

Magnetic Susceptibility of Insulating and Semiconducting Strontium Titanate

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The magnetic susceptibility of strontium titanate with and without charge carriers has been measured at 300, 78, and 4.2°K. Insulating SrTiO₃ shows a magnetic moment, which is partly diamagnetic and partly (Van Vleck) paramagnetic. The free-carrier contribution is mainly paramagnetic because of the high density of states. As the concentration of carriers is increased the temperature dependence disappears. At the highest concentration (~6×10²⁰/cc), pure Pauli paramagnetism is observed. The density-of-states effective mass at the bottom of the conduction band deduced from these measurements is 5m₀, in good agreement with values from transport experiments.

INTRODUCTION

IONIC salts without a magnetic moment in the ground state usually are diamagnetic. However, in many crystals contributions from higher energy states lead to an additional positive susceptibility (Van Vleck paramagnetism). Both parts are approximately temperature-independent. Occasionally the Van Vleck term is the larger of the two, as in the case of rutile (TiO₂).¹

When conduction electrons are added to the crystal—either by doping the material or by thermal excitation—a third term will appear resulting from the para- and diamagnetism of the free carriers.

This paper deals with SrTiO₃ in which all three terms can be observed and separated. The pure diamagnetic term for the unreduced material is simply the sum of the diamagnetic susceptibilities of the individual ions. The Van Vleck contribution depends on the energy band structure. The third term (due to free electrons) yields directly a value for the density-of-states effective mass at the bottom of the conduction band.

EXPERIMENTAL ASPECTS

The magnetic susceptibility was measured by the Faraday method using a high-sensitivity vertical-beam balance.²

A SrTiO₃ sample was cut from a single-crystal boule and ground into a small cylinder, 10 mm high and 3 mm in diameter, with a round bottom; the weight of this

specimen was 0.3624 g. Experiments started with measurements on the fully oxidized material at 300, 78, and 4.2°K. Subsequently this sample was reduced three times and reoxidized once between the second and third reduction. These treatments are listed in Table I together with the carrier concentrations *n*. The latter are deduced from measurements of the Hall coefficient ($R_H = 1/nec$) made on rectangular specimens that underwent the same reduction procedures.

The estimated uncertainty of the susceptibility measurements is ±2% or ±5×10⁻¹⁰ cm³ g⁻¹, whichever is larger.

Pure Strontium Titanate

Results on the fully oxidized sample of SrTiO₃ are shown in the first and fourth rows of Table I. The lower negative value observed at 4.2°K is probably due to paramagnetic impurities like Fe, Cr, etc. As mentioned above, the susceptibility of an insulating crystal consists of a pure diamagnetic term and a term representing Van Vleck paramagnetism³:

$$\chi_m = -\frac{Le^2}{6mc^2} \sum_i \langle r_i^{-2} \rangle_{av} + 2L \sum_{n,n'} \frac{|\langle n | \mu_z | n' \rangle|^2}{E_n - E_{n'}} \quad (1)$$

The “pure” diamagnetic part is supposed to be found by simply adding the diamagnetic susceptibilities of

TABLE I. Characteristics of a sample of SrTiO₃ before and after several hydrogen reductions.

Sample	Treatment	<i>n</i> (4.2°K) cm ⁻³	T _{deg} °K	χ or Δχ (10 ⁻⁷ cm ³ g ⁻¹)			
				300°K	78°K	4.2°K	(<i>m</i> [*] / <i>m</i> ₀) _{4.2}
<i>P</i>	pure	χ = -1.02	-1.00	-0.92	...
<i>R</i> ₁	28 h, 950°C hydrogen	6×10 ¹⁸	28	Δχ ₁ = +0.037	+0.073
<i>R</i> ₂	5 h, 1200°C hydrogen (carbon boat)	7.5×10 ¹⁹	148	Δχ ₂ = +0.270	+0.523	+0.928	5.1
<i>P</i> '	reoxidized 18 h 700°C, air	χ = -1.016	-1.012	-0.919	...
<i>R</i> ₃	27 h, 1370°C hydrogen (carbon boat)	5.3×10 ²⁰	550	Δχ ₃ = +1.704	+1.763	+1.719	4.9

¹ F. E. Senftle, T. Pankey, and F. A. Grant, *Phys. Rev.* **120**, 820 (1960).

² G. A. Candela and R. E. Mundy, *Rev. Sci. Instr.* **36**, 338 (1965).

³ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 210.

the constituent ions. Using tabulated data⁴ for Sr^{2+} [$(-17 \pm 2) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$], Ti^{4+} [$(-5 \pm 2) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$], and O^{2-} [$(-10 \pm 2) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$], the first term is calculated to be $(-52 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$. Subtracting this amount from the average experimental value of Table I ($-18.6 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$), one finds a Van Vleck paramagnetism in SrTiO_3 of $(+33 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$. When the same method is applied to the susceptibility of pure rutile (TiO_2),¹ ($+5.4 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$), the Van Vleck term appears to be $(+30 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$. The close agreement between the Van Vleck paramagnetic contribution in these two substances is very satisfying considering the expected similarity in electronic band structure.⁵ It confirms the idea that the valence and conduction bands are pretty much determined by the $(\text{TiO}_6)^{2-}$ -octahedron.

Reduced Strontium Titanate

The magnetic susceptibility of the charge carriers in SrTiO_3 is obtained by determining the susceptibility of reduced samples of SrTiO_3 and subtracting the "pure" diamagnetic and Van Vleck contributions. The resulting values for 3 different concentrations of electrons (each at 300, 78, and 4.2°K) are presented in Table I.

Conduction electrons contribute both a diamagnetic moment (translational motion) and a paramagnetic moment (electron spin). In both cases the susceptibility depends on the prevailing statistics.

The total susceptibility can be written as follows⁶:

$$\chi(T) = \frac{n\mu^2 F_{1/2}'(\zeta)}{kT F_{1/2}(\zeta)} \left(1 - \frac{m^2}{3m^{*2}} \right), \quad (2)$$

where n = number of charge carriers, $\mu = (g/2)\mu_B$, μ_B = Bohr magneton, $F_{1/2}$ and $F_{1/2}'$ = integral functions of $\zeta = E_F/kT$ (E_F = Fermi energy), and m^* = density-of-states effective mass at the bottom of the conduction band. One notices that the spin moment μ depends on the g factor. For conduction electrons g is usually (but not always) close to the free-electron value of 2.0023. Preliminary results from electron spin resonance experiments indicate that $g = 2.0 \pm 5\%$.⁷

For complete degeneracy the electronic susceptibility becomes independent of temperature (Pauli paramagnetism)⁶:

$$\chi(0) = (4m^*\mu^2/h^2)(3\pi^2n)^{1/3}(1 - m^2/3m^{*2}). \quad (3)$$

⁴ W. Klemm, *Z. Anorg. Allgem. Chem.* **244**, 377 (1940); **246**, 347 (1941); and P. W. Selwood, *Magnetochemistry* (John Wiley & Sons, Inc., New York, 1956), p. 78.

⁵ A. H. Kahn and A. J. Leyendecker, *Phys. Rev.* **135**, A1321 (1964).

⁶ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), 2nd ed., pp. 155, 168.

⁷ T. Chang (private communication).

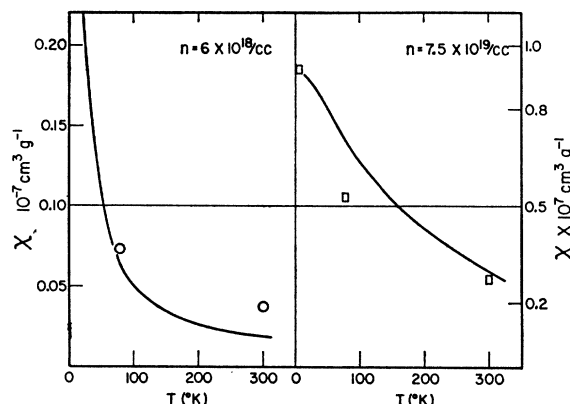


FIG. 1. Magnetic susceptibility of electrons in SrTiO_3 after the first and second reductions. The solid lines represent calculated values using Eq. (2).

The data of Table I show that Eq. (3) applies at all three temperatures only after the third reduction (R_3). In this case the degeneracy temperature is considerably higher than 300°K. When the sample is less reduced (R_1 and R_2), Eq. (2) has to be used. However, all three samples are highly degenerate at 4.2°K and consequently Eq. (3) is applicable at this temperature. It should be noted that all parameters except m^* are known and hence it is possible to calculate the density-of-states effective mass. The values are listed in the last column of Table I. Considering the accuracy of the susceptibility measurement and the possible errors in g and n , these results are good to $\pm 8\%$. The value of m^* found in this experiment is in excellent agreement with the one derived from thermoelectric and Hall data.⁸ The temperature as well as the concentration dependence of m^* appears to be negligible.

It is now possible to check the susceptibilities measured at the two higher temperatures. Using our result $m^* = 5m_0$, the carrier concentrations from our Hall data, and the tabulated values for $F_{1/2}(\zeta)$ and $F_{1/2}'(\zeta)$,⁹ the susceptibilities have been calculated between 4.2 and 300°K; these values together with the experimental data are shown in Fig. 1. It is seen that the temperature dependence is reasonably well represented by Eq. (2).

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⁸ H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).

⁹ O. Madelung, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, pp. 58, 59; $F_n'(\zeta) = nF_{n-1}(\zeta)$ for $n > 0$ (see Ref. 6, p. 332).