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Low-Temperature Heat Capacities of Superconducting Degenerate Semiconductors*

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UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

August 20, 1970

ERRATA

TO: All recipients of UCRL-19164

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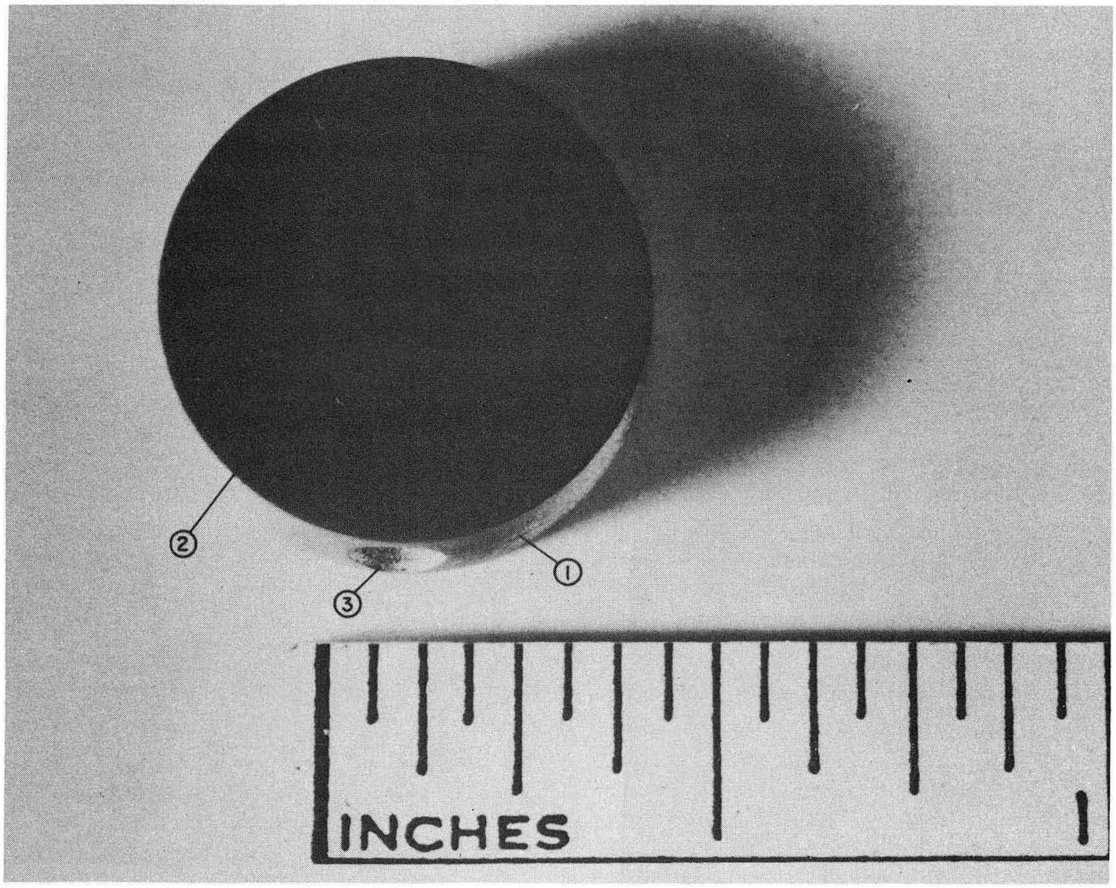
SUBJECT: UCRL-19164, "The Preparation and Characterization of Electron Beam, Vapor Deposited, Germanium Films," by Charles Sterling Portwood III, (M. S. Thesis), June 1970.

Please correct the title on the cover and the abstract page to read as listed above.

Please replace page 17 with attached corrected figure.



XBB 6910-6538A

Fig. 7. Germanium coated molybdenum substrate.

DESCRIPTION OF FIGURE 7

Object Number	Name of Piece of Equipment	Function and Specifications of Piece of Equipment
(7-1)	Molybdenum substrate	To hold germanium film
(7-2)	Germanium film	One of the end products of this study.
(7-3)	Set screw socket	To accept set screw

Abstract

We have measured the low-temperature heat capacities of a number of samples of SnTe and $SrTiO_3$ with varying carrier densities n_c. For SnTe, the Debye temperature θ_D is practically independent of n_c. The coefficient of the electronic heat capacity γ varies regularly with n_c but in a more complicated way than expected for a simple band. The $SrTiO_3$ samples all show appreciable deviation from the temperature dependence expected for the sum of lattice and electronic contributions and, consequently, the values of γ and θ_D are uncertain. For a Nb-doped $SrTiO_3$ sample the increase in heat capacity with applied magnetic field is very much smaller than for a reduced sample with similar n_c. This provides further support for our earlier suggestion that the difference in T_c between Nb-doped and reduced samples, and possibly the maximum in T_c for reduced samples, are related to the presence of paramagnetic ions.

Introduction

The superconductivity of degenerate semiconductors is a subject of continuing interest. This is due primarily to the large range of carrier density over which superconductivity can be observed in these materials. Such materials provide an opportunity to study the effect of carrier density on the superconducting interaction, relatively free of the complications of changes in band structure and phonon spectrum which are important in most alloy systems. A knowledge of certain normal-state properties is essential to a comparison of experiments with theory, and low-temperature heat capacity measurements provide information on two of these -- the density of states at the Fermi surface, N(0), and the Debye temperature, θ_D.

Of the superconducting degenerate semiconductors studied so far, tin telluride, SnTe, and strontium titanate, $SrTiO_3$, have been investigated in the greatest detail[1,2]. In each of these materials charge carriers may be introduced either by the incorporation of impurities into the lattice or by deviations from stoichiometry. In the case of SnTe, it is well established that T_c increases monotonically with n_c, irrespective of doping mechanism, whereas for $SrTiO_3$ the behavior is more complex. In $SrTiO_3$, when carriers are produced by reduction, which removes oxygen and generates two electrons per oxygen vacancy, a sharp maximum in the T_c versus n_c curve is observed at $n_c \approx 7\times10^{19}\,cm^{-3}$. For the impurity doped material, in which carriers are produced by the substitution of Nb^{+5} for Ti^{+4}, T_c shows the same general behavior for low n_c

values, but the critical temperatures of the niobium-doped samples are higher than those of the reduced samples and there is no well defined maximum[2,3].

Several theoretical models based on the BCS theory have been developed to explain the superconductivity of degenerate semiconductors. These differ markedly in their choice of the dominant contribution to the electron-phonon interaction. Surprisingly good agreement with experiment is obtained by each of the theories, possibly due to the presence of an adequate number of adjustable parameters[2,4].

The primary purpose of the present investigation was to obtain values of N(0) and θ_D as functions of n_c for SnTe and $SrTiO_3$. For SnTe samples with high carrier densities the heat capacity measurements extended below the critical temperature T_c, and the new date further confirm the existence of bulk superconductivity which was first demonstrated in our earlier work[5].

Sample Preparation

The SnTe samples were sintered cylinders (approximately 3/4" diameter by 1" length) prepared by powder metallurgical techniques.

Most of the $SrTiO_3$ samples were polycrystalline specimens prepared by sintering the insulating ceramic at about 1400°C. The material was subsequently reduced by heating at about the same temperature in a mixture of CO and CO_2 with the gas composition adjusted for the desired oxygen vacancy concentration. The Nb-doped sample was a boule of approximately 50 carats, grown by the flame fusion technique.

The Hall constant R_H, from which n_c was inferred, and T_c were determined in separate experiments on small samples cut from the ends of the heat capacity samples.

Results and Discussion

Tin Telluride

The observed heat capacity C of SnTe, at the lowest temperatures, could be fitted to the expression

$$C = \gamma T + \alpha T^3 \tag{1}$$

by a least squares analysis, as would be expected for a normal degenerate semiconductor. Some typical data are shown in Fig. 1. The relatively high carrier concentration silver doped sample exhibits a heat capacity peak consistent with the onset of superconductivity throughout the sample. The peak was removed by the application of a magnetic field of 2000 Oe. No increase of heat capacity with magnetic field was observed for this material. The values of γ and θ_D derived from α in the usual way, are summarized in Table I, and plotted as a function of n_c in Fig. 2. The short range of validity of the T^3 approximation for the lattice heat capacity (see Fig. 1) limits the accuracy with which θ_D can be determined, but the weak dependence of θ_D on n_c is probably real. The maximum θ_D value occurs for the sample with the highest vacancy concentration and may be a consequence of the effect of vacancies on the phonon spectrum. For most samples γ, which is proportional to N(0), falls close to the line representing an $n_c^{1/3}$ dependence, as is usually assumed, but which does not seem to have been investigated previously. The deviations from $n_c^{1/3}$ are,

Figure Captions

Figure 1 Typical low-temperature heat capacities of SnTe samples.

Figure 2 Dependence of T_c and normal-state parameters on carrier concentration for SnTe. The dashed line represents an $n_c^{1/3}$ dependence.

Figure 3 Dependence of apparent values of normal-state parameters on n_c for $SrTiO_3$ samples. The dashed line represents an $n_c^{1/3}$ dependence. The open symbols are from Refs 7 and 8.

Figure 4 A comparison of the effect of magnetic field on the heat capacities of reduced and Nb-doped $SrTiO_3$ samples.

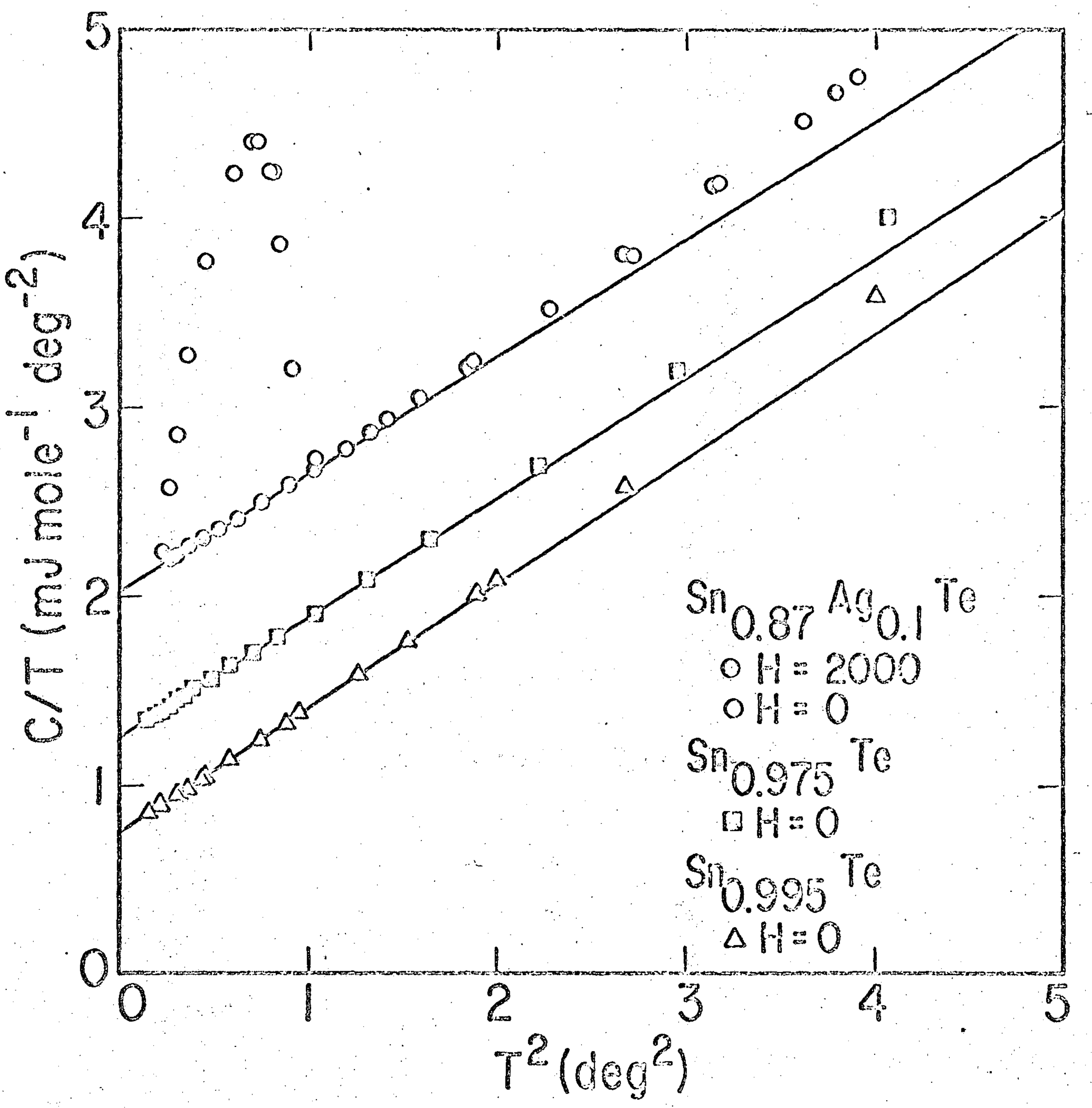

5
4
3
2
1
0
C/T (mJ mole^{-1} deg^{-2})
0
1
2
3
4
5
T^2(deg^2)
$Sn_{0.87}Ag_{0.1}Te$
○ H = 2000
○ H = 0
$Sn_{0.975}Te$
□ H = 0
$Sn_{0.995}Te$
△ H = 0

Figure 1

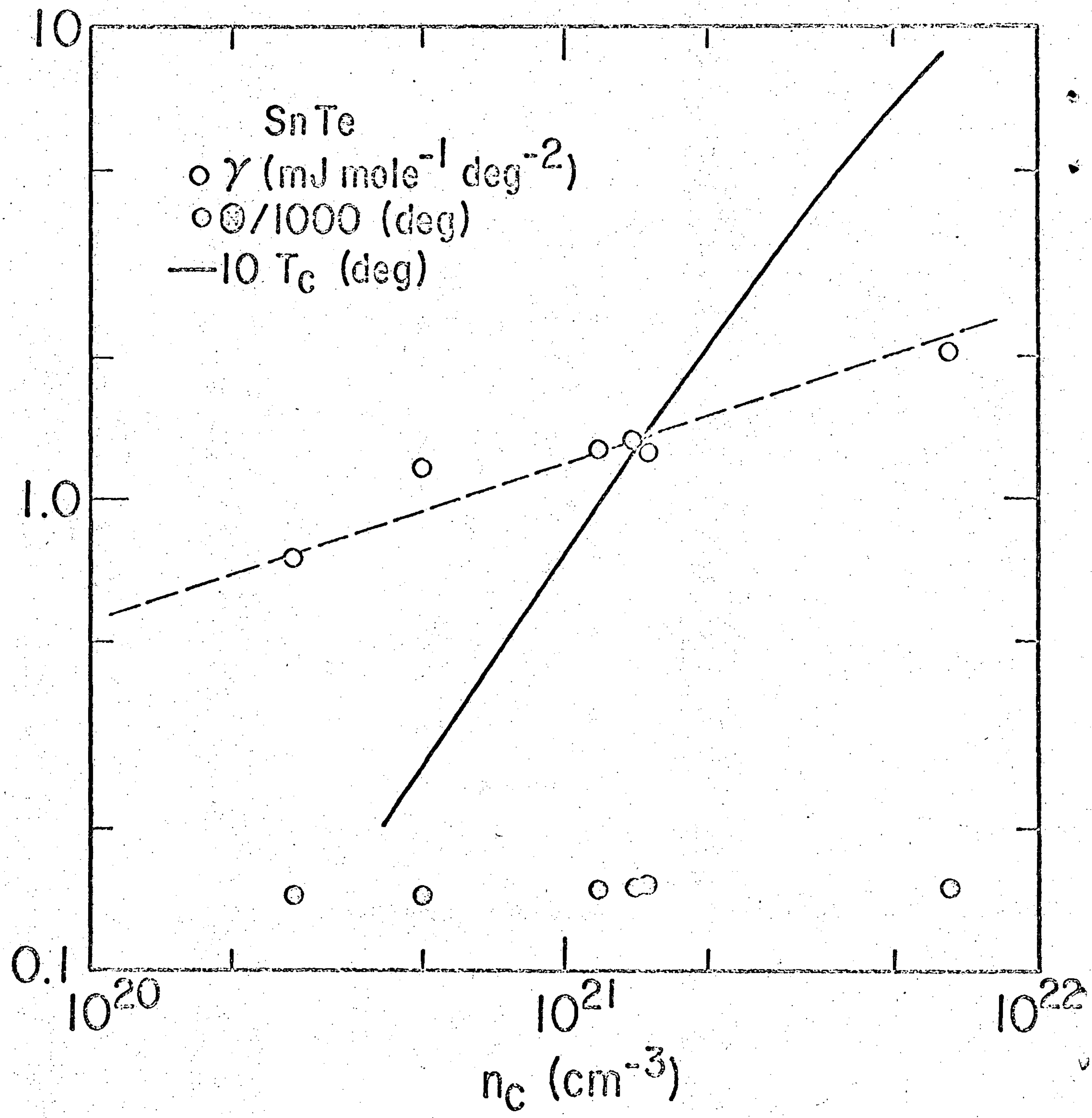

10
1.0
0.1
SnTe
○ γ (mJ mole⁻¹ deg⁻²)
○ Θ/1000 (deg)
— 10 Tc (deg)
10^20
10^21
10^22
nc (cm⁻³)

Figure 2

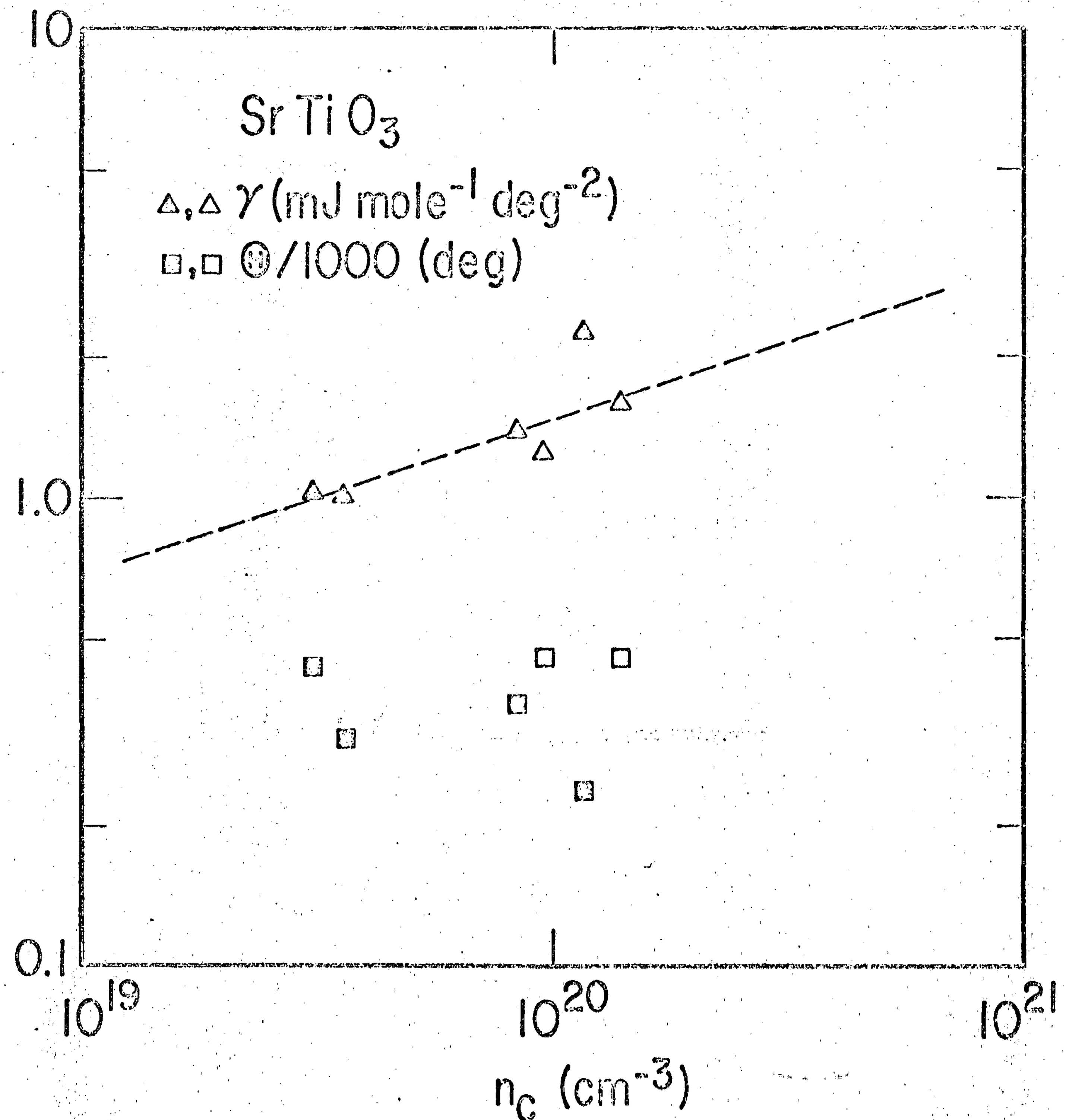
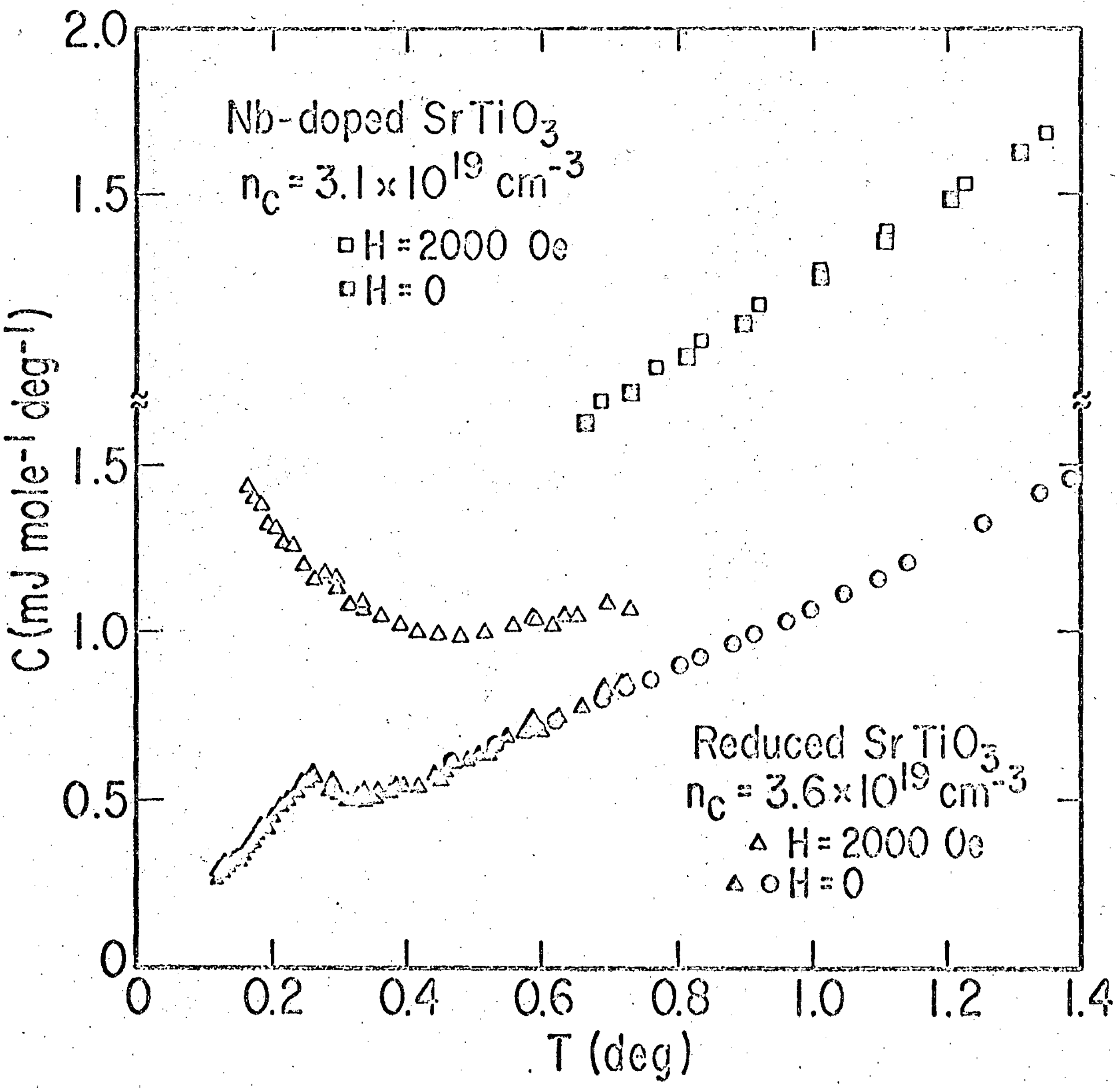


Figure 3



Nb-doped SrTiO3
nc = 3.1×10^19 cm^-3
□ H = 2000 Oe
□ H = 0
Reduced SrTiO3
nc = 3.6×10^19 cm^-3
△ H = 2000 Oe
△ ○ H = 0
C (mJ mole^-1 deg^-1)
T (deg)
2.0
1.5
1.5
1.0
0.5
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

Figure 4

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