de Haas–van Alphen effect in two-dimensional thin films of pure bismuth

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Numerical evaluations have been carried out of the electron and/or hole density, the electronic energy density, the electronic magnetization, and the magnetic susceptibility in ultrathin films of pure bismuth. Electrons and holes were assumed to be performing two-dimensional motions in the film plane. Two orientations of the films were considered: films normal to the trigonal axis and to the bisectrix axis. The Lax nonparabolic, ellipsoidal energy model for bismuth electrons was applied to the energy-momentum relation. The magnetization and susceptibility exhibit de Haas–van Alphen-type oscillations which are unique, both quantitatively and qualitatively, to the semimetallic bismuth films.

I. INTRODUCTION

In sufficiently thin films, the effect of size quantization[1] would become indispensable when electronic properties in the films are to be studied. The quantizations to the electronic energy spectrum become more pronounced in thin films of thickness comparable to the de Broglie wavelength of the electrons. The extreme quantum size effect in ultrathin metallic films would push beyond the Fermi level all but the ground energy level of that part of motion along the film-thickness direction. In ultrathin films of semimetallic crystals, however, the theoretical consequence of the extreme quantum effect may vary depending on the boundary conditions to be used at the film edges. Using the vanishing-wave-function boundary condition,[1] semimetal-semiconductor transition would occur in ultrathin films; and if the vanishing-gradient boundary condition is used, the electrons and holes in ultrathin semimetallic films would perform essentially two-dimensional motions[2,3] in the film plane at low temperatures. Experimental evidence[4,5] suggests that the electrons and holes in semimetallic bismuth films of thickness below about 200 Å are likely in a status of two-dimensional motion.

With the progress in the fabrication of high-quality ultrathin films, in which the single crystallinity may mostly be retained, it is expected that more experimental studies will be performed on the two-dimensional motions of charge carriers in ultrathin films of pure bismuth. It would thus be desirable to provide certain theoretical studies on the two-dimensional bismuth films. In this paper, the magnetic-field-dependent de Hass–van Alphen oscillations of the electronic magnetization and susceptibility will be numerically evaluated in ultrathin bismuth films where the electrons and holes perform two-dimensional motions.

General discussions on the magnetic properties in these films under extreme size quantizations, including magnetic transitions between diamagnetic and paramagnetic states, have been given both for metallic films[6] and for semimetallic films.[7] In Ref. 7, discussions were based on a simple semimetallic energy-band structure, consisting of one conduction band (electrons) and one valence band (holes), and having a simple quadratic energy-momentum relationship. In real bismuth, however, there is a unique and rather complicated energy-band structure; there are three, instead of one, electron bands and one overlapping hole band; besides, the energy-momentum relationship is much more complicated[8–10] than a simple quadratic one. Using the nonparabolic and ellipsoidal two-band model[8] and effective masses in real bismuth,[11] we shall present results of numerical evaluations on the de Haas–van Alphen oscillations in ultrathin films of bismuth, which we believe would provide a much closer and thus more meaningful picture, both qualitatively and quantitatively, of the oscillations.

In Sec. II, theoretical backgrounds will be outlined for the numerical evaluations. The evaluations will include the carrier density, the energy, the magnetization, and the susceptibility. Two specific orientations of the films will be considered: films normal to the trigonal axis and normal to the bisectrix axis. In films normal to the trigonal axis, there would be no magnetic-field-induced transition from a semimetallic state to a semiconducting state, while in films normal to the bisectrix axis, such transition would be possible. Results will also be qualitatively different in the two cases. For bismuth films normal to the binary axis, results are qualitatively similar to those of the former in the two cases and will not be presented. Results and discussions will be presented, respectively, in Secs. III and IV for the aforementioned two cases.

II. THEORETICAL BACKGROUNDS

According to the nonparabolic, ellipsoidal model,[8] the energy levels of electrons and holes in a two-dimensional (ultrathin) bismuth film placed in a transverse magnetic field B assume the following forms, respectively:

Electrons: $$E_n(1+E_n/E_g) = (n+\tfrac{1}{2})\hbar eB/m_cC \pm \tfrac{1}{2}\hbar eB/m_sC\ , \quad (1)$$

Holes: $$E_p = (N+\tfrac{1}{2})\hbar eB/M_cC \pm \tfrac{1}{2}\hbar eB/M_sC, \quad (2)$$

where E_g is the energy gap between the conduction band

TABLE I. Magnetic field values of level crossings between an electron energy level and a hole energy level.

	Films⊥trigonal	Films⊥bisectrix
B_0(kG)		1.39×10^3
B_1(kG)	2.19×10^2	4.65×10^2
B_2(kG)	1.05×10^2	3.61×10
B_3(kG)	6.83×10	3.33×10
B_4(kG)	5.02×10	3.11×10
B_5(kG)	4.94×10	1.77×10
B_6(kG)	3.48×10	1.70×10
B_7(kG)	3.44×10	1.64×10
B_8(kG)	2.93×10	1.58×10
B_9(kG)	2.55×10	1.14×10
B_{10}(kG)	2.25×10	1.11×10

and the valence band underneath it at the L point of the energy-band structure; m_c and M_c are the orbital cyclotron effective masses; m_s and M_s the spin effective masses; and n and N assume 0, 1, 2, . . . , . The numerical values of the effective masses can be found in Refs. 11 and 2. There are three equivalent electron-energy ellipsoids symmetrically located with respect to the trigonal axis. There is only one hole band. Equation (1) measures electron energies from the bottom of the electron band, while Eq. (2) measures hole energies from the top of the hole band. Thus, the electron and hole bands overlap, and the overlap energy for bismuth[11] is 38.5 meV. At zero temperature, each and every occupied electron level must be lower than any of the occupied hole levels; in other words, E_n in Eq. (1) must be less than $E_o - E_p$ in Eq. (2), where $E_o = 38.5$ meV is the energy overlap.

To reveal the de Haas–van Alphen effect, we shall consider 0° temperature for simplicity. In a given magnetic field B, the charge carriers (electrons and holes) accommodate themselves to the lower energy levels in the expressions (1) and (2), respectively, where each level has a degeneracy $D = AeB/hC$, A being the area of the film, such that the total number of conduction electrons equals that of holes. This is the charge neutrality condition. When the magnetic field is increased, all of the values of E_n and E_p increase with a possible exception for the lowest E_n or E_p. In bismuth films perpendicular to the trigonal axis, the lowest hole level decreases in value in an increasing magnetic field because $M_s < M_c$, while in films normal to the bisectrix axis, the bottom level of electrons remains nearly stationary, since $m_s \cong m_c$. Thus, with an increasing magnetic field, the number of occupied levels either in Eq. (1) or in Eq. (2) decreases discontinuously. Such discontinuous variations occur whenever there is a crossing between an electron level and a hole level.

In a given magnetic field, the numbers of the occupied levels in Eqs. (1) and (2) can be determined using the charge neutrality condition. The density (number per unit area) of either electrons or holes and the total energy of the charge carriers can then be evaluated with a little work on a personal computer. The magnetization is the negative derivative of the energy with respect to the field and the susceptibility is the derivative of the magnetization. The discontinuous variations of the occupied level

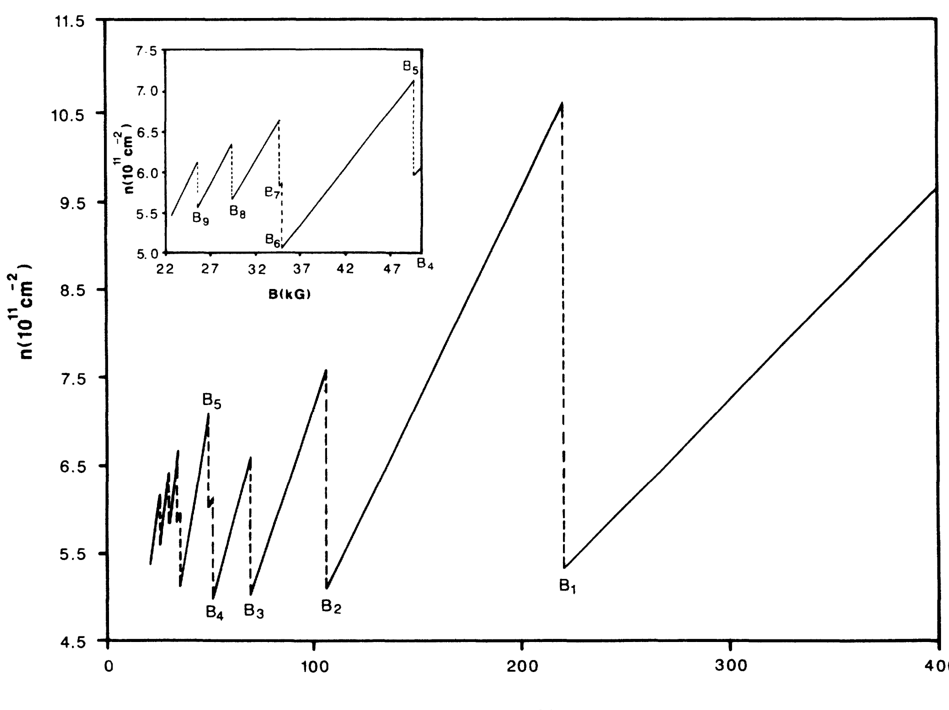

FIG. 1. Density of electrons and holes versus magnetic field in a two-dimensional bismuth film, film⊥trigonal axis.

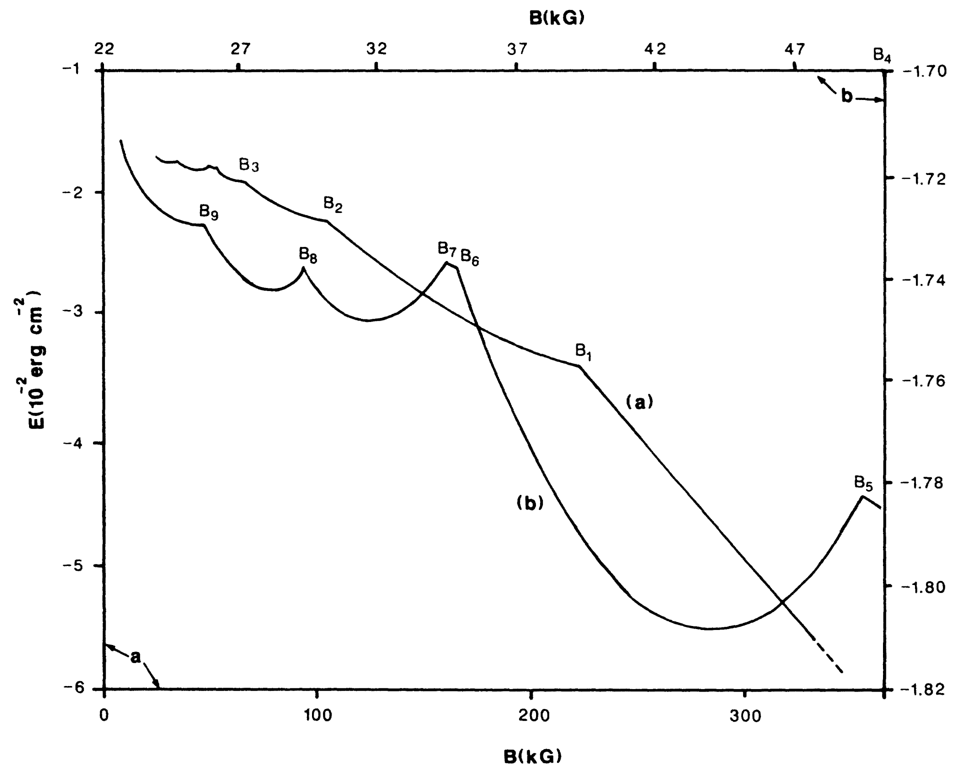

FIG. 2. Energy density versus magnetic field in a two-dimensional bismuth film, film ⊥ trigonal axis.

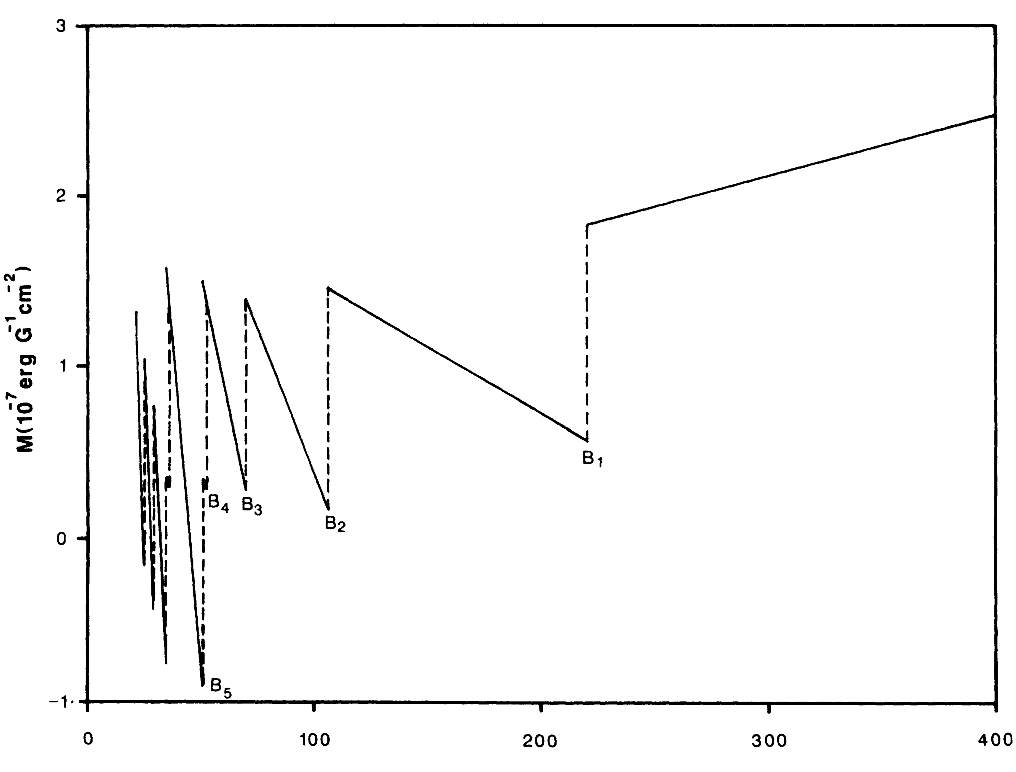

FIG. 3. Magnetization versus magnetic field in a two-dimensional bismuth film, film ⊥ trigonal axis.

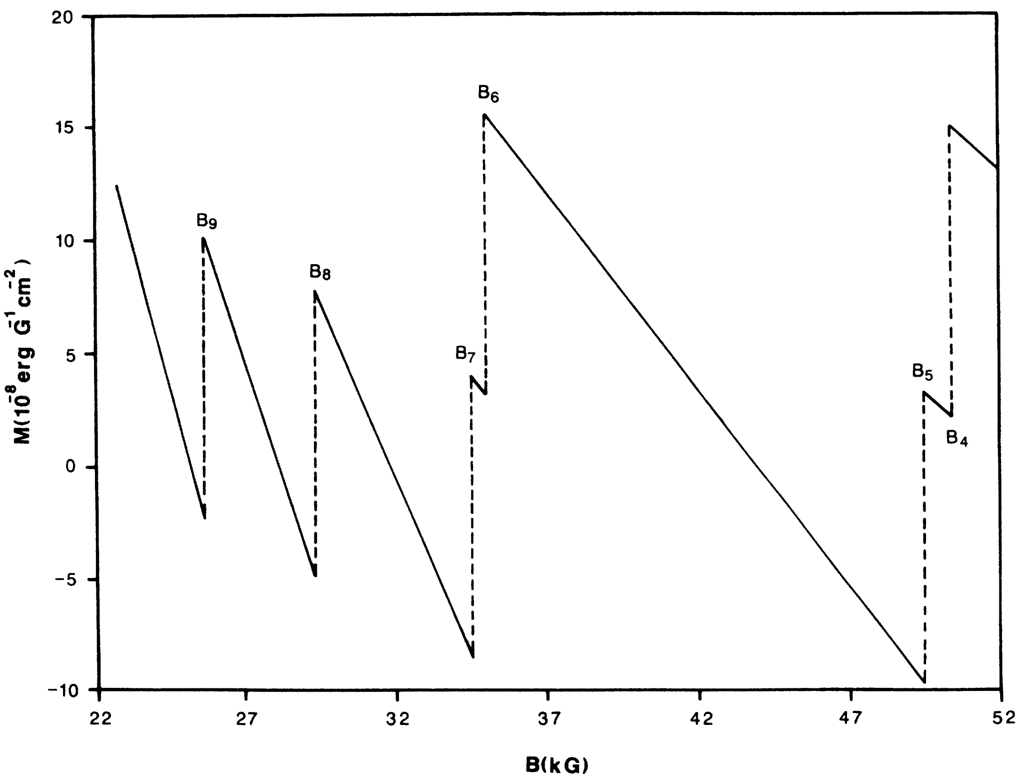

FIG. 4. Magnetization versus field, bismuth film ⊥ trigonal axis.

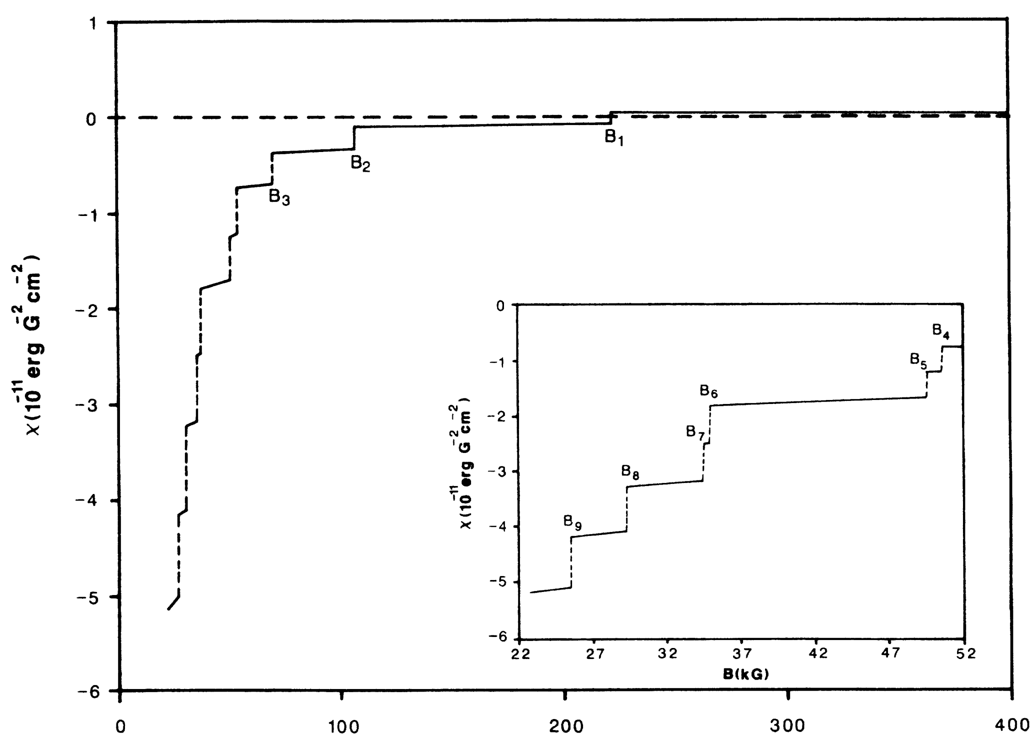

FIG. 5. Magnetic susceptibility versus magnetic field in a two-dimensional bismuth film, film ⊥ trigonal axis.

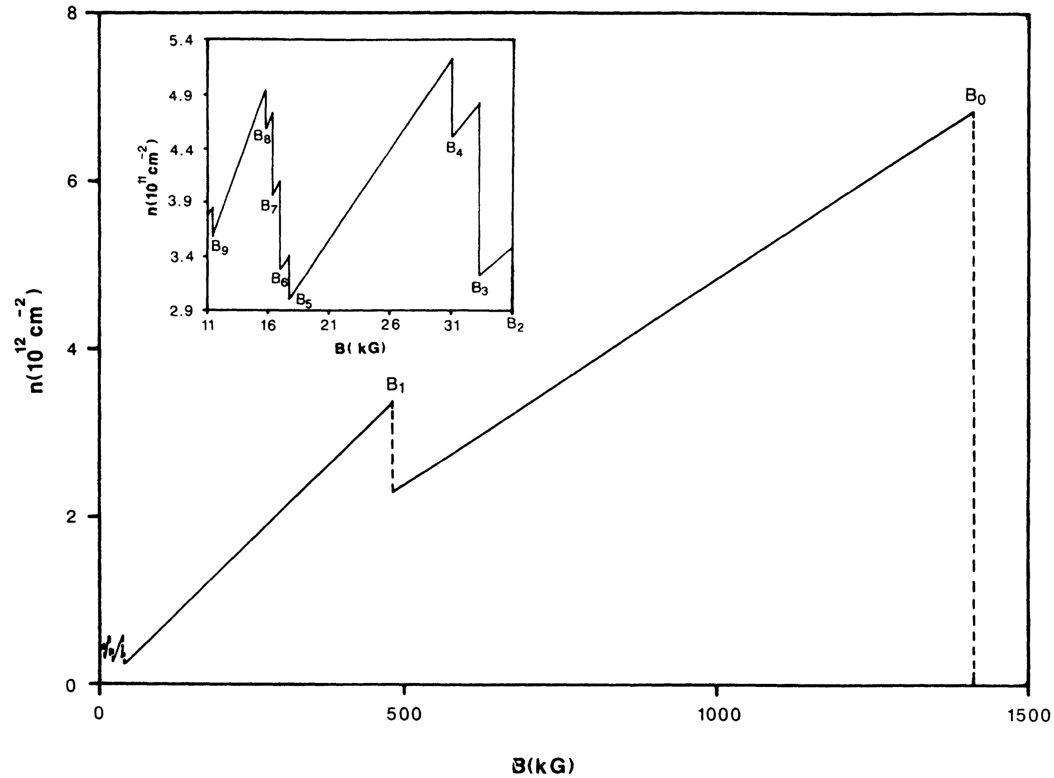

FIG. 6. Density of electrons and holes versus magnetic field in a two-dimensional bismuth film, film ⊥ bisectrix axis.

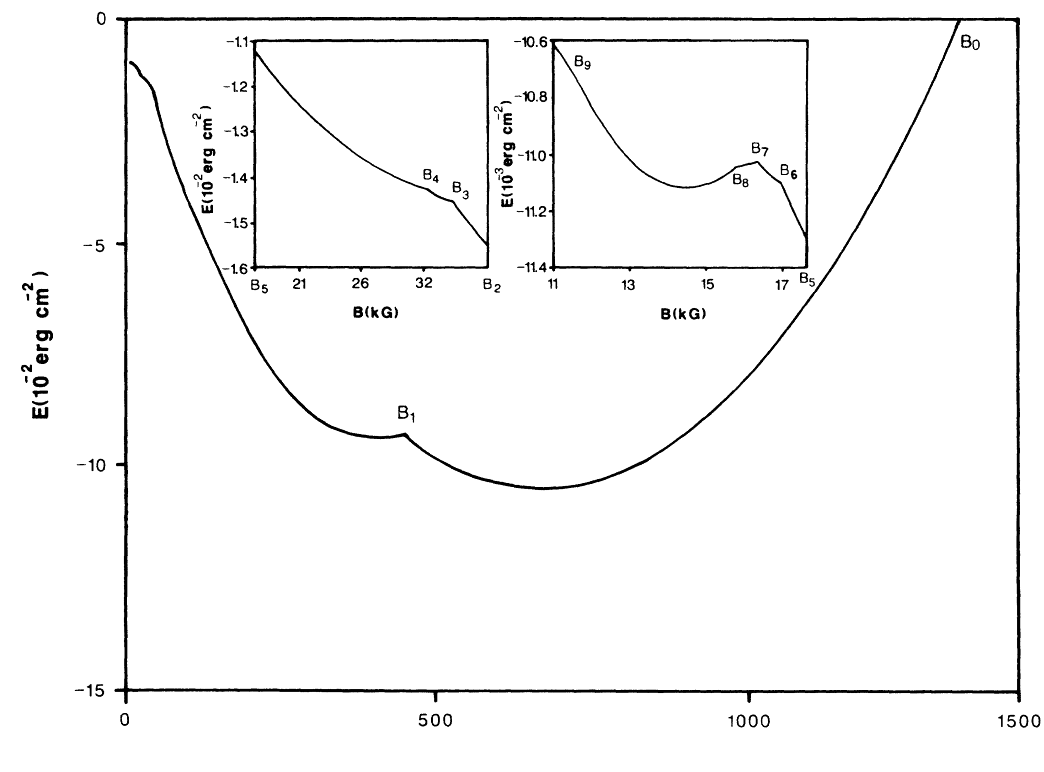

FIG. 7. Energy density versus magnetic field in a two-dimensional bismuth film, film ⊥ bisectrix axis.

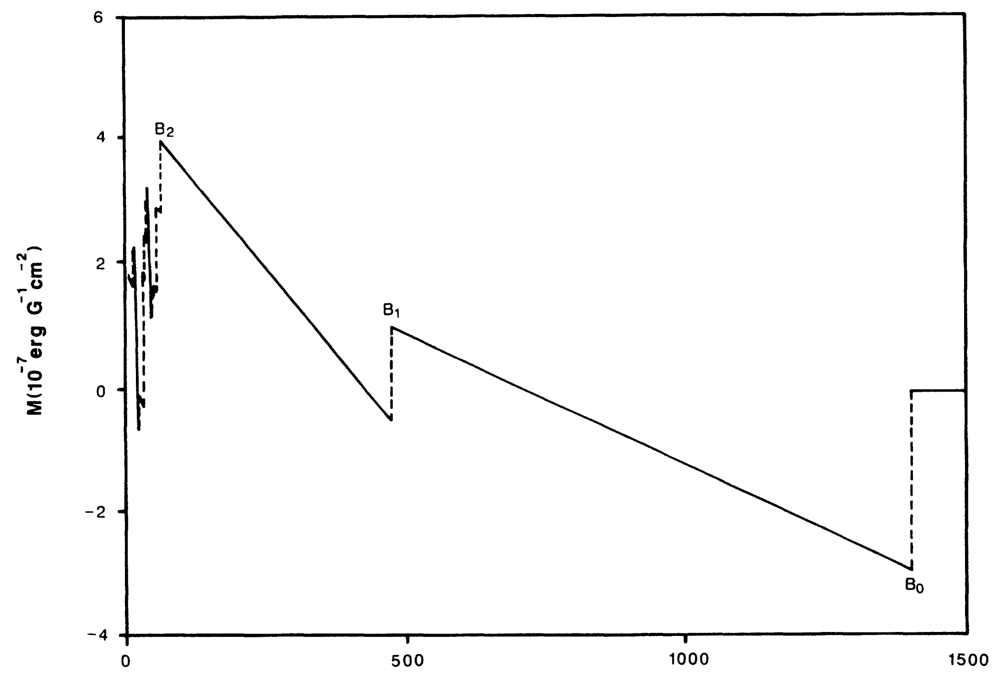

FIG. 8. Magnetization versus magnetic field in a two-dimensional bismuth film, film ⊥ bisectrix axis.

numbers result in the sharp oscillations of the magnetizations—*the de Haas–van Alphen oscillations.*

III. FILMS NORMAL TO THE TRIGONAL AXIS

In ultrathin films of pure bismuth, normal to the trigonal axis, the charge carriers perform two-dimensional motions in a plane perpendicular to the trigonal axis, whose energies are described by Eqs. (1) and (2), respectively, where[2] $m_c = 0.0140$, $m_s = 0.0239$, $M_c = 0.064$, and $M_s = 0.033$, in units of a free electron mass.

In Table I are listed the field values at which energy-level crossings occur. In magnetic fields higher than B_1, all but the lowest of the hole energy levels have crossed over the lowest electron level, and thus these lowest levels, corresponding to $n = 0$ and $N = 0$ and the minus signs of the spin terms in Eqs. (1) and (2), respectively, are the only levels occupied by electrons and holes, respectively. The number of holes in each level equals the degeneracy D. Each electron level in Eq. (1) can accommodate, however, a maximum of $3D$ electrons, since there are three equivalent electron bands in bismuth films normal to the trigonal axis. In $B > B_1$, the number of either electrons or holes is D, or the density (number per unit area) equals eB/hC, which increases linearly with the magnetic field. Numerical evaluation indicates that the lowest energy level of holes remains higher than the lowest electron level even the magnetic field is increased further; in other words, $E_o - E_p(0-) > E_n(0-)$, where $0-$ corresponds to N or $n = 0$, and the minus sign of the spin terms in Eq. (1) or (2). Thus, the films remain semimetallic. When the magnetic fields B are $B_1 > B > B_2$, the hole levels $E_p(0-)$ and $E_p(0+)$ are positioned above $E_n(0-)$, and there are D holes each in $E_p(0-)$ and $E_p(0+)$ and $2D$ electrons in $E_n(0-)$. Such analyses can go on. In general, in fields $B_{s-1} > B > B_s$, there are S hole levels occupied by SD holes, and the same number of SD electrons are accommodated in $[s/3]+1$ electron levels, where $[s/3]$ is the integer part of $s/3$. The value of B_s is determined by the crossing of the $(s+1)$th hole level, based on the value in Eq. (2), through the $([s/3]+1)$th level of electrons given

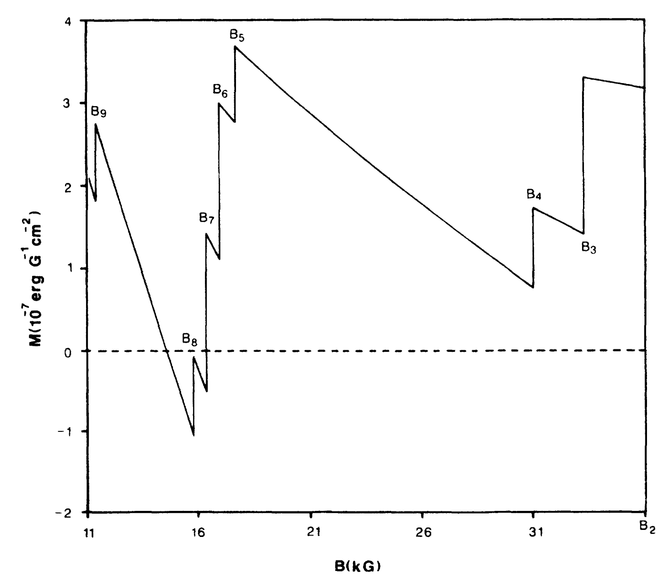

FIG. 9. Magnetization versus field, bismuth film ⊥ bisectrix axis.

in Eq. (1). The discontinuous variation of the carrier density with the magnetic field is shown in Fig. 1. Besides the discontinuous change at each B_s, the density increases linearly with the field. The spacings in field between two consecutive discontinuities are somewhat regular, but some are much narrower (e.g., between B_4 and B_5, and between B_6 and B_7, etc.), resulted in by the three to one degeneracy ratio of the electron and hole levels, and the numerical values of the effective masses.

The energy of each electron can be obtained by solving Eq. (1) for E_n, where E_g is known[11] to be 15.3 meV. Taking the conduction-band bottom as zero energy, a hole in energy level E_p contributes the amount of $-(E_o-E_p)$ to the total energy, since a hole means a missing electron. The electronic energy of the film is the sum of the energies contributed by the conduction electrons and an equal number of holes accommodated in the occupied levels in Eqs. (1) and (2), respectively. Figure 2 shows the magnetic field dependence of the energy. At the fields listed in Table I, the energy is continuous itself, although its slope varies discontinuously. Between any two neighboring fields B_s and B_{s+1}, the energy varies somewhat quadratically with B. The contribution to the energy by the holes is quadratic, since each energy in Eq. (2) as well as the degeneracy D is linearly proportional to B. The contribution of the electrons, because of the nonparabolic feature in Eq. (1), however, is not quite quadratic.

The magnetization and susceptibility have outstanding discontinuities at the fields listed in Table I. Between any two consecutive fields listed, the magnetization is approximately linear and the susceptibility is not too far from being a constant. The striking differences of the de Haas–van Alphen oscillations in the two-dimensional bismuth films from those in an isotropic Fermi gas are the following. First, only in $B > B_1$, the magnetization increases with B and the susceptibility is positive; in any field range below B_1, the magnetization decreases with B and the susceptibility is negative. Second, in some field ranges between B_s and B_{s+1} of those listed in Table I, the magnetization undergoes a positive-negative transition, while in other field ranges it remains positive. Third, the oscillations exhibit poor periodicity due to the nonparabolic feature in the electron energy spectrum and the 3:1 ratio of the level degeneracies of electrons and holes. The field-dependent magnetization and susceptibility in a two-dimensional bismuth film normal to the trigonal axis are shown in Figs. 3–5.

IV. FILMS NORMAL TO THE BISECTRIX AXIS

In bismuth films normal to the bisectrix axis, two among the three electron-energy ellipsoids are equivalent and have the same effective masses:[2] $m_c=0.00363$, $m_s=0.003\,44$, in the unit of free electron mass. For these two electron bands, each energy level in Eq. (1) has a degeneracy of $2D$. The single electron band has $m_c=0.001\,83$ and $m_s=0.001\,72$, while the hole band has $M_c=0.21$ and $M_s=2.57$. The spin effective mass of holes is too large to produce any appreciable spin splittings of the energy spectrum and we shall approximate the situation by neglecting the spin splittings completely, i.e., $M_s \cong \infty$. Thus each hole level carries a degeneracy of $2D$. Besides, we shall apply the two-band[8] approximation

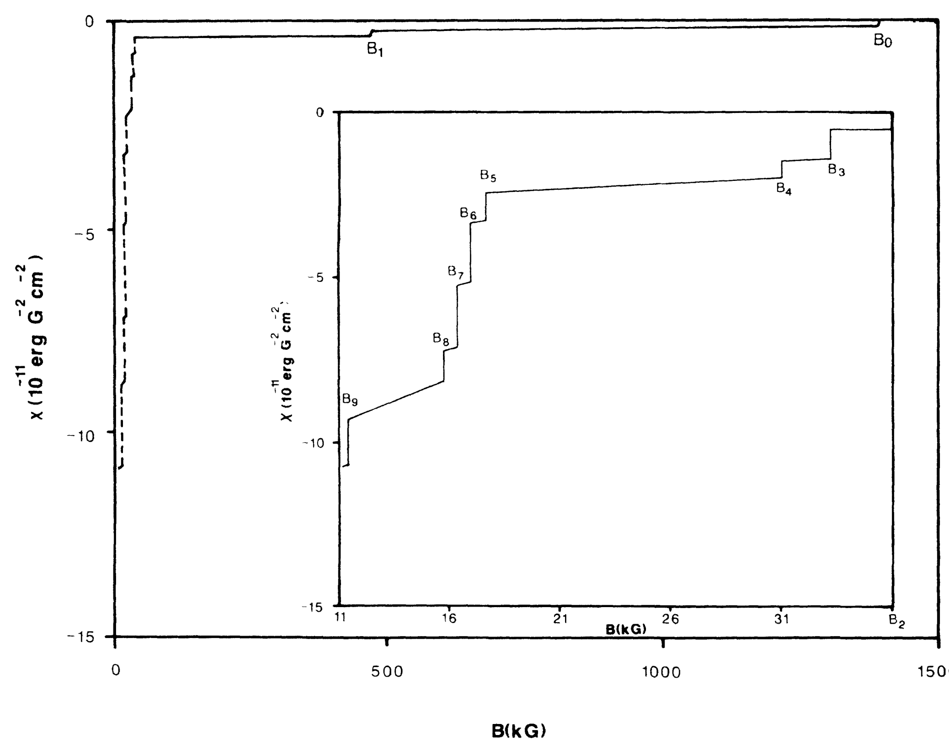

FIG. 10. Magnetic susceptibility versus magnetic field in a two-dimensional bismuth film, film ⊥ bisectrix axis.

or $m_s \cong m_c$. Thus, the twin electron bands have $m_c \cong m_s \cong 0.003\,53$, and the single electron band has $m_c \cong m_s \cong 0.001\,77$.

As in films normal to the trigonal axis, in $B > B_1$ there is one hole level and one electron level that are occupied, but the number of either electrons or holes equals $2D$. However, in films normal to the bisectrix axis, the lowest hole level $E_p(0-)$ may cross over the lowest electron level $E_n(0-)$ at B_0 (see Table I), beyond which ($B > B_0$) an energy gap starts to emerge and the semimetallic-semiconducting state transition would take place. In fields below B_0, the film remains semimetallic and the evaluations for the carrier density, energy density, magnetization, and susceptibility are similar to those in Sec. III. The results, however, are certainly different, as expected. In films normal to the trigonal axis, the three electron bands are equivalent and each energy level has a degeneracy of $3D$; in films normal to the bisectrix axis, however, there are two unequivalent electron bands, one has a degeneracy of $2D$ and the other has D. There has been no severe difficulty in identifying those occupied levels of electrons and holes in a given field B, although it was time consuming. The results are shown in Figs. 6–10. The figures are quite self-explanatory.

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