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Electrical Properties of Stannic Oxide Single Crystals

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The Hall coefficient and electrical resistivity have been measured on single-crystal specimens of *n*-type SnO_2 between 80 and 900°K. Data were obtained on samples in the "as grown" state, as well as on crystals which were thermally equilibrated in oxygen. A single-donor-level analysis on heat-treated crystals with donor concentrations (N_D) between 1×10^{16} and 5×10^{17} cm^{-3} resulted in values of the "density-of-states" effective mass $m^{(N)}=0.22m$. Values of the donor ionization energy E_D were found to decrease with increasing N_D. At infinite dilution E_D has an estimated value of 0.15 eV. Room-temperature thermoelectric-power measurements resulted in calculated values of $m^{(N)}$ between 0.12 and 0.18m. Antimony-doped crystals of SnO_2 with $N_D>6\times10^{18}$ cm^{-3} appeared to be degenerate above 80°K. The low-temperature Hall mobility was found to decrease with decreasing donor concentration. A qualitative treatment of the data appears consistent with the hypothesis of impurity-level transport. Mobility above 300°K was analyzed by considering polar-optical modes of vibration as being the dominant lattice scattering mechanism. Both the perturbation and intermediate-coupling theories were in reasonable agreement with experimental values using a Debye temperature $\Theta_l\sim500$°K.

I. INTRODUCTION

STANNIC oxide, an extrinsic *n*-type semiconductor, has been used extensively for many years, in the form of conducting thin films and ceramics. Several investigations of both the electrical and optical properties of polycrystalline SnO_2 have appeared in the literature.[1–6] However, the majority of these studies have been restricted to measurements over a narrow temperature range on completely degenerate samples (electron concentrations exceeding 10^{19}/cm^3) with variations in preparation and impurity content, giving rise to differences in sample behavior. The difficulties associated with the interpretation of bulk transport properties on polycrystalline materials have been summarized by several authors.[7,8]

Kohnke[9] has reported on some electrical and optical properties of natural crystals of SnO_2 (cassiterite). His conclusions, as well as those of earlier workers, indicate that most of the transport properties are consistent with a broad-band-defect semiconductor model, as one might expect from comparison with other materials such as ZnO, In_2O_3, and CdS in which the conduction band is formed from *s* orbitals. Unfortunately, cassiterite usually contains objectionable concentrations of electrically active impurities, which make interpretation of specific donor and acceptor levels extremely difficult. Recently, detailed optical analyses of the ultraviolet absorption edge of SnO_2 have been made on vapor-grown crystals.[10] Studies of the infrared spectra of these crystals[11] have contributed information on effects due to free-carrier and lattice absorption.

The purpose of this paper is to present an investigation of some electrical transport properties of SnO_2 single crystals prepared in this laboratory. In the present study, we report on the temperature dependence of the resistivity and Hall effect from 80–900°K on undoped as-grown crystals, and on crystals subsequently heat treated in oxygen. Data are also presented for crystals intentionally doped with antimony. In addition, the thermoelectric power of several crystals was measured near room temperature.

II. EXPERIMENTAL PROCEDURE

Single crystals of stannic oxide were prepared by a vapor-transport technique, which involves the decomposition of SnO_2 powder (99.9995%) in a helium-oxygen ambient.[12] The resulting crystals are transparent rods free from any visible flaws, approximately 1–2 mm on a side and 10–20 mm in length.

Both optical microscopy and x-ray diffraction confirmed their tetragonal structure and indicated the growth axis to correspond to the crystallographic *c* axis. Recent studies of etch pits and dislocations in vapor-grown crystals[13] indicate a bulk dislocation density in the range 10^1–10^3/cm^2 which is well below the density believed to be effective in influencing electrical properties. A typical mass-spectrographic analysis on un-

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doped samples indicated the presence of Al and Fe in the range one to two parts in 10^5.

Doping with antimony was accomplished by modifying the crystal-growing apparatus previously described[14] to include a source for maintaining a constant partial pressure of impurity vapor during growth.

A four-probe dc method was used to measure high-temperature resistivity. Specific details have been described elsewhere.[14] Hall-effect and resistivity measurements below 575°K were made by mounting the sample as shown in Fig. 1. The apparatus was enclosed in a Dewar system similar to that described by Ure.[15] All samples reported on had a total variation in resistivity along their length of less than 5%. No variation in either the resistivity or Hall constant was found with magnetic-field strengths up to 10^4 G. Because of the growth habit, measurements were made with the current parallel to the c axis of the crystal. Indium metal, applied with an ultrasonic soldering gun, was found to be the most satisfactory electrode material. It was frequently necessary to "form" contacts electrically in order to decrease resistance and noise at the voltage contacts. No adverse effects were noted due to this treatment.

The thermoelectric power of SnO_2 versus platinum was measured near room temperature using a technique reported by Middleton and Scanlon.[16] Matched 0.005-in. Pt-Pt 10% Rh thermocouples were forced into holes drilled directly into the samples. Failure to imbed thermocouples, frequently resulted in nonreproducible results.

As-grown undoped crystals of SnO_2 were found to show large differences between their surface and bulk conductivities, the surface having the lower conductivity. By alternately lapping the crystal surface and measuring the difference in electrical resistance between the bulk and surface, estimates could be made of the depth and conductivity of the surface compared to the bulk properties. Typically, a crystal cooled at a rate of 10°C/minute from its growth temperature (approximately 1600°C) was found to contain a 25–50-micron-deep surface layer (10^6 Ω cm or greater) compared to a uniform bulk resistivity on the order of 0.01 Ω cm. Quenching in air or liquid nitrogen was found to decrease the thickness of the insulating surface layer. Koffyberg[13] has also noted that a gradient in dislocation density exists between the surface and bulk of vapor-grown crystals. The dimensions of this gradient correlate well with the results of electrical measurements reported above. It appears that these data are consistent with a model based on a gradient in stoichiometry as a result of oxygen diffusion into the crystal during the cooling period. All measurements reported were made on crystals which were lapped to remove any surface inhomogeneities. Samples which were equilibrated below their growth temperature were quenched in liquid nitrogen to ensure uniform defect concentrations.

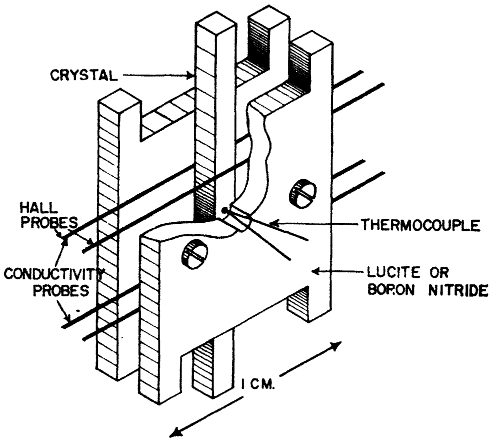

FIG. 1. Sample holder for Hall-effect and resistivity measurements.

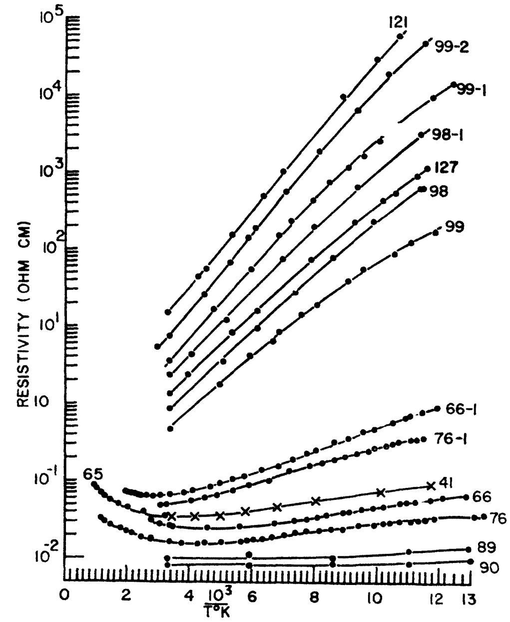

FIG. 2. Electrical resistivity as a function of $1/T$ between 80 and 900°K for as-grown, heat-treated and antimony-doped crystals.

Electrical Measurements

The temperature dependence of the electrical resistivity for several crystals of SnO_2 is shown in Fig. 2. Sample descriptions as well as a summary of heat treatment times and temperatures are given in Table I. Samples 66 and 76 were quenched from above 1575°C and are transparent and brown in color. Crystals 41 and 65 were not quenched and are colorless. It was

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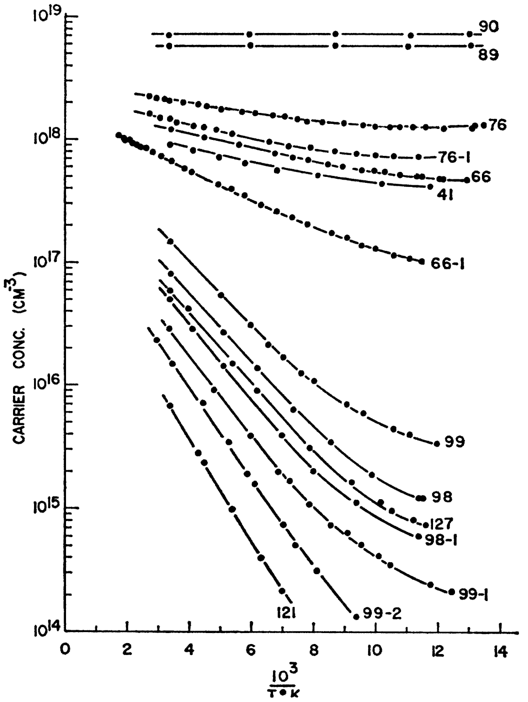

FIG. 3. Electron concentration as a function of $1/T$ for as-grown, heat-treated and antimony-doped crystals.

found that quenched crystals could be bleached by heating for several hours at approximately 1000°C (samples 66–1 and 76–1). Data on the effect of heat treating crystals in oxygen at temperatures between 1170 and 1390°C are indicated by curves labeled 99, 98, 127, 98–1, 99–1, 99–2, and 121. Equilibration times were determined by heat treating until the carrier concentration at 300°K reached a constant value.

Hall measurements on single crystals of SnO_2 indicated only n-type conductivity. Carrier-concentration data for samples described above are plotted in Fig. 3. The number of electrons n was calculated assuming a single-band-conduction model and noninteracting carriers using the expression $n=(\mu_H/\mu)(1/R_He)$ where R_H is the Hall coefficient and e the charge on the electron. The scattering factor μ_H/μ was assumed to be equal to $\frac{3}{8}\pi$. Figure 4 shows the temperature dependence of the Hall mobility as calculated from the carrier concentration and resistivity data of Figs. 2 and 3. Measurements on sample 66–1 were extended to 575°K in

TABLE I. Thermal history of SnO_2 samples.

Sample	Thermal treatment after growth	Equilibration temperature (°C)	Equilibration time (h)
76	as grown (air quenched)	...	...
66	as grown (air quenched)	...	...
65	as grown	...	...
41	as grown	...	...
76–1	sample 76 bleached in dry argon	1030	11.5
66–1	sample 66 bleached in dry argon	1030–1060	23
99	O_2 pressure 1 atm	1390	67
98	O_2 pressure 1 atm	1367	75
127	O_2 pressure 1 atm	1364	62
98–1	O_2 pressure 1 atm	1360	161
99–1	O_2 pressure 1 atm	1330	140
99–2	O_2 pressure 1 atm	1290	71
121	O_2 pressure 0.06 atm	1165	282
89 90	as grown antimony-doped (≈300 ppm Sb)	... ...	... ...

TABLE II. Thermoelectric power of SnO_2.

Sample	Temperature (°K)	R_H(cm^3 C^{-1})	$Q_{(Pt)}$(μV deg^{-1})
65	303	3.9	−183
75	335	4.4	−135
127–*H*	328	8.5	−263

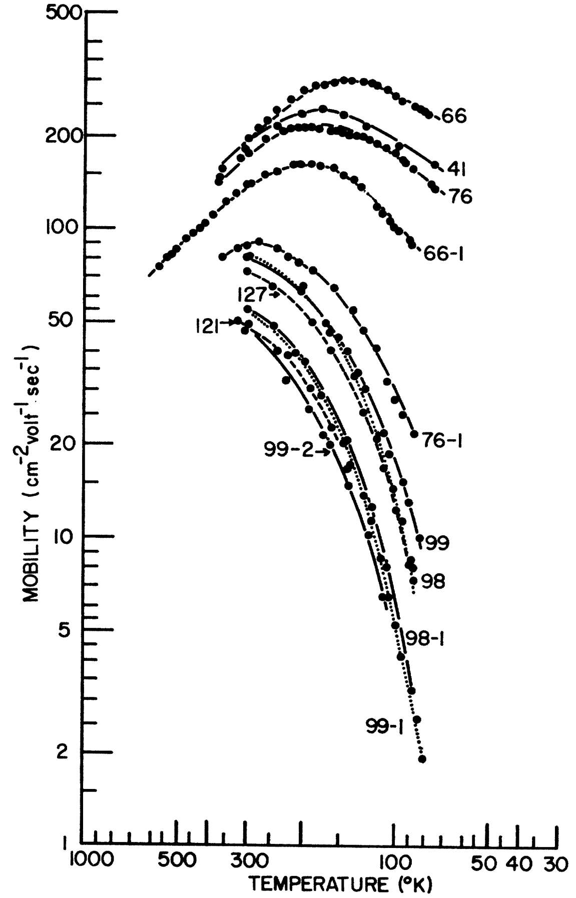

FIG. 4. Hall mobility as a function of temperature for as-grown and heat-treated crystals.

order to gain an estimate of the contribution due to lattice scattering processes.

Values of thermoelectric power Q of undoped SnO_2 together with the temperature and Hall constant are presented in Table II.

III. DISCUSSION

Carrier Concentration Analysis

In Fig. 3 samples 89 and 90, containing antimony, appear to approach complete degeneracy at temperatures as low as 80°K. The fact that there is no variation in carrier concentration with temperature is taken as evidence that the shallow donor impurity band, resulting from antimony doping, has merged with the bottom of the main conduction band. This observation is also generally in agreement with the results of studies on polycrystalline films containing antimony as an impurity.[17] The addition of antimony results in an increase in electron concentration consistent with the substitution of a 5+ for a 4+ valent cation.[18]

The relationship between clear and quenched crystals does not appear to be a simple one. The visible brown color, characteristic of quenched samples, which appears as an additional optical absorption on the long-wavelength side of the ultraviolet edge, can be removed by heating crystals to about 1000°C. The effects of thermal treatment sufficient to cause bleaching are a substantial decrease in the carrier concentration and Hall mobility (Fig. 4) as seen by comparing curves #66-1 and 76-1 with #66 and 76. At the present time, however, it has not been demonstrated conclusively that a single electronically active defect can be associated with the bleaching process. Similar behavior in quenched crystals of ZnO doped with Zn has been reported by other workers,[19] but the exact relationship between optical absorption, thermal bleaching, and electrical activity still remains uncertain.

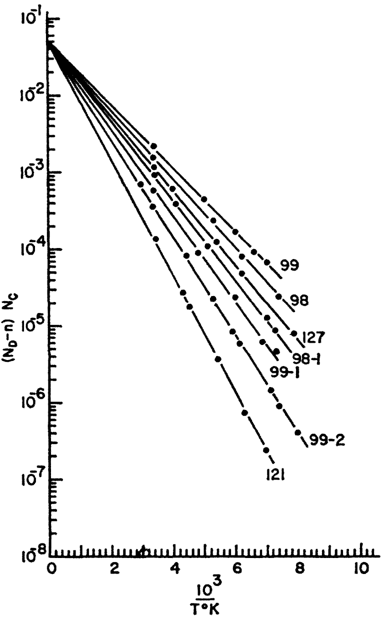

FIG. 5. Single-donor analysis of the carrier concentrations of crystals equilibrated in oxygen between 1165 and 1390°C.

TABLE III. Values of the activation energy and donor concentration obtained from Fig. 5.

Sample	N_D(cm^{-3})	E_D(eV)
99	5.7×10^{17}	0.081
98	2.6×10^{17}	0.090
127	1.9×10^{17}	0.099
98-1	1.6×10^{17}	0.104
99-1	7.6×10^{16}	0.108
99-2	4.8×10^{16}	0.125
121	1.5×10^{16}	0.138

The remaining curves in Fig. 3 indicate that thermal equilibration at successively lower temperature, while maintaining a fixed oxygen pressure, results in a decrease in the measured carrier concentration. This behavior is consistent with a decrease in the degree of off-stoichiometry as a result of either vacancies in the anion sublattice or the presence of interstitial cations. Structural considerations appear to rule out the possibility of oxygen at an interstitial position.

Further inspection of Fig. 3 shows that for crystals equilibrated in oxygen, a linear relationship exists between log n and $1/T$ above 120°K. Below this temperature noticeable curvature occurs. This is believed to result from impurity-level effects and will be discussed further in the section dealing with low-temperature mobility. An analysis of heat-treated crystals has been made on the assumption that a single nondegenerate donor level is active over the temperature range above 120°K and that compensation by acceptors is negligible. Under these conditions the relationship between the carrier concentration n in the conduction band, the total number of donors N_D, and the ionization energy of the donor level E_D can be written as[7]

$$n^2/(N_D-n)N_c=(m^{(N)}/m)^{\frac{3}{2}}D^{-1}\exp(-E_D/KT)\,,\quad(1)$$

in which the density of states at the band edge N_c is equal to $2(2\pi mkT/h^2)^{3/2}$ and $m^{(N)}$ is the density-of-states effective mass. The spin degeneracy of the donor states D refers to the number of ways an electron may occupy a particular state. A value of $D=2$ has been used in the present calculations on the assumption that contributions from excited states are negligible. A plot of the logarithm of the left side of Eq. (1) versus $1/T$°K should result in a straight line whose slope gives E_D

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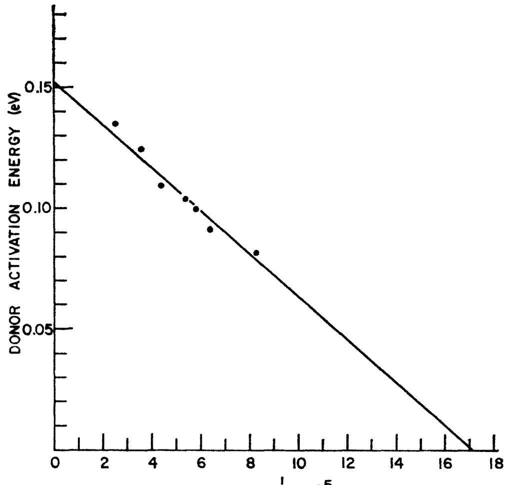

FIG. 6. Donor ionization energies as a function of donor concentration for crystals equilibrated in oxygen.

and whose intercept is equal to $(m^{(N)}/m)^{3/2}D^{-1}$. An initial estimate of values for N_D was made by inspection of the high-temperature end of Fig. 3. These values were then further refined to give the best straight-line fit to the experimental data over the entire temperature range. The plots of Eq. (1) for equilibrated samples are shown in Fig. 5. It can be seen that all curves have a common intercept equal to 0.05. The assumption that $D=2$ leads to a value of the effective mass $m^{(N)}$ equal to 0.22 m. Values of E_D and N_D obtained from Fig. 4 are summarized in Table III.

The decrease of the donor ionization energy E_D with increasing donor concentration, as indicated in Table III, is an effect commonly observed in both elemental and compound semiconductors. Pearson and Bardeen[20] have proposed a model to explain this effect, based on the hypothesis that at moderate impurity concentration there is an appreciable electrostatic attraction between an electron and ionized impurity center, which increases with increasing donor concentration. Their results for boron-doped silicon samples could be expressed as

$$E=E_0-aN^{1/3}, \qquad (2)$$

where E_0 is the ionization energy at infinite dilution, E is the ionization energy for a given concentration of donors, N is the number of donors, and a is a constant. This relation also appears to apply to the present case of donor impurities in SnO_2 as shown by the plot of donor ionization energy versus concentration in Fig. 6. The equation describing the data may be written as

$$E_D=0.15-8.7\times10^{-8}N_D^{1/3}(\text{eV}) . \qquad (3)$$

The donor ionization is estimated to approach zero at a donor concentration of 5.5×10^{18} cm^{-3}. At infinite dilution a value of $E_D=0.15$ eV is predicted.

Measurement of the thermoelectric power in conjunction with the Hall coefficient can also be used to calculate the density-of-states effective mass. The total thermoelectric power of a semiconductor Q_T may be written as

$$Q_T=Q_e+Q_p, \qquad (4)$$

where Q_e is the electronic contribution due to diffusion of electrons or holes in a thermal gradient and Q_p is a phonon-drag term associated with the interaction of charge carriers with the lattice vibrations. Contributions from Q_p are most important at low temperatures and generally diminish as the temperature increases. Calculations of $m^{(N)}$ were made in the present case for values of Q measured above 300°K and hence contributions from Q_p were assumed to be negligible. According to Johnson,[21] the relationship between Q_E and the effective mass of a nondegenerate semiconductor in the range in which lattice scattering predominates is given by

$$Q_E=(k/e)[\ln\{2(2\pi m^{(N)}k/h^3)^{3/2}\} \\ -\ln n+|\Delta E|/kT+\tfrac{3}{2}\ln T], \qquad (5)$$

where $|\Delta E|$ is the average kinetic energy of a carrier moving in a temperature gradient which is of the order of $2kT$ at 300°K. Measurements of Q and n on crystals reported in Table II result in calculated values of $m^{(N)}$ in the range 0.12 to 0.18m which is in reasonable agreement with $m^{(N)}=0.22m$ obtained from analysis of the Hall-effect data.

Hall Mobility

Study of the Hall mobility, in conjunction with the diffusion of imperfections in compound semiconductors, can supply information as to the types of defects resulting from variation of the cation-to-anion ratio, since the temperature dependence of the mobility frequently reveals the scattering mechanisms present in the crystal.

In a polar material, such as SnO_2, one would expect that at higher temperatures the electron mobility will be determined by a combination of both optical and acoustical modes of lattice vibrations, while contributions from centers such as neutral and ionized impurities would be expected to be the chief mechanisms limiting mobility at lower temperatures.

It is evident from Fig. 4 that heat treatments at various temperatures have a marked effect on the magnitude and temperature dependence of the electron mobility, particularly at lower temperatures. In general, it can be noted that samples having higher carrier concentrations exhibit both an impurity-dominated range

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at temperatures below about 150°K and a region at higher temperatures in which lattice scattering becomes the dominant mechanism limiting mobility. However, lowering the carrier concentration by thermal treatment also results in lower electron mobilities. With decreasing electron concentrations, the maxima in Fig. 4 are also shifted to higher temperatures to the extent that processes associated with impurity scattering dominate the mobility up to 300°K. Comparison of the experimental data with the predicted mobility behavior for a single-band model shows that the temperature dependence at low temperatures and concentrations is considerably larger than the $T^{+1.5}$ dependence predicted for ionized impurity scattering. In addition, the dependence of mobility on the concentration of scattering centers is found to follow a direct rather than the inverse theoretical relationship. These observations suggest that conduction may not be limited to a single band, particularly at low temperatures.

Mott[22] has recently reviewed multiple transport processes particularly with application to elemental semiconductors. At high temperatures, in an n-type material, current is carried almost exclusively by electrons in the main conduction band in equilibrium with electrons on donor impurities. In the low-temperature range, where virtually all of the donors remain un-ionized, overlap of the wave function of an electron with other donors is sufficient to allow transport of carriers between impurity centers without activation into the main conduction band. This mechanism has been termed impurity conduction. At intermediate temperatures, both processes make contributions to the total charge transport. In general, the total conductivity may be written as

$$\sigma = n_1\mu_1 e + n_2\mu_2 e\,, \tag{6}$$

where n_1 and μ_1 are the carrier concentration and mobility in the conduction band and n_2 and μ_2 refer to the same quantities for the impurity carriers. The Hall coefficient R may be expressed as

$$R = \frac{1}{e}\left[\frac{n_1\mu_1\mu_{1H} + n_2\mu_2\mu_{2H}}{(n_1\mu_1 + n_2\mu_2)^2}\right] \tag{7}$$

(where μ_H and μ are the Hall and drift mobility, respectively), and the Hall mobility as

$$\mu_H = \frac{n_1\mu_1\mu_{1H} + n_2\mu_2\mu_{2H}}{n_1\mu_1 + n_2\mu_2}\,. \tag{8}$$

Based on such a model and neglecting any temperature variation in the mobilities, a maximum in the Hall coefficient is predicted when

$$n_1\mu_1 e = n_2\mu_2 e\,. \tag{9}$$

The behavior of μ_H in this general region represents an average of the mobilities of the two processes with the variation in temperature reflecting both the rate at which carriers, from the conduction band, are returning to donor impurity level, as well as the temperature dependence of the individual mobilities, μ_1 and μ_2. The mobility μ_2 of an electron in the impurity level, particularly at low donor concentrations, is expected to be very small since it depends on interaction between widely spaced impurities. Therefore, in the case where $\mu_1 \gg \mu_2$, a sharp temperature variation in the Hall mobility should occur. It can also be seen from Table III and Fig. 4 that, in addition to $\mu_1 \gg \mu_2$, the variation in donor activation energy E_D also serves to increase the electron concentration n_2 on the impurity level, resulting in a greater ratio of the total current being transported between un-ionized donors, tending to decrease the measured mobility at lower temperatures.

In the present study, since data are restricted to above 80°K, the precise temperature at which a maximum in R_H occurs has not been measured, although it can be noted in Fig. 3 that all samples approach the predicted inflection at lower temperatures. The temperature at which this occurs is generally higher for larger values of N_D, which is consistent with the theoretical behavior of R_H. Similarly, it is not possible to arrive at a quantitative value of μ_2 for even the lowest mobilities observed, although by examination of Fig. 4 and from similar observations on ZnO[23] one would expect values of μ_2 for samples 99–1, 98–1, and 99–2 to be well below 1 cm^2/V sec. Measurements of the transverse magnetoresistance at 4.2°K[24] also are interpretable in terms of an impurity-level transport mechanism.

Contributions from lattice scattering processes appear to limit the electron mobility above about 300°K. Because of impurity-band effects and the onset of diffusion above about 500°C, analysis of lattice scattering mechanisms has been limited to samples having an electron concentration at room temperature of approximately 5×10^{17}/cm^3 and above. The dependence of mobility on temperature for samples 76, 66, and 66–1 can be approximated by the formula $\mu = \mu_0 T^{-n}$, where n has a value of about 1.1. This is considerably less than the $T^{-1.5}$ dependence characteristic of scattering by the acoustical vibrations of the lattice. In this treatment, it is assumed that impurity effects are unimportant above 350°K. Furthermore, polar scattering by acoustical-mode lattice vibrations can be neglected since the structure of SnO$_2$ is centrosymmetric. Polar scattering by optical-mode lattice vibrations appears then to be an important mechanism limiting the high-temperature electron mobility.

The calculation of mobility due to optical-mode scattering has been treated by two approaches. The

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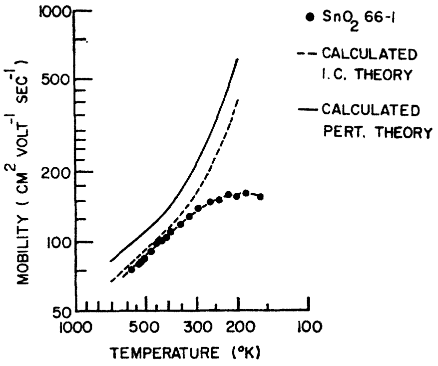

FIG. 7. Hall mobility as a function of temperature for sample 66–1. Solid line represents dependence calculated from the perturbation theory. Broken line represents calculated mobility values predicted by intermediate-coupling theory.

first is a perturbation theory of Fröhlich and Mott[25] and Howarth and Sondheimer,[26] while the second is an "intermediate-coupling" theory proposed by Lee, Low, and Pines.[27] The expression for optical-mode scattering mobility resulting from the perturbation theory is

$$\mu_{\text{pert}}=\frac{1}{2\alpha\omega_l}\frac{e}{m^*}\frac{8}{3\sqrt{\pi}}\frac{\chi(Z)(e^Z-1)}{(Z)^{1/2}}, \tag{10}$$

where ω_l is the longitudinal optical-mode frequency, $Z=h\omega_l/kT=\Theta_l/T$. The dimensionless parameter α, called the "coupling constant," is a measure of the strength of interaction between the longitudinal-optical modes and the conduction electrons. The term $\chi(Z)$ is a slowly varying function with limits of 1 and $\frac{3}{8}(\pi Z)^{1/2}$. The parameter α is defined by

$$\alpha=(e^2/h)(m^*/2h\omega_l)^{1/2}(K-K_0/KK_0), \tag{11}$$

where K and K_0 are the static and optical dielectric constants, respectively. For stannic oxide, K is estimated to be 23 (Ref. 28) and $K_0=n^2=4$.

The intermediate-coupling theory results in the following expression for mobility limited by polar scattering:

$$\mu_{I.C.}=(1/2\alpha\omega_l)(e/m^{(P)})(m^*/m^{(P)})^2 f(\alpha)\exp(Z)-1, \tag{12}$$

where $f(\alpha)$ varies slowly from a value of 1 for $\alpha=0$ to 1.4 for $\alpha=6$. The effective mass of the polaron, i.e., the electron plus associated optical phonons, can be approximated by

$$m^{(P)}=m^*(1+\alpha/6) \tag{13}$$

when $\alpha<6$.

The intermediate-coupling theory is valid for values of α as large as 6 but is restricted to temperatures less than Θ_l. The perturbation theory has no temperature restrictions but formally requires α to be much less than unity.

Solution of Eq. (11) in conjunction with values of $m^*\sim 0.2m$ gives a value of α for SnO_2 equal to about 0.7. The best temperature fit to the observed mobility data shown in Fig. 4 requires $\Theta_l\sim 500$°K. Both the perturbation and intermediate-coupling theories were solved and resulted in nearly identical values for mobility over the temperature range 350–600°K. Agreement between both the calculated and experimental values as shown in Fig. 7 appears satisfactory. No attempt at further refinements to obtain a more exact fit between experimental and calculated values seems warranted in view of uncertainties in estimating contributions from other scattering mechanisms.

IV. CONCLUSIONS

We have reported Hall-effect and resistivity measurements for a variety of SnO_2 crystals between 80° and 900°K. Above about 120°K, a single-donor-level model was found to describe the data on carrier concentration versus reciprocal temperature and to yield estimates of both the electron effective mass as well as the variation of activation energy with donor concentration. Values of the effective mass obtained from thermoelectric-power measurements were in good agreement with those obtained from the above treatment. Both the Hall effect and mobility data at low temperature appear consistent with the hypothesis of impurity-level transport, although additional data at lower temperatures are necessary before a quantitative description will be possible.

The high-temperature mobility was treated by considering polar optical-mode scattering as being the dominant lattice scattering mechanism. The effects of other scattering mechanisms were not quantitatively considered due to the limited knowledge of the band structure of stannic oxide.

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