where

$$I' = (2/\pi) \int d\mathbf{x}\, x^{-2} \exp(-bx^2 + 2\mathbf{x}\cdot\mathbf{K}), \quad \text{(B7b)}$$

with $b = b_m + b_{m'}$ and $\mathbf{K} = b_m\mathbf{k} + b_{m'}\mathbf{k}'$. Equation (B7b) becomes, after several transformations,

$$I' = 4(\pi/b)^{1/2} \int_0^1 \exp(K^2t^2/b)dt, \quad \text{(B8a)}$$

which is related to the confluent hypergeometric function

$$I' = 4(\pi/b)^{1/2}\, {}_1F_1(\tfrac{1}{2};\tfrac{3}{2};K^2/b). \quad \text{(B8b)}$$

Since the integral, Eq. (B8a), is evaluated a large number of times in the course of a calculation of core-exchange matrix elements with plane waves, it was necessary to develop high-speed methods for determining its value. By tabulating the function and interpolating the value of the function by a central-difference technique we were able to reduce the calculation time (on an IBM 7074) to a maximum of 0.5 msec per integral. Fortunately, we were able to compare our calculated values to a table of the function prepared by Lohmander.[27] The calculated points compared to 8 digits and the interpolated points to 4 digits. Thus, we expect an accuracy of about 2–3 significant digits in the core-exchange matrix elements with plane waves.

Since the derivatives in Eq. (B7) make the equations more complicated, the least-squares technique was biased to keep the power of the polynomials as small as possible.

An accurate method for calculating core-valence exchange integrals where core functions are represented by linear combinations of Slater functions has been described recently by Brinkman and Goodman.[22]

[27] B. Lohmander and S. Rittsen, Kgl. Fysiograf. Sallskap. Lund, Forh. 28, 45 (1958).

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Shubnikov–de Haas Effect in $SrTiO_3$†

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The magnetoresistance of semiconducting $SrTiO_3$ has been investigated in high magnetic fields (up to 150 kOe). In the temperature range 1.4–2.1°K, for fields of more than 50 kOe, well-developed Shubnikov–de Haas–type oscillations have been observed. The data support a conduction band consisting of spheroids along the ⟨100⟩ crystalline axes, having 3 minima at the points X_3. The periods of oscillation as well as the temperature dependence of the amplitude and the magnetic field saturation lead to the following values for the transverse and longitudinal effective masses: $m_t = 1.5m_0 \pm 15\%$; $m_l = 6.0m_0 \pm 30\%$.

INTRODUCTION

The observation of quantum effects in the electronic properties of metals and semiconductors has been and is being used extensively to probe the energy-band structure of such solids. Cyclotron resonance, oscillatory susceptibility (de Haas–van Alphen effect) and oscillatory magnetoresistance (Shubnikov–de Haas effect) are the three most popular phenomena being investigated.

Considering the interest in the electronic properties of $SrTiO_3$, the question arose whether these experiments could be applied fruitfully to the further exploration of its band structure. A promising theoretical calculation of the electronic energy scheme[1] exists, and a majority of relevant experiments[2–7] seems to confirm this band picture. However, no direct measurement of the tensor elements of the effective mass has been attempted thus far. The application of the magnetic quantum effects to a material like $SrTiO_3$ poses con-

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[2] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. 134, A442 (1964).
[3] A. S. Barker, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structures of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1965).
[4] Manuel Cardona, Phys. Rev. 140, 651 (1965).
[5] H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. 143, 648 (1966).
[6] H. P. R. Frederikse and G. A. Candela, Phys. Rev. 147, 583 (1966).
[7] O. N. Tufte and E. L. Stelzer, Phys. Rev. 141, 675 (1966).

siderable problems. The basic conditions for observation of these effects are (see, e.g., Ref. 8)

$$\omega_c\tau > 1\,, \tag{1a}$$

$$\hbar\omega_c > kT\,, \tag{1b}$$

and

$$E_F > kT\,, \tag{1c}$$

where

$$\omega_c = eH/m_c c\,, \tag{1d}$$

τ = collision time,

$$E_F = (\hbar^2/2m_D)(3\pi^2 n)^{2/3} = \text{Fermi energy}, \tag{1e}$$

m_c = cyclotron mass (in a plane $\perp H$),

m_D = density-of-states effective mass,

n = concentration of charge carriers,

H = magnetic field,

and

c = velocity of light.

These conditions nearly always require that experiments be conducted at low temperatures and in high magnetic fields. In the case of $SrTiO_3$, the requirements are particularly difficult to satisfy experimentally because of the large effective masses ($m_D = 5m_0$ and $m_c > m_0$). It will be shown that the very intense and steady magnetic fields up to 150 kOe produced by an air-core solenoid at the Naval Research Laboratory were essential to the success of this undertaking.

The calculation referred to above[1] predicted energy surfaces in $SrTiO_3$ similar to those of silicon: a set of 3 or 6 ellipsoids of revolution with axes directed along the ⟨100⟩ axes in the Brillouin zone. [Crystal structure: cubic $O_h^1(Pm3m)$; the Brillouin zone is a simple cube.] The transverse mass m_t at X_3 should be about $1m_0$, while the longitudinal mass m_l was estimated to be $(20\text{–}50)m_0$. Plasma edge measurements by Barker[3] confirm the order of magnitude of m_t (assuming that $m_l \gg m_t$). Low-field magnetoresistance experiments[5] indicate that the geometry of the ellipsoids is indeed like that of Si; however, m_l, although quite large, appears to be smaller than $10m_0$.

The purpose of the present experiments was to investigate whether the magnetoresistance of $SrTiO_3$ showed an oscillatory behavior in magnetic fields of 100 or 150 kOe, and whether the results could be interpreted in terms of the suggested energy-band picture assuming quadratic dependence of energy on wave vector throughout.

EXPERIMENTAL DETAILS

Samples used in these experiments were cut from several monocrystalline boules of $SrTiO_3$ using an ultrasonic device and a diamond saw. The specimens were rectangularly shaped ($1\times1\times10$ mm^3) with side arms several mm long which provided large areas for the lead contacts. A set of three samples with the current direction oriented along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ crystal axes were prepared from each boule. One of these was doped with niobium (Nb-5), while the other two received a hydrogen-reduction treatment (HR-49 and HR-51). Hall measurements indicated that all samples contained 4 to 8×10^{18} electrons per cc over the entire temperature range.[5] The mobilities at liquid-helium temperatures varied from 1370 cm^2/V sec for sample HR-51 to 10 500 cm^2/V sec for sample Nb-5. Special care was taken to reduce the contact resistance to the lowest value attainable. By different "forming processes" it was possible to reduce the contact resistance to a value of the order of the bulk resistance of the specimen in each case.

A total of six runs were made. Samples were immersed in liquid helium and placed in the magnetic field with the current $J\|H$. During the last run a ⟨110⟩ sample was rotated in the magnetic field such that one could observe the magnetoresistance with $H\|$⟨110⟩, $H\|$⟨111⟩, as well as with $H\|$⟨001⟩. In the latter case the nonoscillatory part was largely subtracted through application of a (linear) bucking voltage. Resistances were measured using a nanovoltmeter and the result plotted versus the magnetic field on an x-y recorder (0–150 kOe in 3 min).

Experiments at 4.2°K showed only weak oscillations; besides, the thermal conductivity of the liquid helium above the λ point was too small to carry away the heat generated at the contacts. Hence most measurements were made at 1.4 or 1.5°K up to 2.1°K.

RESULTS AND DISCUSSION

Some of the recorder tracings are shown in Figs. 1, 2, and 3. Because maxima and minima will occur whenever

$$E_F = (n+\tfrac{1}{2})\hbar\omega_c \pm \tfrac{1}{2}g\mu H = (n+\tfrac{1}{2}\pm\delta)\hbar\omega_c\,, \tag{2}$$

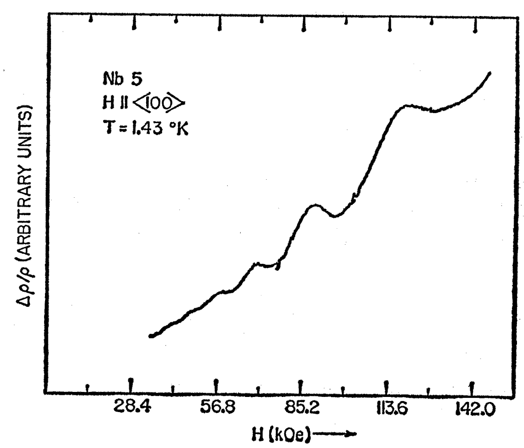

FIG. 1. Oscillatory magnetoresistance of Nb-doped $SrTiO_3$ at 1.43°K. I and $H\|$⟨100⟩.

[8] H. P. R. Frederikse and W. R. Hosler, Phys. Rev. **110**, 880 (1958).

it is customary to plot the positions of the 1st, 2nd, $\cdots$, nth extremum against the corresponding values of $1/H$, as shown in Fig. 4.[9] Beyond the first few levels ($n=1,2$) spin splitting gives rise only to a phase shift δ.[10] Furthermore, the Fermi energy E_F [Eq. (1e)] can be calculated because $m_D=5m_0$,[2,6,11] and n is known from measurements of the Hall coefficient; the number of minima is assumed to be either 3 or 6. The cyclotron frequency is given by Eq. (1d), and hence

$$\Delta(1/H)=(e\hbar/m_c)(1/E_F). \qquad (3)$$

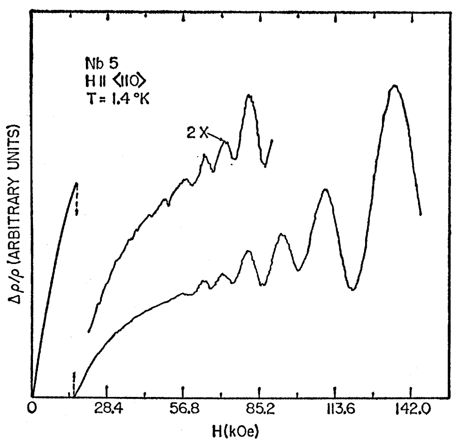

FIG. 2. Oscillatory magnetoresistance of Nb-doped $SrTiO_3$ at 1.4°K. I and $H\|\langle110\rangle$.

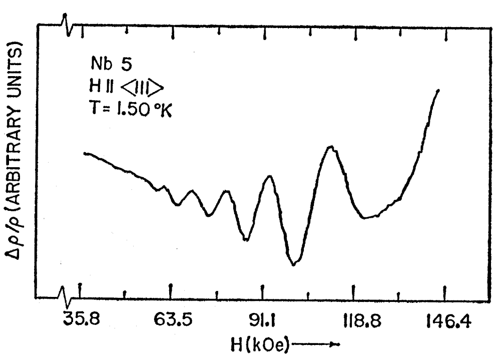

FIG. 3. Oscillatory magnetoresistance of Nb-doped $SrTiO_3$ at 1.5°K. $I\|\langle110\rangle$ and $H\|\langle111\rangle$.

Values of $\Delta(1/H)$ for three samples are listed in Table I. The first column, labeled Nb-5, refers to rotation of the ⟨110⟩ sample in the magnetic field, while the second Nb-5 column contains data from three different samples (⟨100⟩, ⟨110⟩, and ⟨111⟩). The agreement from sample to sample is of the order of 10% or better.

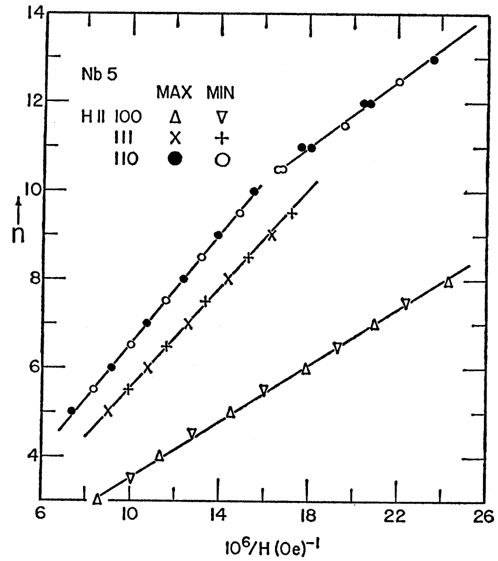

FIG. 4. The "oscillation number" n (integer or half-integer) as a function of the reciprocal magnetic field. Maxima: △, $H\|\langle100\rangle$; ●, $H\|\langle110\rangle$; ×, $H\|\langle111\rangle$. Minima: ▽, $H\|\langle100\rangle$; ○, $H\|\langle110\rangle$; +, $H\|\langle111\rangle$.

Each period leads directly to a cyclotron resonance mass m_c [Eq. (3)]. This quantity can be expressed in terms of the transverse and logitudinal masses m_t and m_l depending on the orientation of the energy surfaces and the direction of H. The largest period and hence the smallest m_c will be observed for the smallest cross section of the spheriods perpendicular to H. This will be the ⟨100⟩ direction if the spheroids have their longest dimension along the ⟨100⟩ axes. Similalry, one finds the largest periods for ⟨110⟩ spheriods when $H\|\langle110\rangle$, and for ⟨111⟩ spheroids when $H\|\langle111\rangle$. The results of Table I indicate that the case of ⟨100⟩ spheroids applies. Consequently two periods are being observed when $H\|\langle100\rangle$ or $H\|\langle110\rangle$ and one period for H in the ⟨111⟩ direction.

In this case the different m_c's are related to m_t and m_l in the following manner:

$$H\|100 \quad m_c=m_t \qquad (4a)$$

or

$$m_c=(m_tm_l)^{1/2}, \qquad (4b)$$

$$H\|110 \quad 1/m_c^2=\tfrac{1}{2}[(1/m_t^2)+(1/m_tm_l)] \qquad (4c)$$

or

$$m_c=(m_tm_l)^{1/2}, \qquad (4d)$$

$$H\|111 \quad 1/m_c^2=\tfrac{1}{3}[(1/m_t^2)+(2/m_tm_l)]. \qquad (4e)$$

TABLE I. Periods of oscillation.

		$\Delta(1/H)$ (10^6 Oe)$^{-1}$			
		Nb-5 rotation	Nb-5 individual	*HR*-49	*HR*-51
⟨100⟩	*a*	3.1	3.07	$\cdots$	$\cdots$
	b	$\cdots$	$\cdots$	$\cdots$	(1.71)
⟨110⟩	*a*	2.65	2.4	$\cdots$	$\cdots$
	b	1.60	1.62	1.53	$\cdots$
⟨111⟩		1.79	1.66	1.77	$\cdots$

[9] A. H. Kahn and H. P. R. Frederikse, Solid State Phys. 9, 257 (1959).
[10] M. H. Cohen and E. I. Blount, Phil. Mag. 5, 115 (1960); Y. Eckstein and J. B. Ketterson, Phys. Rev. 137, A1777 (1965).
[11] E. Ambler, J. H. Colwell, W. R. Hosler, and J. F. Schooley, Phys. Rev. 148, 280 (1966).

TABLE II. Cyclotron mass, transverse and longitudinal mass tensor elements for sample Nb-5, assuming 3 or 6 ellipsoids along ⟨100⟩ direction. Masses in units of m_0.

			$\nu=6$			$\nu=3$	
	m_c	m_t	m_l	K	m_t	m_l	K
⟨100⟩ a	1.50	1.50	1.54	1.03	1.46	6.6	4.5
⟨110⟩ a	1.72	1.63	1.31	0.81	1.27	8.7	6.9
b	2.86	0.42	19.4	46.0	1.72	4.75	2.8
⟨111⟩	2.56	2.23	0.7	0.31	1.64	5.25	3.2
Average					1.52	6.3	4.3

For $m_t<m_l$ the largest period corresponds to (4a) and the smallest to (4b) and (4d). Hence the assignment is straightforward; the order of the periods indicated in Table I follows the same sequence as the Eqs. (4a)–(4e). In principle one can deduce m_t and m_l from the different m_c's by solving the above equations in various ways. Because the differences between the m_c's are rather small, this method does not lead to accurate results.

Another approach is to combine each of the Eqs. (4a)–(4e) with the expression for the density-of-states effective mass

$$m_D=\nu^{2/3}(m_t^2 m_l)^{1/3}, \tag{5}$$

where ν= number of minima. The results using the latter method are shown in Table II for both $\nu=3$ and $\nu=6$; the value adopted for m_D is 5 m_0, an average from three different experiments.[2,6,11] It is clear that the values for m_t, m_l, and $K(=m_l/m_t)$ are much more consistent for $\nu=3$ than for $\nu=6$. It is gratifying that on the basis of the three-valley model the figure for the transverse mass, $m_t=1.5\ \pm15\%$, is, within the limit of error, the one predicted by theory; the agreement with Barker's results is satisfactory, too. Although the value for K shows a somewhat larger margin of error (2.8–6.9), the average value compares favorably with the result obtained from low-field magnetoresistance experiments[5]: $K=3.0$–4.5.

SATURATION AND DAMPING

A few experiments were performed to explore the field saturation of the magnetoresistance. Such a measurement allows for another check on the value for K as can be seen from the following formulas[12]:

$$M_{110}{}^{110}=\frac{(K-1)^2}{K(K+5)}, \tag{6a}$$

$$M_{111}{}^{111}=\frac{2(K-1)^2}{9K}. \tag{6b}$$

[12] M. Shibuya, Phys. Rev. 95, 1385 (1954).

At 4.2°K the saturation value for sample Nb-5 appeared to be

$$\langle 110\rangle:\quad \Delta\rho/\rho\approx 0.3\rightarrow K\approx 4.5\,(\text{or } 0.30),$$
$$\langle 111\rangle:\quad \Delta\rho/\rho\approx 0.4\rightarrow K\approx 3.5\,(\text{or } 0.28).$$

However, one should realize that any saturation value under 0.5 leads to $1<K<6$.

It is also interesting to analyze the temperature and magnetic-field damping of the oscillations. Again, values for the band parameters may be derived from such measurements. Several authors[13,14] have shown that the magnitude of the oscillatory magnetoresistance is given by

$$\frac{\Delta\rho}{\rho_0}=CTH^{-1/2}\exp\left[-\frac{2\pi^2k(T+T')}{\beta^*H}\right]\cos\left[\frac{2\pi E}{\beta^*H}-\frac{\pi}{4}\right].$$

In this expression $\beta^*=e\hbar/m_cc$, C is a constant, T' describes the collision broadening, and it is assumed that $2\pi^2k(T+T')\geq\beta^*H$. Plotting the log of the extremal values $(\cos=\pm1)$ of $[(\Delta\rho/\rho_0)H^{1/2}]$ versus $1/H$, one should obtain straight lines with slope $-[2\pi^2k(T+T')]/\beta^*$. From a number of such plots at different temperatures, T' and β^* (hence m_c) can be calculated.

The amplitudes of the oscillations have been measured on sample Nb-5 (⟨110⟩ direction) at 1.4 and 4.2°K. The results indicate $m_c=3.0\ m_0$, hence $m_t=1.54\ m_0$, $m_l=6.0\ m_0$, and $K=3.9$. The value of T' is about 0°K. Similar experiments on HR-49-(⟨110⟩) lead to $m_c=1.95\ m_0$ and $K=4.3$. In the case of HR-49-(⟨111⟩) the results are $m_c=3.5\ m_0$ and $K=2.6$.

CONCLUSIONS

Shubnikov–de Haas-type measurements on n-type $SrTiO_3$ favor the many-valley structure for the conduction band. The picture with three minima at the edge of the Brillouin zone in the ⟨100⟩ direction fits considerably better than the assumption of six minima. The transverse and longitudinal effective masses are larger than m_0 and are in good agreement with earlier results from low-field magnetoresistance experiments.

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[14] G. E. Zilberman, Zh. Eksperim. i Teor. Fiz. 29, 762 (1955) [English transl.: Soviet Phys.—JETP 2, 650 (1956)].