5/2^+ \gamma_M 0.03715$

$1/2^+ \text{EC, } \beta^+$

$11/2^- \text{complex } \text{Te}\textsuperscript{121} 154d 296$

$1/2^+ \text{complex } \text{Te}\textsuperscript{121} 17d$

$\text{Sb}\textsuperscript{121}$

Figure 9. Simplified decay scheme for antimony 121

(From Ruby\textsuperscript{108})
fraction as the stannates, but the FWHM is 2.7 mm/sec.\textsuperscript{108}

The source used in these experiments is a CaSnO\textsubscript{3}(Sb\textsuperscript{121})
1.5 mCi source of 37.2 keV Mossbauer gamma rays, obtained
commercially from New England Nuclear Corporation. A
typical pulse-height spectrum is shown in Figure 10.

6. The Absorbers and Filters

The isotopic abundance of Sb\textsuperscript{121} is 57%, so that enriched
Sb\textsuperscript{121} is not needed for absorber studies. The thickness of
the absorbers used has been reported to be 2-8 mg/cm\textsuperscript{2}.
Ruby\textsuperscript{108} commented that absorbers of 10 mg/cm\textsuperscript{2} of antimony
will be black. Antimony absorbers can be used even if
rather dilute in antimony. The author calculated the anti-
mony thickness required to observe a Mossbauer spectrum with
a 1/e absorption, and found that a concentration of 7.6x10\textsuperscript{18}
antimony atoms/cm\textsuperscript{2} was needed. The calculation procedure is
shown in Appendix I.

Ruby\textsuperscript{108} found that a one-eighth inch aluminum filter
is sometimes useful to decrease the flux of 24 keV x-rays
entering the proportional counter. A graded shield of
aluminum, brass and lead was used by the author to protect
the proportional counter tube from stray radiation that
might get through the aluminum casing, rather than the thin
detector window.

7. Detectors

Gamma rays can be detected using proportional counters,
scintillation counters, or semiconductor radiation detectors.
Scintillation counters have relatively poor resolution at low
Figure 10. Typical pulse-height-analyzer spectrum for antimony 121 source

(From Puritt et al.)
energies, making it difficult to separate x-rays from the desired gamma rays. Lithium-drifted germanium detectors are very inefficient and are useful only for energy resolution. Proportional counters are limited in use to the energy range below 40 keV, since their efficiency drops sharply with increasing energy. Their energy resolution, however, is much better than scintillation counters in the region where they are useable. Gas-filled proportional counters can be built to suit individual needs and are the easiest to use. Ruby reported that a proportional counter filled with a mixture of xenon and methane gas at two atmospheres is very suitable for detection of the gamma ray spectrum of antimony. A thin beryllium window, about 0.010 inch thick and one inch in diameter, limits the detection area. Ruby et al. have used a xenon-methane gas proportional counter at two atmospheres with a two-inch square and ten mil thick beryllium window.

B. Apparatus

A diagram of the apparatus is given in Figure 11. Each component of importance will be briefly discussed in terms of design and operation. However, it should be mentioned that there are several alternatives to this type of system. The Mossbauer effect is usually observed either in the constant velocity or constant acceleration mode, depending on the method used to cause the Doppler shift of the gamma radiation. The purpose of the motion device is to provide energy modulation for a Mossbauer effect absorption spect-
A. CSP-200 FET Preamp.
B. LA-200 Linear Amp.
C. Single Channel Analyzer

Figure 11. Block diagram of Mossbauer spectrometer
rometer, using the Doppler shift of the gamma ray to examine a region of the spectrum near its unperturbed energy. It is desirable to have a linear energy scale and a spectrum which is flat in the absence of absorption. The constant velocity mode is the most economical way to achieve this, as all one needs are a motor, detector, and scalar. The constant velocity can be produced by turntables, lathes, or by gated counting on oscillatory systems such as cams or pendulums, but electro-mechanical transducers are best. The spectrum is acquired by counting for a fixed time at equally spaced velocity values. The utility of such a constant velocity spectrometer system is usually limited by the stability of the counting system. The more advantageous system (constant acceleration mode) sweeps repeatedly through the range of velocities of interest, storing the instantaneous counting information in a large number of scalers, a multichannel analyzer (MCA). The constant acceleration mode also gives a linear velocity scale, since equal lengths of time are spent in equal velocity increments, though the drive motion is parabolic in time. The synchronization between the mechanical motion and the analyzer is accomplished by using the last bistable in the channel counting circuit (which can represent a constant acceleration plot) and integrating it to give the corresponding triangular velocity waveform. This is then used to generate a drive signal to an electro-mechanical transducer.

One method of presenting the data on a linear velocity
scale requires that the velocity signal be added to the gamma ray counts and then stored, using the pulse height analysis feature of the MCA. Thus the counts are stored in channels corresponding to a particular increment of velocity. The chief disadvantage with this system is that any non-linearity in the velocity appears as a modulation of the nonabsorption spectrum, making it difficult to detect weak broad absorption peaks. A second scheme of converting velocity into a channel number is provided by using the MCA as a time analyzer, where it is allowed to step at a clock-controlled rate through its channels (time sequenced scalar mode). Synchronism between the mechanical motion and the analyzer is maintained by triggering the analyzer once per cycle or by using the analyzer itself as the waveform generator.

1. The Multichannel Analyzer (MCA)

The multichannel analyzer occupies a central position in the apparatus. A 400 channel RIDL model 24-2 analyzer, with $10^6$ bits of memory per channel, is used for data storage. For data accumulation we use the time sequenced scaler mode, advanced by a crystal-controlled time base generator built by Austin Science Associates, Timing Unit TU-100. This offers a choice of 100 or 400 microseconds dwell time per channel and a scan rate for 400 channels of 25 and 6 Hz respectively. The analyzer generates a 7.5 Hz square wave called the 200-200 bistable, which is used to generate the drive signal. The gamma ray spectrum of the source is determined and the detector system is set optimal-
ly by using the pulse height analysis mode of the MCA. (The analog to digital converter is operated in coincidence with an independent single channel analyzer, allowing a faster selection of the Mossbauer pulses to be stored.)

2. The Drive System

This part of the apparatus produces the Doppler modulation of the source and sets the dwell time per channel for data accumulation. A Mossbauer spectroscopy velocity drive model S3 unit, built by Austin Science Associates, with constant acceleration motion, is used. The drive has a velocity range from 0 to 60 cm/sec with less than one percent nonlinearity. The control electronics consists of four sections:

(1) an input clipping stage which amplifies, d.c. corrects, and squares off the input from the MCA bistable;

(2) an integrator which converts this square wave to a triangular wave;

(3) a computing amplifier, which compares the velocity return signal from the motor with a selected fraction of this triangular wave and synthesized an error signal; and

(4) a four-transistor high-power voltage follower, capable of sending up to six amperes into the 1.4 ohm armature winding of the motor.

The motor, Mossbauer Linear Motor K3 built by Austin Science Associates, is based on Kankeleit's\textsuperscript{14} design. A light bulb is included in the output circuit as a current limiter during periods of overloading to protect the motor.
coils from burnout. A diagram of the motor construction is shown in Figure 12. The two coils provide the driving force and the velocity feedback signal required in this system. The springs are designed to provide rigid centering of the coils with as light a spring force as possible. The center shaft of the motor is light-weight in order to reduce the mass mounted on the spring, and the source is mounted at the end of the shaft. The motor can be mounted vertically, if necessary.

The optimum operating frequency depends upon how the drive is used. Heavy loads, as when the source is located at the end of a long push rod, require additional time at the point where the sense of the acceleration is reversed. In the present experiments low velocities (1.5 cm/sec) were used, and the source was located at the end of a long push rod because these studies required cryogenic applications (see Figure 13). Thus a spectrum scanning frequency of 25 Hz was used. This is equivalent to allowing 100 microseconds dwell time per channel.

3. The Absorbers and Dewar

The absorbers consisted of both single crystal and powders placed on masking tape and mounted between the source and detector in a dewar capable of holding temperatures down to 4.2°K. The stainless steel dewar was designed and built by Austin Science Associates for Mossbauer low temperature studies and is seen in Figure 13. The insulation is provided by a vacuum of $10^{-5}$ torr in the outer chamber, which rises to about $10^{-3}$ torr over a period of five weeks. The
I, E  Alnico V castings
D, G, J  Armco iron
A, C, F, H, K  Aluminum
B  Phosphor bronze
L  Phenolic plastic, reinforced

Figure 12. Mossbauer linear motor K3
A. Inner Chamber  
B. Push Rod  
C. Source Holder  
D. Copper Cup Heater

Figure 13. Mossbauer stainless steel dewar
central chamber contains the liquid nitrogen. When filled (approximately six liters) the nitrogen boils off in a period of three days, when the vacuum is $10^{-5}$ torr. The liquid helium is also transferred to this chamber, after the latter is cooled to liquid nitrogen temperature. However, it was learned that a full dewar of liquid helium will last for only six to eight hours. The inner chamber is where the pushrod, source, and absorber are kept. This chamber is dry and helium gas is constantly passed through it. The motor is enclosed in a polyethylene bag which is filled with helium gas, thus preventing the drive from freezing up at both nitrogen and helium temperatures. The source and absorber are placed in a wire wound copper cup, enabling temperature variation of both. The source could also be kept in the dewar and the absorber at room temperature outside the dewar. The samples are restricted to be less than one and one-half inch in diameter, due to the geometry of the inner cylinder. The powder samples were sprinkled onto masking tape mounted on a brass ring, and then the sample and ring were taped securely to the copper cup. The temperature was monitored with a copper-constantan thermocouple, measured with a Leeds and Northrup potentiometer. The gamma rays passing through the absorber left the Dewar through two mylar windows. The dewar was elevated above the detector by a tripod which had a two inch hole in the center for gamma ray transmission. The source-sample-detector geometry is shown in Figure 14.
Figure 14. Source-absorber-detector geometry
Cosine broadening due to spread of velocities obtained from finite source and absorber size has been discussed by Spijkermann\textsuperscript{145}. It is given by:

$$\Delta V = V(1 - \cos \theta) = \Gamma / n$$

where $V$ is the velocity of motion,

$\theta$ is the angle of propagation of the gamma ray with respect to the direction of motion,

$\Gamma / n$ is the fractional broadening of $\Gamma$.

The smaller the angle, the smaller the effect, but the count rate is also reduced. When the source is closer to the detector, giving a larger solid angle, more counts are observed on one half of the spectrum. When using the triangular wave mode, cancellation of this effect can be achieved by adding the two spectra. No noticeable cosine broadening was seen in these investigations.

4. The Detector System

The gamma ray spectrum was detected with a two atmosphere xenon-carbon dioxide ($97\% \text{Xe} - 3\% \text{CO}_2$) gas-filled proportional counter with a one inch diameter, 0.010 inch thick beryllium window. The detector electronics used were an Austin Science Associates CSP-200 FET preamplifier, and a LA-200 linear amplifier.

The pulse-height discriminators of either the RIDL 33-14A single channel analyzer, operating in delayed coincidence with the analog-to-digital converter, or the MCA's analog-to-digital converter, were used for pulse selection. The former method allowed more accurate pulse selection and was the scheme used in this study. The windows for the
desired gamma ray peak were bracketed by setting the upper and lower levels of the discriminator on the analog-to-digital converter, while observing the whole spectrum using the MCA in the pulse height analysis mode. Using the delayed coincidence circuit of the analog-to-digital converter, the pulse height spectrum was run in the anticoincidence mode and stored in the MCA. Using the coincidence circuit, the window and threshold of the single channel analyzer were set to bracket the desired peak. Thus only counts passing through the set single channel analyzer were collected and stored for comparison. Once the windows were set for maximum detection of the desired peak, the pulses were directed to the data input for the timed sequence scaler (TSS) mode of operation of the MCA.

The detector tube used a dc potential of 2700 volts supplied by a Keithley 242 high voltage supply. An RIDL 49-30A scaler having a $10^7$ count capacity and a 0-60 minute timer were used to measure the total count rate being stored in all 400 channels of the MCA. This scaler was used to determine absorber thickness, drifts in SCA settings and condensation of air in the inner chamber of the stainless steel dewar.

Because the 37.2 keV gamma rays exceeded the energy necessary to eject a K electron from a xenon atom, an escape peak appeared (see Figure 10) whose energy of 7.5 keV was determined by

$$E_{es} = E_i - E_f$$

(33)
where \( E_i \) is the incident energy of the gamma rays 
(37.2 keV),

\( E_f \) is (in this case) the K-emission edge energy for xenon which is 29.7 keV. 

The high probability of ejecting a K electron, combined with the detector's higher count efficiency for the low energy processes, resulted in an escape peak somewhat more intense than the 37.2 keV gamma ray peak of Sb\(^{121}\). By setting the single channel analyzer window on the escape peak, the counting rate was enhanced.

5. Data Readout

The stored data in the MCA were read onto one-inch wide paper tape, using a Tally 420 PR perforator. This punched tape registers the channel number (0-399 channels) and a six digit number representing the number of counts in that channel. The information registered on the data tapes was then converted to punched cards, compatible with the UMR IBM 360-model 50 computer. The data were processed by computer curve fitting programs.

6. Data Processing

A computer program provided by NBS\(^1\) called Parlors (Parabolic-Lorentzian) was used to give a least-squares fit to a linear approximation of the Lorentzian line shape. This program is capable of fitting as many as twenty separate absorption peaks, and resolving peaks separated by approximately three-fourths of the line half width at half maximum. A background parabola is considered to approximate the affects of non-linearity in the drive or certain geometric
effects due to the source moving with respect to the detector. The data and the computed fit are plotted on one plot for comparison. A residual error plot can be used to show any missed peaks or bad fits. The peak positions, half widths, baseline values, peak height and area, maximum number of counts and also the error analysis\textsuperscript{148} are listed in the output of the program. The program which requires about four minutes of computer time for the analysis and plots, is described and referenced in Appendix II.

A computer program edited by Shaw\textsuperscript{149} called Shawfit, was also available to make a least-squares fit of the Mössbauer spectra of antimony. The relative intensities for the eight lines resulting from the 7/2 to 5/2 dipole transitions in the antimony absorber are determined from the squares of the appropriate Clebsch-Gordon coefficients and are expressed as constraints in the program. In searching for optimal values of the five least-squares parameters of baseline (the nonresonance counting rate), linewidth, quadrupole splitting, isomer shift and fractional absorption (uncorrected for background), the program depends on the investigator's ability to give reasonable estimates of these parameters, which are then refined by successive iterations. Since the program is dependent on the bias of the investigator, the initial parameters have to be chosen with some care. If the absorption line is broad, the investigator might assume an unresolved splitting, when in reality none exists. It is for this reason that this program was not
used in reporting the results. However, it should be mentioned that the results from the Parlors program have been used for initial guesses in the Shawfit program which then gave identical results.

7. Velocity Calibration

The velocity scale of the spectrum was calibrated by using the six peaks of a standard iron foil, which have splitting values of 1.6793, 6.1561, and 10.6267 mm/sec\textsuperscript{150}, (Figure 15). From the calibration, the isomer shift values were converted from channel numbers to velocities. For these studies all of the isomer shift values are made relative to InSb rather than to the CaSnO\textsubscript{3}(Sb\textsuperscript{121}) source.

8. The Experiment

The antimony-doped silicon experiments consisted of three to twenty-seven day runs, accumulating from 12,000 to about 50,000 counts per channel. The absorption peak intensities varied from 3 to 12 percent depending on the concentration of antimony in the sample, with the higher antimony concentrations resulting in more intense peaks. The bismuth-antimony alloy studies consisted of two to twenty-eight day runs, accumulating from 12,000 to 110,000 counts per channel. The absorption peak intensities varied for these alloys from 2 to about 25%, for 5 to 100 atomic percent antimony in the Bi-Sb alloys respectively.

The count rate was checked before, during, and after each run in order to detect electronic drifts or condensation of air in the stainless steel dewar's inner chamber, as
Figure 15. Metallic iron splitting useful for calibration (Spijkerman150)
mentioned previously. The temperature was maintained at 78°K for both the CaSnO$_3$(Sb$^{121}$) source and the absorbers. In addition, two runs were made at 4.2°K. The source and absorber were allowed to stabilize at liquid nitrogen temperature (approximately twenty minutes), and the temperature was checked using a thermocouple and potentiometer, before the counts were allowed to accumulate. The gamma ray pulse height spectrum was checked periodically, especially if the total count rate as measured by the scaler indicated drifting. The InSb absorber was run periodically, thus providing a standard for the isomer shifts and also providing a consistent check on the system.

C. X-Ray Diffraction Measurements

Using an exceptionally precise camera construction, together with a number of refinements of experimental technique, Straumanis$^{151}$ obtained very accurate lattice spacing measurements from the observed line positions in the back-reflection region. He eliminated errors due to uniform film shrinkage and inexact knowledge of the camera and film radii by placing the film in the asymmetric position. Line shifts due to absorption in the sample were eliminated by utilizing lines in the back-reflection region, decreasing the sample diameter, and making the sample more transparent to x-rays. The temperature must be constant during exposure, as the sharpness of the lines is impaired due to thermal expansion and contraction of the lattice, variations of a few tenths of a degree affecting the fifth decimal
place of the lattice constant. The line positions are measured by a comparator of high precision with a discrimination of $\pm 0.001 \text{ mm}$. 

This method was used in the lattice constant measurements of the Si-Sb alloys. The temperature was maintained at 24.0$\pm$0.5°C during the exposures. Appendix II illustrates the measurements and calculations involved in a precision determination of the lattice constant of high purity silicon by the Straumanis method.

A Siemen's x-ray diffractometer was used to check the Bi-Sb alloys for impurity phases and to find the lattice parameters to within 0.01 Å. The results were compared with published data$^{76,97}$ and were found to be in agreement. For these alloys, precision measurements using the Straumanis method were not done, as changes in the lattice parameter were large and have been reported previously to only two decimal places.

D. Resistivity Measurements

The resistivity of semiconductors can be measured quite accurately using a four-point probe. The basic model for resistivity measurements is shown in Figure 16, and the experimental circuit used for measurements is illustrated schematically in Figure 17. The four-point probe was built by the author. It consists of four spring loaded sharp needles. The four sharp probes were placed on a flat surface of the material to be measured. Current was passed through the outer electrodes and the floating potential was
Figure 16. Model for the four-point probe for resistivity measurements
(From Valdes$^{154}$)
Figure 17. Circuit used for four-point probe resistivity measurements
(From Valdes\textsuperscript{154})
measured across the inner pair. If the flat surface on which the probes rest is adequately large, and the crystal is large, the semiconductor may be considered a semi-infinite volume. This condition holds if the nearest probe is no less than three times the probe spacing from any boundary of the crystal, other than the one on which the measurements are being made.\textsuperscript{153} Valdes\textsuperscript{154} and Uhlir\textsuperscript{155} have derived an expression for the resistivity:
\begin{equation}
\rho = \frac{V}{I} \left[ 2\pi / \left\{ \frac{1}{s_1} + \frac{1}{s_2} - \frac{1}{(s_1+s_2)} - \frac{1}{(s_2+s_3)} \right\} \right]
\end{equation}
where \( V \) is the potential difference between the inner probes, \( I \) is the current through the outer pair of probes, \( s_1, s_2, s_3 \) are the probe spacing.
Whenever \( s_1 = s_2 = s_3 = s \), the equation simplifies to
\begin{equation}
\rho = \frac{V}{I} (2\pi s).
\end{equation}
One must require or assume the following properties when using these relations to find experimental results:\textsuperscript{153}

1. The resistivity of the material is uniform in the area of measurement.
2. Measurements are made on surfaces having a high recombination rate.
3. The surface on which the probes rest is flat with no surface leakage.
4. The four probes used for the resistivity measurements must contact the surface at points that lie in a straight line.
5. The diameter of the contact between the semiconductor and probe is small compared to the distance between
probes, a ratio of one to ten or greater.

For measurements involving a non-infinite volume of semiconductor, the resistivity equations previously given must be corrected. A variety of different conditions and the correction factors, have been given by Uhlir\textsuperscript{153} and Irvin\textsuperscript{156}. Irvin\textsuperscript{156} has presented a plot showing the relation between the resistivity measured at a temperature of 300\textdegree{}K for n-type and p-type silicon and the donor or acceptor concentration. The plot is shown in Figure 18.

E. Density Measurements

Density measurements are of prime importance in crystal structure determinations and in establishing the number of atoms per unit cell. Whether solid solutions are interstitial or substitutional in nature can also be determined.

The hydrostatic weighing method, based on Archimedes principle, was used to determine the bulk densities of the samples. This method involves weighing the sample in air and in a liquid of known density. Xylene was chosen as the immersion liquid, due to its low vapor pressure and low surface tension. A Sartorius micro-balance, enclosed in a constant temperature box, was used to make all the required measurements. The densities were then tabulated using the equation:

\[
d_t^s = \frac{M_1}{(M_1-M_2+M_3)} \left( d_t^H - d_t^a \right) + d_t^H
\]

where \( M_1 \) is the weight of sample in air,

\( M_2 \) is the weight of sample plus suspension cup in liquid,
Figure 18. Resistivity of silicon at 300°K as a function of acceptor or donor concentration

(From Irvin$^{156}$)
M₃ is the weight of suspension cup in liquid,
d₄ is the density of liquid in which the sample and
cup were suspended at temperature, t, and,
d₄₄₄₄ is the density of air at temperature, t, and
barometric pressure, H.

The density values of commercial xylene used in these comput-
ations were calculated from the equation:

\[ \text{d}_{\text{t}} = 0.881866 - 0.8173 \times 10^{-3} t \]  \hspace{1cm} (37)

The density of air was calculated from the equation:

\[ \text{d}_{\text{a}}^{\text{H}, \text{t}} = \left[ \frac{0.001293}{(1 + 0.00367t)} \right] \left( \frac{H}{76} \right) \] \hspace{1cm} (38)

where t is the room temperature,
H is the barometric pressure in cm Hg.

F. Samples

The antimony-doped silicon samples were obtained from
the Monsanto Corporation (Table VI). The alloys were single
crystals except for the ends of some of the ingots. The
samples were sliced into one centimeter thick disks with a
diameter of 2.54 centimeters, using a diamond cut-off saw.
The disks were then cleaned with dilute nitric acid and
used as absorbers for our Mossbauer experiments and
resistivity measurements.

Powder samples of the Si-Sb alloys were prepared by
grinding the samples in an automatic mortar and pestle for
a given time. The powders were checked using a Siemen's
x-ray diffractometer, and no impurity phase was seen except
for the powder of the polycrystalline end of the ingots.
**TABLE VI**

SAMPLES OBTAINED FROM MONSANTO CORPORATION

<table>
<thead>
<tr>
<th>Resistivity, Ohm-cm</th>
<th>Sb Concentration, Atoms/cc*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0141</td>
<td>2.8x10^{18}</td>
</tr>
<tr>
<td>0.0109</td>
<td>4.5x10^{18}</td>
</tr>
<tr>
<td>0.009</td>
<td>6.2x10^{18}</td>
</tr>
<tr>
<td>0.007</td>
<td>9.2x10^{18}</td>
</tr>
</tbody>
</table>

*The conversion of measured resistivity to concentration was taken from Irvin\textsuperscript{156}.*
The powder samples were lightly packed in a polyethylene cap and used as absorbers for these studies.

The Bi-Sb alloys were prepared using the solid-solubility curve shown by Hansen\textsuperscript{71}. All of the samples were prepared using 99.93\% pure bismuth and 99.92\% pure antimony. The alloys were prepared by direct weighing of calculated atomic percentages of bismuth and antimony using a microbalance to make about ten grams of the alloy. The alloys contained 5, 10, 15, 20, 25, 35, 40, 45, 55, 65, and 75 atomic percent antimony.

The sample was placed inside a dry, clean fused quartz tube closed at one end. The tube, with its contents, was next evacuated to a pressure less than $10^{-5}$ mm Hg, and the other end of the tube was sealed. The sample was then placed into a nichrome wire cage and suspended inside a vertical cylindrical electric furnace which was heated at 675°C for one hour. Then the temperature was dropped to approximately 125°C above the liquidus temperature of the alloy. To insure that the two metals were thoroughly mixed, the tube was removed several times and vigorously shaken. These operations were carried out for about three hours; then the molten alloy was rapidly cooled by immersing the tube into ice water. This was done to avoid inhomogeneous alloys. The Bi-Sb alloy was annealed for 48 hours at approximately 75°C below the solidus temperature of the alloy. The ingot was then washed in diluted nitric acid, ground into a fine powder, sealed in a clean glass tube
under vacuum, and annealed for an additional 24 hours at approximately 100°C below the solidus temperature of the alloy. The samples were checked using a Siemen's X-ray diffractometer for impurity phases.

A small amount of the Bi-Sb alloy was sprinkled onto masking tape, and used as an absorber for the Mossbauer spectrum.
IV. EXPERIMENTAL RESULTS AND DISCUSSION

The results are presented in this section in the form of tables and graphs. The materials investigated were antimony-doped silicon and the complete solubility range of bismuth-antimony alloys. The results are presented separately as there is no relationship between the two alloys, except for semimetallic to semiconductor transitions dependent on antimony concentration.

The velocity scale was calibrated using a Co$^{57}$ source and an iron foil, both supplied from the New England Nuclear Corporation. The calibration spectrum was obtained at room temperature and the channels were converted to velocities from the observed hyperfine splitting of iron as shown in Figure 15.

An InSb absorber was used as a standard reference for determining the relative isomer shift values in channels. The isomer shift values observed between InSb and the absorber in channel numbers were then converted to velocity using the results of the iron foil calibration. Thus the isomer shift values reported in these studies are given relative to InSb and in the units of mm/sec. The InSb absorber, obtained from Alfa Inorganics Ventron Corporation, was specified as 99.99% pure. X-ray diffraction analysis of the InSb powder using the Siemens x-ray diffractometer showed no impurity phases.

A. Antimony-Doped Silicon
The semiconductor ingots were obtained from the Monsanto Corporation with the measured resistivity and given antimony concentration in the silicon lattice as listed in Table VI. The ingots were sliced into one centimeter disks, faces perpendicular to the <111> growth axis, of diameter 2.54 centimeters to use as Mossbauer absorbers. The resistivities of the five samples (four listed single crystals and the end product of one ingot which was polycrystalline) that were to be used as Mossbauer absorbers were measured with the four-point probe built in this laboratory. The method is described in section III-D. The resistivities, measured at various temperatures, for the five slabs are given in Table VII. The resistivities measured at room temperature for the four single crystals were in reasonable agreement with the values given by Monsanto. Annealing the samples did not affect the resistivity values, as can be seen in Table VII. The polycrystalline slabs showed a very low resistance and the number of antimony atoms/cc was determined from Figure 18 to be $30 \times 10^{18}$ atoms/cc. A plot of the resistivity vs. $1/T$ is shown in Figure 19.

The resistivities of these samples indicated that the conductivity is almost temperature independent, except for the ingot with an antimony concentration of $2.8 \times 10^{18}$ atoms/cc, which showed strong temperature dependent behavior. Hence, these results indicate that the $2.8 \times 10^{18}$ Sb atoms/cc sample behaves as a typical semiconductor but the 4.5, 6.2, 9.2 and $30 \times 10^{18}$ Sb atoms/cc samples are metallic in behavior.
TABLE VII

RESISTIVITY OF SILICON-ANTIMONY INGOTS WITH DIFFERENT CONCENTRATIONS OF ANTIMONY

FOR DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Nominal Concentration Given By Monsanto</th>
<th>300°K</th>
<th>196°K</th>
<th>78°K</th>
<th>4.2°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8x10^{18} Sb atoms/cc</td>
<td>.0141 ohm-cm</td>
<td>.0178 ohm-cm</td>
<td>.0375 ohm-cm</td>
<td>7.5 ohm-cm</td>
</tr>
<tr>
<td>4.5x10^{18}</td>
<td>.0105</td>
<td>.0100</td>
<td>.0096</td>
<td>.0075</td>
</tr>
<tr>
<td>6.2x10^{18}</td>
<td>.009</td>
<td>.0089</td>
<td>.0087</td>
<td>.0041</td>
</tr>
<tr>
<td>9.2x10^{18}</td>
<td>.007</td>
<td>.0068</td>
<td>.0066</td>
<td>.0026</td>
</tr>
<tr>
<td>9.2x10^{18}*</td>
<td>.0024</td>
<td>.0025</td>
<td>.0023</td>
<td>.0011</td>
</tr>
<tr>
<td>2.8x10^{18}**</td>
<td>.0143</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5x10^{18}**</td>
<td>.0103</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.2x10^{18}***</td>
<td>.0032</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Polycrystalline end of ingot. From the resistivity value, the concentration was found
Table VII (continued)

to be $3 \times 10^{19}$ Sb atoms/cc (Figure 18.)

**Annealed at 250°C for 26 hours.

***Polycrystalline end of ingot heated at 800°C for 2 hours and at 1000°C for 5 hours in H$_2$ atmosphere.
(Antimony concentrations in terms of $10^{18}$ Sb atoms/cc) --

Figure 19. Resistivity vs. $1/T$ for antimony-doped silicon
This behavior has been previously reported for moderately-doped samples and is due to impurity band conduction as described in section II-B. The critical concentration for the formation of impurity bands in n-type silicon, as given by Conwell\textsuperscript{29}, is greater than $10^{17}$ donor atoms/cc. The impurity band overlaps the conduction band in n-type silicon at donor concentrations of $2 \times 10^{19}$ atoms/cc or greater. Between these two impurity concentration limits the semiconductor is said to be moderately doped and has an impurity band in the forbidden gap. Hence, the Si-Sb samples used in these studies are considered to possess impurity bands and to be moderately-doped.

By using the etching technique described by Dash\textsuperscript{160} and depositing gold on the surface of the sample, etch pits were observed to be absent, as indicated by the scanning electron microscope. Thus the antimony-doped silicon single crystal ingots were shown to be dislocation-free as Monsanto has claimed.

The Mossbauer spectra of antimony-doped silicon absorbers were collected with both the CaSnO$_3$(Sb$^{121}$) source and the various antimony-doped absorbers at 78°K. The count rate, using optimum geometry for the 1.5 mCi CaSnO$_3$(Sb$^{121}$) source and the single crystal absorbers, was found to vary from 15 to 30 counts per sec for 400 channels. Generally 15,000 counts/channel were collected for the Mossbauer spectrum; however, for the lowest antimony concentrations approximately 50,000 counts/channel were collected. The
percentage absorption effect varied with the antimony concentration, from 3% to 12% at $2.8 \times 10^{18}$ Sb atoms/cc and $30 \times 10^{18}$ Sb atoms/cc, respectively. The data accumulation period ranged from four days for the highest antimony concentration samples to about four weeks for the lowest concentration. A typical Mossbauer spectrum for the antimony-doped silicon is shown in Figure 20.

The trend of isomer shift values showed that the s-electron density was lower in antimony-doped silicon than in InSb. The isomer shift value was found to decrease as the concentration of antimony in the silicon lattice increased. This means that the total s-electron density at the antimony nuclear site increases as the antimony concentration increases. This change in s-electron density is surprising, as this means that the number of s-electrons is increasing or the shielding of the s-electrons by the p-orbitals is decreasing as the antimony concentration increases. No net change in isomer shift values resulted from annealing of the samples. Thus the increase in s-electron density at the antimony nuclear site as the antimony concentration is increased in the silicon lattice is probably not due to ordering or clustering of the antimony atoms, as annealing would have changed these effects. The isomer shift values are given in Table VIII for the different single crystal and polycrystalline samples with the various absorber preparation techniques.

No difference in isomer shift value was found, within
Figure 20. Typical Mossbauer absorption spectrum of antimony-doped silicon at 78°K
### TABLE VIII

**ISOMER SHIFT VALUES FOR ANTIMONY-DOPED SILICON**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorber Temp.</th>
<th>Source Temp.</th>
<th>$\delta_{1-200}$, relative to InSb (mm/sec)</th>
<th>$\delta_{201-400}$, relative to InSb (mm/sec)</th>
<th>$\delta_{ave}$, relative to InSb (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.8 \times 10^{18}$ Sb atoms/cc</td>
<td>78°K</td>
<td>78°K</td>
<td>1.34±.13</td>
<td>1.30±.17</td>
<td>1.32±.15</td>
</tr>
<tr>
<td>$4.5 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>1.09±.09</td>
<td>1.07±.09</td>
<td>1.08±.09</td>
</tr>
<tr>
<td>$6.2 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>0.88±.09</td>
<td>0.82±.11</td>
<td>0.86±.10</td>
</tr>
<tr>
<td>$9.2 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>0.69±.08</td>
<td>0.68±.08</td>
<td>0.68±.08</td>
</tr>
<tr>
<td>$9.2 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>0.67±.09</td>
<td>0.70±.09</td>
<td>0.68±.09</td>
</tr>
<tr>
<td>$30 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>-3.13±.08</td>
<td>-3.08±.10</td>
<td>-3.11±.09</td>
</tr>
<tr>
<td>$9.2 \times 10^{18}$</td>
<td>300°K</td>
<td>78°K</td>
<td>-0.69±.16</td>
<td>-0.61±.15</td>
<td>-0.65±.15</td>
</tr>
<tr>
<td>$6.2 \times 10^{18}$</td>
<td>4.2°K</td>
<td>4.2°K</td>
<td>0.76±.21</td>
<td>0.59±.21</td>
<td>0.68±.21</td>
</tr>
<tr>
<td>$6.2 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>0.81±.13</td>
<td>0.87±.15</td>
<td>0.84±.14</td>
</tr>
<tr>
<td>$9.2 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>0.61±.14</td>
<td>0.67±.16</td>
<td>0.64±.15</td>
</tr>
<tr>
<td>$30 \times 10^{18}$</td>
<td>78°K</td>
<td>78°K</td>
<td>-3.02±.12</td>
<td>-3.03±.14</td>
<td>-3.02±.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.58±.20</td>
<td>0.58±.19</td>
<td>0.58±.19</td>
</tr>
</tbody>
</table>
Table VIII (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorber Temp.</th>
<th>Source Temp.</th>
<th>Isomer Shift, $\delta$, relative to InSb (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta_{1-200}$</td>
</tr>
<tr>
<td>30x10$^{18}$***</td>
<td>78°K</td>
<td>78°K</td>
<td>2.92±0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.62±0.05</td>
</tr>
<tr>
<td>30x10$^{18}$****</td>
<td>78°K</td>
<td>78°K</td>
<td>2.86±0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.84±0.06</td>
</tr>
</tbody>
</table>

*Sample annealed at 250°C for 26 hours.

**Powdered samples with particle size less than 30 microns.

***Slab heated in H$_2$ atmosphere at 800°C for 2 hours.

****Slab heated in H$_2$ atmosphere at 1000°C for 5 hours.
experimental error, for single crystal slab absorbers with the same concentration of antimony. Hence no effect was seen that could be attributed to particle size or perhaps surface states.

For the single crystal absorber of silicon with 9.2x10^{18} Sb atoms/cc two experimental conditions (source and absorber at 78°K, and absorber at 300°K while the source was at 78°K) yielded values for the isomer shift which compared within the experimental error. Ruby et.al.\textsuperscript{132} have reported that the isomer shift values for Sn-Sb absorbers when absorber and source were maintained at 78°K, as compared to when the source was at 78°K and absorber was kept at 200°K, gave identical results within the experimental error. The isomer shift values for the 6.2x10^{18} Sb atoms/cc absorber with both source and absorber at 4.2°K, as compared to both source and absorber at 78°K, were identical within limits of experimental error.

The isomer shift values for the 30x10^{18} Sb atoms/cc absorber indicated a Si-Sb semiconductor phase and a second impurity phase. The impurity phase isomer shift value corresponded to the isomer shift value for antimony metal which had been previously reported to be -2.8±0.3\textsuperscript{114}, -3.07±.07\textsuperscript{127}, and -3.07±.02\textsuperscript{132}. Thus the impurity phase was recognized as antimony metal precipitating from the silicon lattice. An antimony metallic precipitate phase had been reported by Kodera\textsuperscript{49} when the antimony concentration in silicon was approximately 2.9x10^{19} atoms/cc. Hence we see the antimony
metal phase precipitating from the silicon lattice at about the solubility limit given by Kodera.49

After the \(30 \times 10^{18}\) Sb atoms/cc sample had been heated in a hydrogen atmosphere for two hours at 800°C, the isomer shift value corresponding to the semiconductor phase increased while the isomer shift value for the antimony metallic phase remained practically constant. Continued heating of the same sample for five hours at 1000°C in a hydrogen atmosphere produced a more pronounced positive isomer shift value for the semiconductor phase than the above heat treatment. Again, however, the metallic phase isomer shift value remained practically constant. Bublik et.al.41 have shown that annealing of moderately-doped semiconductor samples produced a net decrease in the concentration of carriers. The observed change in isomer shift values for the semiconductor phase indicates similar behavior. The resistivity of this sample increased after the prolonged heat treatment at 1000°C (Table VII). This could however be the result of loss of antimony atoms from their lattice sites in the silicon matrix.

The change in the isomer shift value as a function of antimony concentration, observed at 78°C, is shown in Figure 21. The isomer shift vs. antimony concentration (\(10^{18}\) to \(10^{19}\) atoms/cc) for the single-phase single crystal samples were fitted to a straight line by linear least-squares. Figure 22 shows this linear relationship which is in good agreement with the experimental values. Due to the poly-
Figure 21. Isomer shift values for antimony-doped silicon
Figure 22. Isomer shift values for single crystals of antimony-doped silicon.
crystalline sample having two phases and the antimony concentration being somewhat uncertain, this data point has been omitted from the linear least-squares fit and Figure 22. As mentioned previously this behavior was not expected. Hence the observed linewidths were carefully considered, as perhaps a means of detecting any microscopic inhomogeneity in the samples thus explaining this observed change in s-electron density at the antimony nucleus. The linewidths were found to be a little larger (2.5 mm/sec) than the theoretical value of 2.1 mm/sec, but of reasonable value for a single well-resolved peak. These are the narrowest linewidths that have been observed and reported with the sources available. (No electric field gradient was to be expected at the antimony nuclear site, as the nearest neighbors have tetrahedral structure.) The linewidths were found to be relatively constant for the four single crystals but the two phase, Si-Sb and Sb, polycrystalline material showed broadening linewidths, as seen in Table IX. The linewidths for the single crystal samples showed no broadening that could be attributed to a change in environment of the antimony nucleus, such as clustering. The narrow linewidths and absence of extra peaks in the single-phase samples indicates that the antimony occupies only one site in the silicon lattice. The broadened linewidth for the semiconductor phase of the polycrystalline material could be due to a combination of the antimony metallic phase in the silicon lattice and clustering of the antimony atoms. The
TABLE IX
FULL WIDTH HALF MAXIMUM VALUES FOR ANTIMONY-DOPED SILICON

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorber Temp.</th>
<th>Source Temp.</th>
<th>Full Width Half Maximum (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8x10^{18} Sb atoms/cc</td>
<td>78°K</td>
<td>78°K</td>
<td>$\Gamma_{1-200}$</td>
</tr>
<tr>
<td>4.5x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.48±0.35</td>
</tr>
<tr>
<td>6.2x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.51±0.26</td>
</tr>
<tr>
<td>9.2x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.39±0.34</td>
</tr>
<tr>
<td>9.2x10^{18}*</td>
<td>78°K</td>
<td>78°K</td>
<td>2.53±0.26</td>
</tr>
<tr>
<td>30x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.60±0.24</td>
</tr>
<tr>
<td>9.2x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.33±0.34</td>
</tr>
<tr>
<td>9.2x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>3.35±0.38</td>
</tr>
<tr>
<td>30x10^{18}</td>
<td>78°K</td>
<td>78°K</td>
<td>2.34±0.55</td>
</tr>
<tr>
<td>9.2x10^{18}**</td>
<td>78°K</td>
<td>78°K</td>
<td>2.27±0.34</td>
</tr>
<tr>
<td>30x10^{18}**</td>
<td>78°K</td>
<td>78°K</td>
<td>2.39±0.40</td>
</tr>
</tbody>
</table>
Table IX (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorber Temp.</th>
<th>Source Temp.</th>
<th>( \Gamma_{1-200} )</th>
<th>( \Gamma_{201-400} )</th>
<th>( \Gamma_{ave} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3 \times 10^{18}*** )</td>
<td>78°C</td>
<td>78°C</td>
<td>3.02±0.21</td>
<td>2.88±0.19</td>
<td>2.95±0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.22±0.19</td>
<td>2.43±0.19</td>
<td>2.33±0.19</td>
</tr>
<tr>
<td>( 3 \times 10^{18}**** )</td>
<td>78°C</td>
<td>78°C</td>
<td>3.21±0.33</td>
<td>3.12±0.30</td>
<td>3.17±0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.11±0.21</td>
<td>2.35±0.22</td>
<td>2.23±0.21</td>
</tr>
</tbody>
</table>

*Sample annealed at 250°C for 26 hours.

**Powdered samples with particle size less than 30 microns.

***Slab heated in \( \text{H}_2 \) atmosphere at 800°C for 2 hours.

****Slab heated in \( \text{H}_2 \) atmosphere at 1000°C for 5 hours.
heat treatment of the polycrystalline sample could reduce the clustering and result in producing the observed change in value of the isomer shift, as seen for the semiconductor phase in this sample.

As the observed Mossbauer parameters gave no information as to why the s-electron density should change so greatly, the lattice parameter was checked for changes using x-ray diffraction. The Straumanis method was used, as is explained in section III-C. The radiation used was CuK$_{\alpha}$, and the back reflection lines (444$_{\alpha_1}$) were used to determine the lattice constant. These back reflection lines correspond to approximately an 80$^\circ$ Bragg angle. The samples were hand ground using a mortar and pestle, keeping the sample in liquid nitrogen while grinding. The liquid nitrogen was used to keep dislocations to a minimum and to prevent oxidation. The powder was screened through a 400 mesh sieve, which meant that the sifted particles were less than 38 microns in size. The film was placed in an asymmetric position inside a Straumanis camera and exposed for three hours. During exposure the temperature of the sample was maintained at 24.0±0.5°C. The results are given in Table X, including the refraction correction as given by Straumanis et.al.\textsuperscript{161}

The lattice constant was found to increase as the antimony concentration increased and reached saturation at approximately 30x10$^{18}$Sb atoms/cc as seen in Figure 23. The lattice parameter was expected to increase due to the differences in convalent radii of antimony and silicon, 1.35
TABLE X

LATTECE CONSTANTS FOR ANTIMONY-DOPED SILICON

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a_0) (Non-annealed)(^a)</th>
<th>(a_0) (Annealed)(^a, b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>5.4306±0.0001Å</td>
<td>5.4304±0.0001Å</td>
</tr>
<tr>
<td>2.8x10(^{18}) Sb atoms/cc</td>
<td>5.4307±0.0001</td>
<td>5.4305±0.0001</td>
</tr>
<tr>
<td>4.5x10(^{18}) Sb atoms/cc</td>
<td>5.4310±0.0001</td>
<td>5.4307±0.0001</td>
</tr>
<tr>
<td>6.2x10(^{18}) Sb atoms/cc</td>
<td>5.4313±0.0001</td>
<td>5.4308±0.0001</td>
</tr>
<tr>
<td>9.2x10(^{18}) Sb atoms/cc</td>
<td>5.4315±0.0001</td>
<td>5.4309±0.0001</td>
</tr>
<tr>
<td>30x10(^{18}) Sb atoms/cc</td>
<td>5.4316±0.0001</td>
<td>5.4311±0.0001</td>
</tr>
</tbody>
</table>

\(^a\)Corrected for refraction as given by Straumanis et al.\(^6\)

\(^b\)Annealed at 250°C for 26 hours, (Prolonged annealing resulted in no further change in lattice constant.)
Figure 23. Lattice constants for antimony-doped silicon
and 1.176 Å respectively. However, for an antimony concentration of \(10^{19}\) atoms/cc the measured change in lattice constant, \((83\times10^{-5} \text{Å})\), is approximately five times greater than the calculated increase, \((16\times10^{-5} \text{Å})\)\(^1\), considering the above values for the covalent radii. Bublik et al.\(^1\) have reported measuring a change in the lattice constant of antimony-doped silicon \((10^{19}\text{Sb atoms/cc})\) of \(15\times10^{-5} \text{Å}\) as compared to their calculated change of \(16\times10^{-5} \text{Å}\). They have reported a surface dislocation density of \(10^{3}/\text{cm}^{2}\) for their samples. The samples used in these studies were dislocation-free crystals. Bublik et al.\(^1\) also reported precise measurements of lattice constants for antimony-doped germanium \((0.67\times10^{19}\text{Sb atoms/cc})\), for which they measured an increase in lattice constant of \(49\times10^{-5} \text{Å}\) with respect to the lattice constant of germanium. However their calculated change in lattice constant was given as zero, found by considering the concentration of antimony and the difference in covalent radii of germanium and antimony.

As these changes in lattice constants were much greater than those previously observed and calculated\(^1\), a reason for this abrupt behavior was sought. It was believed that stress was the major cause for the disagreement with the previously reported measured change in lattice constants and disagreement with Vegard's law. Perhaps the stress was created by grinding the samples into fine powders to be used in x-ray diffraction analysis. The powdered samples were annealed at 250°C for 26 hours and the lattice constants
were measured again and found to be smaller than those previously measured for the nonannealed samples (see Figure 23 and Table X). The difference in lattice constant for the annealed sample with antimony concentration of 9.2x10^{18} atoms/cc compared to the annealed silicon was measured to be 51x10^{-5}Å, which compares better with the calculated difference of 16x10^{-5}Å. Prolonged annealing (76 hours at 250°C) produced no further decrease in the lattice constants. This difference in lattice constants is still somewhat larger than predicted by Vegard's law, but the values are believed correct. Disagreement with Vegard's law has been observed previously for low impurity concentration in alloys (the measured lattice constant always being greater than predicted by Vegard's law). There seems to be no apparent reason for this behavior. In this particular case, the disagreement with Vegard's law may have been the result of the particular compositions that were studied in which the semiconductor alloy changes from a single-phase to a two-phase material (approaching the solubility limit) as the concentration of antimony is increased in silicon.

Saturation of the lattice constant for the 30x10^{18} Sb atoms/cc sample indicates that additional antimony atoms are precipitating from the silicon lattice as antimony metal. The metallic antimony lattice structure is rhombohedral with \( a_0 \) given as 4.506Å and \( \alpha = 57^\circ 6.5' \). It is known that group V impurities enter the silicon lattice by substitution for normal atoms, rather than by
going into interstitial positions. To confirm this density measurements were performed on the antimony-doped silicon samples by the method described in section III-E. These measurements provide a means of determining if the antimony atoms are going into the lattice substitutionally or interstitially. If the antimony atoms should be going into interstitial sites, the lattice constant would increase more than expected from Vegard's law, and perhaps this would also increase the s-electron density at the antimony nucleus. However, the results indicated that the density was relatively constant for the four single-phase single crystal samples. The density values and the computed number of atoms per unit cell, \( n' \), are given in Table XI. These results indicate that indeed the antimony atoms are going into the silicon lattice substitutionally. Thus the lattice is not expanding due to the antimony atoms being in interstitial positions in the single-phase samples.

The measured density and calculated \( n' \) values did increase for the \( 3 \times 10^{18} \) Sb atoms/cc, two-phase, polycrystalline sample. This behavior was expected due to the metallic antimony phase.

The value of \( n' \) should be close to the ideal value of \( n=8.000 \) if the lattice of silicon is perfect, free of an excess of vacant sites, interstitials and other imperfections within the limits of error. This was the case for the four single-phase single crystalline samples.

Vegard's law predicts a linear increase in lattice
TABLE XI

DENSITY VALUES AND NUMBER OF ATOMS PER UNIT CELL
FOR ANTIMONY-DOPED SILICON

<table>
<thead>
<tr>
<th>Samples (Dislocation-free)</th>
<th>Density, $\rho$ (gm/cc)</th>
<th>$n' = \rho \frac{a^3N_0}{at.\text{wt.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>2.32904± .00009$^a$</td>
<td>8.00004± .00009$^b$</td>
</tr>
<tr>
<td>2.8x10$^{18}$ Sb atoms/cc</td>
<td>2.3293 ± .0003</td>
<td>7.998 ± .001</td>
</tr>
<tr>
<td>4.5x10$^{18}$ Sb atoms/cc</td>
<td>2.3291 ± .0003</td>
<td>7.998 ± .001</td>
</tr>
<tr>
<td>6.2x10$^{18}$ Sb atoms/cc</td>
<td>2.3292 ± .0003</td>
<td>7.997 ± .001</td>
</tr>
<tr>
<td>9.2x10$^{18}$ Sb atoms/cc</td>
<td>2.3294 ± .0003</td>
<td>7.997 ± .001</td>
</tr>
<tr>
<td>30x10$^{18}$ Sb atoms/cc</td>
<td>2.3417 ± .0003</td>
<td>8.028 ± .001</td>
</tr>
</tbody>
</table>

$^a$From Henins and Bearden$^{163}$

$^b$From Straumanis et.al.$^{161}$
constant as the antimony concentration is increased, if the antimony atoms are going into the lattice sites substitutionally. Therefore as the polycrystalline sample has an antimony metallic phase, as well as a semiconductor phase, and a value of \( n' \) larger than 8.000 this data point was omitted from a plot of the lattice constant vs. antimony concentration between \( 10^{18} \) and \( 10^{19} \) atoms/cc. Figure 24 shows that linear relationship between the lattice constant and the concentration of single crystals of antimony-doped silicon for the annealed and nonannealed samples.

That the antimony atoms are going into the lattice sites substitutionally and that the lattice constant and s-electron density are increasing as the antimony concentration increases, may imply a correlation between the isomer shift value and the lattice constant. A linear least-squares fit is shown in Figure 25 for the lattice constant plotted against isomer shift value for the single-phase samples. The increase in s-electron density at the antimony nucleus, observed as the concentration of antimony in silicon increases, could be the result of either an increase in the number of s-electrons or a decrease in the number of p-electrons, because p-electrons tend to screen the nucleus from electrons of s character, or perhaps both effects occurring simultaneously.

A linear least-squares fit of isomer shift vs. lattice constant for the four single-phase single crystal samples and also for the two-phase polycrystalline sample is plotted
Figure 24. Lattice constants for single crystals of antimony-doped silicon

\[ a_0 = 5.4306_0 + (0.9963_4 \pm 0.1513_7) y \]

Nonannealed

\[ a_0 = 5.4304_5 + (0.6012_2 \pm 0.0788_4) y \]

Annealed
Figure 25. Isomer shift vs. lattice constant for annealed single crystal antimony-doped silicon

\[ \delta = 7931.9 - (1460.4 \pm 110.5) a_0 \]
in Figure 26. The isomer shift vs. lattice constant for these samples also has a linear relation.

Ruby et al.\textsuperscript{132} have done Mossbauer studies of Sn-Sb alloys in which they reported that the isomer shift behavior indicated changes in the s-electron density which must result principally from changes in the occupation of p (or higher order angular momentum) states. They have reported that their data were consistent with the idea that each atom in the alloy is strongly screened. Rigney and Flynn\textsuperscript{134} have also attributed the variation and magnitude of the Knight shift of antimony in liquid solutions of antimony and tin to s-structure saturation and p-wave scattering alone. Ruby et al.\textsuperscript{132} have mentioned that the volume of the unit cell increases with increasing antimony concentration in these alloys. For the antimony-rich alloys, the s-electron density at the antimony nucleus increased and the isomer shift value became more negative as the antimony concentration was increased. This suggests that the change in s-electron density could be a volume effect. However for the tin-rich alloys the s-electron density decreased as the antimony concentration increased. Hence the volume change and s-electron density change relation are unlikely to give a complete explanation.

It is seen that at higher antimony concentrations there is a marked increase in $|\psi(0)|^2$, the electron density at the nucleus. The observed increase is many orders of magnitude greater than the direct contribution of the conduction
Figure 26. Isomer shift vs. lattice constant for annealed antimony-doped silicon
electrons at the nucleus (as the concentration is increased from $10^{18}$ to $10^{19}$ Sb atoms/cc), and must come about through some other effect. The increase in the isomer shift is about one tenth that caused by the addition of one s-electron to the antimony atom.

In these Mossbauer studies there is a linear relationship between the change in s-electron density at the antimony nucleus and the change in lattice constant (volume) of the antimony-doped silicon lattice as the antimony concentration is increased. From the results of previous studies it seems reasonable to postulate that the increase in s-electron density at the antimony nucleus, which implies that the isomer shift becomes more negative, is due to decreasing p-electron shielding, resulting in a net increase in observable s-electron character as the antimony concentration is increased in the antimony-doped silicon lattice.

B. Bismuth-Antimony Alloys

The lattice structures of bismuth and antimony are hexagonal with lattice constants for the $a_0$ parameter of 4.546Å and 4.308Å and for the $c_0$ parameter values of 11.862Å and 11.273Å respectively. A continuous solid solution of the same structure type exists between bismuth and antimony, as given by Hansen.

Bismuth-antimony alloys were prepared as discussed in section III-F. The resulting powders were checked for impurity phases using the Siemens x-ray diffractometer. No impurity phases were found in the Bi-Sb alloys.
radiation used was CuKα for the lattice constant measurements at room temperature. The resulting diffraction pattern was displayed on graph paper from which the 2θ diffraction angles were measured. Only the (110) and (006) diffraction lines were used to determine the a₀ and c₀ lattice constants. These diffraction lines correspond to diffraction angles of 2θ equal to 42 and 48 degrees respectively. The lattice constants measured for these alloys are given in Table XII. They are in good agreement with the values reported by Cucka and Barrett. A plot of the lattice constants against atomic percent antimony in bismuth is shown in Figure 27. The anomalous behavior in the c₀ lattice constant in the range between 4 and 8 atomic percent antimony in these alloys, as reported by Jain, was not observed in these measurements. Neither did Cucka and Barrett confirm the anomalies which Jain showed in the lattice constant of the c₀-axis. Both lattice constants of the Bi-Sb alloys vary linearly in the composition range of 0 to 75 atomic percent antimony. However, above 75 atomic percent antimony the c₀ lattice constant deviates from a linear relationship while the a₀ value retains the linear slope.

The rhombohedral crystal structures of bismuth and antimony semimetals indicate that they all have structures which are weak distortions of more symmetrical cubic structures. Consider two, interpenetrating, fcc sublattices, displaced relative to each other along a body diagonal while having a slight deformation, and the resulting structure is
TABLE XII

LATTICE CONSTANT VALUES FOR BISMUTH-ANTIMONY ALLOYS

AT ROOM TEMPERATURE

<table>
<thead>
<tr>
<th>Sample (Atomic %)</th>
<th>( a_0 (\text{Å}) )</th>
<th>( c_0 (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4.546\textsuperscript{a}</td>
<td>11.862</td>
</tr>
<tr>
<td>Bi\textsubscript{95}Sb\textsubscript{5}</td>
<td>4.54\textsubscript{2±.01}</td>
<td>11.85\textsubscript{9±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{90}Sb\textsubscript{10}</td>
<td>4.52\textsubscript{4±.01}</td>
<td>11.81\textsubscript{2±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{85}Sb\textsubscript{15}</td>
<td>4.51\textsubscript{8±.01}</td>
<td>11.79\textsubscript{8±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{80}Sb\textsubscript{20}</td>
<td>4.50\textsubscript{6±.01}</td>
<td>11.78\textsubscript{0±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{75}Sb\textsubscript{25}</td>
<td>4.47\textsubscript{9±.01}</td>
<td>11.74\textsubscript{0±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{70}Sb\textsubscript{30}</td>
<td>4.46\textsubscript{4±.01}</td>
<td>11.69\textsubscript{0±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{65}Sb\textsubscript{35}</td>
<td>4.44\textsubscript{9±.01}</td>
<td>11.66\textsubscript{0±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{60}Sb\textsubscript{40}</td>
<td>4.44\textsubscript{0±.01}</td>
<td>11.63\textsubscript{6±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{55}Sb\textsubscript{45}</td>
<td>4.42\textsubscript{5±.01}</td>
<td>11.60\textsubscript{8±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{50}Sb\textsubscript{50}</td>
<td>4.39\textsubscript{0±.01}</td>
<td>11.51\textsubscript{5±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{45}Sb\textsubscript{55}</td>
<td>4.37\textsubscript{2±.01}</td>
<td>11.48\textsubscript{3±.01}</td>
</tr>
<tr>
<td>Bi\textsubscript{40}Sb\textsubscript{60}</td>
<td>4.30\textsubscript{4±.01}</td>
<td>11.27\textsubscript{5±.01}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Wychoff\textsuperscript{162}
Figure 27. Lattice constant values for bismuth-antimony alloys
(The error in measured lattice constants is ±0.01Å.)
that of bismuth, antimony and their alloys\textsuperscript{165}.

The powders of the Bi-Sb alloys were used as Mossbauer absorbers. Both the CaSnO\textsubscript{3}(Sb\textsuperscript{121}) source and Bi-Sb alloy powder absorber were maintained at 78\textdegree{}K for the Mossbauer studies. The count rate varied from 22 to 36 counts/sec for 400 channels. The Mossbauer spectra were obtained over periods of 2 to 28 days, for a total number of counts per channel ranging from 10,000 to 110,000. The percentage absorption effect varied from 4 to 28. The samples with the least atomic percentage of antimony required a larger accumulation of counts (because of the small percentage absorption effect) and thus long periods of observation if the Mossbauer parameters were to be defined within small limits of error. A typical Mossbauer spectrum for the Bi-Sb alloys is shown in Figure 28.

The results of the isomer shift measurements are given in Table XIII. The isomer shift value was observed to become more negative in the region where the alloy makes a transition from semimetallic to semiconductor, approximately 5 atomic percent antimony. The isomer shift value reached its maximum negative value at approximately 20-25 atomic percent antimony. Where behavior of the alloy indicated a semiconductor to semimetallic transition, between 45-55 atomic percent antimony, the isomer shift value shifted to a less negative value and gradually grew to an even less negative value as the atomic percent of antimony was increased.

Montgomery and Ruby\textsuperscript{131} have pointed out that in a
Figure 28. Mossbauer spectrum for bismuth-antimony alloy at 78°K
<table>
<thead>
<tr>
<th>Sample (Atomic %)</th>
<th>Isomer Shift Relative to InSb (mm/sec)</th>
<th>( \delta_{1-200} )</th>
<th>( \delta_{201-400} )</th>
<th>( \delta_{\text{ave}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(<em>{95})Sb(</em>{5})</td>
<td>-2.93±0.10</td>
<td>-3.06±0.11</td>
<td>-3.00±0.10</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{90})Sb(</em>{10})</td>
<td>-3.07±0.08</td>
<td>-3.22±0.07</td>
<td>-3.14±0.07</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{85})Sb(</em>{15})</td>
<td>-3.15±0.06</td>
<td>-3.29±0.07</td>
<td>-3.22±0.06</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{80})Sb(</em>{20})</td>
<td>-3.21±0.05</td>
<td>-3.27±0.05</td>
<td>-3.24±0.05</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{75})Sb(</em>{25})</td>
<td>-3.23±0.04</td>
<td>-3.31±0.05</td>
<td>-3.27±0.04</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{65})Sb(</em>{35})</td>
<td>-3.21±0.04</td>
<td>-3.23±0.04</td>
<td>-3.22±0.04</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{60})Sb(</em>{40})</td>
<td>-3.20±0.04</td>
<td>-3.22±0.04</td>
<td>-3.21±0.04</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{55})Sb(</em>{45})</td>
<td>-3.14±0.04</td>
<td>-3.22±0.04</td>
<td>-3.18±0.04</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{45})Sb(</em>{55})</td>
<td>-3.05±0.03</td>
<td>-3.16±0.03</td>
<td>-3.11±0.03</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{35})Sb(</em>{65})</td>
<td>-3.08±0.03</td>
<td>-3.14±0.03</td>
<td>-3.11±0.03</td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{25})Sb(</em>{75})</td>
<td>-3.04±0.04</td>
<td>-3.10±0.04</td>
<td>-3.07±0.04</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-3.02±0.03</td>
<td>-3.08±0.03</td>
<td>-3.05±0.03</td>
<td></td>
</tr>
</tbody>
</table>
metallic alloy electrostatic charges are subject to powerful screening by conduction electrons. Thus it seems reasonable that as the valence and conduction bands overlap in the metallic behavior region of the Bi-Sb alloys, the conduction electron screens the s-electrons more strongly, resulting in a net decrease of s-electron density at the antimony nucleus. When the alloy transfers from semimetallic to semiconductor behavior, a gap appears between the conduction and valence bands resulting in a lesser conduction electron screening effect and a net increase in measurable s-electron density at the Sb nucleus. A plot of isomer shift, \( \delta \), against atomic percent antimony (Figure 29) shows this type of behavior.

These results are consistent with the resistivity values reported by various investigators. The resistivity of the Bi-Sb alloys with antimony concentrations between 5 and 45-55 atomic percent increased as the temperature was lowered below 100°K. Thus in this region the Bi-Sb alloys were deduced to be intrinsic semiconductors. The resistivity was measured to be a maximum between 15 and 25 atomic percent antimony, correlating with the peak observed in the isomer shift. The Bi-Sb alloys have been shown to possess semimetallic behavior for antimony concentrations of 0 to 5 and 45-55 to 100 atomic percent below 100°K. The increase in resistivity for the semiconductor region as compared to the semimetallic regions at 78°K is roughly an order of magnitude.
Figure 29. Isomer shift vs. atomic percent antimony in bismuth-antimony alloys.
The band structure has been calculated for bismuth and showed two points in the Brillouin zone where the valence and conduction bands overlapped, providing the carriers for the semimetallic characteristics of bismuth. These symmetry points were labeled T and L. Dresselhaus and Mavroides showed that carriers were not present at L nor T in the band structure for antimony. Golin and Lerner et al. suggested that the L-point energy gap (in the band structure) does not remain constant but changes with antimony alloying.

Blount and Cohen have explained the semimetallic-semiconductor transition for the Bi-Sb alloys in terms of the band structure, and their theory is consistent with the change in value of the isomer shift for these alloys. The addition of antimony causes the light mass bands to shift relative to the heavy bands resulting in a decrease of overlapping between the light conduction band and the heavy valence band. Thus an energy gap emerges and remains until the antimony concentration exceeds 45-55 atomic percent, where the alloy again displays semimetallic behavior. It seems likely, from these results, that the light conduction band has started overlapping some other set of bands in a manner which will be in accordance with the structure of antimony (Figure 6).

Brown and Silverman attempted to explain the semimetallic-semiconductor-semimetallic transitions by other models, but concluded that Blount and Cohen's model for Bi-Sb alloys containing between approximately 10 and 45-55
atomic percent antimony may be qualitatively correct.

From the linewidth values given in Table XIV, it is interesting to note the behavior of FWHM plotted against atomic percent antimony (Figure 30) for the Bi-Sb alloys. This behavior may also result from some type of order-disorder transition in the Bi-Sb compositions. The FWHM was measured to be greater in the metallic behavior region than observed in the semiconductor region. Though the single-line Mossbauer absorption spectra were broad for some absorbers, there was no evidence for the eight-line quadrupole hyperfine splitting which would have been apparent from asymmetry of the absorption lines.

The linewidth (4.34±0.42 mm/sec) for the 5 atomic percent antimony alloy was very broad, and attempts were made to fit the Mossbauer data to an eight line spectrum. However the Parlors and Shawfit computer programs could not resolve the absorption spectrum for eight lines. Perhaps an impurity phase is present in the alloy, causing the broad linewidth, but several attempts showed that the data could not be fitted to a two line absorption spectrum with either of the computer programs. Dokuzoguz et.al.\textsuperscript{122} have reported linewidths for Ni-Sb alloys which ranged from 3.49±0.08 to 5.0±0.4 mm/sec, the largest linewidth corresponding to the sample with the least concentration of antimony. They have attributed these large linewidths to the imperfect nature of their source as well as due to unresolved quadrupole splitting. It is believed that the large linewidth
### TABLE XIV

**FULL WIDTH HALF MAXIMUM VALUES FOR BISMUTH-ANTIMONY ALLOYS**

<table>
<thead>
<tr>
<th>Sample (Atomic %)</th>
<th>( \Gamma_{1-200} )</th>
<th>( \Gamma_{201-400} )</th>
<th>( \Gamma_{ave} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(<em>{95})Sb(</em>{5})</td>
<td>4.38±0.42</td>
<td>4.30±0.42</td>
<td>4.34±0.42</td>
</tr>
<tr>
<td>Bi(<em>{90})Sb(</em>{10})</td>
<td>3.15±0.37</td>
<td>2.96±0.28</td>
<td>3.06±0.32</td>
</tr>
<tr>
<td>Bi(<em>{85})Sb(</em>{15})</td>
<td>2.78±0.22</td>
<td>2.98±0.24</td>
<td>2.88±0.23</td>
</tr>
<tr>
<td>Bi(<em>{80})Sb(</em>{20})</td>
<td>2.67±0.18</td>
<td>2.83±0.23</td>
<td>2.75±0.20</td>
</tr>
<tr>
<td>Bi(<em>{75})Sb(</em>{25})</td>
<td>2.58±0.17</td>
<td>2.66±0.15</td>
<td>2.62±0.16</td>
</tr>
<tr>
<td>Bi(<em>{65})Sb(</em>{35})</td>
<td>2.60±0.17</td>
<td>2.71±0.18</td>
<td>2.65±0.17</td>
</tr>
<tr>
<td>Bi(<em>{60})Sb(</em>{40})</td>
<td>2.66±0.15</td>
<td>2.74±0.13</td>
<td>2.70±0.14</td>
</tr>
<tr>
<td>Bi(<em>{55})Sb(</em>{45})</td>
<td>2.85±0.13</td>
<td>2.74±0.12</td>
<td>2.80±0.12</td>
</tr>
<tr>
<td>Bi(<em>{45})Sb(</em>{55})</td>
<td>3.02±0.10</td>
<td>3.11±0.11</td>
<td>3.07±0.10</td>
</tr>
<tr>
<td>Bi(<em>{35})Sb(</em>{65})</td>
<td>3.07±0.10</td>
<td>3.12±0.11</td>
<td>3.10±0.10</td>
</tr>
<tr>
<td>Bi(<em>{25})Sb(</em>{75})</td>
<td>3.19±0.14</td>
<td>3.24±0.14</td>
<td>3.21±0.14</td>
</tr>
<tr>
<td>Sb</td>
<td>3.14±0.14</td>
<td>3.21±0.16</td>
<td>3.17±0.15</td>
</tr>
</tbody>
</table>
Figure 30. FWHM vs. atomic percent antimony in bismuth-antimony alloys
measured for the 5 atomic percent antimony alloy could be due to the antimony environment being inhomogeneous, as well as to an unresolved splitting.

Montgomery and Ruby\textsuperscript{121} have reported that the linewidths measured in the Pd-Sb alloys tend to increase with increasing antimony concentration. However for the Bi-Sb alloys this effect was not observed.

Cucka and Barrett\textsuperscript{97} have shown that the atomic positional parameter, \( z \), remained practically constant in the Bi-Sb alloys in the range of 0 to 12 atomic percent antimony. Above 12 atomic percent antimony the atomic positional parameter increased as the antimony concentration increased. This value must decrease at some antimony composition, however, as pure antimony has a smaller value for the atomic positional parameter than pure bismuth, (0.23364 as compared to 0.23400\( \text{Å} \)).\textsuperscript{170} This change in the atomic positional parameter may produce the measurable decrease in linewidth found in these studies for the antimony composition range of 10 to 45 atomic percent, as in this range the value of \( z \) is closer to the value for a cubic lattice of 0.250 and therefore the atoms should be in higher symmetry environments.

However, the linewidth behavior may be explained more rigorously by the band structure of the Bi-Sb alloy system. There is a higher density of conduction electrons in the semimetallic regions as opposed to the semiconductor region for the Bi-Sb alloys. This density increase in conduction
electrons results in an increased interaction with the s-electron core of the atoms, creating a local deformation of the lattice.

Perhaps the most important effect of the lattice deformation is the attendant increase in the effective mass of the electron. Because the ion cores are set into motion when the electron moves, the electron acts as if its mass was increased.\textsuperscript{13} Smith\textsuperscript{78} has reported that the electron effective mass for a Bi-Sb alloy with 5 atomic percent antimony was one half that for pure bismuth and that the hole masses are essentially unchanged.

From previous studies, it is believed that the observed linewidth behavior is due to the semimetallic regions having a larger lattice deformation than the semiconductor range of Bi-Sb alloys. Thus it is proposed that this enhanced deformation of the lattice in the semimetallic regions broadens the linewidths because of unresolved quadrupole splitting while the semiconductor region has a much smaller lattice deformation and measured narrower linewidths.

The measured values for the isomer shift and linewidth of -3.05±0.03 and 3.15±0.17 mm/sec respectively for antimony metal agrees very well with the values previously reported\textsuperscript{127} as being -3.07±0.07 and 2.85±0.07 mm/sec, respectively.
V. SUMMARY AND CONCLUSIONS

The results obtained in these Mossbauer investigations, x-ray diffraction studies and resistivity measurements are given below, with indications for further studies.

A. Antimony-Doped Silicon

The primary results obtained from the antimony-doped silicon absorber samples can be summarized as follows:

1. The isomer shift value was observed to decrease linearly as the antimony concentration increased between $10^{18}$ and $10^{19}$ atoms/cc. The observed increase in s-electron density at the antimony nucleus as the antimony concentration increases is many orders of magnitude greater than the direct contribution of the conduction electrons at the nucleus. This change in s-electron density at the antimony nucleus represents an s-electron transfer of 0.1 electron. The isomer shift showed no change in value for annealed samples as compared to nonannealed samples.

2. The lattice constant of the antimony-doped silicon was found to increase linearly between the antimony concentrations of $10^{18}$ and $10^{19}$ atoms/cc. The lattice constants decreased when the powder samples were annealed at 250°C for 26 hours. The changes in the measured lattice constants between the annealed and nonannealed samples were believed to be the result of annealing the residual stress, created by grinding the single crystal chips. The increase in lattice constants for the annealed samples are three times greater than
expected from Vegard's law. Density measurements showed that the antimony atoms were in substitutional lattice sites for antimony concentrations of $10^{18}$ to $10^{19}$ atoms/cc. The single-phase single crystal samples were found to be dislocation-free as claimed by Monsanto. Deviations from Vegard's law have been observed by other investigators for low impurity concentrations in alloys. Perhaps this observed deviation is an effect due to the narrow region of study and some abnormal behavior at the solubility limit of antimony-doped silicon, which is $2.9 \times 10^{19}$ antimony atoms/cc.

3. The isomer shift, when plotted against lattice constant for antimony concentrations in the region of $10^{18}$ to $10^{19}$ atoms/cc, exhibits a linear relation. The conclusion is that the expansion of the lattice on doping silicon with antimony is accompanied by an increase in the $s$-electron density at the antimony nucleus. The expansion of the lattice would be expected to result in drawing the $p$-electrons further from the nucleus. This reduces the shielding of the $s$-valence electrons causing them to contract toward the nucleus, and resulting in an increase in the $s$-electron density at the antimony nucleus. These are the results that have been seen experimentally by the isomer shift and lattice constant data.

It is concluded that the increased lattice constant causes the $p$-orbitals to push outward, which enhances the $s$-electron density at the antimony nucleus.

Several secondary results were obtained in these studies
of antimony-doped silicon which can be summarized as follows:

1. Four-point probe resistivity measurements showed that between 2.8 and $4.5 \times 10^{18}$ antimony atoms/cc the behavior of antimony-doped silicon changed from semiconductor to semimetallic.

2. The second phase of the polycrystalline sample with antimony concentration of $30 \times 10^{18}$ atoms/cc has been attributed to antimony metal. This is consistent with the results reported by Kodera, who found an antimony metallic phase in antimony-doped silicon with an antimony concentration of $2.9 \times 10^{19}$ atoms/cc or greater.

3. The powder samples with particles less than thirty microns in size showed the same isomer shift values within limits of experimental error as the bulk crystalline samples. Thus no change in isomer shift resulted from a particle size effect.

4. The annealed sample with concentration of $30 \times 10^{18}$ Sb atoms/cc showed an increase in isomer shift value for the semiconductor phase as compared to the same absorber without heat treatment. Prolonged annealing at a higher temperature produced more drastic changes in the isomer shift, which became more positive. The isomer shift value for the antimony metallic phase remained constant throughout the annealing. This change in the semiconductor phase behavior could be explained as due to a net decrease in the number of charge carriers, which has been observed by Bublik et al. from
Hall measurements with annealed moderately-doped n-type and p-type germanium samples. A difference was found in the measured resistivity for the annealed as compared to the non-annealed sample of $3 \times 10^{18}$ Sb atoms/cc, with the annealed sample having the larger resistivity value.

5. No difference was observed in the isomer shift value when the $9.2 \times 10^{18}$ Sb atoms/cc absorber was kept at 78°K as compared to the spectrum when the absorber was maintained at 300°K, the source being at 78°K for both spectra. Isomer shifts values reported for Sn-Sb alloys using similar temperature environments were shown to be temperature independent between absorber temperatures of 78°K and 200°K.

6. The isomer shift value observed for the $6.2 \times 10^{18}$ Sb atoms/cc absorber, with both it and the source at 4.2°K, was found to be equivalent to the isomer shift value measured with the same absorber and source at 78°K. However, as the $6.2 \times 10^{18}$ Sb atoms/cc absorber has metallic behavior, a change in the value of the isomer shift would not be expected between 78°K and 4.2°K, as the extra electron provided by the antimony atoms is "free" at both temperatures. The absorber with an antimony concentration of $2.8 \times 10^{18}$ atoms/cc shows semiconductor behavior, (high resistivity at 4.2°K) so perhaps a change in isomer shift value would be detected between the temperature at which the extra electron should be relatively "free" (78°K) and the temperature at which the extra electron is fairly well "localized" (4.2°K). Using the s-electron density value at the antimony nucleus in
silicon given by Feher\textsuperscript{164} at 4.2°K, the calculated change in isomer shift value between the "localized" and "free" electron state should be 0.14 mm/sec. This value is obtained by considering Feher's given s-electron density value for the "localized" state and a free electron gas system, to obtain the s-electron density at the antimony nucleus for a "free" electron state with the appropriate values substituted in equation 27. This would mean that the isomer shift value should become more negative for the 2.8x10\textsuperscript{18} Sb atoms/cc absorber measured at 4.2°K, as compared to the measured isomer shift value for 78°K absorber temperature. Because of the small change in isomer shift, however, a measurement of the effect would require two long periods of data accumulation, one spectrum with both the absorber and source maintained at 78°K and the other spectrum with the source and absorber at 4.2°K. The periods of observation would be about a year, which is not a practical experiment for this absorber.

B. Bismuth-Antimony

The results obtained from the Bi-Sb alloy absorber samples can be summarized with conclusions as follows:

1. The a\textsubscript{0} and c\textsubscript{0} lattice constants for the Bi-Sb alloys decreased linearly with increasing antimony concentration up to about 75 atomic percent. Above 75 atomic percent antimony, the c\textsubscript{0} lattice constant deviated from a linear slope while the a\textsubscript{0} value retained the linear relation. The lattice constants were in agreement with the values previously
reported$^{76,97}$, but anomalous behavior in the $c_0$-axis was not seen for antimony concentrations of 4 to 8 atomic percent, as reported by Jain$^{76}$.

2. The isomer shift was found to be most negative in the antimony concentration range of 10 to 45-55 atomic percent, showing a maximum negative value at approximately 20 to 25 atomic percent antimony. The isomer shift value indicates that the $s$-electron density at the antimony nucleus is larger in the semiconductor region than in the semimetallic regions of the Bi-Sb alloy system. It is known that conduction electrons screen the $s$-valence electrons greatly in a metallic alloy.$^{131}$ Thus the shielding by the conduction electrons of the $s$-valence electrons would be greater in the semimetallic regions than in the semiconductor range. Therefore the $s$-electron density at the antimony nucleus would be greater in the semiconductor region as opposed to the semimetallic regions, which is verified by the isomer shift data. This conclusion is in agreement with the bismuth, and Bi-Sb alloy band model proposed by Blount and Cohen$^{76}$ and results from other structural studies.$^{165-169}$ Blount and Cohen's model$^{76}$ is identical with the existing ideas of how the energy spectrum of Bi-Sb alloys changes as proposed by other authors.$^{82,84,85,90,93}$

3. The linewidth showed a minimum value in the semiconductor range as compared to the semimetallic behavior regions. This implies that the 10 to 45-55 atomic percent antimony compositions have a more symmetrical environment, or that these
semiconductor alloys have more order than the regions of alloys displaying semimetallic behavior. These results agree with the atomic positional parameter values for bismuth, antimony and Bi-Sb alloys$^{97,170}$, which indicate that the Bi-Sb alloys with antimony concentration greater than 12 atomic percent have higher symmetry than either pure bismuth or antimony.

This particular behavior in the measured linewidth vs. atomic percent antimony can, however, be explained by the lattice deformation caused by the conduction electrons interaction with the s-electron core of the atoms. Because of the increased density of conduction electrons, the lattice deformation is expected to be larger for the semimetallic regions than for the semiconductor region of the alloy system. The larger lattice deformation could cause an increase in the measured linewidth due to unresolved quadrupole splitting. This is in agreement with the experimental data which shows a narrower linewidth in the semiconductor region as compared to the semimetallic regions.

4. The Mossbauer studies show that the semiconductor range may be a more ordered system and has a larger s-electron density at the antimony nucleus than the semimetallic regions. These results seem to imply a correlation between the lattice distortion and band structure. Cucka and Barrett$^{97}$ have suggested that perhaps the addition of more than 12 atomic percent antimony shifts the bands so as to increase the atomic positional parameter, $z$, and at the same
time change the residual resistivities. Kao et al.\textsuperscript{66} have suggested that the energy gap in bismuth and its alloys may be associated with the displacement of the sublattices, and the overlap of the hole and electron bands may be associated with the rhombohedral distortion and spin-orbit interaction. Brandt and Shchekochikhina\textsuperscript{90} have shown that changes in the energy spectrum of the bismuth electrons can be fully explained by the changes in lattice parameter of bismuth under the influence of antimony impurities.

5. Band structure studies can be done with single crystals of Bi-Sb alloys using Mossbauer spectroscopy. Single crystals are needed to do directional Mossbauer studies, in which investigation of the valence band and conduction band overlap at the L and T symmetry points in the Brillouin zone can be done. It may be difficult to prepare large, homogeneous, Bi-Sb single crystal alloys. However once the large single crystals are grown, directional studies would not be difficult and would be of considerable importance for the band structure determination of antimony and Bi-Sb alloys.

Semiconductor-semimetallic-semiconductor transitions have been observed with the Bi-Sb alloys placed under external conditions such as magnetic fields or pressure.\textsuperscript{94}, \textsuperscript{171,172} Hence Mossbauer studies could be done using these absorbers placed in magnetic fields or under pressure.
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VITA

James Ralph Teague was born March 16, 1946, in Asheville, North Carolina. He attended primary and secondary schools in Asheville, graduating from Clyde A. Erwin High School in 1964.

He received his B.A. from the University of North Carolina-Asheville in Physics in 1967. During the latter part of studies at UNCA he was also employed as a Research Assistant in the Physical Research and Development Division of American Enka Corporation, where he co-authored five publications.

He received his M.S. from the New Mexico Highlands University in Physics in 1968. Title of his thesis was, "Development of a Soft X-ray Spectroscopy System".

He has been enrolled in the Graduate School at the University of Missouri-Rolla since 1968. During his graduate program at UMR, he was a research assistant supported by the Atomic Energy Commission and the U.S. Air Force.

He married the former Dianne McIntyre in 1965, and they have one son, Jeffrey David.
APPENDICES

A. Absorber Thickness Calculation

The effective absorber thickness can be calculated from the equation:
\[ T = f n a_0 t, \]  
(A-I-1)
where \( f \) is the fraction of gamma rays absorbed without energy loss,
\( n \) is the number of atoms per cubic centimeter,
\( a \) is the fractional abundance of the resonantly absorbing atoms,
\( a_0 \) is the absorption cross section at resonance,
\( t \) is the absorber thickness.

For a \( 1/e \) absorption, the amount of antimony needed to observe a Mossbauer spectrum is given as: \[ n \approx \frac{1}{\sigma_0}. \]

The resonance absorption cross section can be calculated from the equation:
\[ \sigma_0 = \frac{\lambda^2}{2\pi} \left[ \frac{1+2I_E}{1+2I_G} \right] \left[ \frac{1}{1+\alpha} \right], \]  
(A-I-2)
where \( \lambda \) is the wavelength of the emitted gamma ray,
\( I_E \) and \( I_G \) are the nuclear spins of the excited state and ground state respectively,
\( \alpha \) is the internal conversion coefficient of the gamma transition.

With the substitution of these known values for the Sb\(^{121}\) nucleus in equation (A-I-2), the resonance absorption cross section was calculated to be \( 2.3 \times 10^{-19} \text{ cm}^2 \).

From the known value of \( \sigma_0 \), the number of antimony atoms
per square centimeter needed to observe this Mossbauer spectrum was shown to be $7.6 \times 10^{18}$ within less than an order of magnitude. Mossbauer spectra were obtained for antimony concentrations of $2.8$ and $4.5 \times 10^{18}$ atoms/cc. However the spectra had a percentage absorption of 3 and 5 and required accumulation periods of 17 and 27 days respectively.
B. Parlor Computer Program Modified for IBM 360-50

The Parlor program makes a least-squares fit of the data to as many as twenty Lorentzian line shapes and a background parabola. This parabola approximates the effects of nonlinearity in the drive or certain geometric effects due to the source moving with respect to the detector.

The program takes the initial guesses for peak positions and halfwidths and attempts to fit the data to a theoretical Lorentzian line. If the values do not agree, new values of peak positions and halfwidths are calculated and the next iteration is begun. The program stops if the difference between iterations is less than the specified error or after a specified number of iterations, whichever comes first. The program faults if the least square matrix is singular, because no unique inverse can be found for it. The program tries to make adjustments for large errors by altering the halfwidth until usable values are acquired.

The program prints out the parameters of the fit, error analyses, and plots of the data and theoretical fit. The program consists of the main control program and three subroutines: READLD, DPINUS, and PARLOR. READLD reads in the data and prepares it for analysis. DPINUS is a double precision matrix inversion routine used in solving the least square matrix. PARLOR does the curve fitting and output control, including the error analysis and plotting.

The computer program was listed in Canner's thesis and is not reproduced here. However, the instructions were
different, as he had inserted a correction factor for his iron studies which was not needed in these antimony studies. These instructions are listed on the following pages.
Instructions for Using PARLORS Program for Evaluating Mossbauer Spectra

The data cards are arranged in the following order:

I. **Card 0** NSETS Format (I2)
   
   This is the total number of data sets to be fit at this time. If 200 (400) channels are the full spectrum then each 200 (400) channels adds one to NSETS. This card must be included once each time the program is used.

II. All succeeding data cards are needed for each spectrum.

   **Card 1** MØ(1), MØ(2), MØ(3), MØ(4) Format (4I2)
   
   These four variables control different output modes.

   - MØ(1) = 0 plots on calcomp plotter.
     = 1 plots on high speed printer.
   - MØ(2) = 0 no residue plot is obtained.
     = 1 residue plot is obtained.
   - MØ(3) = 0 no numerical data is printed out.
     = 1 numerical data is printed (normalized data, calculated, and residual)
   - MØ(4) = 0 1-400 channels are called for at once.
     = 1 1-200 channels are called for at once.
     = 2 1-200 channels are called for at once and an impurity correction, called Be-Fe impurity here, can be made.
negative 1-400 channels are called for at once and data is folded.

**Card 2**

**IT, ER Format (I2, F14.4)**

**IT=** Number of iterations called for (maximum).

If the refinement criterion is not met after IT iterations the message "convergence not met in specified number of iterations" is printed out as well as data. Depending upon the scatter of the data IT is usually from 5 to 20.

**ER=** acceptable error of fit between iterations.

For poor data use 0.1 channel down to 0.001 for very good data.

**Card 3**

**OV Format (F4.0)**

The number of overflows of $10^6$ counts in memory.

0.0 for less than 999,999 cts.
1.0 between 1,000,000 and 1,999,999 cts.
2.0 between 2,000,000 and 2,999,999 cts., etc.

**Card 4**

Title or label cards Format (18A4) generally used to identify sample.

**Card 5**

**Card 6**

Format (18A4) another label card.

This card is generally used to identify channels of interest. When the spectrum only uses 200 channels, i.e. MO(4)=1,2,
this is the first data card needed for the analysis of channels 201-400.

**Card 7**

J Format (I3)

This card activates the bad channel routine which permits the program to ignore any channel which has bad data. There must be one card present for each bad channel plus a blank card. (For no bad channels two blank cards are needed.)

J=bad channel number + 1.

**Card 8**

P(NL), H(NL), ER (NL) Format (3F7.4)

P(NL) = peak position in channel numbers + 1

H(NL) = the half-width at half maximum intensity in channel numbers.

ER(NL) = individual error, in channel numbers, of peak. If this is not specified the value ER from Card 2 is assumed. One of these cards for each peak plus a blank card to end this routine.

Note for Card 7 and Card 8: Fortran IV does not accept a zero subscript. The channel numbers of 000-199 on the spectrometer must be changed to 001-200 for use with the program. This accounts for the +1 term which must be subtracted from the final answer. If (MØ(4) = 1 or 2) then all peaks
between 200-399 must be converted to channel numbers below 200 by subtracting each peak from 400.

Blank card - to stop peak guesses.

RW(J) Format(10(2X,F6.0))

Data cards. Format must be as shown, i.e., 10 channels per card with the first two columns blank and then six digits etc.

The data input is arranged for use with both a triangle wave spectrum or a flyback spectrum. For the triangle wave, two mirror image spectrum are generated in channels 1-200 and 201-400. There are two methods for analyzing the data.

1) The data for each half can be analyzed separately.

2) The data can be folded by adding the two halves;

\[ y(I) = y(I) + y(401-I). \]

The folding routine is useful to subtract out the geometric background contribution present with large amplitudes of source motion. The separate analysis is useful for estimates of nonlinearity and other errors can be seen and corrected.

For flyback or sawtooth velocity waveform, the 1-400 channel data format is used.
C. Precision Determination of the Lattice Constant of Silicon, using Back-reflection Lines (Method of Straumanis).

Determiniation of the effective film circumference

<table>
<thead>
<tr>
<th>Item</th>
<th>Reflections about line B</th>
<th>Reflections about line A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position of line in region b</td>
<td>220</td>
<td>311</td>
</tr>
<tr>
<td>Position of line in region c</td>
<td>117.4415 mm</td>
<td>122.3647 mm</td>
</tr>
<tr>
<td>Twice the distance of A from scale zero</td>
<td>179.9445</td>
<td>175.0353</td>
</tr>
<tr>
<td>MEAN VALUE = 297.3939 mm</td>
<td>297.3860</td>
<td>297.4000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Reflections about line A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position of line in region b</td>
<td>444α₁</td>
</tr>
<tr>
<td>Position of line in region a</td>
<td>60.4815 mm</td>
</tr>
<tr>
<td>Twice the distance of B from scale zero</td>
<td>36.7172</td>
</tr>
<tr>
<td>MEAN VALUE = 97.1987 mm</td>
<td>97.1987</td>
</tr>
</tbody>
</table>

Film circumference = 297.3930-97.1987 mm = 200.1943 mm

Degrees per mm on film = 90°/200.1943 mm = 0.4495632°/mm
Determination of the Lattice Constant

Bragg's law is given as

\[ n\lambda = 2d \sin \theta \]  

(A-III-1)

where \( d \) is the interplanar spacing given as:

\[ d_{hk1} = (h^2 + k^2 + l^2)^{1/2}a_o \]  

(A-III-2)

for a cubic lattice. Therefore one has the equation relating the lattice constant to the Bragg angle, which is

\[ a_o = \frac{\lambda}{(2 \sin \theta)}(h^2 + k^2 + l^2)^{1/2} \]  

(A-III-3)

<table>
<thead>
<tr>
<th>Item</th>
<th>Reflection about the line A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position of line in region b</td>
<td>60.4815 mm</td>
</tr>
<tr>
<td>Position of line in region a</td>
<td>36.7172 mm</td>
</tr>
<tr>
<td>Difference (( \phi ) in mm)</td>
<td>23.7643 mm</td>
</tr>
<tr>
<td>( \phi ) in mm</td>
<td>23.7643 mm</td>
</tr>
<tr>
<td>( \phi ) in degrees (( \phi \times 0.4495632 ))</td>
<td>10.6836°</td>
</tr>
<tr>
<td>( \theta ) in degrees</td>
<td>79.3164°</td>
</tr>
<tr>
<td>( \sin \theta )</td>
<td>0.982664</td>
</tr>
<tr>
<td>( a_o (\text{Å}) )</td>
<td>5.43063Å</td>
</tr>
<tr>
<td>( a_o ) corrected for refraction (( \text{Å} ))</td>
<td>5.43067Å</td>
</tr>
</tbody>
</table>

Therefore the lattice constant, \( a_o \), for nonannealed dislocation-free silicon measured at 24.0±0.5°C is 5.43067Å.