Magnetic field dependence of the carrier density and magnetization in a bismuth thin film

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The electrons and holes in a bismuth film placed in a transverse magnetic field assume three-dimensionally quantized energy spectra. The nonparabolicity of the conduction band and the unique effective masses result in a peculiar magnetic field dependence of the thermodynamical quantities in the film (normal to the trigonal axis). In particular, the carrier density and the magnetization exhibit unusual field dependences, quite different from that for an ordinary de Haas–van Alphen effect. Lax's energy-band model for bismuth electrons, and experimental effective masses, with modification to account for the quantum size effect, were used in the evaluations.

I. INTRODUCTION

In a previous work,[1] we have studied the de Haas–van Alphen effect in an ultrathin film of semimetal bismuth. Once the film thickness is sufficiently reduced, the quantum size effect would have pushed beyond the Fermi level all but the ground energy levels of the electrons and the holes, respectively, and the charge carriers would perform essentially two-dimensional motions. The electrons in semimetal bismuth are well known for having a complicated energy spectrum, featuring the nonparabolic ellipsoidal Fermi surface among a few of the most commonly used models.[2] Accordingly, the de Haas–van Alphen effect exhibits more peculiar oscillations as reported in Ref. 1.

It is conceivable that the de Haas–van Alphen effect as well as other thermodynamic quantities would exhibit significantly different features in films where the quantum size effect is neither extremely pronounced nor negligible so that the motion of the charge carriers would be neither two dimensional (2D) nor the same as in a bulk crystal. In fact, the electrons and/or holes would perform a three-dimensionally (3D) quantized motion and the energy spectrum would be three-dimensionally quantized: the size quantization that quantizes the energy along the film-thickness direction and the magnetic-field-induced quantization that quantizes the energy in the plane of the film, assuming the magnetic field is applied perpendicular to the film. We shall use 3D for these films. It is conceivable that analyses of the de Haas–van Alphen effect and of other thermodynamical quantities in a 3D film would provide useful information for the Fermi surface, the cyclotron effective mass, the spin effective mass, and the longitudinal effective mass.

To our knowledge, there have been few experimental studies on the de Haas–van Alphen oscillations in a 3D film. In this paper we shall provide results of numerical analyses of a few thermodynamical quantities, including the magnetization and the magnetic susceptibility, in 3D films of semimetal bismuth. It was noticed, interestingly, that the combination of the nonparabolic feature of the electron-energy spectrum[2] and the unique masses of electrons and holes in bismuth would result in the peculiar magnetic-field dependence of the thermodynamical quantities. We believe such peculiarities would be of interest to experimentalists. Experimental work in the future may either confirm such predictions or provide information to improve the theory for the study of bismuth thin films.

In the work in Ref. 1, the effective masses used in the analyses were directly from a report by Smith *et al.*,[3] where bulk crystals of semimetal bismuth were studied. It has been reported[4] that in thin films the quantum confinement would modify, maybe significantly, the cyclotron as well as the longitudinal effective masses. Also from the work of Smith *et al.*, the energy gap E_g between the conduction band and the valence band directly underneath it assumed a constant value of 15.3 meV. This constant, which is a characteristically important parameter associated with the nonparabolic band model[2] of bismuth electrons, would obviously be subject to an increase should the bottom of the conduction band (the lowest energy level of the electrons in the conduction band) move up due to the quantum size effect. We have taken the quantum effects on the effective masses and on the energy gap E_g into account in this work.

In a pure bismuth crystal, the number of electrons in the conduction band is naturally equal to the number of holes in the valence band which overlaps the conduction band. This is the charge-neutrality condition that has been used extensively until recently in connection with studies on semimetal bismuth. Recently, in the papers by Hoffman *et al.*,[5] Lu *et al.*,[6] and ourselves,[7] a hole-majority condition was suggested to replace the charge-neutrality condition in bismuth thin films to accommodate a possible energy-band bending due to surface effects. However, a reliable quantitative expression of the condition has not been experimentally established and a primitive test indicated that the feature of the peculiar magnetic-field dependence reported in this paper would not be significantly modified if the charge-neutrality condition is substituted by a hole-majority condition. Thus, in order to explore the fundamental features in a 3D film of bismuth, we shall use the charge-neutrality condition for a simpler and more concrete computation.

Theoretical background for this study will be given in Sec. II, results and discussion in Sec. III, and a summary in Sec. IV.

II. THEORY

The electrons and holes in a 3D bismuth film, according to Lax's nonparabolic-ellipsoidal model,[2] assume the follow-

TABLE I. Effective masses (Refs. 3 and 4) in a bismuth thin film normal to the trigonal axis.

	Electron	Hole
Cyclotron	$1.72\times10^{-2}m_0$[a]	$6.4\times10^{-2}m_0$
Spin	$2.39\times10^{-2}m_0$	$3.3\times10^{-2}m_0$
Longitudinal	$2.97\times10^{-3}m_0$	$6.9\times10^{-1}m_0$

[a] m_0 is the free electron mass.

ing quantized energy levels, respectively: for electrons,

$$E_e\left(1+\frac{E_e}{E_g}\right)=\left(n+\frac{1}{2}\right)\hbar\frac{eB}{m_c c}\pm\frac{1}{2}\hbar\frac{eB}{m_s c}+\frac{\hbar^2\pi^2}{2m_l d^2}l^2, \quad (1)$$

and for holes,

$$E_p=\left(N+\frac{1}{2}\right)\hbar\frac{eB}{M_c c}\pm\frac{1}{2}\hbar\frac{eB}{M_s c}+\frac{\hbar^2\pi^2}{2M_L d^2}L^2, \quad (2)$$

where the cyclotron effective masses m_c and M_c, the spin effective masses m_s and M_s, and the longitudinal effective masses m_l and M_L assume the numerical values given in Table I. The magnetic quantum numbers n and N assume integers 0, 1, 2,... and each level has a degeneracy of $g=A(eB/hc)$, where A is the area of the film. The size quantization numbers l and L assume integers 1, 2, 3,... . The conduction band consists of three symmetrically located energy ellipsoids while the hole valence band has only one energy ellipsoid.

E_g, a characteristic parameter in the nonparabolic ellipsoidal model for the bismuth electrons (when $E_g\rightarrow\infty$, the energy spectrum goes to a parabolic one), is the energy difference from the top of the valence band (directly underneath the electron conduction band) to the lowest electron energy level in the conduction band. From Eq. (1), the lowest energy level E_0 satisfies

$$E_0\left(1+\frac{E_0}{E_g}\right)=\frac{1}{2}\hbar\frac{eB}{m_c c}-\frac{1}{2}\hbar\frac{eB}{m_s c}+\frac{\hbar^2\pi^2}{2m_l d^2}. \quad (3)$$

The first two terms on the right-hand side of Eq. (3) have a positive net value and the right-hand side is zero only when $B=0$ and $d\rightarrow\infty$. When E_0 is zero, $E_g=15.3$ meV (Ref. 3), and when $E_0\neq0$, we should have $E_g=15.3\,\text{meV}+E_0$. Let us denote the right-hand side of Eq. (3) by E^* and use meV as the unit for energies; we obtain

$$E_g=\tfrac{1}{4}\{3\times15.3+E^*+[E^{*2}+(15.3)^2+6\times15.3\times E^*]^{1/2}\} \quad (4)$$

Thus E_g is 15.3 meV when $E^*=0$, and is increasing with E^*, which would increase with increasing magnetic field, and with decreasing film thickness.

Most of our evaluations were for $T=0$. Given a magnetic field B and a film thickness d, the energy levels can be numerically sorted by a computer. Since each quantized energy level carries a known degeneracy, the number of electrons can be equal to that of the holes only when certain levels are occupied, respectively, given that at $T=0$ each and every occupied electron level must be lower in energy than any of the occupied hole levels and the energy overlap of the electron band and the hole band is a known constant[3] of 38.5 meV. Thus, the number of the carriers can be evaluated as a function of B and d (at $T=0$). The total energy, magnetization, and the magnetic susceptibility can then be worked out also as functions of B and d. For $T\neq0$, the Fermi distribution function must be used and the computations just require a modified computer program.

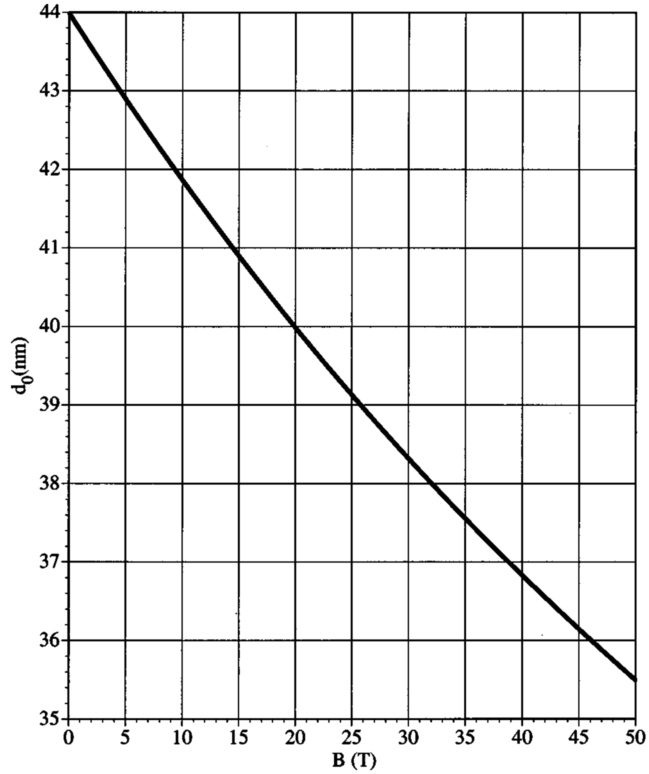

FIG. 1. Semiconductor-semimetal transition diagram: film thickness d_0 (where semiconductor-semimetal transition occurs) versus magnetic field.

III. RESULTS AND DISCUSSION

A. Semimetal-semiconductor transitions

We have reported in a previous work[7] that under the vanishing-wave-function boundary condition and in zero magnetic field there would be a transition from a semimetallic state to a semiconducting state when the film is reduced to a certain thickness denoted by d_0. Since changing the magnetic field B would also move the energy levels, one may expect a magnetic-field-induced transition as well. However, our results showed that the magnetic field would not induce a transition of a semimetallic bismuth film (normal to the trigonal axis) to a semiconducting film. This means if the film is a semimetallic film in zero or low magnetic fields, then it would remain semimetallic even when a strong magnetic field is applied; and if a film of reduced thickness starts with a semiconducting state in zero or low fields, it may return to a semimetallic state when the fields are sufficiently strong. Figure 1 shows a phase diagram in the d-B plane; semiconducting states on the left side of the curve and semimetallic states on the right.

Two characteristic features in the energy-band structure in bismuth lead to this interesting result. First, the lowest magnetic level of holes moves away from, instead of toward, the

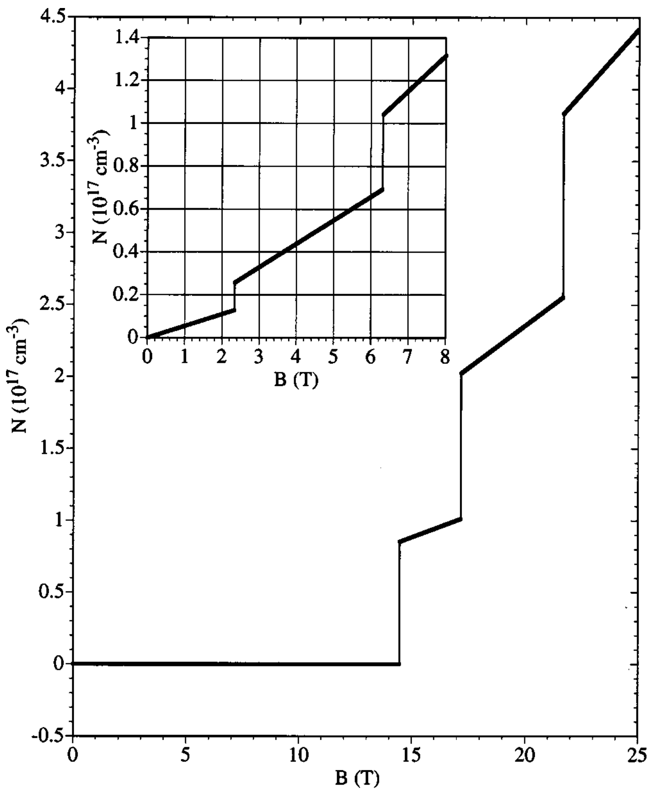

FIG. 2. Carrier density versus magnetic field; $T=0$, film thickness is 410 Å; inset 440 Å.

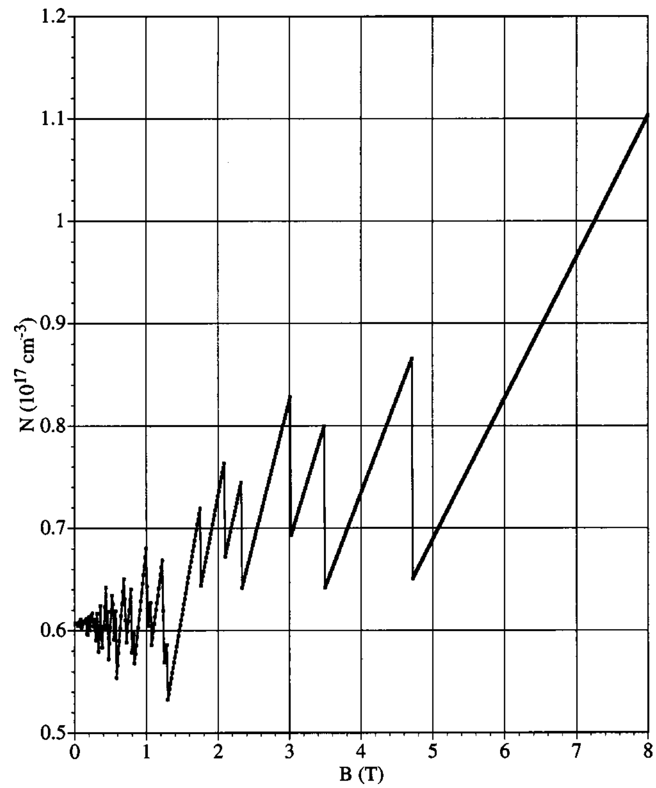

FIG. 3. Carrier density versus magnetic field; $T=0$, film thickness is 525 Å.

Fermi level since M_s is smaller than M_c in Eq. (2), and second, although the lowest magnetic level of electrons does move upward, its motion with increasing magnetic field is significantly reduced by the nonparabolic feature in Eq. (1). The overall separation between the lowest levels, respectively, of the electrons and holes actually increases with increasing field; this means increasing the magnetic field would not induce a semimetal to semiconductor transition.

B. Carrier density

Figure 2 shows the electron and/or hole density as a function of the applied magnetic field in a film of thickness 410 Å. The evaluations were for $T=0$ (temperature). At low temperatures, the dependence (not shown) would remain similar, but exhibit smooth corners at the discontinuities. The thickness was arbitrarily chosen below the largest $d_0=440$ Å in Fig. 1. In lower fields, the film is a size-induced semiconductor and has zero carrier density at $T=0$. In larger than an on-set magnetic field (for the 410-Å film, this is about 14 Tesla) the film would have returned to a semimetallic status. This is because the lowest hole level [$N=0$, negative spin, and $L=1$ in Eq. (2)] moves upward ($M_s<M_c$) in an increasing magnetic field faster than the lowest electron level [$n=0$, negative spin, and $l=1$ in Eq. (1)] which also moves upward ($m_c<m_s$). Once this hole level is above the electron level, the density would be $g/Ad=eB/hcd$, where $d=410$ Å. Since the hole longitudinal effective mass is relatively large, the hole levels $L=2$, 3, 4,... ($N=0$, negative spin) are all near the $L=1$ level and move up at the same rate in an increasing field. Thus, at $B\approx 17$ T, the $L=2$ hole level, which is below the $L=1$ level, would be crossing the lowest electron level and become occupied. The electron and/or hole density is now $2(eB/hcd)$. When $B\geqslant 22$ T, the density would be $3(eB/hcd)$. Here the occupied hole levels are $N=0$, negative spin, and $L=1$, 2, 3 with each level accommodating g holes; the occupied electron level is $n=0$, negative spin, $l=1$, which accommodates $3g$ electrons. Each segment in Fig. 2 is linear with B and the slope of the third segment is three times larger compared to that of the first. In fields as high as 50 T, the $N=0$, negative spin, $L=4$ hole level, which may well be above the $n=0$, negative spin, $l=1$ electron level, would remain unoccupied, because the $n=0$, positive spin, $l=1$ or the $n=0$, negative spin, $l=2$ electron level remains higher in energy. Thus the occupied levels remain to be three hole levels and one electron level. Such density-versus-field dependence applies to any thickness below the largest d_0 in Fig. 1. For a larger or smaller thickness, each corresponding step up would occur at a lower or higher magnetic field, and each corresponding slope would be smaller or larger (inversely proportional to the thickness), respectively. In particular, a film of thickness of 440 Å would start to be semimetallic even in low magnetic fields. This is shown as an inset in Fig. 2.

The carrier density versus magnetic field in a film of 525 Å is shown in Fig. 3. This thickness is larger than the largest d_0 in Fig. 1, so the film would remain semimetallic in a magnetic field of any intensity. However, this thickness is still quite low, so the quantum size effect would be pronounced. In fact, only the $l=1$ [in Eq. (1)] electron levels are occupied for $0<B<\infty$. In low magnetic fields $B\approx 2$ Tesla, two electron levels are filled with electrons; they are $n=0$, $\pm$ spin, and $l=1$, while the hole levels are $N=0$, $-$ spin, and $L=1$ through 5, plus another $N=1$, $-$ spin, and $L=1$ level.

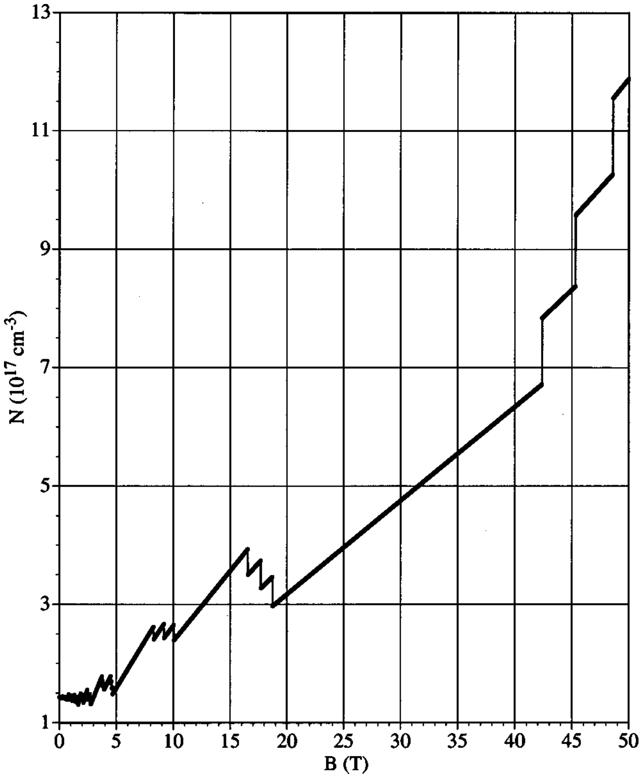

FIG. 4. Carrier density versus magnetic field; $T=0$, film thickness is 915 Å.

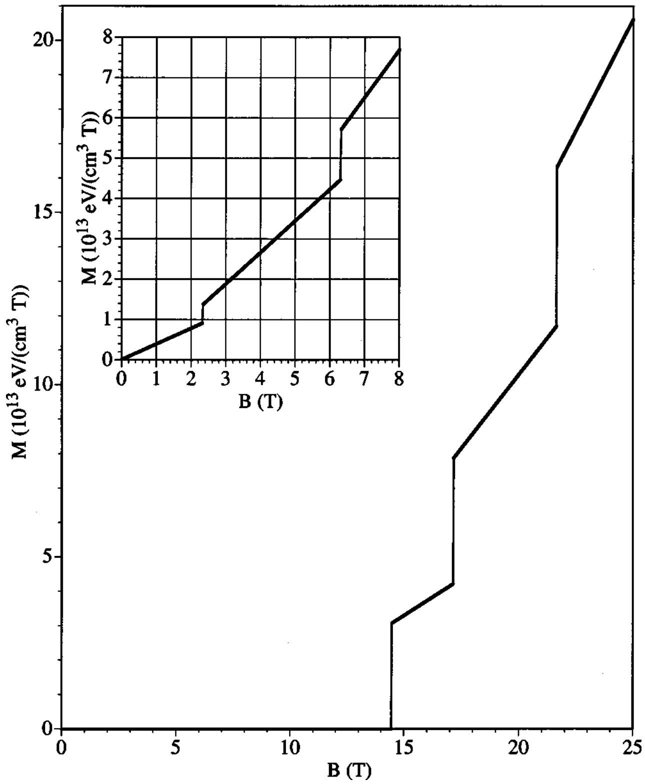

FIG. 5. Magnetization versus magnetic field; $T=0$, film thickness is 410 Å; inset 440 Å.

When the field is increased to a little less than 5 T, the remaining occupied levels are one level ($n=0$, $-$ spin, $l=1$) for electrons and three levels ($N=0$, $-$ spin, $L=1$, 2, 3) for holes. Increasing the field strength further would not change the occupied levels, although the density would increase linearly because the degeneracy is proportional to the field. Figure 3 provides oscillations qualitatively similar to those learned in a 2D film or in a bulk crystal of semimetal bismuth. In an increasing magnetic field, occupied levels of higher energy of electrons and holes, respectively, cross over each other and become unoccupied, resulting in a sudden drop in the density.

Figure 4 provides the plot for a film of 915 Å, a much larger thickness. We see a ''normal'' field dependence in lower fields and peculiar dependence in higher fields. By ''normal'' we mean normal level crossings that result in a drop of the density (cf. Fig. 3), while by ''peculiar'' we mean the abnormal crossings that open up unoccupied levels and increase the density. We have already seen such peculiar dependence in Fig. 2. The unique energy band structure and effective masses in bismuth make this dependence possible. The density increases linearly with the field between two steps (either step up or step down). This is a general feature, since the density is proportional to the degeneracy which is proportional to the field.

The level crossings in the plots may appear in groups of three, i.e., three step ups or three step downs in a row, as can be seen in Figs. 2 and 4. This is simply because each electron level is triply degenerate due to the three energy ellipsoids in the conduction band.

C. Magnetization and susceptibility—peculiar de Haas–van Alphen effect

The charge-neutrality condition determines which levels of electrons and holes, respectively, are occupied at $T=0$ in a film of known thickness in a given magnetic field. The energy levels are those in Eqs. (1) and (2), respectively. The total energy of the carriers can thus be readily calculated. The magnetization (per unit volume) at $T=0$ is simply $M=-\partial E/\partial B$, where E is the energy per unit volume. When plotting against the magnetic field, the carrier density, the energy density, and the magnetization in a given film should exhibit discontinuities at the same field intensities (the energy itself is continuous, but its slope should be discontinuous). The explanation for the discontinuities, as well as for the step ups and/or step downs in the plots, should be the same as given in the first two parts in this section, and will not be repeated. Three M versus B plots are shown in Figs. 5–7 in films of thicknesses similar to those in Figs. 2–4.

In a typical de Haas–van Alphen effect, the energy of a Fermi gas of N electrons in an increasing magnetic field rises following a drop in the number of occupied levels (at $T=0$, for simplicity) and goes down before the next level drop. While the magnetization exhibits fragmental straight lines, each assuming negative to positive values, the susceptibility is always positive, indicating that the electron system remains paramagnetic. In a semimetal bismuth film, however, there are electrons and holes and the conduction band consists of three energy ellipsoids while the hole valence band has only one. Calculation of the energy showed that, except in thicker films in low magnetic fields where occupied levels were plenty and an increase of energy with increasing

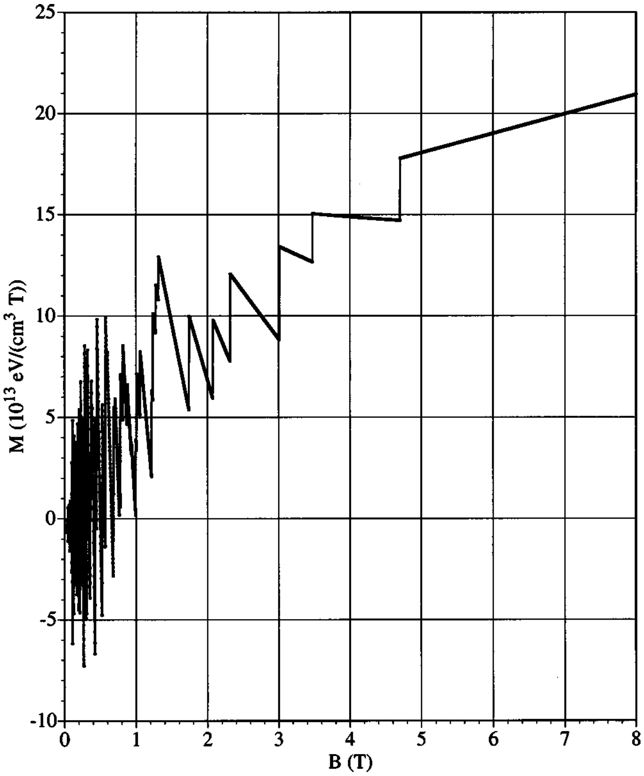

FIG. 6. Magnetization versus magnetic field; $T=0$, film thickness is 525 Å.

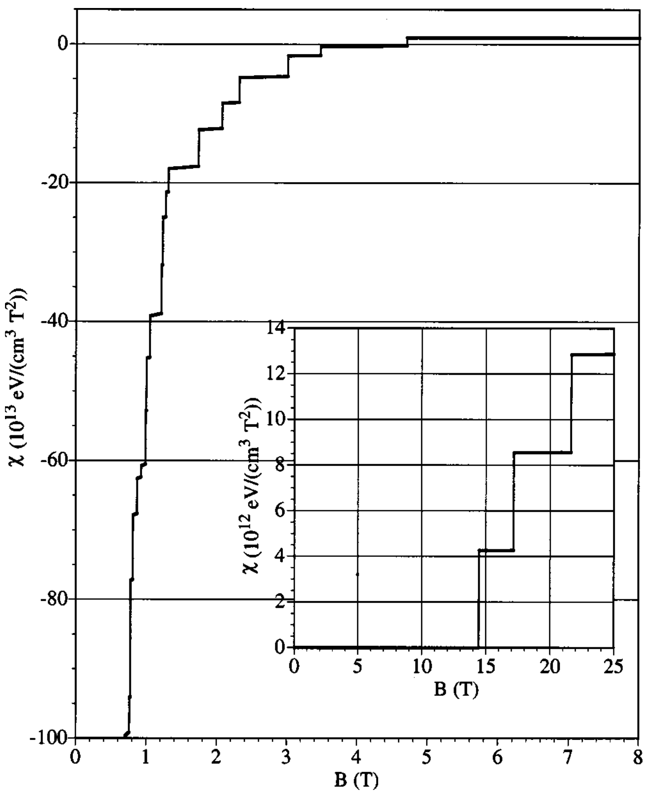

FIG. 8. Magnetic susceptibility versus magnetic field; $T=0$, film thickness is 525 Å; inset 410 Å.

magnetic field could be seen, the energy most commonly decreased with the increasing field, resulting in positive magnetizations, as shown in Figs. 5–7.

The magnetization M, except at the discontinuities, seems to be linear with the field. The right-hand sides of the energy equations (1) and (2) are linear in B, and the degeneracy of each level is also proportional to B; thus, without the nonparabolic feature on the left-hand side of Eq. (1), the total energy of the carriers would be quadratic in B resulting in a linear dependence of the magnetization with the field. The parabolicity should qualitatively cause deviation from such linear dependence; however, in the figures shown thus far the deviations are quantitatively too small to be noticed (cf. see the nonconstant susceptibilities between two ''steps'').

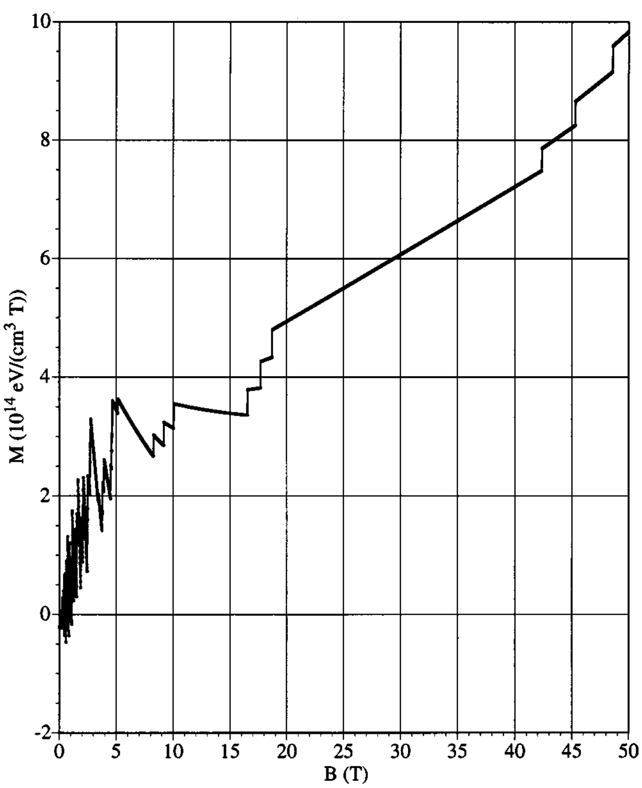

FIG. 7. Magnetization versus magnetic field; $T=0$, film thickness is 915 Å.

In thinner films (e.g., 410 Å), the lowest unoccupied levels of electrons and holes, respectively, open up for occupation in an increasing magnetic field and the film would be turned into a semimetal from a semiconductor. The total energy would thus exhibit a monotonic decrease; the magnetizations would be positive and increase linearly with the field, so the susceptibility would be positive and the semimetallic film is paramagnetic. Films thicker than 440 Å are always semimetallic. In these films, the normal crossings of an electron level over a hole level in an increasing magnetic field eliminate these levels for occupation. Immediately following a crossing, the closest occupied levels of electrons and holes, respectively, are relatively far apart, so the increase of the degeneracy g with the field would cause a fast decrease in the energy and a positive, but larger in magnitude, magnetization.

Shown in Figs. 6 and 7, the magnetizations are positive and most of them have negative slopes. These are the ''normal'' de Haas–van Alphen–type oscillations in a semimetal, where the susceptibilities are negative. In Fig. 5 as well as in the high field limit in Figs. 6 and 7, ''peculiar'' de Haas–van Alphen oscillations are shown, where the susceptibilities are positive. Thus, both diamagnetism and paramagnetism could be seen in films thicker than 440 Å, while only paramagnetism would exist in thinner films. In a thicker film diamagnetism is in lower fields and paramagnetism is in higher fields. Shown in Fig. 8 are the magnetic susceptibility in a couple of films. The nonconstant susceptibilities between two consecutive level crossings are the result of the nonparabolic feature of the electron-energy band. The deviation from being a constant appears, however, to be inappreciable.

IV. SUMMARY

The spin effective mass M_s of holes in semimetal bismuth is smaller than the cyclotron effective mass M_c [Eq. (2)] and thus the lowest hole (energy) level would move in an increasing magnetic field away from the Fermi level. Such motion is opposite to a normal motion commonly seen with larger spin effective mass. This abnormality in the effective masses of holes plus the nonparabolicity of the energy-momentum relationship in the conduction band leads to peculiar magnetic-field dependence of the carrier density, the magnetization, and the susceptibility.

With an increasing magnetic field, there are two kinds of energy-level crossings. A normal crossing occurs when an electron level moves up (in terms of energy), crosses over a downward-moving hole level, and eliminates the occupation of these two levels leading to a sudden drop in the density of electrons and/or holes. An abnormal crossing is due to the upward-moving hole levels [$N=0$, $-$ spin in Eq. (2)], when one of them overtakes an electron level and opens up these two levels for occupation leading to an abrupt increase in the density.

Abnormal level crossings generally occur in higher magnetic fields and correspond to an abrupt increase in carrier density and a positive susceptibility (paramagnetism). Normal crossings lead to a drop in the carrier density and generally a negative susceptibility (diamagnetism). There are only abnormal level crossings in thinner films.

Once experimental results become available, comparison with the results presented in this paper would verify the applicability of the basically bulk model of the energy-band structure to thin films, check numerically the effective masses, and suggest the appropriate boundary condition. The peculiar field dependence of the carrier density and the magnetization, as well as the field-induced diamagnetism to paramagnetism transition may provide both experimental and practical interests.

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