# S. H. Koenig†

# Transport Properties and Band Structure in Bismuth, Antimony and their Alloys

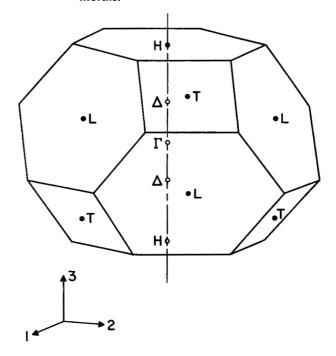
Abstract: We shall interpret the galvanomagnetic properties of bismuth, antimony and the Bi-Sb alloy system in terms of bands of carriers known to exist in the pure semimetals. In our interpretation, the new carriers, presumed holes, observed by several investigators in antimony must have slightly warped oblate ellipsoidal energy surfaces to account for the galvanomagnetic data of Juretschke et al, rather than tilted ellipsoidal surfaces. These new holes, together with the well established holes in bismuth and the Shoenberg electrons in both bismuth and antimony, account for the anomalous Hall coefficients of antimony. Consideration of qualitative features of the nearly free electron model of Jones and Harrison suggests that a linear variation of the spatial potential upon alloying bismuth with antimony is sufficient to account for the considerable changes observed in the transport properties of the alloy system. This model also suggests that the conduction band minima in bismuth are located at different points in the Brillouin zone from those in antimony. Experimental support for these hypotheses is discussed.

## Introduction

The band structure of the rhombohedral Group V semimetals in the vicinity of the Fermi surface is a subject of continuing discussion. A variety of oscillatory magnetic and galvanomagnetic phenomena in bismuth, the prototype semimetal, and in antimony and arsenic as well, has been successfully interpreted with what we shall call the "classic" model. In this model for bismuth, the electron Fermi surfaces are three ellipsoids, or near ellipsoids, as proposed by Jones, 1 Blackman 2 and Shoenberg, 3 located at points L in the Brillouin zone (Fig. 1) and, if only two carriers are present, the hole Fermi surface consists of a single ellipsoid of revolution, as suggested by Abeles and Meiboom,4 located at points H. Both the electrons and holes are characterized by very prolate energy surfaces. The long, or heavy mass, axis of the hole ellipsoid is normal to the hexagonal zone face which it intersects, and the long electron axes are approximately normal to the pseudohexagonal zone faces, being rotated approximately 6° from a bisectrix (2) axis toward the trigonal (3) axis in the sense shown. In the ellipsoid princi-

\* Now at Thomas J. Watson Research Center. † IBM Watson Laboratory, Columbia University.

Figure 1 First Brillouin zone for Group V semimetals.



pal axes, the heavy electron mass is approximately 1.7 free electron masses, while the transverse masses are both about 0.01 free electron masses. The hole masses are about 0.8 and 0.07 free electron masses in the longitudinal and transverse directions, respectively.<sup>5</sup>

The classic model accounts for many of the observed properties of the semimetals, but there is growing evidence that it is not complete. A number of observers have recently reported evidence for a nonclassic carrier in antimony, from quantum oscillatory experiments. In this paper, we shall examine this evidence and show how these new carriers, together with the classic carriers, permit an unambiguous interpretation of the room temperature galvanomagnetic properties of pure antimony, and also suggest a particularly simple model for the relative motions of bands near the Fermi surface in the bismuthantimony alloy system.

#### **Bismuth**

Let us first review the electrical transport properties of bismuth in the light of the known band structure. Various low temperature<sup>4,11,12</sup> galvanomagnetic measurements are in substantial agreement that the drift mobility of the classic electrons is roughly isotropic, being approximately 15% greater along the threefold axis than in the trigonal plane. The classic hole drift mobility in the trigonal plane is about half that of the electrons, but is much smaller in the trigonal direction, so that the total conductivity of bismuth is greater perpendicular to the threefold axis than parallel to it. For a magnetic field in the trigonal plane, the Hall mobility for the electrons is much greater than for the holes, so that this component of the Hall tensor is negative. For a magnetic field perpendicular to this plane, on the other hand, the electron Hall mobility is low, while that for the holes is somewhat larger, resulting in a small, positive Hall constant. Zitter's<sup>11</sup> analysis of the low field galvanomagnetic effects, using the classic model, shows that the mobility components for each carrier are sensibly proportional to the inverse effective mass tensor components as determined from cyclotron resonance by Galt et al. and by Kao. In fact, despite the very considerable mass anisotropy, the electron and hole relaxation times are found to be constant over the Fermi surface within experimental error, that for the holes being  $\sim$ 2.5 times that for electrons.

Finally, we remark that it has occasionally been suggested<sup>13</sup> that there are one or more additional groups of carriers in bismuth, typically with a heavy mass and low Fermi energy to account for the linear term in the low temperature heat capacity.<sup>14,15</sup> While such carriers might not be observable in low field galvanomagnetic experiments, the higher field measurements of Mase et al.,<sup>12</sup> in which a reversal of the sign of the small Hall coefficient is observed, seem definitely to preclude such carriers.

Further, the absence of the helicon or "whistler" mode of propagation in Alfven wave experiments has also established that the mobile classic carriers in bismuth constitute a plasma neutral to within 1%, the limit of the experiment. Charge neutrality would then require the very unlikely condition that any additional carriers consist of equal densities of heavy holes.

Although it is improbable that two new groups of carriers exist in bismuth with equal number density and opposite sign, there is an additional condition upon these hypothetical carriers: no temperature variation, within  $\pm 5\%$ , is observed either in the de Haas - van Alphen period<sup>3</sup> or the classic electron cyclotron mass<sup>17</sup> up to 20°K, from which it may be concluded that the Fermi energy for the classic carriers, and hence for any new carriers, does not vary by more than a fraction of a millivolt. Thus, either the densities of states for the new carriers are essentially equal to each other, or their Fermi energies are both several times 20°K in energy. The former possibility merely compounds the improbable while the latter, assuming masses of the order of the free electron mass, would require a density of new carriers much greater than that of the classic carriers; the heat capacity contribution of these carriers would be greater than the largest reported values. More significantly, such carriers must contribute-by any reasonable estimate-at least one part in 10<sup>4</sup> to the electrical conductivity. Yet, transverse magnetoresistance measurements at 4.2°K show an approximate H<sup>2</sup> dependence (after elimination of the oscillatory component) up to 20 kG or higher, with no sign of saturation; 18 the resistance increase at this field is greater than 106, and there is no trace of nonclassic carriers. 19 Additionally, no evidence for other than classic carriers has been found in microwave transport,<sup>5</sup> for either the Faraday or the Azbel'-Kaner field configuration, up to values of magnetic field corresponding to a cyclotron mass of  $2m_0$ .

From the two classic carrier model, one may compute the contribution to the linear term in the heat capacity to be given by  $\gamma = 52 \text{ erg/deg}^2$  mole. This is to be compared with the value 210 ergs/deg<sup>2</sup> mole reported by Phillips<sup>14</sup> and the much larger value 670 ergs/deg2 mole found by Kalinkina and Strelkov, 15 who did not, however, correct for the nuclear heat capacity. It would seem that the discrepancy between the specific heat in the classic model and the experimental value is large and significant. However, we must note that  $\gamma$  for Bi is two orders of magnitude smaller than for typical metals so that the maximum carrier contribution to the specific heat, occurring at the lowest temperature to which Phillips fitted his data, was less than 10% of the total specific heat, compared to 5% scatter in the data at this temperature. Taking into account the thermometric uncertainties which Phillips discusses, particularly the position of 0°K on his temperature scale, we feel there is no fundamental objection to the classic model from the determination of  $\gamma$ .

#### Antimony

While antimony has not yet been subject to as extensive experimental investigation as bismuth, there is good quantitative agreement on the properties of the conduction band among a variety of low temperature experiments. The electron Fermi surface in antimony consists of a set of prolate tilted ellipsoids, similar to the classic electrons in bismuth, with their long axes rotated approximately 36° from the bisectrix axis toward the trigonal, but in the opposite sense from bismuth. From cyclotron resonance (which is the experiment that identifies the classic, tilted carriers as electrons) and the various quantum oscillatory effects, the effective masses and number density per ellipsoid have been obtained; representative values are

$$m_{1'} = 0.06 m_0; \quad m_{2'} = 1.8 m_0; \quad m_{3'} = 0.05 m_0$$

in the ellipsoid principal axis system and

$$n_{\rm e} = 1.4 \times 10^{19}/{\rm cm}^3$$
.

From the infrared absorptance measurements of Nanney<sup>22</sup> and the inverse effective mass components, it may be verified that there are but three electron ellipsoids, so that the total electron concentration is

$$N_{\rm e} = 4.2 \times 10^{19} / {\rm cm}^3$$

in agreement with the room temperature galvanomagnetic experiments.<sup>9</sup>

The valence band of antimony appears to be somewhat more complex than that of bismuth. In the cyclotron resonance experiments in which the tilted carriers were identified as electrons, <sup>21</sup> Datars and Dexter observed a strong hole resonance for the magnetic field along the trigonal axis and an isotropic absorption for the field in the trigonal plane (in addition to the electron resonances). Assuming these resonances to be due to the same carrier, a hole with an ellipsoidal Fermi surface of revolution about the trigonal axis, the inverse mass tensor components are

$$m_1 \simeq m_2 \simeq 0.09 m_0; \quad m_3 = 0.8 m_0,$$

remarkably similar to the inverse masses of the bismuth classic holes.

Recently, a number of authors have observed a new carrier in antimony.<sup>6-8</sup> Interpreting their data within the framework of a three tilted ellipsoids model, these authors concluded these new carriers, presumably holes, to be a set of highly prolate ellipsoids with a small tilt angle for the heaviest mass direction from the bisectrix axis and with a number density approximately equal to that of the electrons. However, none of the experiments reported

to date give evidence of the shorter periods which should be associated with three ellipsoids of carriers, although these periods were within experimental range. We have suggested<sup>23</sup> that this new section of the antimony Fermi surface consists, rather, of one or (probably) two warped oblate ellipsoids centered along the trigonal axis. We estimate the carrier density to be

$$n_W \simeq 6 \times 10^{18}/\text{cm}^3$$
,

and the mass anisotropy to be  $\sim$ 6:1 and to vary  $\sim$ 20% with direction. Assuming the heavy carriers observed by Datars<sup>24</sup> in cyclotron resonance with **H** along the trigonal axis to be these warped carriers, the approximate mass parameters and Fermi energy  $\xi$  become

$$m_1 \sim m_2 = 0.4 m_0$$
,  $m_3 = 0.96 m_0$ ,  $\xi \simeq 60$  meV.

In their recently reported de Haas-Shubnikov measurements, Rao et al.<sup>8</sup> have indeed found a similar model to be equally consistent with their data. However, the totality of low temperature oscillatory and cyclotron resonance experiments do not permit choosing one interpretation over the other.

In order to clarify the situation regarding the Sb valence band, we have turned to the room temperature galvanomagnetic measurements of Freedman, Epstein and Juretschke. 9,10 These authors find the conductivity and Hall constants of antimony to be approximately isotropic, with an anomalous (i.e., hole-like) sign for both Hall constants.25 Now, one can estimate from the known electron parameters, assuming an isotropic relaxation time, the contributions of the antimony electrons to both total conductivity and Hall constant to be approximately isotropic; therefore the hole contribution must be isotropic also. The tilted hole model, with the parameters derived from the low temperature data, far from meets these requirements. In fact, this model gives a negative value for the Hall constant for the field parallel to the trigonal direction. It is also interesting to note that Epstein and Juretschke<sup>10</sup> analyzed their galvanomagnetic data using tilted electrons and tilted holes, but were unable to find a unique fit to their data.

In our interpretation, the valence band is composed of both the warped, oblate ellipsoid of new carriers and the prolate ellipsoid of classic holes. The classic holes provide the Hall conductivity in the trigonal plane necessary for the Hall constant to be positive when the magnetic field is along the trigonal direction, while the new carriers with a low mass in the trigonal direction provide the mobility necessary to make the second of the two Hall constants positive. An analysis of the Sb data <sup>9,10</sup> in our model yields the proportion of new holes to be 30% of the total (which requires that there be two warped ellipsoids); assuming one ellipsoid of classic holes then leads to a Fermi energy of 180 meV. This model also properly predicts the

relative magnitudes of the five magnetoresistance coefficients; to explain the non-zero value of the longitudinal magnetoresistance for current along the trigonal direction, the warping is in fact essential.

Additionally, the three carrier model which we have proposed predicts that the effect of doping Sb *p*-type by the addition of a Group IV element would be to increase the conductivity in the trigonal plane at the expense of that in the trigonal direction (because of the increased proportion of classic holes relative to new holes in view of their greater density of states); this is in agreement with observation.<sup>10</sup> The alternative (three tilted ellipsoid) model predicts the converse.

# The free electron approximation

Our three band model for the Fermi surface in antimony has a particularly attractive interpretation in the nearly free electron approximation which has had such success with the polyvalent metals.<sup>26</sup> The fifth Brillouin zone for the Group V semimetals (Figure 2) was described thirty years ago by Jones; this zone contains exactly ten electrons. In the spirit of the nearly free electron approximation, we expect electrons due to overlap of the free electron sphere into the sixth and higher zones at points on the zone surface closest to the zone center, the face centers B and C. In the first or Brillouin zone, B corresponds to T and C to L. We agree with Mase<sup>27</sup> and Harrison<sup>28</sup> that the electron overlap in bismuth occurs at points C of the large zone, that is, points L of the Brillouin zone. This interpretation is consistent with the fact that the heavy electron axes are very nearly normal to the pseudohexagonal faces which contain L. In antimony, because of the greatly different electron tilt angle, we suggest that the electron overlap occurs at B, as originally proposed by Jones for bismuth. In the reduced zone, this corresponds to the T points, centers of the approximately square faces, and would locate the heavy electron axes normal to these faces, as is observed.

Mase's calculations do not admit electrons in the vicinity of T, whereas the free electron construction by Harrison<sup>28</sup> does, as expected, allow electrons at either L or T. The large difference in this respect between the free electron and tight binding approaches presumably is due to a greater sensitivity of tight binding calculations to relativistic effects, and in particular to the fact that Mase included spin-orbit effects but did not include the Darwin shift. This shift has recently been shown to have a profound influence on the band structure calculations of PbTe,<sup>29</sup> a material with a band structure closely related to that of Bi.<sup>23</sup> The free electron model, however, works very well for lead itself.<sup>26</sup>

Again referring to the large zone, hole states are most likely to be occupied at the corners farthest from the zone center. These are the points A<sub>1</sub>, corresponding to the H

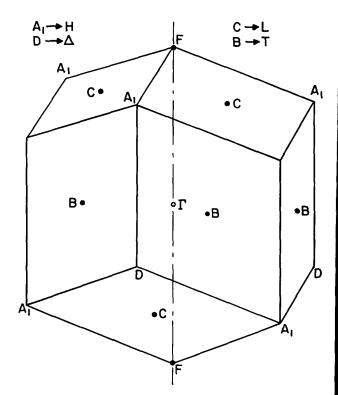


Figure 2 Jones zone (5th Brillouin zone) for the Group V semimetals. The correspondence of important points with the Brillouin zone is indicated.

points of the reduced zone, and the points D which are the  $\Delta$  points of the small zone, with a multiplicity of two. In bismuth, in which the band overlap is very small, we expect occupied hole states at  $A_1$  only, as these states are farthest from the zone center; this is the accepted picture for Bi. In antimony, with its greater overlap, we suspect that hole states at D become occupied, thus placing a group of carriers of the symmetry we have inferred at  $\Delta$ .

# Bi-Sb alloys

The effect of alloying bismuth into antimony would be twofold. First, the lattice potential would be increased, increasing the energy gap at B, as found by Harrison. Second, the increase in the spin-orbit coupling with increasing bismuth content would lower the gap at C, as found by Mase. For some intermediate alloy concentration—close to the pure bismuth end—the electron energies at B and C would cross at an energy higher than the valence band, resulting in an alloy which would be a semiconductor over a range of concentrations, as the bismuth-antimony system is well known to be. 31,32

The model presented here predicts several effects which are in agreement with experiment. First: in pure bismuth, the hole states at D should lie very close under the Fermi level. In their galvanomagnetic experiments at 77°K,

Abeles and Meiboom<sup>4</sup> found the hole conductivity anisotropy in bismuth substantially less than that known at helium temperatures.<sup>11</sup> Thus suggests the presence of additional holes with the opposite conductivity anisotropy to the classic bismuth holes, as would be produced by thermal activation of the holes at D. Further, in their piezoresistance experiments at 77°K, Jain and Jaggi<sup>33</sup> have found similar evidence for these new carriers as they reduced the electron overlap with strain. Finally, Brown and Silverman,<sup>34</sup> in magnetoresistance studies in a heavily doped *n*-type bismuth—15% antimony alloy, have found evidence for two distinct sets of electron ellipsoids, as predicted at the crossing of the electron bands at B and C.

## References

- H. Jones, Proc. Roy. Soc. (London) A147, 396 (1934); A155 653 (1936).
- 2. M. Blackman, Proc. Roy. Soc. (London) A166, 1 (1938).
- D. Shoenberg, Proc. Roy. Soc. (London) A170, 341 (1939).
  Several corrections to this paper are to be found in J. S. Dhillon and D. Shoenberg, Phil. Trans Roy. Soc. (London) A248, 1 (1955).
- 4. B. Abeles and S. Meiboom, Phys. Rev. 101, 544 (1956).
- J. K. Galt, W. A. Yager, F. R. Merritt, B. B. Cetlin, and A. D. Brailsford, *Phys. Rev.* 114, 1396 (1959); Y. H. Kao, *Phys. Rev.* 129, 1122 (1963).
- Y. Eckstein, Phys. Rev. 129, 12 (1963); J. B. Ketterson, Phys. Rev. 129, 18 (1963); J. Ketterson and Y. Eckstein, Phys. Rev. 132, 1885 (1963).
- 7. Y. Saito, J. Phys. Soc. Japan 18, 452 (1963).
- G. N. Rao, N. H. Zebouni, C. G. Grenier, and J. M. Reynolds, *Phys. Rev.* 133, A141 (1964).
- S. J. Freedman and H J. Juretschke, *Phys. Rev.* 124, 1379 (1961).

- S. Epstein and H. J. Juretschke, *Phys. Rev.* 129, 1148 (1963).
- 11. R. N. Zitter, Phys. Rev. 127, 1471 (1962).
- S. Mase, S. von Molnar, and A. W. Lawson, *Phys. Rev.* 127, 1030 (1962).
- c.f. L. S. Lerner, *Phys. Rev.* 127, 1480 (1962); 130, 605 (1963), for a discussion of heavy carriers and earlier references.
- 14. N. E. Phillips, Phys. Rev. 118, 644 (1960).
- I. N. Kalinkina and P. G. Strelkov, Soviet Phys.—JETP 7, 426 (1958).
- 16. G. A. Williams (private communication).
- Y. H Kao, R. L. Hartman, and R. D. Brown III, Bull. Am. Phys. Soc. 9, 96 (1964).
- 18. P. B. Alers and R. T. Webber, Phys. Rev. 91, 1060 (1953).
- 19. We thank Leo Esaki for this argument.
- 20. D. Shoenberg, Phil. Trans. Roy. Soc. A245, 1 (1952).
- 21. W. R. Datars and R. N. Dexter, Phys. Rev. 124, 75 (1961).
- 22. C. Nanney, Phys. Rev. 129, 109 (1963).
- J. J. Hall and S. H. Koenig, Bull. Am. Phys. Soc. 8, 51 (1963).
- 24. W. R. Datars, Can. J. Phys. 40, 1784 (1962).
- 25. M. C. Steele, Phys. Rev. 99, 1751 (1955), and R. D. Brown III (private communication) have found the Hall constants for Sb to be positive over the entire range from 4° to 300°K. Rao et al. (Reference 8, above) assume the Hall constant for H parallel to the trigonal axis to be negative on the basis of a model for their data, but apparently have not measured the sign.
- A. V. Gold, *Phil. Trans. Roy. Soc.* (London) A251, 85 (1958); W. Harrison, *Phys. Rev.* 118, 1190 (1960).
- 27. S. Mase, J. Phys. Soc. Japan 13, 434 (1958); 14, 584 (1959).
- 28. W. Harrison, J. Phys. Chem. Solids 17, 171 (1960).
- L. E. Johnson, J. B. Conklin and G. W. Pratt, Jr., Phys. Rev. Letters 11, 538 (1963).
- 30. A. L. Jain and S. H. Koenig, Phys. Rev. 127, 442 (1962).
- 31. A. L. Jain, Phys. Rev. 114, 1518 (1959).
- S. Tanuma, J. Phys. Soc. Japan 16, 2349 (1961); 16, 2354 (1961).
- 33. A. L. Jain and R. Jaggi (private communication).
- D. M. Brown and S. J. Silverman, IBM Journal 8, 253 (1964). (This conference).

# Discussion

A. W. Lawson: Hewitt and Williams [Phys. Rev. Letters 12, 216 (1964)], at Riverside, have determined the quadrupole coupling constant in bismuth to be  $58.5 \pm 2$  Mc/s. This is twice as large as that obtained by Phillips from specific heat data, and implies a much smaller contribution to the electronic specific heat from the holes. It may remove the necessity for assuming "heavy" holes in bismuth.

R. N. Dexter: I wish to point out that the early Datars and Dexter cyclotron resonance of holes in antimony is not qualitatively reliable since only the X-Y plane was observed and we now know (Rao, Ketterson) that an accidental, experimental near-degeneracy exists between the electron and hole cyclotron resonance in this plane. Although later work on cyclotron resonance appears to be suitable for direct comparison with the present model, the early work is not because of poor resolution.

J. J. Hall: We agree that, because of poor resolution in the early work, the Azbel'-Kaner cyclotron resonance of holes in antimony may not be reliable. However, you did clearly observe a hole resonance in the Faraday configuration with the magnetic field perpendicular to the trigonal plane. The experimental near degeneracy between electrons and holes, observed by Rao et al. and by Ketterson and Eckstein, was for their quantum oscillatory periods rather than for their cyclotron masses. If,

as in another model, equal densities of electrons and holes were distributed among three ellipsoids each, then the cyclotron masses would also be nearly degenerate, as you state.

I wish to emphasize that the Shoenberg tilted-ellipsoid model is very general, and may fit a variety of data. The fact that this model fits some data well over a limited range does not, however, mean that the model is necessarily the correct description of the Fermi surface. We have presented an alternative model which we feel is equally consistent with the low-temperature data and which *does* permit an understanding of the galvanomagnetic properties of antimony.

W. E. Henry: You mentioned the effect of strain on the hole concentration. How was the strain applied and what was the effect of hydrostatic pressure on the hole concentration?

*Hall:* This question concerns the work of Jain, Jaggi and Weibel. Their strain was applied in the trigonal direction by simple compression with a "push-rod". The effect of hydrostatic pressure on the carrier concentration that they report [*Physics Letters* 7, 181 (1963)] is a fractional change of  $8 \times 10^{-5}$  for both electrons and holes.

Y. Eckstein: No one has really seen the short-period Shoenberg electrons in de Haas - van Alphen or de Haas - Shubnikov data. Our own results in the X-Z plane seemed to indicate a spread in tilt angles, but the data of Reynolds et al. suggest definitely

245

two tilt angles. Can you explain their results by your warped surface?

- S. H. Koenig: All oscillatory data so far can be fitted to either tilted ellipsoids or our model. To make a choice one has to go to transport data. We can understand the sign of the Hall constant and its change with doping only in terms of classical holes and these other warped surfaces, and not three tilted ellipsoids alone.
- S. Epstein: How well does your model explain the tin-doped antimony galvanomagnetic data of Epstein and Juretschke, and what does it say about the carrier contribution per added tin atom?

Hall: In general, it does not appear that the change in hole concentration is proportional to the amount of tin added. However, the change in the conductivity and Hall constant anisotropy which you observe in your 0.2% alloy is completely consistent with the model we have presented. Our model does not fit the 0.8% data. It must be borne in mind, however, that a 0.8 atomic percent density of tin atoms in antimony is greater than the total carrier concentration, so that the relative position of conduction and valence bands may change. This may account for the fact that the *electron* density in your 0.8% tin sample does not seem to have changed appreciably from pure antimony in our model.

Epstein: Our galvanomagnetic data are being reinterpreted in terms of two tilted ellipsoidal Fermi surfaces and an untilted one along  $k_z$ . A contribution of one carrier per tin atom is not inconsistent with our preliminary computations. This compares with roughly 0.3 of one carrier obtained by scaling our two-

band tilted model for pure antimony to fit both the 0.2 and 0.8 atomic % data [Phys. Rev. 129, 1148 (1963)]. The latter result is consistent with overlapping bands which either shift or do not shift on alloying. I feel that distortion need not be invoked to analyze the 0.8% data in terms of either shifting or nonshifting bands. By "distortion" I mean changes in effective mass with alloying (due to changes in either Fermi level or Fermi surface topology).

M. H. Cohen: If I may turn from facts to band structure calculations, I should like to make a few remarks about the relations between the model proposed by Hall and Koenig and our own band structure calculations. First, although the actual bands may be regarded as derived from the free electron bands, the splittings of degeneracies and shifts of levels may be quite large, of the order of several volts, so that caution must be used in making arguments based only on the free electron model. Secondly, the possibilities that arise for both holes and electrons from our calculations are in agreement with those proposed by Hall and Koenig. In our notation, these would be electrons at X and/or at L, that is, the centers of the square face and the pseudohexagonal face respectively, and holes near T, the real hexagonal face normal to the trigonal axis. The situation for holes near T is complex and depends on the magnitude of the spin-orbit splitting. For large spin-orbit splitting as in bismuth, only holes at T should exist. For smaller spin-orbit splitting one could get either a warped surface at and near T or one could get both holes at T and holes near what was the cross over point before spin-orbit coupling was included, if the cross over is sufficiently far from T. It seems difficult to find at present, in our rough calculations, hole ellipsoids elsewhere in the zone which would conform to the 3 or 6 ellipsoid picture.