

## Oxygen-Deficient SrTiO<sub>3-x</sub>, x = 0.28, 0.17, and 0.08. Crystal Growth, Crystal Structure, Magnetic, and Transport Properties

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The grossly nonstoichiometric perovskites SrTiO<sub>3-x</sub> with  $x = 0.28, 0.17,$  and  $0.08$  were prepared from a reaction of Sr<sub>2</sub>TiO<sub>4</sub>, TiO, and TiO<sub>2</sub> at 1500°C. For  $x = 0.28$  relatively large single crystals were obtained. Also for this sample the crystal symmetry was found to depend on the rate of cooling from the reaction temperature and the annealing conditions. Rapidly cooled samples are tetragonal  $a = 3.9177(3)$  Å,  $c = 3.8878(5)$  Å. Samples annealed in vacuum at temperatures of 1000 to 600°C are cubic  $a = 3.9075(3)$  Å with no change in cell volume. Single crystal data from a tetragonal sample indicate slight preferential occupancy of one oxygen position in  $P4/mmm$ . No evidence for any supercell due to defect ordering could be seen by TEM in either cubic or tetragonal samples. The  $x = 0.28$  crystals show metallic resistivity,  $\rho(300\text{ K}) = 6 \times 10^{-4}$  ohm-cm and temperature-independent paramagnetism,  $\chi_m = 118 \times 10^{-6}$  cm<sup>3</sup> mole<sup>-1</sup>. Hall effect data from 300 to 4.2 K analyzed on a single carrier model give a temperature-independent  $n$ -type carrier density of  $2.4 \times 10^{21}$  cm<sup>-3</sup>. This is a factor of 3.9 less than that expected if the creation of each oxygen vacancy results in the production of two carriers in a single band. Hall data for  $x = 0.17$  and  $0.08$  samples give similar results corresponding to densities of  $2.1$  and  $1.4 \times 10^{21}$  cm<sup>-3</sup>, respectively, in the same temperature range. These densities are 2.7 and 1.9 times less than the expected single-band value, respectively. Such results point to a two-band model with a large effective mass in one of the bands. © 1991 Academic Press, Inc.

### Introduction

Strontium titanate SrTiO<sub>3</sub> has the cubic perovskite structure at room temperature (1). The stoichiometric compound becomes tetragonal at 108 K (2) and is ferroelectric at 45 K (3). Oxygen-deficient SrTiO<sub>3-x</sub> has also been studied. For very small values of  $x$ , which can be achieved by reducing in high vacuum, the materials are either semiconductors or metallic depending on the

conditions and doping levels (4). Superconductivity in the millikelvin range has been reported for H<sub>2</sub>-reduced samples and Ti-gettered samples (5). An extensive study of the variation of  $T_c$  with carrier density indicates a maximum for  $T_c$  of 0.3 K at about  $9 \times 10^{19}$  cm<sup>-3</sup> (5). Although the extent of nonstoichiometry in these compounds could not be measured, if one assumes no change in lattice constant and that one O<sup>2-</sup> vacancy introduces two carriers, then  $x$  in SrTiO<sub>3-x</sub> is estimated as 0.011 for  $n = 9 \times 10^{19}$  cm<sup>-3</sup>. Superconductivity is found in another titanium oxide, the spinel LiTi<sub>2</sub>O<sub>4</sub> with  $T_c \approx 11$  K (6). This is a mixed valence oxide with

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one Ti<sup>3+</sup> and one Ti<sup>4+</sup> per formula unit in the octahedral sites of the spinel structure. This gives on average one-half a *d*-electron per Ti atom and assuming that the *d*-electron density is the carrier density,  $n \approx 1.3 \times 10^{22} \text{ cm}^{-3}$ . In the SrTiO<sub>3-x</sub> system, an *x* value corresponding to such a carrier density would be  $\sim 0.4$ . Such grossly oxygen-deficient SrTiO<sub>3-x</sub> systems have been reported but little characterization work has been done (7). Although the comparison of LiTi<sub>2</sub>O<sub>4</sub> and SrTiO<sub>2.6</sub> is clearly superficial and expectations of similar behavior would be extremely naive, an investigation of the latter could be intriguing.

A parallel line of investigation concerns the crystal chemistry of such a grossly nonstoichiometric system. It is well known that in compounds which can be regarded as grossly nonstoichiometric perovskites, e.g., the brown millerites such as Ca<sub>2</sub>FeAlO<sub>5</sub> or CaFeO<sub>2.5</sub>, the oxygen vacancies are ordered (8). The ordering mechanism is usually conservative in that the defects are assimilated, which results in supercells based on the simple perovskite structure. In the original report of SrTiO<sub>2.5</sub> (7) it was claimed that this material was cubic with a lattice constant unchanged from the stoichiometric SrTiO<sub>3</sub>. This is a surprising result and merits a more detailed investigation.

## Experimental

### *Sample Preparation and Crystal Growth*

Starting materials were SrCO<sub>3</sub> (Baker Reagent), TiO<sub>2</sub> (Alfa Inorganics 99.9%), and Ti sponge (Alfa Inorganics 99.9%). Sr<sub>2</sub>TiO<sub>4</sub> was prepared by firing SrCO<sub>3</sub> and TiO<sub>2</sub> in the correct proportions at 1200°C for 3 days in air. The product was identified as Sr<sub>2</sub>TiO<sub>4</sub> by X-ray powder diffraction. TiO and TiO<sub>1.5</sub> (Ti<sub>2</sub>O<sub>3</sub>) were prepared by arc melting TiO<sub>2</sub> and Ti sponge in the correct proportions. The Ti/O ratio of the products

was checked by thermogravimetric oxidative weight gain.

### *SrTiO<sub>2.72</sub>*

Sr<sub>2</sub>TiO<sub>4</sub> and TiO were weighed in the ratio of 1 : 1, well ground with an agate mortar and pestle in acetone, and pressed into pellets. The pellets were placed in a molybdenum tube, evacuated, and then sealed under 0.5 atmosphere argon by arc welding. This was heated at 1500°C in a radio frequency induction heating furnace under vacuum ( $\sim 10^{-5}$  Torr) for 2 days, and then cooled to room temperature over a period of 10 hr. Dark blue-violet single crystals were obtained with dimensions up to  $5 \times 4 \text{ mm}^3$ . A smaller amount of polycrystalline material was also formed in a different part of the crucible but this was not analyzed.

The oxygen content of the crystals was determined by thermogravimetric oxidation in a Netzsch STA 409 system in dry air. The sample was heated to 1000°C and the value of *x* was found to be 0.28(2) assuming oxidation to SrTiO<sub>3.00</sub>. Note that the crystals are more oxidized than the starting materials.

### *SrTiO<sub>2.83</sub>*

The starting materials were Sr<sub>2</sub>TiO<sub>4</sub> and TiO<sub>1.52</sub> in the ratio of 1 : 1. The mixture was sealed in a Mo tube as above and heated in a RF induction heating at 1500°C for 2 days and then quenched to RT in 1 hr. No melting of the sample was observed and no large crystals were formed.

A 465.7-mg sample was oxidized in air at 900°C and the weight gain was found to be 7.0 mg for an oxygen content of 2.83 or  $x = 0.17$ .

### *SrTiO<sub>2.92</sub>*

The starting materials were Sr<sub>2</sub>TiO<sub>4</sub>, TiO<sub>1.52</sub>, and TiO<sub>2</sub> in a 1 : 0.5 : 0.5 molar ratio. The mixture was sealed in a molybdenum crucible and heated in a radio fre-

quency induction heating furnace at 1550°C for 2 days and then quenched to rt in 1 hr.

A 725.6-mg sample was oxidized in air at 900°C and the weight gain was found to be 5.0 mg, giving an oxygen content of 2.92 or  $x = 0.08$ .

#### *X-Ray Diffraction*

Powder X-ray diffraction data were obtained on a Nicolet I2 automated diffractometer and also with use of an IRDAB Model XDC 700 Guinier camera with monochromated  $\text{CuK}\alpha_1$  radiation and a Si internal standard. Experimental details for a single crystal study of the  $x = 0.28$  sample are described in a later section.

#### *Magnetic Susceptibility*

Data were obtained with a Quantum Design S.Q.U.I.D. magnetometer in the temperature range 4.2 to 300 K. The magnetometer is calibrated with a sample of high purity palladium.

#### *Electron Microscopy*

Samples were investigated in a Philips CM12 transmission electron microscope. The samples were obtained from crushed single crystals supported on holey carbon films.

#### *Electrical Transport Properties*

$\text{SrTiO}_{3-x}$  samples were cut into rectangular pieces with typical dimensions of  $3.5 \times 1.5 \times 0.3 \text{ mm}^3$ . Samples were provided with six contacts using silver paste. The two current contacts were made by painting silver paste onto the entire area of the end faces of the sample to ensure a uniform current injection. Both the resistivity and the Hall effect measurements were carried out with the standard four probe method in the temperature range 1.3 K (4.2 K for Hall effect) to 300 K. All Hall and conductivity voltages were measured with a Keithley-181 nanovoltmeter. Conventional current and field reversal procedures were used to elim-

inate thermal drifts, Hall contact mismatch offset, and magnetoresistance effects.

## **Results and Discussion**

#### *Structural Characterization of $\text{SrTiO}_{3-x}$ , $x = 0.28$*

Small portions of the single crystals comprising most of the charge were ground to a fine powder and examined using Guinier film methods. Small crystals were also selected for precession photographs. Both methods showed unequivocally that the crystals had tetragonal symmetry. Shoulders on low angle reflections such as [100] could be observed from powder diffractometer data. The results from a typical Guinier film are shown in Table I for a crystal of composition  $\text{SrTiO}_{2.72}$  (2) as determined by TGA.

During characterization of the products of several crystal growth runs and of the products of annealing experiments where crystals were heated in evacuated ( $\sim 10^{-5}$  torr), sealed quartz ampules under a variety of temperature-time schedules, we noted a correlation between crystal symmetry, lattice constants, and the sample history. This is summarized briefly in Table II.

Note that the more rapidly a sample is cooled (B) from the reaction temperature, the greater the degree of the tetragonal distortion. Also, samples annealed in vacuum become cubic (C) with no change in cell volume. Sample (A) was annealed to produce sample (C). All samples, when oxidized in air, revert to the cubic  $\text{SrTiO}_{3.00}$  with a smaller lattice constant than the reduced phases.

A small single crystal from batch (A) was selected for data collection on a Nicolet P2<sub>1</sub> diffractometer using  $\text{MoK}\alpha$  radiation at room temperature. The details are summarized in Table III. Intensities of two standard reflections were monitored throughout the data collection.

TABLE I  
GUINIER CAMERA X-RAY DIFFRACTION DATA  
FOR SrTiO<sub>2.72</sub>

$d_{\text{cal}}^a$	$d_{\text{obs}}$	$h k l$	$I_{\text{obs}}$
3.918	3.913	1 0 0	w+
3.888	3.889	0 0 1	w
2.770	2.769	1 1 0	s
2.760	2.757	1 0 1	s+
2.256	2.256	1 1 1	m
1.959	1.958	2 0 0	s-
1.944	1.944	0 0 2	m-
1.752	1.753	2 1 0	w
1.749	1.749	2 0 1	w
1.741	1.741	1 0 2	w
1.597	1.597	2 1 1	m+
1.591	1.591	1 1 2	m
1.385	1.385	2 2 0	m-
1.380	1.379	2 0 2	m
1.306	—	3 0 0	—
1.305	1.305	2 2 1	w-
1.301	1.301	2 1 2	w
1.296	—	0 0 3	—
1.239	1.239	3 1 0	m-
1.238	1.238	3 0 1	m-
1.230	1.230	1 0 3	m-
1.180	1.180	3 1 1	w+
1.174	1.174	1 1 3	w
1.128	1.128	2 2 2	m-

<sup>a</sup>  $a = 3.9177(3)$  Å,  $c = 3.8879(5)$  Å.

The unit cell parameters are in excellent agreement with those from the Guinier powder experiment. No systematic ab-

sences were observed and the highest symmetry space group consistent with this observation,  $P4/mmm$ , was chosen for refinement.

The structure was refined by full matrix least-squares using the program SHELX 76 (9). The positional parameters were derived from the cubic SrTiO<sub>3</sub> (1). Scattering factors and anomalous dispersion terms were taken from the usual source (10, 11). A total of 916 X-ray diffraction intensities were corrected for absorption with the use of the  $\psi$ -scan technique and averaged ( $R_{\text{int}} = 0.037$ ) to give 89 unique reflections. The final anisotropic refinement based on 13 variables and 89 observations resulted in an  $R$  index on  $F$  of 0.016, with  $\Delta/\sigma$  not exceeding 0.005 is  $R_w(F) = 0.016$ , where the weighting scheme is  $w = 1.0/(\sigma(F_0)^2 + 0.001F_0^2)$ . The error in an observation of unit weight is 0.68.

A final electron density map exhibited no features. The highest and lowest residual peaks were 0.80 e/Å<sup>3</sup> and -0.65 e/Å<sup>3</sup>, respectively. No unusual trends are observed from an analysis of  $F_0$  vs  $F_c$  as a function of  $F_0$ ,  $(\sin \theta)/\lambda$ , and Miller indices. Table IV lists fractional coordinates and equivalent isotropic thermal parameters. The anisotropic thermal parameters are given in Table V.

A list of selected bond distances and angles may be found in Table VI. The  $x$  value found by refining the O occupancies,  $x = 0.40(6)$  is within  $2\sigma$  of the TGA results. As the TGA-determined composition is characteristic of the bulk crystals upon which

TABLE II  
CORRELATION OF LATTICE CONSTANTS AND SAMPLE HISTORY FOR SrTiO<sub>2.72</sub>

Conditions	$a$ (Å)	$c$ (Å)	$V_{\text{CELL}}$ (Å <sup>3</sup> )
A 1500°C to RT, 10 hr	3.9177(3)	3.8879(5)	59.67(1)
B 1500° to RT, 1 hr	3.9240(3)	3.8780(5)	59.71(1)
C Vac-annealed 800°C 4 days	3.9075(3)	—	59.66(1)
D Oxidized in air	3.9047(3)	—	59.53(1)

TABLE III  
Summary of Intensity Collection and Refinement of SrTiO<sub>2.72</sub>

$a(\text{\AA})$	3.917(2)
$c(\text{\AA})$	3.889(1)
$V(\text{\AA}^3)$	59.67
$Z$	1
Space group	$D_{4h}^1 - P4/mmm$ [No. 123]
Crystal shape, dimension (mm <sup>3</sup> )	Cube, $0.25 \times 0.25 \times 0.25$
Radiation	Graphite monochromated MoK $\alpha$ ( $\lambda(K\alpha_1) = 0.70926\text{\AA}$ )
Scan type	$\theta-2\theta$
Scan range (deg.)	1.2 below $K\alpha_1$ to 1.2 above $K\alpha_2$
Scan speed (deg./min.) <sup>a</sup>	5.86–29.3
$\lambda^{-1} \sin\theta$ , limits ( $\text{\AA}^{-1}$ )	0.0492–0.7576
Data collected	$\pm h, \pm k, \pm l$
No. of unique data	89
No. of variables	13
$R(F)$	0.016
$Rw(F)$	0.016

<sup>a</sup> Dependent on prescan.

the physical measurements have been made the single crystal data have been labeled with this composition.

The structure of SrTiO<sub>2.72</sub> changes slightly as a result of the distortion to tetragonal symmetry. As there are now two oxygen sites in the tetragonal cell, the occupation of O atoms in these two sites are not equal. The O(1) site (occupancy = 80(2)%) has more vacancies than the O(2) site (occupancy = 90(2)%). This seems to be related to the contraction of the structure along the  $c$ -axis.

Electron diffraction experiments were conducted to detect any superstructure resulting from possible oxygen ordering in both the tetragonal and the cubic phases. The crystals were annealed in sealed Mo or quartz tubes at temperatures ranging from 600 to 1200°C for periods up to several weeks. However, no evidence for a superlattice was observed in any of the several tens of crystals examined.

For the other compositions investigated,  $x = 0.17$  and  $0.08$ , there was no evidence for distortion from cubic symmetry. Indexed Guinier powder data and derived unit cell constants are given for both in Ta-

TABLE IV  
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR SrTiO<sub>2.72</sub>(6)

Atom	Site	$x$	$y$	$z$	Beq( $\text{\AA}^2$ ) <sup>a</sup>	Occupancy
Ti	1a	0	0	0	0.53	1
Sr	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.27	1
O(1)	1b	0	0	$\frac{1}{2}$	0.53	0.80(2)
O(2)	2f	0	$\frac{1}{2}$	0	0.40	0.90(2)

<sup>a</sup> Beq =  $(8^2/3)U_{ij} a_i^* a_j^* (a_i \cdot a_j)$ .

TABLE V  
ANISOTROPIC THERMAL PARAMETERS FOR SrTiO<sub>2.72</sub>(6)

Atom	$U_{11}$	$U_{22}$	$U_{33}$
Ti	0.0041(3)	$U_{11}$	0.0020(5)
Sr	0.0079(3)	$U_{11}$	0.0042(3)
O(1)	0.0113(14)	$U_{11}$	-0.002(2)
O(2)	0.0077(11)	0.0016(10)	0.0051(13)

TABLE VI  
SELECTED BOND DISTANCES (Å) AND ANGLE  
(DEGREES) FOR SrTiO<sub>2.72</sub>(*b*)

Ti-O(1) × 2	1.945(1)	Sr-O(1) × 4	2.770(1)
Ti-O(2) × 4	1.959(1)	Sr-O(2) × 8	2.760(1)
O(1)-Sr-O(2)	59.88(1)		

bles VII and VIII. The relative intensities are the same at this level of accuracy as those reported for the corresponding reflections (averaged when necessary) in Table I.

#### Electrical Transport Properties

Electrical resistivity data are shown in Fig. 1. All three samples are clearly metallic. As mentioned, single crystal samples were available only for SrTiO<sub>2.72</sub> so quantitative comparisons between samples are not useful but all three have similar temperature dependencies. For all samples the resistivities were nearly constant in the temperature range 1.3 to 50 K with values between 1.6 and 3.2 × 10<sup>-4</sup> ohm-cm. Similar low-temperature resistivities were noted for more lightly doped SrTiO<sub>3</sub> samples (4.5) but in these cases the room temperature values were 10<sup>2</sup>-10<sup>3</sup> times greater, while in

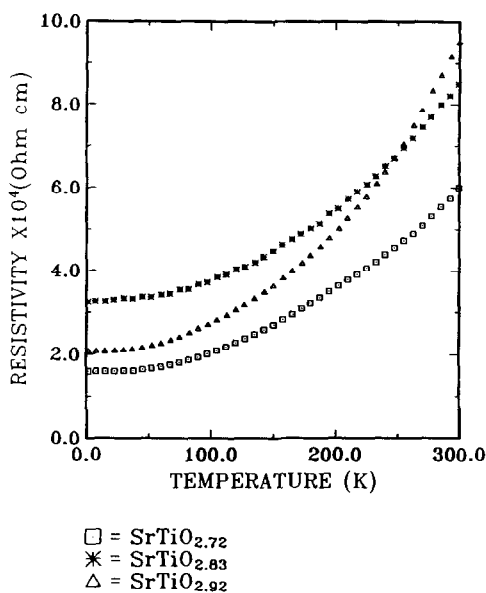


FIG. 1. Electrical resistivity versus temperature for SrTiO<sub>3-x</sub>. □, *x* = 0.28; \*, *x* = 0.17; △, *x* = 0.08.

the present case the increase is only a factor of four to five at room temperature. Attempts to fit the data between 50 and 300 K to a simple power law in the temperature were not successful.

From Fig. 2 it is clear that the Hall coeffi-

TABLE VII  
CALCULATED AND OBSERVED X-RAY DIFFRACTION  
DATA FOR SrTiO<sub>2.83</sub>

<i>d</i> <sub>cal</sub> <sup>a</sup>	<i>d</i> <sub>obs</sub>	<i>h k l</i>
3.9089	3.9080	1 0 0
2.7640	2.7624	1 1 0
2.2568	2.2571	1 1 1
1.9545	1.9553	2 0 0
1.7481	1.7487	2 1 0
1.5958	1.5963	2 1 1
1.3820	1.3823	2 2 0
1.3030	1.3030	2 2 1, 3 0 0
1.2361	1.2357	3 1 0
1.1786	1.1785	3 1 1
1.1284	1.1284	2 2 2

<sup>a</sup> *a* = 3.9089(3) (Å), cell volume = 59.73(1) Å<sup>3</sup>.

TABLE VIII  
CALCULATED AND OBSERVED X-RAY DIFFRACTION  
DATA FOR SrTiO<sub>2.92</sub>

<i>d</i> <sub>cal</sub> <sup>a</sup>	<i>d</i> <sub>obs</sub>	<i>h k l</i>
3.9057	3.9078	1 0 0
2.7618	2.7603	1 1 0
2.2550	2.2563	1 1 1
1.9529	1.9524	2 0 0
1.7467	1.7474	2 1 0
1.5945	1.5939	2 1 1
1.3809	1.3813	2 2 0
1.3019	1.3017	2 1 1, 3 0 0
1.2351	1.2351	3 1 0
1.1776	1.1776	3 1 1
1.1275	1.1273	2 2 2

<sup>a</sup> *a* = 3.9057(3) (Å), cell volume = 59.58(1) Å<sup>3</sup>.

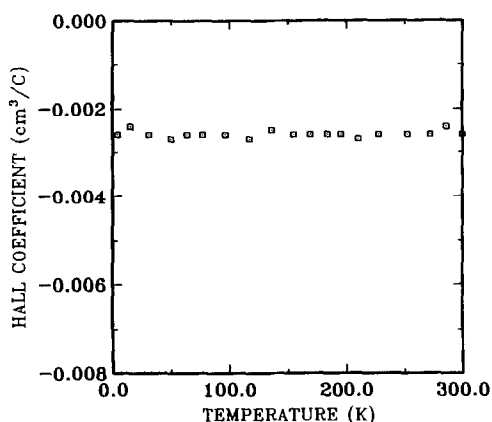


FIG. 2. Temperature dependence of the Hall coefficient for  $\text{SrTiO}_{2.72}$ .

cient for  $\text{SrTiO}_{2.72}$  is temperature independent. The same behavior was found for the other two samples and the values are listed in Table IX.

From the observed sign, the charge carriers are electrons. Note that the Hall coefficient increases systematically from  $x = 0.28$  to  $0.08$ , which is the expected trend. Also in Table IX are listed values of the charge carrier concentration obtained assuming a single carrier band,  $R_H = -1/nec$ . When these values are compared to carrier concentrations calculated from the  $x$  values on the assumption that a single  $\text{O}^{2-}$  vacancy donates two electrons to a single conduction band, discrepancies are noted. The ob-

served values,  $n_H$ , are always lower (by a factor of 3.9 for  $x = 0.28$ ) than the expected values,  $n_t$ . The ratio  $n_t/n_H$  decreases systematically, in fact linearly, with  $x$ . This result can be understood, qualitatively, on a two-conduction band model assuming that one of the bands has a much greater effective mass than the other. In this case the lower band would have the smaller  $m^*$  and carriers in this band would dominate the resistivity and the Hall data. As the total electron concentration increases the upper band will become more populated with a proportionately larger number of carriers being lost to these high  $m^*$  states. Qualitatively, this explanation is consistent with band structure calculations for stoichiometric  $\text{SrTiO}_3$  (12, 13), which show a multiple conduction band with a nearly flat band in the  $\langle 100 \rangle$  directions degenerate with a relatively broad band. The high concentrations of random oxygen vacancies in these samples would also tend to cause a narrowing of the energy bands and might introduce localization at certain defect concentrations introducing a finite concentration of trap sites which could also act as sinks for the missing charge carriers.

The effect of the high defect concentrations is seen in the Hall mobility data for  $\text{SrTiO}_{2.72}$  plotted in Fig. 3. The mobility is weakly temperature dependent and is in the range  $4.3$  to  $16 \text{ cm}^2/(\text{V sec})$ . The small value of the low temperature mobility is remark-

TABLE IX  
ROOM TEMPERATURE HALL COEFFICIENTS AND EFFECTIVE  
CHARGE CARRIER CONCENTRATIONS OF  $\text{SrTiO}_{3-x}$

Sample	$x$	$R_H$ ( $10^{-3} \text{ cm}^2/\text{C}$ )	$n_t$ ( $10^{21} \text{ cm}^{-3}$ )	$n_H$ ( $10^{21} \text{ cm}^{-3}$ )	$n_t/n_H$
2	0.28	-2.57	9.38	2.43	3.86
3	0.17	-3.01	5.70	2.08	2.74
4	0.08	-4.33	2.68	1.44	1.86

Note.  $n_t$ , carrier density estimated from  $x$  (TGA);  $n_H$ , carrier density calculated from Hall effect.

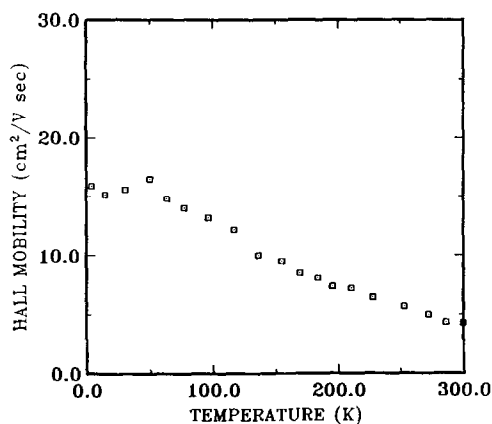


FIG. 3. Temperature dependence of the Hall mobility for SrTiO<sub>2.72</sub>.

able when compared to previous studies on more lightly reduced,  $n \approx 10^{19} \text{ cm}^{-3}$ , SrTiO<sub>3</sub> (4). In these studies the room temperature Hall mobilities are similar to those reported here, 5 to 6.5 cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup>, but in most cases low temperature values exceed 10<sup>3</sup> cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup>. The systems studied here differ fundamentally in the concentration of oxygen vacancies, which are on the order of  $5 \times 10^{21} \text{ cm}^{-3}$  for SrTiO<sub>2.72</sub>, exceeding those of the previous studies by three orders of magnitude. At such a defect concentration the average separation between the oxygen vacancies is about 6 Å, assuming a random distribution, and this is smaller than the expected mean free path for the conduction electrons at low temperatures. Thus it is reasonable to conclude that the temperature-independent resistivity and Hall mobility below about 50 K can be ascribed to scattering by oxygen vacancies.

#### Magnetic Susceptibility

Magnetic susceptibility data for the  $x = 0.28$  sample is shown in Fig. 4. It is nearly temperature independent in the range 20 to 300 K. Below 20 K there is a sharp upturn which might be due to a localized electron paramagnetic center. The susceptibility for

the other two samples  $x = 0.08$  and 0.17 is strongly temperature dependent in the same range. As the electrical resistivity and Hall effect data indicate that the samples are all intrinsically metallic with temperature invariant carrier densities, the magnetic susceptibilities of  $x = 0.17$  and 0.08 are likely due to paramagnetic impurities or to localized paramagnetic centers associated with the very high concentration of random defects in these materials. In any case it is thus extremely difficult to extract that part of the susceptibility due to the conduction electrons for the  $x = 0.17$  and 0.08 samples so a more detailed analysis will be attempted only for  $x = 0.28$ . There are four components of the temperature-independent susceptibility, namely, the core electron diamagnetism, a van Vleck paramagnetism which depends only on the band structure, and a conduction electron contribution which includes both a paramagnetic and a diamagnetic term. The core diamagnetism and van Vleck paramagnetism have been measured for stoichiometric, insulating SrTiO<sub>3</sub> and the values are  $-52(4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$  and  $33 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ , respectively (14). Although it is not

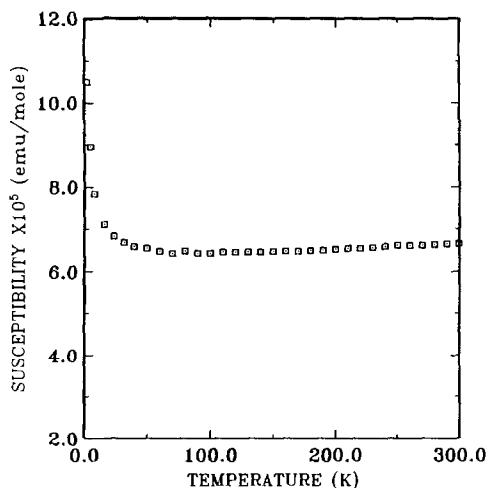


FIG. 4. Magnetic susceptibility versus temperature for SrTiO<sub>2.72</sub>.



obvious that the band structure and thus the van Vleck term is similar for SrTiO<sub>2.72</sub> and SrTiO<sub>3</sub> this will be assumed to a first approximation. The conduction electron contribution is given, assuming parabolic bands, as (15).

$$\chi_m = (4m^* \mu_B^2/h^2)(3n^2)^{1/3} \left(1 - \frac{m^2}{3m^2}\right). \quad (1)$$

Note that this is a volume susceptibility where  $n$  is the carrier density and  $m/m^*$  is the ratio of the electron rest mass to the effective carrier mass. The measured susceptibility for SrTiO<sub>2.72</sub> is  $66(1) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$  which, corrected for core diamagnetism and the van Vleck term, give  $85(4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$  for the conduction electron or Pauli susceptibility. Converting this to a volume susceptibility and using Eq. (1) along with the carrier density found from the Hall effect gives  $m^* \approx 7$ . This is greater than the  $m^* \approx 5$  obtained for more lightly doped samples  $10^{19} < n < 5 \times 10^{20} \text{ cm}^{-3}$  (14), which indicates a higher density of states at the Fermi level for this material. This observation is consistent with the interpretation of the electrical transport results. It is instructive to compare the Pauli susceptibility for  $x = 0.28$  with those for similar perovskite materials with comparable carrier densities. For example the cubic alkali metal tungsten bronzes  $M_x\text{WO}_3$ , are also defect perovskites with a theoretical carrier density given by the  $x$  value. Hall effect data are consistent with this assumption (16). For Na<sub>0.78</sub>WO<sub>3</sub> this density is  $1.4 \times 10^{22} \text{ cm}^{-3}$ , which is very near the value expected for SrTiO<sub>2.72</sub>,  $9.4 \times 10^{21} \text{ cm}^{-3}$ , assuming that two carriers are created in a single conduction band for each O<sup>2-</sup> vacancy. Yet the molar susceptibility for Na<sub>0.78</sub>WO<sub>3</sub> is only  $15 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$  (17), less than one-fourth the value for SrTiO<sub>2.72</sub>. This reflects the broader conduction bands and smaller  $m^*/m$  ratio  $\sim 2$  for the tungsten bronzes (17). Another structurally related material is LaTiO<sub>3</sub> which has

a distorted perovskite structure and an enormous temperature-independent susceptibility of  $-800 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$  (18). This material is likely to have extremely narrow conduction bands and large correlation effects as evidence by the onset of anti-ferromagnetic order below 125 K (19).

### Summary and Conclusions

Samples of grossly nonstoichiometric SrTiO<sub>3-x</sub> have been prepared and characterized for  $x = 0.28, 0.17,$  and  $0.08$ . Single crystals of  $x = 0.28$  were prepared for the first time. Rapidly cooled crystals of  $x = 0.28$  are tetragonal with some evidence for a slight vacancy site preference from analysis of X-ray diffraction data. No evidence for long range defect ordering was found from either X-ray or electron diffraction. All of the samples are  $n$ -type metallic conductors with a temperature-independent carrier density from 1 to 300 K. Hall mobility data suggest that the carriers are strongly scattered by the high concentration of defects. The measured carrier concentration, assuming that each O<sup>2-</sup> vacancy donates two electrons to the conduction band, is much lower than that calculated from the X-value. This can be understood on a two-band model if one band has a very large effective mass. The magnetic susceptibility for  $x = 0.28$  is temperature independent but strong temperature dependence is found for  $x = 0.17$  and  $0.08$ . Analysis of the Pauli susceptibility for  $x = 0.28$  gives an effective mass of about seven.

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## APPENDIX

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SrTiO<sub>2.6</sub>

<i>h k l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	SIG	<i>h k l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	SIG	<i>h k l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>	SIG
0 1 0	78	77	2	2 4 1	42	43	1	0 3 3	213	214	7
1 1 0	305	323	9	3 4 1	174	175	5	1 3 3	115	115	4
0 2 0	409	406	12	4 4 1	29	27	2	2 3 3	191	195	6
1 2 0	73	72	2	0 5 1	172	171	5	3 3 3	90	89	3
2 2 0	353	365	11	1 5 1	86	85	3	0 4 3	41	41	2
0 3 0	69	69	2	2 5 1	156	158	5	1 4 3	181	180	6
1 3 0	252	254	8	3 5 1	65	66	2	2 4 3	36	35	2
2 3 0	64	63	2	0 0 2	435	409	13	3 4 3	149	151	5
3 3 0	208	201	6	0 1 2	74	74	2	0 5 3	151	148	5
0 4 0	282	281	9	1 1 2	294	298	9	1 5 3	70	69	2
1 4 0	53	54	2	0 2 2	370	369	11	0 0 4	307	297	10
2 4 0	251	253	8	1 2 2	70	68	2	0 1 4	60	61	2
3 4 0	46	43	2	2 2 2	329	322	10	1 1 4	219	218	7
4 4 0	194	193	6	0 3 2	66	65	2	0 2 4	264	267	8
0 5 0	46	46	2	1 3 2	227	229	7	1 2 4	52	54	2
1 5 0	165	166	5	2 3 2	57	58	2	2 2 4	242	243	7
2 5 0	39	40	2	3 3 2	186	186	6	0 3 4	49	48	2
3 5 0	140	139	4	0 4 2	258	256	8	1 3 4	181	180	6
0 0 1	68	65	2	1 4 2	48	49	2	2 3 4	41	42	2
0 1 1	327	330	10	2 4 2	232	233	7	3 3 4	150	151	5
1 1 1	243	234	7	3 4 2	38	38	2	0 4 4	205	205	6
0 2 1	64	64	2	0 5 2	40	41	2	1 4 4	35	34	2
1 2 1	296	302	9	1 5 2	157	154	5	0 0 5	52	51	3
2 2 1	60	60	2	2 5 2	34	35	2	0 1 5	190	187	6
0 3 1	256	261	8	0 0 3	67	68	2	1 1 5	97	97	3
1 3 1	148	148	5	0 1 3	274	268	8	0 2 5	45	43	2
2 3 1	236	233	7	1 1 3	155	154	5	1 2 5	170	172	5
3 3 1	110	110	3	0 2 3	62	62	2	2 2 5	39	37	2
0 4 1	49	50	2	1 2 3	232	239	7	0 3 5	156	158	5
1 4 1	212	212	6	2 2 3	55	55	2				

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