found essentially no change in conductivity in their homogeneous crystal-cleavage experiments with the admission of oxygen. This result must be contrasted with the large change in work function upon oxygen admission which is observed by Gobeli and Allen.[3] The magnitude of the work function change is approximately 0.5 to 0.6 ev and certainly indicates that a chemical reaction has taken place with an appreciable amount of electron transfer. One would also assume that the nature of the silicon-oxygen surface would be such that any conductive mechanisms which might take place would be orders of magnitude smaller than that expected for the clean cleaved-silicon surface. Since PMD would have been able to see changes greater than one micromho/square, an upper limit may be set on the mobility of the electrons in the surface band of states.

$$\mu_{ss}=\sigma_s/qN_s<0.01 \text{ cm}^2/\text{vsec}, \quad (4)$$

where q is the electronic charge, σ_s is the conductivity per square and N_s is the density of atoms on a (111) surface. If there are no peculiar effects due to the nature of the junctions, the cleavage experiments on the *npn* structure allow one to set the upper bound of μ_{ss} two orders of magnitude lower since PMD claimed they could detect a conductance of 10^{-8} mho. Using this value for σ_s the upper bound for μ_{ss} is less than 10^{-4} cm^2/volt sec.

These extremely low values of the surface state mobility may arise from experimental artifacts. However, if experimental difficulties are excluded, it suggests that the overlap of the nonbonding orbitals of adjacent-surface atoms is very small. Thus if a Shockley-type band were to exist it would have to be very narrow. These results have great theoretical significance but the experiments will have to be repeated with this problem in mind before any conclusions can be reached. As an alternative explanation it may be assumed that the states which have been removed from the valence band do not coalesce with those removed from the conduction band. In this model the lower band would be full while the upper band would be empty. No conduction would be expected. This splitting of the surface states into two sets may arise by adjacent surface atoms bonding to each other directly or through the lattice. The resolution of these problems calls for additional experimental work.

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Electron Spin Resonance in Antimony

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Electron spin resonance of conduction electrons in antimony has been investigated at 34.3 kMc/sec and 1.5°K. The results were consistent with the theory of Cohen and Blount for the g factor of conduction electrons in Bi and Sb. The principal axes of the g tensor coincided with those of the tilted-ellipsoidal Fermi surface. The parameters of the electron spin resonance were determined to be $g_1=3.4$, $g_2=29.5$, $g_3=3$. Resonance was also observed from transitions that involved both an orbital transition and a Zeeman transition.

I. INTRODUCTION

THE g factor of conduction electrons in antimony was shown by Cohen and Blount to be large for orientations of an antimony crystal in a magnetic field when the spin-orbit coupling was large compared to the band gap.[1] This theory was followed by the observation of a large g factor for one orientation of antimony.[2] The present paper reports an experimental study of electron spin resonance in antimony with the purpose of presenting values of the parameters of the g factor for antimony.

When an antimony crystal is in a magnetic field, there may be four different electronic transitions between energy levels caused by Landau and Zeeman splitting. The transitions are shown in Fig. 1 where

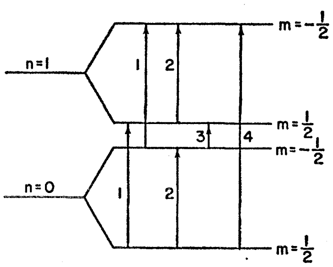

FIG. 1. Energy level diagram showing the Zeeman splitting of Landau levels $n=0$, 1 for conduction electrons in antimony.

[1] M. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960).
[2] G. E. Smith, J. K. Galt, and F. R. Merritt, Phys. Rev. Letters 4, 276 (1960).

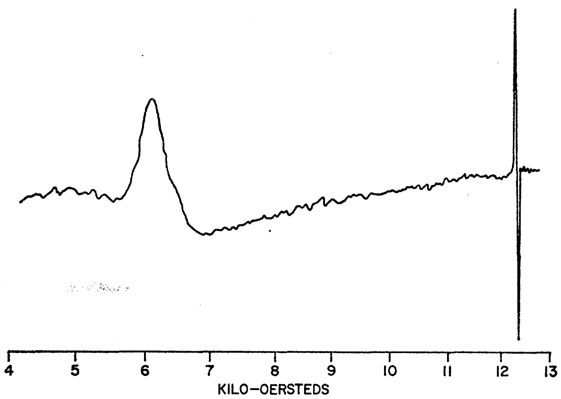

FIG. 2. Electron-spin resonance signal in antimony at 6.4 koe for the magnetic field 4° from a binary axis in the binary-bisectrix plane and an E.P.R. signal at 12.25 koe from a small sample of DPPH. Derivative of absorption measured at 34.3 kMc/sec.

the notation corresponds to that of Smith *et al.*[2] Type-1 transitions are the transitions responsible for cyclotron resonance and take place between two successive Landau levels having the same spin state. The cyclotron resonance in antimony is not dealt with in this paper but is reported elsewhere.[3,4] Type-2 transitions are pure spin resonance and are the subject of this paper. Types-3 and -4 transitions involve both an orbital transition and a Zeeman transition. We report strong evidence that the last two transitions do occur in antimony.

The conduction electrons in antimony are situated on a tilted-ellipsoidal Fermi surface.[5] The crystal structure of antimony is rhombohedral and the three-fold symmetry axis is called the trigonal axis. We denote the three ellipsoids that are not related by reflection symmetry by the letters used in the cyclotron resonance paper.[4] The axes of ellipsoid a are parallel to axes $1'$, $2'$, $3'$ in the crystal where $1'$ is parallel to a binary axis. Axis $3'$ is tilted an angle θ from the trigonal axis of the crystal. Ellipsoids b and c are symmetrically displaced by a rotation of $\pm 2\pi/3$, respectively, about the trigonal axis from ellipsoid a.

II. EXPERIMENTAL PROCEDURE

A microwave spectrometer operating at 34.3 kMc/sec was used to take measurements of the derivative of absorption as a function of magnetic field. Samples prepared with a flat shiny surface formed the end wall of a TE_{111} cavity in the spectrometer. In all experiments, the sample surface was parallel to H and was in a horizontal plane. The temperature of the sample and cavity was 1.5°K. During an experiment, the direction of the magnetic field with respect to the polarization of the microwave field was set by rotating the magnet on its base. The orientation of the sample was adjusted by rotating a stainless steel shaft which extended from above the Dewar to a gear train that was connected to the bottom half of the cavity. A full description of the apparatus is given elsewhere.[4]

III. EXPERIMENTAL RESULTS

The anisotropy of the spin resonance is closely related to that of the cyclotron resonance of electrons. The anisotropy of both resonances results from the shape and tilt of the tilted-ellipsoidal Fermi surface of antimony. Consequently, for a general direction of the dc field in the crystal, there are three spin resonance signals. The study of the spin resonance and its distinction from all other types of transitions (1, 3 and 4) required a careful study of the resonance pattern for magnetic field directions in the binary-bisectrix plane and bisectrix-trigonal plane. The study was aided by data taken with $H \| H_{rf}$ and with $H \perp H_{rf}$ since electron spin resonance occurred only with the second geometry. Results for three orientations will be discussed here.

We would expect, according to the theory of Cohen and Blount, one spin-resonance signal at high magnetic fields from electrons on ellipsoid a when H is close to the binary axis. Figure 2 shows the high-field signal that was observed when H was in the binary-bisectrix plane and 4° from the binary axis. We recognize this signal as electron spin resonance rather than cyclotron resonance because it is an absorption maximum, its line shape is approximately Dysonian, it is not observed with $H \| H_{rf}$, and no subharmonic resonance is associated with it. Spin resonance signals of electrons on ellipsoids b and c for the orientation of Fig. 2 lie within the cyclotron-resonance pattern and are not shown here.

Figure 3 shows data taken with H parallel to the trigonal direction. For each of the four electronic transitions, the three signals that occur for a general magnetic field direction become one signal for the trigonal direction. Consequently, the trace for this orientation is relatively simple. The spin resonance is derived from the data by considering the difference between Fig. 3(a) taken with $H \| H_{rf}$ and 3(b) taken with $H \perp H_{rf}$: in Fig. 3(b) the signal which is on the high-field side of the fundamental resonance attributed to the light hole is considered to be spin resonance of conduction electrons. Its g value is 17. For the trigonal direction, the type-4 transition occurred too close to the second subharmonic of the light hole resonance to be resolved from it. Thus, there is no evidence of a type-4 transition in Fig. 3. For many other orientations, type-4 resonance was resolved, or at least partially distinct, from the cyclotron resonance signals.

Data taken with the magnetic field along the bisectrix axis are shown in Fig. 4. The spin resonance of electrons on ellipsoids a and c is easily discerned at 2100 oe corresponding to a g factor of 12. The spin resonance of electrons on ellipsoid b has a g value of 23.5 for the bisectrix direction, and is only slightly resolved from

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[4] W. R. Datars, Can. J. Phys. (to be published).
[5] D. Shoenberg, Phil. Trans. Roy. Soc. London **A245**, 1 (1952).

the fundamental resonances of the light holes and of the electrons on ellipsoid *b*. Type-4 transitions from electrons on ellipsoids *a*, *b*, *c*, are also evident.

With H along the trigonal direction and perpendicular to H_{rf} there was a weak signal, approximately 1000 oe wide, at 7000 oe. It was an absorption maximum. Its shape was very sensitive to any misalignment from the trigonal axis. It appeared to be the superposition of three signals, indicating that it was resonance of electrons on the tilted-ellipsoidal Fermi surface. Since type-3 transitions are expected to occur at quite high fields when the g-factor is large, we believe that the resonance at 7000 oe is a type-3 transition. For most other orientations, the type-3 transition was not observed, presumably due to insufficient sensitivity at high fields.

For the electrons on any one ellipsoid, the magnetic field for the type-4 transition is lower than the fundamental resonance field of the cyclotron resonance. The anisotropy in the resonance field of type-4 transitions is determined by the orientation dependence of the cyclotron mass and the g factor. Furthermore, to be identified with the type-4 transition, the resonance which is observed with $H\perp H_{rf}$, should be absent with $H\|H_{rf}$. Resonances with the above properties were observed for most crystal orientations. The zero point of the absorption derivative curve was taken as the position of resonance. Accuracy in measuring the position of resonance was limited by its close proximity to the cyclotron resonance of electrons and holes, and by uncertainty in the position of the resonance field for a resonance that combines a spin transition with a cyclotron resonance transition.

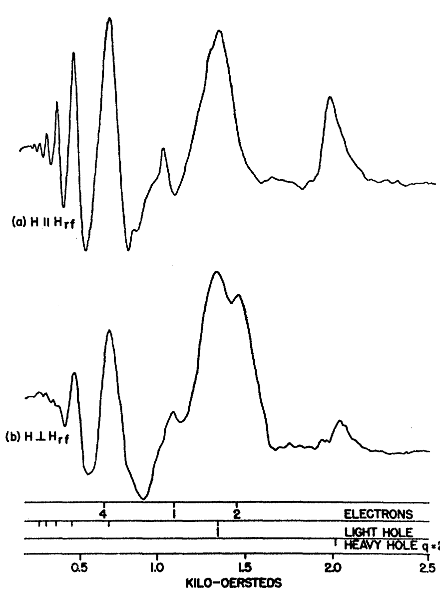

FIG. 3. Resonance spectrum in antimony with H parallel to the trigonal axis and with (a) $H\|H_{rf}$ (b) $H\perp H_{rf}$ and its decomposition into transitions of types 1–4 and subharmonic resonances of cyclotron resonance. Derivative of absorption measured at 34.3 kMc/sec.

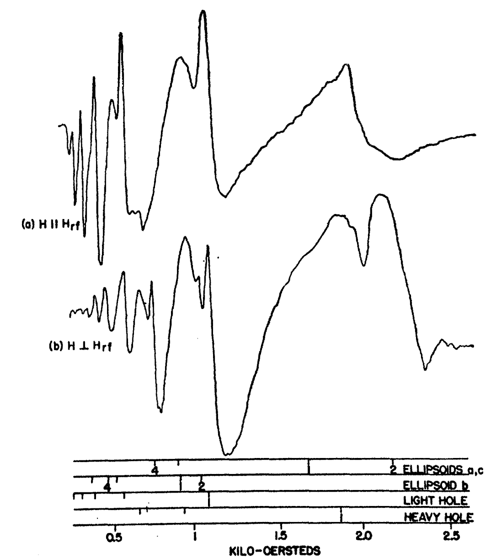

FIG. 4. As Fig. 3 but with H parallel to the bisectrix axis.

IV. ANALYSIS AND DISCUSSION

A. Transitions (3 and 4)

From the relationship of transitions (3 and 4) to cyclotron and electron spin resonance, we define effective masses m_3^* and m_4^* of type-3 and type-4 transitions, respectively, where

$$m_3^* = m_s m_c/(m_s - m_c) \tag{1}$$

$$m_4^* = m_s m_c/(m_s + m_c) \tag{2}$$

Here, $m_s = 2/g$ is the spin mass and m_c is the cyclotron mass in units of the free-electron mass m_0. A comparison of the observed and calculated values of m_4^* is a check of the spin-mass and cyclotron-mass values. There is not sufficient accuracy in m_4^* to warrent this comparison for all magnetic-field directions. The values of m_4^* for principal magnetic-field directions are listed in Table I. Equation (2) was used to calculate m_4^* from cyclotron-mass values[4] and spin-mass values.

The effective mass m_3^* for a trigonal direction is 0.51 according to Eq. (1) with $m_s = 0.11$ and $m_c = 0.092$. The observed value of the effective mass of the resonance attributed to a type-3 transition for this orientation is 0.57. The agreement between the observed and calculated m_3 is not strikingly good. However, we

TABLE I. Experimental and calculated values of the effective mass m_4^* (in units of the free electron mass) used to describe type-4 transitions of electrons on ellipsoids *a*, *b*, *c*.

Direction of H	Ellipsoid *a* Observed	Ellipsoid *a* Calc.	Ellipsoid *b* Observed	Ellipsoid *b* Calc.	Ellipsoid *c* Observed	Ellipsoid *c* Calc.
Binary axis	0.21	0.21	0.045	0.043	0.045	0.043
Bisectrix axis	0.068	0.071	0.038	0.035	0.068	0.071
Trigonal axis	···	0.050	···	0.050	···	0.050

conclude from the properties of the resonance that a type-3 transition was observed.

B. Electronic *g* Factor

The electron spin resonance will be analyzed in terms of the spin Hamiltonian

$$\mathcal{H}=g\beta_0 H \quad (3)$$

where β_0 is the Bohr magnetron and g is the effective spectroscopic splitting factor with the form[1]

$$g=[(\lambda_{1''})^2 g_1^2+(\lambda_{2''})^2 g_2^2+(\lambda_{3''})^2 g_3^2]^{\frac{1}{2}}. \quad (4)$$

Here, λ_1'', λ_2'', λ_3'' are the direction cosines of H relative to the principal axes ($1''$, $2''$, $3''$) of the tensor describing g. The theory of Cohen and Blount predicts that axis $1''$ is parallel to axis $1'$ and that $2''$ and $3''$ are close to $2'$ and $3'$, respectively. The present study of the spin resonance reveals that $2''$, $3''$ actually coincide with $2'$, $3'$. Thus, the angle between axis $3''$ of the g tensor and the trigonal direction is equal to the tilt angle of the ellipsoidal Fermi surface and has a value of 36°.

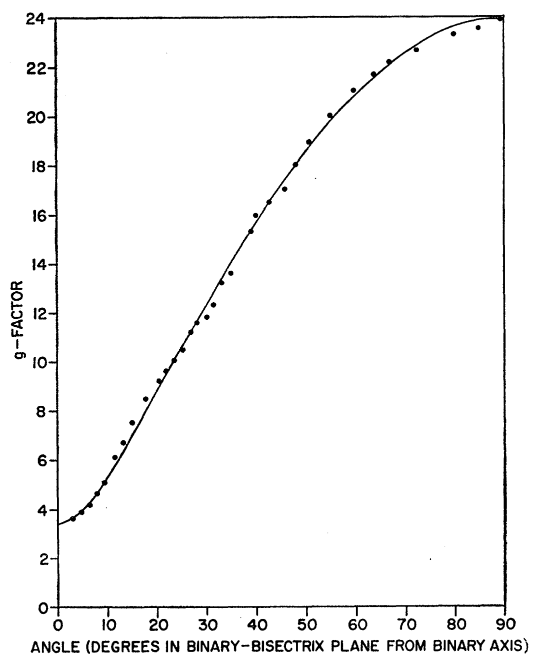

FIG. 5. The g factor of conduction electrons on ellipsoid a in antimony for magnetic-field directions in the binary-bisectrix plane.

The g factor of the conduction electrons was determined from the zero point of the absorption-derivative curve and the width of the spin resonance according to the theory of electron spin resonance.[6,7] The g factor changed from 3.4 to 24 as H was rotated through 90° from axis $1'$ of ellipsoid a as shown in Fig. 5. For $H\|$ axis $3''$ the spin-resonance signal was very broad at 9.5 koe, corresponding to a g-value of 3. The result of the analysis of these data is

$$g_1=3.4 \quad g_2=29.5 \quad g_3=3. \quad (5)$$

Each of the values is believed to be accurate to ±5%. A plot of Eq. (4) for the binary-bisectrix plane using the parameters (5) is given in Fig. 5 for ellipsoid a.

Following the theory of Cohen and Blount,[1] let us consider the one-level case in which there is one energy level close to the energy minimum in the conduction band. In bismuth, the spin-orbit splitting is larger than this band gap for all directions except in the neighborhood of the axis $2'$. If this condition exists also in antimony, the one-level approximation yields for antimony

$$g_1=2 \quad g_2=36 \quad g_3=2. \quad (6)$$

Then the spin mass m_s is equal to the cyclotron mass for the magnetic field direction $2'$. The conditions necessary in the determination of parameters (6) are not as applicable to antimony as to bismuth since the band gap is larger and the spin-orbit splitting is smaller for antimony than for bismuth. The general agreement between parameters (5) and (6) is evidence that the conditions are quite well satisfied in antimony. Probably the band gap is not much smaller than the spin-orbit splitting in antimony since g_1 and g_3 are is slightly larger and g_2 is somewhat smaller than the corresponding values predicted by theory.

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[7] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).