Magnetoresistance of Semiconducting $SrTiO_3$†

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(Received 20 September 1965)

The magnetoresistance of reduced and doped $SrTiO_3$ was measured at 4.2°K in fields up to 8000 Oe. The effect was studied for directions of primary current and magnetic field along the major crystalline axes. Results are in agreement with the theoretical prediction of 3 (or 6) energy minima on the ⟨100⟩ axes. Assuming an isotropic collision time, the effective-mass ratio is either 4.0 or 0.34.

INTRODUCTION

RECENTLY, the compound $SrTiO_3$ has attracted renewed attention not only as a "pseudoferroelectric,"[1] but also as a semiconductor[2] and superconductor.[3] The semiconducting properties were investigated, since it appeared that conduction electrons could be introduced by means of chemical reduction or by doping (e.g., niobium). Information about the conduction electrons (effective mass, mobility) prompted an effort to calculate the electronic energy bands.[4] The result of this calculation (based on a tight-binding approximation) was the prediction of a lowest conduction band qualitatively similar to that of silicon. Such a multivalley structure is an important element in the explanation of superconductivity in reduced or doped $SrTiO_3$.[3]

For this and other reasons it is desirable to collect additional data which can illuminate the understanding of the band structure of $SrTiO_3$. A fruitful experiment in this respect is the measurement of the magnetoresistance.

In dealing with a cubic crystal like $SrTiO_3$, a particular selection of current and magnetic-field directions will provide the necessary information to choose between a number of probable energy band models. Actually, the crystal structure of $SrTiO_3$ is not exactly cubic at low temperatures: a transition point exists at 110°K,[5] and other small phase transitions may occur below 50°K.[6] However, the relative changes of the lattice constants are of the order of 5×10^{-4}. Furthermore, the crystals show a domain pattern with differently oriented domains. Such a pattern will tend to average out the small deviations from the cubic structure.

† Research supported in part by National Aeronautics and Space Administration.

[1] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1960), Vol. 9, p. 387.

[2] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. 134, A442 (1964).

[3] J. F. Schooley, W. R. Hosler, and Marvin L. Cohen, Phys. Rev. Letters 12, 474 (1964); J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, Marvin L. Cohen, and C. S. Koonce, Phys. Rev. Letters 14, 305 (1965).

[4] A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).

[5] R. O. Bell and G. Rupprecht, Phys. Rev. 129, 90 (1963).

[6] F. W. Lytle, J. Appl. Phys. 35, 2212 (1964).

MAGNETORESISTIVE EFFECT

During the last 15 years the magnetoresistive effect has been studied in great detail experimentally as well as theoretically. All this information has been compiled recently by Beer.[7]

In order to define the pertinent parameters, a few formulas will be quoted. In the weak-magnetic-field region (i.e., $\mu H \ll 10^8$), the magnetoresistance can be represented by the following expression:

$$\Delta\rho/\rho_0=\mu^2H^2f(\zeta)g(p)h(K), \quad (1)$$

where $f(\zeta)$ depends on the degree of degeneracy ($\zeta=E_F/kT$, E_F=Fermi energy); $g(p)$ depends on the scattering mechanism ($\tau\sim E^p$; a simplified model in which the collision time τ is a function of the energy: $p=-\frac{1}{2}$ for phonon scattering, $p=+\frac{1}{2}$ for polar scattering, and $p=\frac{3}{2}$ for ionized impurity scattering[8]); $h(K)$ depends on the shape of the energy surfaces in the regions where the states are occupied by conduction electrons (or holes). This function has different values for different directions of **J** and **H** as shown in columns 3 and 4 of Table I. The magnitude of $\Delta\rho/\rho_0$ is, of course, also dependent on the directions of the current **J** and the magnetic field **H** relative to the crystalline axes. For a cubic material the expression has the form[9]:

$$M_J^H=\Delta\rho/(\rho_0H^2)=b+c(il+jm+kn)^2 +d(i^2l^2+j^2m^2+k^2n^2), \quad (2)$$

where i, j, k and l, m, n are the direction cosines of **J** and **H** with the cubic axes. Column 2 of Table I lists the magnetoresistive quantities M_J^H for particular directions of **J** and **H** in terms of b, c, and d.

The shape of the energy surfaces in k space near the extrema can often be approximated by ellipsoids of revolution. The minimum may be at the center of the Brillouin zone or there may be a number of ellipsoids along a set of the major crystallographic directions. In the latter case, the curvature of the ellipsoids along the spheroid axis is described by an effective mass m_l^*, while the curvature perpendicular to the axis is represented by an effective mass m_t^*. The ratio m_l^*/m_t^*,

[7] A. C. Beer, in *Solid State Physics–Supplement 4*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963).

[8] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1954), 2nd ed., p. 240.

[9] G. L. Pearson and H. Suhl, Phys. Rev. 83, 768 (1951).

TABLE I. Magnetoresistive coefficients in terms of the anisotropy parameter for 3 or 6 spheroids in [100] directions.

	[From Eq. (2)]	Ionized-impurity scattering[a]	Lattice scattering[a]
$M_{100}{}^{100}$	$b+c+d$	0	0
$M_{100}{}^{001}$	b	$\mu^2\left[\frac{8}{9}\frac{(K^2+K+1)(2K+1)}{K(K+2)^2}\frac{F_2F_5}{F_{7/2}{}^2}-1\right]$	$\mu^2\left[\frac{4(K^2+K+1)(2K+1)}{K(K+2)^2}\frac{fF_0}{F_{-1/2}{}^2}-1\right]$
$M_{110}{}^{001}$	b	same	same
$M_{110}{}^{1\bar{1}0}$	$b+d/2$	...	...
$M_{110}{}^{110}$	$b+c+d/2$	$\mu^2\left[\frac{4}{9}\frac{(K-1)^2(2K+1)}{K(K+2)^2}\right]\frac{F_2F_5}{F_{7/2}{}^2}$	$\mu^2\left[2\frac{(K-1)^2(2K+1)}{K(K+2)^2}\frac{fF_0}{F_{-1/2}{}^2}\right]$

[a] D. G. Adrianov and V. I. Fistul, Fiz. Tverd. Tela 5, 1480 (1963) [English transl.: Soviet Phys.—Solid State 5, 1077 (1963)]; R. L. Weiker and B. G. Dick, Jr., J. Appl. Phys. 35, 3511 (1964).

multiplied by the factor τ_t/τ_l, is the quantity K in Eq. (1). The second factor takes into account the possibility of anisotropic scattering. Little knowledge exists concerning the different scattering mechanisms that determine the mobility of electrons in $SrTiO_3$ at 4.2°K. Considering the high dielectric constant of the unreduced titanate and the shielding by charge carriers in the reduced or doped samples, one is inclined to conclude that ionized impurity scattering (strongly anisotropic) plays a minor role. At low temperatures neither the electrons nor the phonons possess sufficient energy to permit much intervalley scattering (isotropic). The main mobility limiting effect may well be intravalley scattering. Herring's work[10] on this subject indicates that the collision time involved in this process often is anisotropic. However, the anisotropy factor τ_t/τ_l is usually between 1.2 and 0.8 unless the energy surface is close to spherical. [In the latter case the collision time ratio can reach a maximum of 2.8 for special values of E_d/E_u (E=deformation potentials: d=dilatational and u=uniaxial).] A third mechanism that probably influences the mobility is scattering by neutral impurities. The corresponding τ is isotropic. The above discussion indicates that the scattering anisotropy may not be negligible. However, considering that the ratio τ_t/τ_l is not very different from unity, this figure will be used in the analysis of the experimental data.

The orientation of the energy ellipsoids (or sphere, if the minimum occurs at $k=0$) leads to specific relationships between the coefficients b, c, and d of Eq. (2)[11]:

$$b+c+xd=0. \tag{3}$$

The four models are distinguished from each other by the following conditions for x and d:

spherical symmetry	$x=0$	$d=0$,
⟨100⟩ type spheroids	$x=1$	$d<0$,
⟨111⟩ type spheroids	$x=0$	$d>0$,
⟨110⟩ type spheroids	$x=-1$	$d>0$.

[10] C. Herring, Bell System Tech. J. 34, 237 (1955).
[11] Reference 7, p. 231.

Moreover, the magnitudes of b, c, and d are determined by functions of K multiplied by factors sensitive to the degree of degeneracy and the scattering mechanism. These terms are listed in the last two columns of Table I. Hence a determination of b, c, and d makes it possible not only to verify the applicability of one of the models, but also to calculate the axial ratio of the energy spheroids.

EXPERIMENTAL

The origin, purity, and preparation of samples of reduced and Nb-doped $SrTiO_3$ have been described previously.[2] The specimens used for the determination of the magnetoresistance were cut in a rectangular shape with side arms; a typical size of the samples is $16\times1.5\times1.5$ mm³.

Because of the relatively small mobilities μ at room temperature and at 78°K, no reliable data could be obtained at these temperatures and all measurements were performed at 4.2°K (where μ ranges from 1400 to 10,000 cm²/volt sec). Limiting the investigation to this single temperature has certain pros and cons. All samples studied were close to complete degeneracy at 4.2°K ($\zeta=E_F/kT=2$, or larger). All other factors being equal, the degeneracy diminishes the size of $\Delta\rho/\rho_0$ considerably.[12]

The nature of the scattering mechanism [$g(p)$ in Eq. (1)] becomes rather unimportant as complete degeneracy is approached. This can easily be verified by calculating the factors $F_2(\zeta)F_5(\zeta)/F_{7/2}{}^2(\zeta)$ and $f(\zeta)F_0(\zeta)/F_{-1/2}{}^2(\zeta)$ which appear in the expressions for b and are shown in Table I. Strong degeneracy corresponds to large ζ; the values of f and F_α are listed in the article by Madelung.[13]

Measurements were made on four sets of samples: three hydrogen-reduced and one Nb-doped. A set consists of three specimens which have their length directions cut along the [100], [110], and [111]

[12] O. Madelung, in *Handbuch der Physik*, edited by S. Flügge (Springer Verlag, Berlin, 1957), Vol. 20, p. 78 (Fig. 2).
[13] Reference 12, pp. 58–59.

TABLE II. Compilation of magnetoresistance coefficients and band structure parameters.

	HR-56	HR-49	Nb-5	HR-51
n (cm^{-3})	1×10^{18}	4.6×10^{18}	6×10^{18}	1×10^{19}
μ_{100} cm^2 V^{-1} sec^{-1}	3 760	2 360	10 500	1 370
μ_{110} cm^2 V^{-1} sec^{-1}	3 400	2 000	9 800	1 540
$b/\mu^2(_{110}{}^{100})$	0.21	0.28	0.28	0.32
$b/\mu^2(110)$	0.32	0.32	0.34	0.31
$c/\mu^2(_{110}{}^{100})$	−0.07	0.04	0.08	0.09
$c/\mu^2(110)$	−0.08	0.05	0.09	0.07
$d/\mu^2(_{110}{}^{100})$	−0.12	−0.26	−0.31	−0.35
$d/\mu^2(110)$	−0.28	−0.25	−0.35	−0.30
$x(_{110}{}^{100})$	1.20	1.24	1.19	1.16
$x(110)$	0.83	1.5	1.23	1.3
$K(_{110}{}^{100})$	3.0 or 0.41	3.7 or 0.36	3.7 or 0.36	4.1 or 0.34
$K(110)$	4.1 or 0.34	4.1 or 0.34	4.4 or 0.33	4.0 or 0.34

directions within 2° as checked by means of x-ray diffraction. Comparing the results on different samples, it appears that $\Delta\rho/\rho_0$ does not consistently scale proportional to μ^2. Except for the Nb-doped samples, the mobilities of the [111] specimens were very different from the other two directions; hence it was decided not to make use of the data on [111] samples. The mobilities of the [100] and [110] samples are much closer in magnitude. Two different procedures were adopted: the pertinent parameters were calculated as an average of data taken on both orientations of samples *and* from results on [110] samples only (see Table II).

The H^2 dependence was checked as shown in Fig. 1; it holds rather well for the hydrogen-reduced samples, but considerable deviations occur for the Nb-doped specimen above ~3500 Oe. In the latter case the coefficients b, c, and d were calculated from magnetoresistance data at 3400 Oe, while results at 7370 or 7600 Oe were used for the HR samples.

A few rotation diagrams are presented in Figs. 2 and 3. The plotted values are averages of measurements

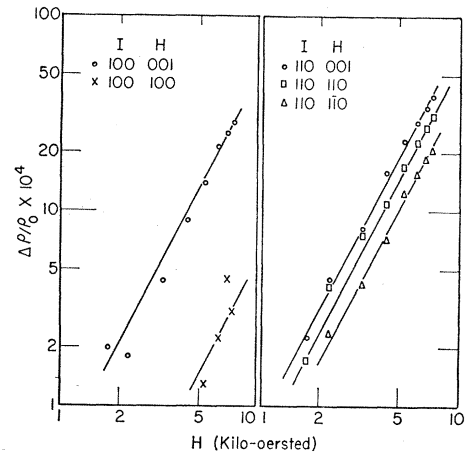

FIG. 1. Magnetic-field dependence of the magnetoresistance $\Delta\rho/\rho_0$ for the (hydrogen-reduced) sample HR-51 at 4.2°K. The solid lines represent an H^2 dependence; the current and magnetic-field directions are given on the graph.

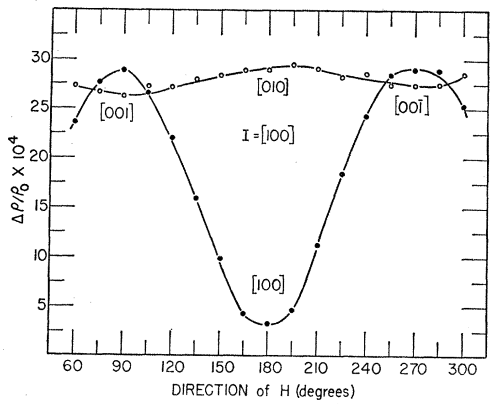

FIG. 2. Angular dependence of the magnetoresistance $\Delta\rho/\rho_0$ for sample HR-51 at 4.2°K with a magnetic field of 7370 Oe and current in the [100] direction. The solid points were obtained by rotating the field about an ⟨010⟩ axis with H in the transverse [001] direction at 90° and in the longitudinal [100] direction at 180°. The open circles are the results obtained when H was rotated about the ⟨100⟩ axis. The cardinal directions of H are indicated on the figure.

with $+H$ and $-H$, a method which eliminates effects proportional to H.

The magnitudes of $M_J{}^H$ indicated in Table I have been read from these diagrams; from these data sets of b, c, d, and x were calculated and are listed in Table II. The values of K (last two rows) were determined from the expressions quoted in the third and fourth columns of Table I. Only those corresponding to b were used because these values are larger and contain fewer errors than those for $(b+c+d/2)$. For near-degeneracy the factors $(8/9)\times(F_2F_5/F_{7/2}{}^2)$ and $4\times(fF_0/F_{-1/2}{}^2)$ are very close to 1,[14] the figure used in the calculation. The expressions in the last two columns of Table I lead to cubic equations; consequently there will be three roots. One of these roots is negative and has no physical significance. Of the other two roots, one is larger than 1, the other smaller than 1. These two possibilities correspond to either prolate or oblate ellipsoids. Without experimental knowledge about the magnitude of m_l or m_t it is impossible to decide which model really applies. The theoretical energy band calculation (Ref. 4) indicates a preference for the prolate ellipsoids (see below).

The reproducibility of the results is very poor. Different surface treatments (sandblasting or etching) produce variations up to 20%. The data presented in this paper were obtained from measurements on etched samples. Even under essentially the same conditions, the magnetoresistance changes by 10% after warm-up to room temperature and subsequent re-cooling. It is possible that this is a result of domain shifting generating different polarization and boundary patterns.

One should realize that the magnetoresistive effects in this investigation are usually not more than 1% of the zero-field resistance. Considering that experimental

[14] Robert S. Allgaier, Phys. Rev. **119**, 554 (1960).

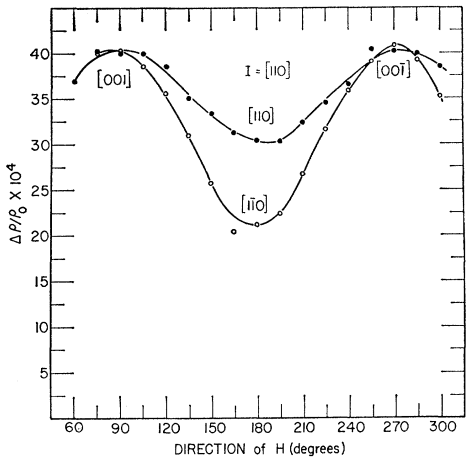

FIG. 3. Angular dependence of the magnetoresistance $\Delta\rho/\rho_0$ for sample HR-51 at 4.2°K with a magnetic field of 7370 Oe and current in the [110] direction. The solid points are measurements with the magnetic field rotated about an $\langle 1\bar{1}0\rangle$ axis where 90° corresponds to H in the transverse [001] and 180° to H in the longitudinal [110] direction. The open circles were obtained by rotating H about an $\langle 110\rangle$ axis. The cardinal directions of H are given on the graph.

conditions limit the primary current to values of 100 mA or less, the observed voltage across the sample is about 1mV, and $\Delta V \approx 10\,\mu V$. The measuring equipment allows a determination of this voltage to within 0.1 or $0.2\,\mu V$. The irreproducibility mentioned above raises the uncertainty to 1 or $2\,\mu V$. However, the deviations seem to be random, and hence, averaging over many different measurements on four samples produces much better final values for x and K.

The maximum error of x is estimated to be 50%. An examination of the graphical solution for K indicates that the accuracy of this parameter is of the order of 25%.

CONCLUSIONS

The conclusions reached from these measurements are the following:

(1) The value of x is close to 1, while d is large and negative (Table II). This combination indicates that the lowest conduction band of $SrTiO_3$ can be approximated by 3 or 6 spheroids along the $\langle 100\rangle$ axes in k space, in agreement with the tight-binding calculation.[4]

(2) Assuming an isotropic collision time, the mass ratio of the spheroids (K) is 4.0 ± 1.0 or 0.34 ± 0.07. Taking the average value of the density-of-states effective mass at 78°K as quoted in Ref. 2 ($m_{av}^*=6$), one can calculate both m_l and m_t from

$$m_{av}^* = (m_t^2 m_l)^{1/3} \nu^{2/3},$$

where ν is the number of minima (3). The result is $m_t=1.9m_0$, $m_l=7.6m_0$ for the higher value of K, or $m_t=4.4m_0$, $m_l=1.4m_0$ for the lower value.

The calculated band structure[4] predicts a transverse effective mass of about $1.3m_0$ and a much larger m_l. On this basis the first set of values (prolate ellipsoids) is preferred. However, the longitudinal mass of $7.6m_0$ suggests that the lowest conduction band ($\Delta_{2'}$) has a width of about 0.13 eV which is a factor 3 or 5 higher than suggested by Kahn and Leyendecker.

These results are in disagreement with the conclusions reached by Tufte and Stelzer,[15] who investigated the piezoresistivity of $SrTiO_3$ at different temperatures; these authors prefer the minimum of the conduction band at the center of the Brillouin zone. It is obvious that refinements of the band calculations and additional experimental information are needed to reach unanimity concerning the electronic energy structure of $SrTiO_3$.

ACKNOWLEDGMENTS

The authors want to thank Dr. A. H. Kahn for helpful discussions and constructive criticism. The assistance of M. I. Cohen in orienting the samples is gratefully acknowledged.

[15] O. N. Tufte and E. L. Stelzer, Phys. Rev. **141**, 675 (1966).