extent to which the wave moving in the film is reflected at the back surface.

[22]The transverse dielectric function as obtained from the Boltzmann equation is given, for example, by Eq. (2.46) of Ref. 1. To obtain Eq. (2.46) of Ref. 1, one need only replace α in Eq. (4.35) above by $ib'Q$, where Q is the magnitude of the wave vector and $b' = (v/\gamma c)/(1 - i\Omega/\gamma)$.

[23]J. N. Hodgson, J. Phys. Chem. Solids 24, 1213 (1963).

[24]M. A. Biondi and A. I. Guobadia, Phys. Rev. 166, 667 (1968).

[25]T. Holstein, Phys. Rev. 88, 1427 (1952).

[26]Equation (5.1) results if the $\tilde{d} \to \infty$ limit is taken in Eq. (9.1) of Ref. 11.

[27]$W = 0.3$ corresponds to a film thickness of 136 Å for K, and 47 Å for Al.

[28]Both δ and α are of order 1 for $\Omega \sim 10^{-3}$ and $\gamma \sim 10^{-3}$.

[29]The expression in Eq. (9.1) of Ref. 11.

[30]Note that this is consistent with (6.13b) and (6.9).

[31]This expression, having already been averaged over v_f, involves only the Fermi velocity, and, thus, corresponds to the general theory wherein physical effects occur only for electrons with the Fermi velocity because of the factor $\partial f_0/\partial \epsilon_k^*$ appearing, for example, in Eqs. (4.11).

[32]L. Bos and D. W. Lynch, Phys. Rev. Letters 25, 156 (1970); D. W. Lynch (private communication).

[33]Equation (3.1) for the surface impedance can be integrated exactly in the region of the extreme anomalous skin effect. See L. E. Hartmann and J. M. Luttinger, Phys. Rev. 151, 430 (1966); 156, 1038 (1967).

[34]Obviously, Eq. (3.1) can be used for all frequencies. However, numerical integration of Eq. (3.1) becomes particularly time consuming when $\Omega > 10^{-1}$. In this frequency range the present theory with $W \to \infty$ is a much more efficient way to obtain results for thick samples.

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Effect of Hydrostatic Pressure on the Fermi Surface of Bi†

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(Received 11 May 1970)

We present data on the pressure dependence of the smallest extremal cross-sectional areas of both the hole and electron sheets of the Fermi surface of Bi. The cross sections were determined from measurements of the frequency of de Haas–van Alphen oscillations detected with the field modulation technique. Pressure derivatives obtained using solid He and fluid He were in excellent agreement, thus removing any doubts about the hydrostatic nature of the stress in the solid-He portions of the work. Values for the pressure derivatives of the effective masses associated with these cross sections were obtained from magnetization-amplitude-versus-temperature measurements in solid He to ~4 kbar. Our values for the pressure derivatives of the cross sections and masses differ in detail from and have somewhat less uncertainty than the most recent literature values. No change in the initial phase of the de Haas–van Alphen oscillations associated with the smallest extremal cross-sectional area of the hole sheet was detected in contrast to the findings of Overton and Berlincourt.

I. INTRODUCTION

Bi was the first metal in which studies of the size and shape of the Fermi surface as a function of pressure were attempted.[1–3] Although much of the earlier work suffered from the inadequacies of the pressure techniques in achieving hydrostatic compression on nonisotropic crystals, it was established that large changes in the electronic energy spectrum were occurring with pressure. These large changes are not surprising in view of the anisotropy of the structure and elastic properties of Bi.

Bi crystallizes in the arsenic structure, which can be thought of as two face-centered-cubic sublattices displaced from each other along a body diagonal with a small rhombohedral distortion along this diagonal. The effect of pressure on the Bi lattice[4] is to change the dimension in the trigonal direction at the fractional rate of -18.1×10^{-4} kbar^{-1} and the dimension perpendicular to the trigonal axis at -6.4×10^{-4} kbar^{-1}. The distance between the sublattices or the atomic positional parameter increases[5] at the fractional rate of $\sim 11 \times 10^{-4}$ kbar^{-1}.

The Fermi surface of Bi is quite simple, consisting of nearly ellipsoidal hole and electron sheets.[6] The hole sheets are located near the point T in the Brillouin zone with their long axes parallel to the trigonal direction. The electron sheets are in the trigonal-bisectrix plane with their long axes tipped ~96° from the trigonal direction in the sense T toward X.[7]

There has been a renewal in interest in the pressure dependence of the semimetals of the arsenic structure (Bi, Sb, and As) with the findings of Brandt and co-workers[8] that the behavior of these metals under conditions of hydrostatic pressure are very different. By measurement of the transverse magnetoconductivity, Brandt *et al.*[8] showed that the number of carriers decreases in Bi and As with pressure, but increases in Sb. We have verified this unexpected behavior in Sb by direct measurements of several of the cross-sectional areas by de Haas–van Alphen studies under pressure.[9] There has been considerable variation in the reported results for the pressure dependence of the cross-sectional areas of the two Fermi-surface sheets of Bi. Recent work on the electron surface by Brandt *et al.*[10] showed good agreement between de Haas–van Alphen measurements using the ice-bomb technique[3] and Shubnikov–de Haas studies using the frozen oil-kerosene method.[11] More recently Itskevich *et al.*[12] have reported extensive studies using the frozen oil-kerosene pressure method on both sheets of the Fermi surface. We have previously observed discrepancies between the results of these types of measurements and our solid-He results.[13] These discrepancies have been most pronounced on highly anisotropic materials at relatively low pressures (<3–5 kbar).

The purpose of this work is to present de Haas–van Alphen studies of the smallest extremal cross-sectional areas of the hole and electron sheets of the Fermi surface of Bi obtained in solid He to ~ 4 kbar. We are able to complement these measurements with direct determinations of the initial change of the cross sections in fluid He by means of the fluid-He phase-shift technique.[14,15] We have also measured the effective masses of both of these cross-sectional areas to ~ 4 kbar. Finally, we have made a careful search for the large change with pressure in the initial phase of the "de Haas–van Alphen" oscillations in the Hall coefficient associated with the hole cross section reported by Overton and Berlincourt.[2] In Sec. II we outline briefly our experimental procedures. Section III consists of our results and discussion and we summarize our findings in Sec. IV.

II. EXPERIMENTAL PROCEDURE

Samples were grown from 99.9999+% pure material from Cominco by the Czochralski technique. This technique eliminated problems arising from the well-known increase in volume of Bi upon freezing which can produce strained crystals if the ingot is confined. Samples were cut to within 2° of the desired orientation (as determined by standard back reflection Laue x-ray techniques) by spark erosion and were typically $\frac{1}{8}$-in.-diam. $\times \frac{1}{2}$ in.-long right circular cylinders.

The de Haas–van Alphen (dHvA) oscillations were detected with the low-frequency modulation technique in fields generated in either a superconducting solenoid or in an electromagnet.[9] Since much of the work was done at low fields (<3 kOe) where a frozen-in flux can be a serious problem in a superconducting solenoid, the field was determined using an NMR probe situated in the immediate proximity of the dHvA sample. The F^{19} resonance in our Teflon NMR sample chamber was usually used at these low fields and the dHvA traces were marked as the field was swept very slowly through the resonance. The calibration of the electromagnet was checked with dHvA periods previously determined in the *in situ* NMR-calibrated solenoid.[16] Periods were determined between essentially the same field values at the various pressures and data were confined as much as possible to sufficiently low fields so that distortion of the wave form of the dHvA signal was minimized. All pressure studies of the dHvA frequencies were conducted near 1.1 °K.

Mass measurements were all made below the λ point at the signal could be seen at the lowest fields (~ 500 G for the electron and ~ 3000 G for the hole cross section) to eliminate as much as possible the strong higher harmonic contributions to the dHvA signal. Five or six temperatures were taken on each run and the mass determined from a best straight-line fit of a $\ln(A/T)$ versus T plot (where A is the amplitude and T is the temperature).

Pressures to ~ 4 kbar were generated by careful isobaric freezing of He about the single-crystal sample.[13] This technique consists of applying pressure in fluid He at a temperature slightly above the freezing point of He at the desired pressure. The pressure vessel is then cooled slowly from the bottom so as to move the solid-fluid line slowly over the single-crystal specimen while maintaining the pressure at a given value to within $\sim 1\%$. Too rapid freezing of the He could result in serious loss of amplitude of the dHvA signal. The fluid-He phase-shift technique was used to determine the initial slope of the dHvA frequency-versus-pressure curve.[14,15] This technique utilizes the usually high phase $2\pi F/B$ (where F is the dHvA frequency and B is the applied field) to obtain directly the pressure derivative. The method is relatively inappropriate for Bi because of the low frequencies involved, but this is compensated somewhat by the large value of the pressure derivatives of the frequencies, so that accuracies approaching $\pm 10\%$ are obtainable.

III. RESULTS AND DISCUSSION

A. Electron Surface

The results for our pressure studies of the electron surface of Bi are shown in Table I. Data were

TABLE I. Pressure derivatives for the cross section and effective mass of the electron sheet of the Fermi surface of Bi. The magnetic field is parallel to $[11\bar{2}0]$ in the frequency measurements and to $[10\bar{1}0]$ in the mass measurements. Values are given in units of 10^{-2} kbar^{-1}. Also shown are comparisons with most recent literature values where we have estimated uncertainties from those quoted in the references.

	Solid He	Fluid He	Literature value
$d\ln F/dP$	$-6.0\ (\pm 0.3)^a$		$-6\ (\pm 1)^b$
	$-6.0\ (\pm 0.3)^c$	$-7\ (\pm 1)^c$	
$d\ln m^*/dP$	$-6\quad(\pm 2)^d$		$-5\ (\pm 3)^e$

[a]Sample S139.
[b]Reference 12.
[c]Sample S160.
[d]Samples S138, S160.
[e]Reference 17.

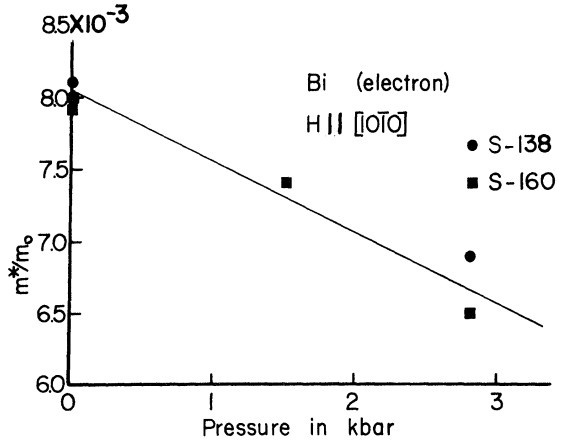

FIG. 2. Effective mass of the smallest extremal cross-sectional area of the electron surface of Bi for $H \| [10\bar{1}0]$ as a function of pressure.

in actuality taken along the $[11\bar{2}0]$ and $[10\bar{1}0]$ crystal directions for a large part of the study, but no effect due to these deviations from the actual direction of minimum area was detected. We show for comparison the recent data of Itskevich *et al.*[12] for this cross section. The error in the phase-shift determination is large because of the low phase of the oscillations even below 1 kOe. Figure 1 shows the results of two runs on separate samples of the dHvA frequency versus pressure for $H \| [11\bar{2}0]$ at 1.1 °K. The cross-hatched region shows the range of slope of the dHvA frequency versus pressure as determined by the phase-shift technique.

Figure 2 shows the data for the effective mass of the electron cross section versus pressure for $H \| [10\bar{1}0]$. Our value for $d\ln m^*/dP$ agrees easily within combined uncertainties with the value given by Itskevich and Fisher.[17] Our value for the pressure dependence of the electron cross section is in substantial agreement with that found by Itskevich *et al.*[12] We have made no attempt to compare with the early data for the pressure dependence of this cross section because much of the disagreement between various investigators is now recognized to stem from difficulties in generating hydrostatic pressures in solid pressure media.[13] We have therefore confined our comparison here and in what follows to the most recent data.

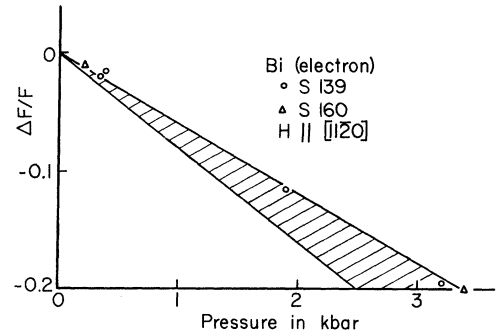

FIG. 1. Smallest extremal cross-sectional area of the electron surface of Bi for $H \| [11\bar{2}0]$ as a function of pressure. The cross-hatched area denotes our estimated uncertainty in the initial slope as determined in fluid He.

B. Hole Surface

Our results for the pressure studies of the hole surface for Bi for $H \| [0001]$ are given in Table II. We also show the results of Itskevich *et al.* The difference between our values for the pressure derivative of the frequency and that reported by Itskevich *et al.*[12] seems to be outside of experimental uncertainty. In Fig. 3 we show the results of runs on two different samples for $H \| [0001]$ at 1.1 °K for the hole frequency versus pressure. The cross-hatched region is again the range of initial slope given by the phase-shift technique in fluid He.

TABLE II. Pressure derivatives for the cross section and effective mass of the hole sheet of the Fermi surface of Bi for $H \| [0001]$. Values are given in units of 10^{-2} kbar^{-1}. We show for comparison recent literature values for these quantities.

	Solid He	Fluid He	Literature value
$d\ln F/dP$	$-6.8\ (\pm 0.3)^a$	$-6.8\ (\pm 0.6)^a$	$-4.6\ (\pm 1.0)^b$
	$-6.8\ (\pm 0.3)^c$		
$d\ln m^*/dP$	$-6.5\ (\pm 2)^a$		$-2\ (\pm 3)^d$

[a]Sample S138.
[b]Reference 12.
[c]Sample S161.
[d]Reference 17.

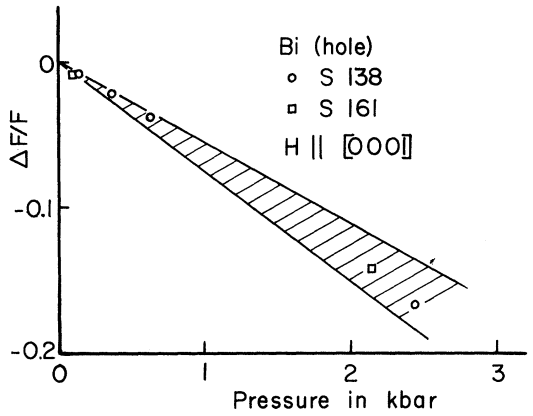

FIG. 3. Smallest extremal cross-sectional area of the hole surface of Bi for $H \| [0001]$ as a function of pressure. The shaded area denotes our estimated uncertainty in the initial slope as determined in fluid He.

In Fig. 4 we show our data for the effective mass of the hole surface versus pressure for $H \| [0001]$. These data were taken at ~3 kOe. Our value for $d\ln m^*/dP$ of $-6.5\ (\pm 2.0)\times 10^{-2}$ kbar^{-1} does not appear to agree with the work of Itskevich and Fisher[17] who report a rate of change over an 8-kbar range of about $-2(\pm 3)\times 10^{-2}$ kbar^{-1}.

We have made a very careful search for the large change with pressure in the initial slope of the dHvA oscillations associated with the hole minimum cross-sectional area reported by Overton and Berlincourt.[2] A similar "anomalous" change of initial phase with temperature had been observed in Zn by Berlincourt and Steele.[18] We were able to show that this was due to the disappearance of one of the spin-split peaks in the magnetization coupled with a change with c/a in the magnitude of the splitting itself.[19] This splitting is related to the g factor and effective mass by the relation

$$(|g|m^*)(2m_0) = \pm \Delta_s F + l \ ,$$

where Δ_s is the splitting between the peaks, F is the dHvA frequency, and l is zero or an integer. Since we observe a large pressure derivative for m^* and the g factor of Bi is extremely large[20] (and might well be expected to have, as does Zn, a different pressure dependence than m^*) it was of interest to check the observations of Overton and Berlincourt. We measured very carefully, using NMR field markers, the positions of the peaks in the magnetization at ~0.2-kbar pressure intervals to ~2 bkar. No change in the initial phase was observed. Brandt *et al.*[10] showed that the phase of the electron surface oscillations for field along the bisectrix direction did not shift to ~7.5 kbar, but their data cannot be compared with the trigonal hole data of Overton and Berlincourt.[2] Itskevich *et al.* subsequently reported no change in the phase of the hole oscillations to ~8 kbar. Therefore it appears to be well established that either the observations of Overton and Berlincourt are in error or that there is something very different in the phase of oscillations in the Hall voltage from that in the magnetoresistance and magnetization.

Itskevich and Fisher analyze their data for the electron sheet in terms of the model of Lax *et al.*[21] Since our values for the frequency and mass for this sheet are in essential agreement with those of Itskevich and Fisher we will not duplicate their analysis. In view of the recently discovered differences in the pressure dependence of the energy spectra of Bi and Sb mentioned in the Introduction, it appears that rather complicated band-structure pictures may be required to account for the observed behavior in these metals.

IV. SUMMARY

We have obtained data on the pressure dependence of the minimum cross-sectional areas of both the hole and electron sheets of the Fermi surface of Bi. Values obtained in solid He and under purely hydrostatic conditions of fluid He are in excellent agreement so there can be no question of nonuniform stress in our solid-He experiments. We have also obtained values for the pressure dependence of the effective masses associated with these minimum cross sections. Our values for both the pressure derivatives of these cross sections and the masses have less uncertainty than those previously reported. Itskevich *et al.*[12] find that the decrease in the size of the electron minimum cross section is larger in magnitude than that for the hole minimum cross section. Our results do not agree with this in that we find that the two derivatives are very similar, with the pressure derivative of the hole surface slightly larger than that of the electron surface. This difference is barely outside the combined esti-

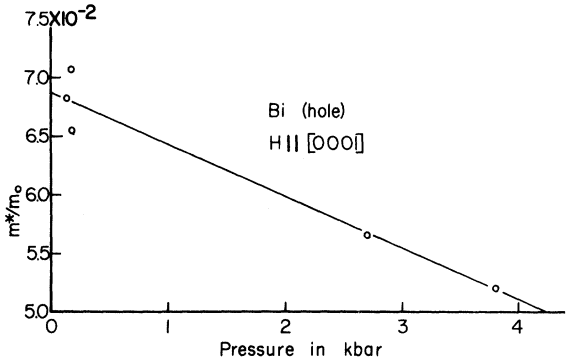

FIG. 4. Effective mass of the hole surface of Bi for $H \| [0001]$ as a function of pressure.

mated uncertainties of the measurements. We have confined the comparison of our data to the most recent published work as it is recognized that much of the disagreement with earlier studies was due to the nonhydrostatic pressure techniques employed. This problem has been discussed elsewhere.[13,22]

Finally, we find no indication of any change in the initial phase of the dHvA oscillations associated with the minimum cross-sectional area of the hole surface.

ACKNOWLEDGMENTS

We are indebted to R. J. Baughman for growing the single-crystal boule from which the samples were cut and to L. Brubaker and R. L. White for technical assistance.

†Work supported by the U. S. Atomic Energy Commission.

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[1]N. E. Alekseevskii and N. B. Brandt, Zh. Eksperim. i Teor. Fiz. 28, 379 (1955) [Soviet Phys. JETP 1, 384 (1955)].

[2]W. C. Overton and T. G. Berlincourt, Phys. Rev. 99, 1165 (1955).

[3]B. I. Verkin, I. M. Dimitrenko, and B. G. Lazarev, Zh. Eksperim. i Teor. Fiz. 31, 538 (1956)[Soviet Phys. JETP 4, 432 1957)]; and references therein.

[4]S. Epstein and A. P. deBretteville, Jr., Phys. Rev. 138, A771 (1965).

[5]B. Morosin and J. E. Schirber, Phys. Letters 30A, 512 (1969).

[6]R. N. Bhargava, Phys. Rev. 156, 785 (1967); and references therein.

[7]L. R. Windmiller, Phys. Rev. 149, 472 (1966).

[8]N. B. Brandt, N. Ya. Minina, and Yu. A. Pospelov, Zh. Eksperim. i Teor. Fiz. 55, 1656 (1968) [Soviet Phys. JETP 28, 869 (1969)]; and references therein.

[9]J. E. Schirber and W. J. O'Sullivan, Solid State Commun.7, 709 (1969); J. Phys. Chem. Solids (to be published).

[10]N. B. Brandt, Yu. P. Gaidukov, E. S. Itskevich, and N. Ya. Minina, Zh. Eksperim. i Teor. Fiz. 47, 455 (1964) [Soviet Phys. JETP 20, 301 (1965)].

[11]E. S. Itskevich, Cryogenics 4, 365 (1964).

[12]E. S. Itskevich, I. P. Krechetova, and L. M. Fisher, Zh. Eksperim. i Teor. Fiz. 52, 66 (1967) [Soviet Phys. JETP 25, 41 (1967)].

[13]J. E. Schirber, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. F. Emrick (Academic, New York, 1965); W. J. O'Sullivan and J. E. Schirber, Phys. Rev. 151, 484 (1966).

[14]I. M. Templeton, Proc. Roy. Soc. (London) A292, 413 (1966).

[15]J. E. Schirber and W. J. O'Sullivan, Phys. Rev. 184, 628 (1969).

[16]W. J. O'Sullivan and J. E. Schirber, Cryogenics 7, 118 (1967).

[17]E. S. Itskevich and L. M. Fisher, Zh. Eksperim. i Teor. Fiz. 53, 1885 (1967) [Soviet Phys. JETP 26, 1072 (1968)].

[18]T. G. Berlincourt and M. C. Steele, Phys. Rev. 95, 1421 (1954).

[19]W. J. O'Sullivan and J. E. Schirber, Phys. Rev. 162, 519 (1967).

[20]G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. 135, A1118 (1964).

[21]B. Lax, J. G. Mavroides, H. J. Zeigler, and R. J. Keyes, Phys. Rev. Letters 5, 241 (1960).

[22]J. E. Schirber, Phys. Rev. 140, A2065 (1965).

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Pseudopotential Determination of Volume Dependence of Residual Resistivity in Binary Alloys*

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Ashcroft pseudopotential form factors are used to predict the volume dependence of residual resistivity in dilute noble-metal alloys. A trend toward negative-volume derivatives for lower-valence impurities is found for all solvents. Reasonable agreement with experimental magnitudes of the volume derivative are noted for many combinations.

I. INTRODUCTION

Since the introduction of solid and fluid helium as pressure-transmitting media, reliable measurements of the volume dependence of the residual resistivity ρ_0 of alloys have been obtained. Dugdale[1] has measured the volume derivatives of the residual resistivity of noble-metal alloys containing monovalent and multivalent impurities. In the case of impurities with valences of 3, 4, and 5, $d\ln\rho_0/d\ln V$