

### V. CONCLUDING REMARKS

Based on the information in Tables II and III, the average value of  $\epsilon_T$  is  $3.64 \pm 0.04$  eV per electron-hole pair in silicon. A search of the literature revealed no other value of  $\epsilon_T$ . Literature values of  $\epsilon$  for  $\alpha$  particles, electrons, and nitrogen atoms are summarized in Table IV. A first examination of the table seems to indicate a decrease in  $\epsilon$  with increasing mass of the bombarding particle. This conclusion must be tempered by the comparatively large difference between values of  $\epsilon$  for electrons, reflecting a large uncertainty in the accuracy of the measured values. Also, Halbert and Blanken-

ship's value<sup>7</sup> for  $\epsilon$  for nitrogen atoms is given as being equal within 1% to the value of  $\epsilon$  for  $\alpha$  particles, which they determined to be  $3.50 \pm 0.05$  eV per electron-hole pair. If the best value of  $\epsilon_\alpha$  of 3.62 is taken to be correct, then the Ref. 7 value for  $\epsilon$  for nitrogen atoms may be in error.

Because of the uncertainties indicated, it is not possible to confirm a trend in energy deposition with particle mass. Further, based on a best value of  $\epsilon_\alpha$  of 3.62 and the value of  $\epsilon_T$  derived herein, it may be concluded that  $\epsilon_T$  and  $\epsilon_\alpha$  are equal, within experimental error.

## Mössbauer Measurements of Tin-Antimony Solid Solutions\*

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The isomer shifts for both  $Sb^{121}$  and  $Sn^{119}$  nuclei have been measured in primary solid solutions of the Sb+Sn system. The experimental results show that the variation of isomer shift with concentration is much weaker than that from one insulating compound to another. This indicates that an increase in the number of electrons per atom hardly changes the number of 5s electrons.

THE isomer shift has been measured for  $Sb^{121}$  and  $Sn^{119}$  nuclei in both tin-rich and antimony-rich Sb+Sn alloys over the complete range of solid solubility. Such measurements show how alloying influences the number and character of the valence electrons of both solvent and solute ions. From these results, one may then draw inferences about the electronic structure of primary solid solutions of polyvalent metals.

Alloys of composition 0, 2, 4, and 6% antimony in tin and 0, 2.5, 5.0, 7.5, and 10% tin in antimony were examined. (All compositions are given in atomic percent.) In the measurements of the  $Sn^{119}$  resonance, both  $CaSnO_3$  and  $Mg_2Sn$  were used as source matrices. The antimony measurements were performed with  $Sb^{121}$  in a  $CaSnO_3$  matrix. For the results reported here, source and absorber were held at 80°K. Measurements were also made with the absorber at 200°K. The composition dependence of the shift at this higher temperature was the same (within experimental error) as that measured at the lower temperature, so only the measurements at 80°K are reported here. A broadened singlet was observed for both  $Sn^{119}$  (width  $\sim 1.6$  mm/sec) and  $Sb^{121}$  (width  $\sim 2.8$  mm/sec) for all alloys. In order to establish that our samples were indeed single-phase alloys, two

methods were used. First, metallographic observation at 300 X after a standard Nital etch showed no second-phase precipitate. Second, x-ray analysis was used to confirm the  $\beta$ -Sn(A5) and antimony (A7) structures.

The results for the experimental isomeric shifts are given in Table I. To compare with earlier work, it is convenient to refer these measurements to  $\alpha$  tin and InSb, respectively, rather than to the  $CaSnO_3$  sources used. This is done by adding  $-1.78$  and  $8.62$  mm/sec to the experimental values. Previous measurements on the Sn+Sb system<sup>1</sup> have been attempted with  $Sn^{119}$ ; there is indication that the material used was often of two phases.

TABLE I. Isomer shifts and electronic charge densities.

Sb (%)	Experimental shifts <sup>a</sup>		Charge densities	
	Sn	Sb	Sn	Sb/1.3
	(mm/sec)			
0	$2.528 \pm 0.003$	$(-11.27 \pm 0.04)^b$	$19.180 \pm 0.02$	$17.58 \pm 0.05$
2	2.539	$-11.29 \pm 0.08$	19.255	$17.59 \pm 0.40$
4	2.541	$-11.14 \pm 0.02$	19.267	$17.41 \pm 0.15$
6	2.547	$-11.08 \pm 0.06$	19.306	$17.38 \pm 0.06$
90	$2.650 \pm 0.005$	$-11.58 \pm 0.02$	$19.990 \pm 0.03$	$17.90 \pm 0.03$
92.5	2.649	-11.581	19.983	17.93
95	2.660	-11.602	20.057	17.98
97.5	2.660	-11.678	20.057	18.02
100		11.690		17.02

\* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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<sup>a</sup> Measured relative to  $CaSnO_3$ .

<sup>b</sup> This point is found from a measurement of the shift between InSb and a source of  $\beta$  tin containing  $Sn^{121m}$  that decays to Sb.

<sup>1</sup> F. Pobell, Phys. Status Solidi **13**, 509 (1966).

The isomeric shifts depend on the electronic charge density at the nucleus, as well as the presently irrelevant quantities  $F(z)$ ,  $E_\gamma$ , and  $\delta\langle r^2 \rangle / r^2$ . A quantitative interpretation of these quantities has been given in an earlier paper.<sup>2</sup> The irrelevant factors can be stripped away by converting from the shifts to charge density at the nucleus from valence electrons using  $\psi^2(\text{Sn}) = 14.20 + 6.65 \times S(\text{Sn})$  and  $\psi^2(\text{Sb}) = 18.84 - 1.45 \times S(\text{Sb})$ . These relations are taken from Figs. 2 and 3 of Ref. 2, the former being slightly modified to include more recent data.<sup>3</sup>

It should be noted that a tin and antimony nucleus in the same isoelectronic configuration do *not* have the same charge densities; the calculations show that the larger nuclear charge of the antimony increases the valence charge density by a factor of 1.3. The antimony densities reported here have been corrected by this factor to facilitate the comparison required to answer the question: What happens to the "extra" antimony electron as antimony is added to the alloy? It should also be noted that the above relations between density and shifts are uncertain<sup>2</sup> by about 10%; correspondingly, the fact that the antimony densities are all some 10% smaller than the corresponding tin is not quite significant. The slope of the densities contains most of the new information of this communication. The charge density at both Sn and Sb nuclei is plotted against the average number of electrons per atom in the alloy in Fig. 1 (four valence electrons per atom being assumed for Sn and five for Sb). The solid lines *S* and *P* are drawn to show the slopes the experimental points would have if the increased number of electrons went completely into (a) the 5s band or (b) the 5p or 5d band.

Figure 1 leads to one main inference concerning the electronic structure of the ions in the alloy: The rate of variation of the charge density at the nucleus of either atom in either a tin-rich or an antimony-rich solution is much less than the slope of line *S*. The charge density at an Sb nucleus when it is surrounded entirely by Sb atoms is much the same as when it is surrounded entirely by Sn atoms, and the same is true for the Sn nuclei. This is in sharp contrast to the behavior in nonconducting compounds of Sn and Sb, for which relatively large variations in isomer shift have been found. The present data are consistent with the idea that each atom in the alloy is strongly screened. The behavior of the isomer shift indicates that changes must occur principally in the occupation of *p* (or higher-angular-momentum) states. The results are consistent

<sup>2</sup> S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **159**, 239 (1967); S. L. Ruby and G. Shenoy, *ibid.* **186**, 326 (1969).

<sup>3</sup> J. K. Lees and P. A. Flinn, J. Chem. Phys. **48**, 882 (1968).

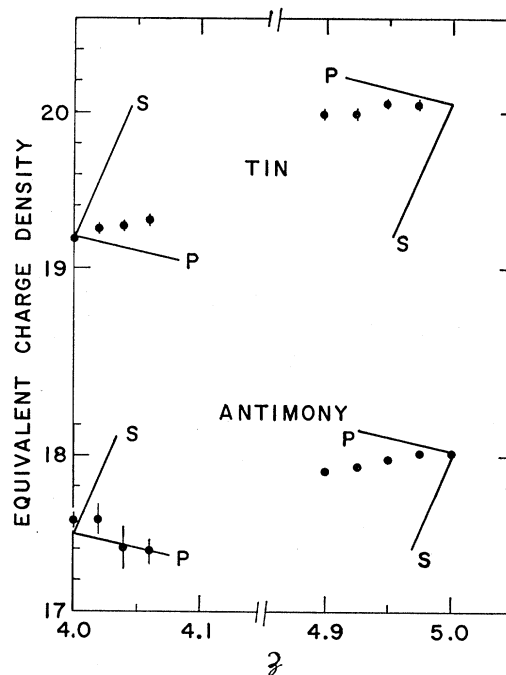


FIG. 1. Effective charge density of valence electrons in units of  $a_0^{-3}$  at  $\text{Sn}^{119}$  and  $\text{Sb}^{121}$  nuclei in tin-antimony alloys, plotted against the electron-per-atom ratio  $z$ . *S* and *P* are the calculated shifts if the added charge from the  $z$  ratio went completely into the 5s or 5p band.

with the finding of Verken *et al.*<sup>4</sup> for  $\text{Sn}^{119}$  nuclei and with the result of Rigney and Flynn,<sup>5</sup> who attribute the variation and magnitude of the Knight shift of Sb in liquid solutions of Sb+Sn to *s*-structure saturation and *p*-wave scattering alone.

It should be noted that the volume of the unit cell increases with antimony concentration in these alloys, and according to pressure experiments on  $\beta$  Sn, this increase should be accompanied by an increase in charge density in the  $\text{Sn}^{119}$  nucleus.<sup>6</sup> Thus, the general slow increase in charge densities as one moves to the right on Fig. 1 may be a volume effect. However, this is unlikely to be a complete explanation because in the tin-rich alloys the  $\text{Sn}^{119}$  density increases with solute concentration, while the  $\text{Sb}^{121}$  density shows a slight decrease.

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<sup>4</sup> B. I. Verken, V. V. Chekin, and A. P. Vinnekov, Zh. Eksperim. i Teor. Fiz. **51**, 25 (1966) [English transl.: Soviet Phys.—JETP **24**, 14 (1967)].

<sup>5</sup> D. A. Rigney and C. P. Flynn, Phil. Mag. **15**, 1213 (1967).

<sup>6</sup> H. S. Moller and R. L. Mössbauer, Phys. Letters **24A**, 416 (1967).