PHYSICAL REVIEW VOLUME 134, NUMBER 2A 20 APRIL 1964

# Electronic Transport in Strontium Titanate

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(Received 5 December 1963)

The conductivity and the Hall and Seebeck coefficients of reduced and doped strontium titanate were measured over the temperature range 4.2–300°K. An average effective mass of about 10 $m_0$ was deduced from these experiments. This value agrees well with the results of a recent energy-band calculation for $SrTiO_3$ based on a tight-binding approximation. Phonon-drag contributions to the Seebeck coefficient appear to be negligible above 50°K. Such a result is expected in view of the very small heat conductivity reported by Sievers.

## INTRODUCTION

STRONTIUM titanate is one of the few titanium compounds which is cubic at room temperature. It has the perovskite structure. Many of its properties are similar to those of the other titanates and titanium oxides. Results of several investigations (elastic constants,[1] electron spin resonance,[2] etc.) indicate that a transition to a tetragonal phase takes place at 108°K. The dielectric constant $\epsilon$ was measured by Weaver[3] from room temperature down to 1.4°K; no anomaly was observed at 108°K. The temperature dependence of $\epsilon$ can be represented by an expression derived by Barrett.[4] Using this formula Weaver finds a Curie temperature of 45°K. The Curie–Weiss law predicts a somewhat lower value of $T_c$ 35°K. At 40°K and below, Weaver observed hysteresis loops. Gränicher[5] has found that $SrTiO_3$ samples can be made to oscillate like a piezoelectric crystal, after being polarized with a dc field of $>600$ V/cm. These and other observations[6] lead one to believe that $SrTiO_3$ is indeed a ferroelectric below $T\approx45°K$. However, the absence of any discontinuity in $\epsilon$ at that temperature remains puzzling. A few years ago Cochran[7] suggested a theory of ferroelectricity in which he tied the phenomenon to the existence of a low-energy, temperature-dependent lattice mode. When the frequency of this mode reaches zero, the crystal becomes unstable and undergoes a phase transition. This mode has been observed in $SrTiO_3$ both optically[8,9] and by means of cold-neutron spectroscopy.[10]

Pure $SrTiO_3$ is transparent in the visible range and up to $\sim5\,\mu$ in the infrared. The energy gap is $\sim3.15$ eV.[11] Upon reduction the material becomes a semiconductor and a broad absorption appears which increases towards the infrared.[11] This absorption produces light blue or dark blue crystals; with strong reduction the samples become opaque.

This paper reports on measurements of conductivity, Hall effect and Seebeck coefficient between 4 and 300°K. The results are discussed in the light of a recent energy band calculations for cubic titanates made by A. H. Kahn of this laboratory.

## EXPERIMENTAL DETAILS

The $SrTiO_3$ samples used in this investigation were cut from boules grown by the National Lead Company.[12] Reduction was achieved by heating the samples at temperatures of 900°C or higher in vacuum (ion-vac.-pump: $5\times10^{-7}$ mm Hg) for long periods of time. Reduction does not occur as easily as in $TiO_2$. The process is speeded up considerably when small amounts of titanium metal (e.g., evaporated films on quartz) are used as getter in the system. The oil of a conventional forepump serves the same purpose.

The sample geometry was usually of the order of $10\times3\times1$ mm$^3$. Samples were provided with 6 contacts using indium solder. Two of these (on the end faces) were used to apply the primary current; two contacts on either side served as connection points for leads to measure the resistivity and Hall effect with appropriate potentiometers.

The apparatus for the determination of the Seebeck coefficient is similar to one described in a previous paper[13] on heat conductivity. The very small heat conductivity of $SrTiO_3$ at low temperatures[14] made it possible to use fairly large temperature gradients and hence to continue measurements down to 7°K in some cases.

The results of these studies are illustrated in Figs. 1–3. The abscissa of Fig. 1 covers the range ∞ to 36°K. Below 36°K the Hall effect is independent of tempera-

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[1] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963); **125**, 1915 (1962).

[2] L. Rimai and G. A. de Mars, Phys. Rev. **127**, 702 (1962).

[3] H. E. Weaver, Phys. Chem. Solids **11**, 274 (1959).

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[5] H. Gränicher, Helv. Phys. Acta **29**, 210 (1956).

[6] R. S. Krogstad, F. W. Lytle, R. W. Moss, and E. B. Moore, Jr., Bull. Am. Phys. Soc. **8**, 470 (1963).

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

[8] A. S. Barker, Jr., and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

[9] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).

[10] R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).

[11] H. W. Gandy, Phys. Rev. **113**, 795 (1959).

[12] Analysis by the Spectrochemistry Section of the National Bureau of Standards on several boules indicates that the following impurities may be present: Al, Ba, Ca, Fe [0.001−0.01%]; Cu, Fe, K, Na, Mg, Mn, Rb, Si (?) [<0.001%].

[13] E. V. Mielczarek and H. P. R. Frederikse, Phys. Rev. **115**, 888 (1959).

[14] A. J. Sievers, III, Bull. Am. Phys. Soc. **8**, 208 (1963).

ture except for sample VR-5 which has too high a resistance to be measured at all below 30°K.

## DISCUSSION

A striking feature of this series of transport measurements is the very low resistivity of most samples at 4.2°K (except for a few lightly reduced specimens, which reached values of $10^{10}$ Ω-cm at 40°K). The Hall-effect behavior parallels that of the resistivity. The temperature independence of $R$ in the low temperature range (below 70, 50, or 30°K depending on the degree of reduction of the samples) is not surprising considering the magnitude of the dielectric constant. Assuming that we are dealing with a hydrogen-like donor, one expects an activation energy $E$ proportional to $\epsilon^{-2}$. As $\epsilon$ is of the order of $10^4$ in this temperature range,[3] $E$ would be $10^{-7}$ to $10^{-5}$ eV even for fairly high values of the effective mass. Hence all charge carriers originating from such shallow donors will be in the conduction band for $T > 1$°K.

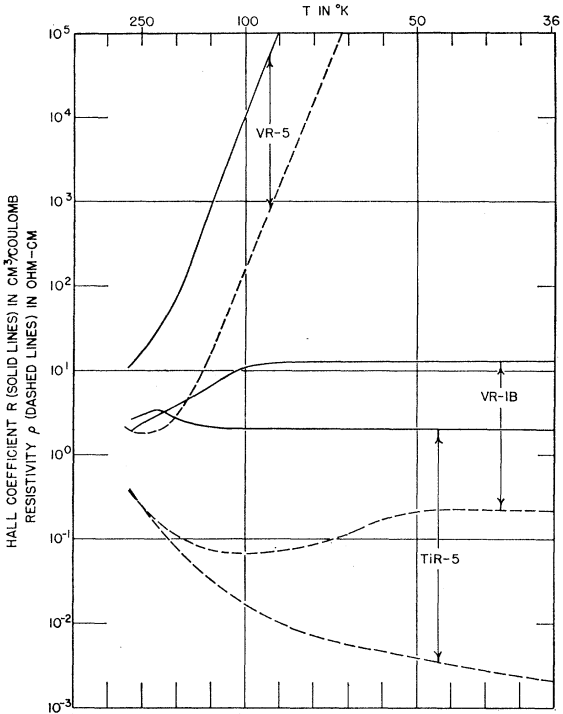

Fig. 1. Resistivity and Hall coefficient of three reduced $SrTiO_3$ samples.

At somewhat higher temperatures both $R$ and $\rho$ of the group of lightly reduced samples show an exponential decrease with rising $T$. The general behavior of this group is strongly suggestive of acceptor-donor compensation in varying degrees. The situation looks similar to that in gold-doped germanium.[15] Reduction introduces a number of very shallow donors. These donors appear to be dominant when their number exceeds 1 to $3(\times 10^{18})$ per cm³, corresponding to $R \approx 2-6$ cm³/C. For "smaller" reductions the compensating centers have a strong influence on the temperature dependence of $R$ and $\rho$. These centers might be foreign ions [like $Al^{3+}$, $Fe^{3+}$ (or $Fe^{2+}$), $Cr^{3+}$, $H^+$], vacancies, interstitials, associated defects or dislocations. One should also mention the possibility of surface states. The compensation is so effective that some samples reach resistivities as high as $10^{10}$ or $10^{12}$ Ω-cm around 30–40°K. In this connection it is important to mention two Nb-doped samples. Nb is probably a hydrogen-like, and hence shallow, donor. One contains about 0.05% Nb and

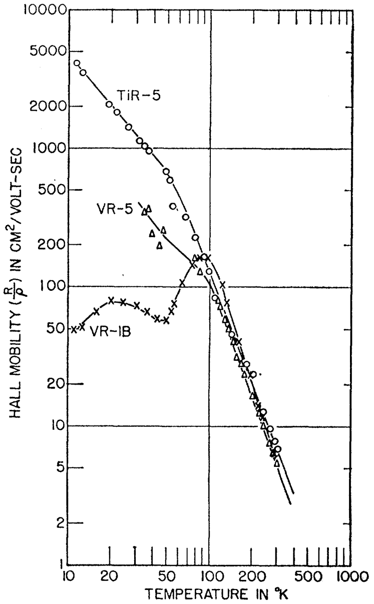

Fig. 2. Hall mobility of reduced $SrTiO_3$ samples as a function of temperature (log-log).

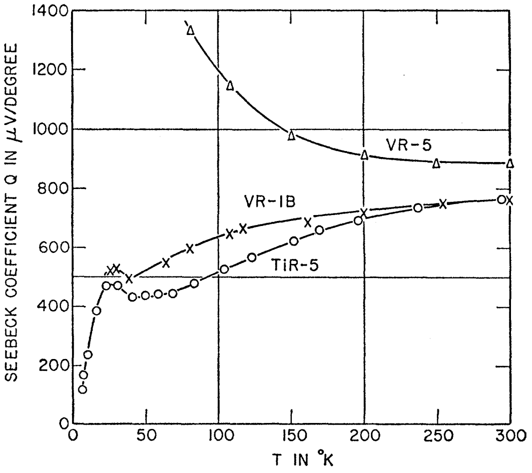

Fig. 3. Seebeck coefficient of reduced $SrTiO_3$ samples.

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[15] W. C. Dunlap, Phys. Rev. **97**, 614 (1955).

TABLE I. Electron parameters of reduced and doped $SrTiO_3$.

| Sample | Preparation | $T$ °K | $\rho$ ohm-cm | $R$ cm³/C | $\mu$ cm²/volt-sec | $Q$ $\mu$V/deg | $m^*/m_0$ |
|---|---|---|---|---|---|---|---|
| VR-1B | 1000°C | 300 | 0.35 | 2 | 5.9 | 750 | 16 |
| | forepump | 78 | 0.086 | 8.9 | 103 | 585 | 6.3 |
| | $\sim 10^{-3}$ cm Hg | 4 | 0.2 | 15 | (75) | ··· | ··· |
| | 28 h | | | | | | |
| VR-5 | 1200°C | 300 | 2 | 10 | 5 | 890 | 16 |
| | Vac-Ion | 78 | $10^3$ | $1.3\times10^5$ | 130 | 1350 | 4.0 |
| | $5\times10^{-7}$ cm Hg | 40 | $\sim 10^{10}$ | $\sim 1.5\times10^{12}$ | ($\sim$150) | ··· | ··· |
| | 10 days | | | | | | |
| TiR-2 | 1200°C | 300 | 0.08 | 0.52 | 6.5 | 600 | 12 |
| | Vac-Ion | | | | | | |
| | 0.1 mg Ti (getter) | 78 | 0.0025 | 0.55 | 220 | 360 | 7.3 |
| | $5\times10^{-7}$ cm Hg | | | | | | |
| | 10 days | 4 | 0.0004 | 0.5 | 1250 | 180(16°K) | ··· |
| TiR-5 | 900°C | 300 | 0.4 | 2.6 | 6.5 | 770 | 16 |
| | Vac-Ion | | | | | | |
| | 0.002 mg Ti (getter) | 78 | 0.009 | 2.1 | 230 | 465 | 6.5 |
| | $10^{-6}$ cm Hg | | | | | | |
| | 3 days | 4 | 0.0006 | 2.0 | 3300 | 115(7°K) | ··· |
| Nb-5 | 0.05 wt % Nb | 300 | 0.20 | 1.3 | 6.5 | $\sim$700 | 15 |
| | (National | 78 | 0.0046 | 1.1 | 240 | $\sim$420 | 7.4 |
| | Lead Company) | 4 | $\sim$0.0001 | $\sim$1.0 | $\sim$1000 | $\sim$90(8°K) | ··· |

has a constant Hall coefficient of 1.3 cm³/C ($n \approx 5\times10^{18}$ cm$^{-3}$). The doping level would predict about 3 or 4 ($\times10^{18}$) cm$^{-3}$ donor states. Another boule was grown with an addition of 0.005% Nb. This crystal is colorless and has a very high room-temperature resistivity of $>10^{10}$ Ω-cm. The amount of Nb in this boule would predict 3 or 4 ($\times10^{17}$) cm$^{-3}$ niobium donor states. Apparently because of a comparable number of compensating centers, hardly any electrons are left in the Nb states or in the conduction band.

The Hall mobility $\mu$ is plotted in Fig. 2. Down to ~100°K $\mu$ does not seem to depend on the degree of reduction or on the particular doping agent, in spite of the widely different resistivities at 100°K. Below that temperature the mobilities diverge considerably. It is somewhat surprising that the samples with the lowest Hall coefficients (at low temperatures) show the highest mobility. Specimens with higher $R$ are probably strongly compensated and contain a larger total number of impurities, reducing the mobility of such samples.

One should keep in mind that $SrTiO_3$ has transition points at 108°K and probably around 40°K. The Hall mobilities of most samples show changes of slope (or more drastic variations, e.g., VR-1B) in the neighborhood of these two temperatures. In the lowest range where the crystal is supposed to be ferroelectric, a domain structure will occur; several authors believe that some sort of domain pattern exists even up to 100°K. The boundaries of these domains may contribute considerably to the scattering of electrons.

In the temperature range 100–300°K the mobility is proportional to $T^{-x}$, where $x$ is between 2.7 and 3.2.[16] A power law is not compatible with polar mode scattering. On the other hand, one-phonon acoustical scattering requires $x=1.5$. It is possible that a temperature-dependent effective mass would increase the value of $x$.[17] When acoustical lattice scattering dominates, $\mu \sim (m^*)^{-5/2}$. The calculated effective masses (see below) seem to vary approximately as $T^{1/2}$. Hence the change of $m^*$ would boost $x$ to about the observed value. However, the change of $m^*$ with $T$ is not understood, and hence the above reasoning should be regarded with reservations.

Another effect which increases the power of $T$ is intervalley scattering. This argument is quite reasonable because a recent study of the energy bands in $SrTiO_3$ puts the minimum of the conduction band at the edge of the Brillouin zone in the [100] direction, giving rise to threefold degeneracy. By the same token it is possible that acoustical and polar mode scattering of similar magnitude give rise to a mobility proportional to about $T^3$.

Kahn's energy-band calculation is based on the tight binding approximation. Starting with a pure ionic model the orbital energies were deduced. Subsequently, crystalline fields and overlap were taken into account. The ionic charge was adjusted to yield the observed energy gap. It appears that the (empty) conduction band is derived predominantly from Ti 3$d$-states and the (filled) valence band mostly from O 2$p$ orbitals. The effective masses of the ellipsoids at the edge of the Brillouin zone are estimated to be: $m^*_{\text{trans}}=1.1\,m_0$ and $m^*_{\text{long}}=20\text{–}50\,m_0$. From these $m^*$'s one can calculate the density-of-states effective mass according to the expression:

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

where $\nu$ is the number of energy minima. The result is $m_{\text{av}}^* \approx 6$ to $13\,m_0$. This is the value of the "bare" mass; polaron effects will probably increase this value somewhat.

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[16] Plotting ln $\mu$ versus $1/T$ does *not* produce a straight line.

[17] F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 339.

Combining our measurements of Seebeck coefficient and Hall effect, the average effective mass may be deduced from experiment. As will be discussed below, there are good reasons to believe that the phonon-drag effect does not contribute to the Seebeck coefficient $Q$ above 50 or 60°K. Hence, we can use the expression for the "pure electronic" part[18] of $Q$:

$$Q_e = -(k/e)[\ln(-R) + \tfrac{3}{2}\ln(m_{av}^*/m_0) + \tfrac{3}{2}\ln T + r + \text{const}]. \quad (2)$$

$r$ depends on the scattering mechanism and has been taken to be 2.5. The results for $m_{av}^*$ are listed in Table I. (Slightly higher values of $m_{av}^*$ would be obtained with $r=2.0$.) Considering the approximate character of the band calculation and the uncertainties with respect to the scattering mechanism [which influence some constants in Eq. (2)], the agreement between theory and experiment is good. It adds strength to the assumption concerning the strong $d$ character of the conduction band in the titanates.

The temperature dependence of the effective mass is surprising. It is possible that the larger values of $m^*$ at room temperature are caused by the fact that the energy bands are filled to higher levels where the curvature is smaller. Or the explanation could be the onset of population of slightly higher conduction bands (at the center of the Brillouin zone) with high effective masses. Also, one can argue that the electron interacts with the polar modes and that a polaron is formed. Several authors claim that the effective mass of the polaron increases with temperature. However, this holds only for the small polaron, a model which is not easily acceptible for $SrTiO_3$.

However, the decrease of $m_{av}^*$ towards lower temperature proves one thing: At liquid-nitrogen temperature and above, the phonon-drag contribution to the Seebeck coefficient is negligible. A glance at Fig. 3 reveals that samples VR-1B and TiR5 show a small maximum at about 25°K.

The absence of any phonon-drag effect above 60°K is understandable on the basis of Cochran's theory[7] of ferroelectric modes. (Recent heat-transport experiments[13] showed a very low thermal conductivity over the entire temperature range 1.4–100°K, in accordance with these ideas). As the energy of the ferroelectric mode decreases with temperature, interaction of this mode with the acoustic phonons will grow. Hence the acoustical-phonon equilibrium will be maintained and the phonon mean free path—especially that of the acoustic phonons with small wave vector—will be small. Thus, little momentum will be transferred to the electrons and a negligible phonon-drag contribution results. If the energy of the ferroelectric mode reaches zero at about 40°K($T_c$), a rearrangement of modes will take place and a phonon-drag contribution to $Q$ is a distinct possibility below the Curie temperature. The heat conductivity shows a maximum at $\sim$30°K. It is therefore not surprising that the Seebeck coefficient also peaks in the neighborhood of this temperature. One would expect that the maximum of $Q$ would occur somewhat higher because the large mean free path of the long-wavelength phonons should reach values comparable with the dimensions of the sample at somewhat higher temperature than the average mean free path of the total acoustical-phonon spectrum. However, such a coincidence of the two maxima has also been observed in experiments on tellurium.[19]

## CONCLUSIONS

(1) Electrons in $SrTiO_3$ can be described by the energy-band model.

(2) The theoretically predicted average effective mass ($6-13\ m_0$) at the bottom of the conduction band agrees rather well with experiment.

(3) Phonon-drag contributions to the Seebeck coefficient are very small in contrast to rutile.[20] Cochran's theory of ferroelectricity explains this behavior satisfactorily.

## ACKNOWLEDGMENTS

The continued interest and advice of Dr. J. H. Becker and of Dr. A. H. Kahn are greatly appreciated.

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[18] Conyers Herring, Phys. Rev. **96**, 1163 (1954).

[19] I. M. Timchenko and S. S. Shalyt, Fiz. Tverd. Tela 4, 935 (1962) [English transl.: Soviet Phys.—Solid State 4, 685 (1962)].

[20] W. R. Thurber, M. S. thesis, University of Maryland, 1963 (unpublished).