bracketed term is 0.73 for $b=40$ and 0.80 for $b=85$. Thus, "freeze-out" makes a substantial contribution to the rate of increase of resistivity above 30 kbar.

The shape of the resistivity-versus-pressure curve above 37 kbar, where it saturates, is difficult to analyze for two reasons: First, the working fluid freezes so that the additional force is seen by the sample as a uniaxial instead of a hydrostatic stress; second, the mobility of the electrons in the [000] valley may be expected to drop due to intervalley scattering when the band-edge separation gets down to 1 or 2 kT.

ACKNOWLEDGMENTS

Electron Mobility in Semiconducting Strontium Titanate

O. N. TUFTE AND P. W. CHAPMAN

Honeywell Corporate Research Center, Hopkins, Minnesota

The electron Hall mobility has been measured in semiconducting $SrTiO_3$ over the temperature range from 1.6 to 550°K. Electron concentrations in the range from 1×10^{17} to 2.5×10^{19} cm^{-3} were obtained by reduction or by doping with niobium. The niobium donor centers remain fully ionized down to the lowest temperatures investigated. The low-temperature mobility in niobium-doped $SrTiO_3$ is approximately 4 times larger than in reduced $SrTiO_3$ over the concentration range investigated, and mobility values up to 2.2×10^4 cm^2/V sec were measured in niobium-doped samples having electron concentrations of approximately 2×10^{17} cm^{-3}. The mobility results are compared with the behavior expected for scattering by ionized defects and polar optical lattice modes at low and high temperatures, respectively.

I. INTRODUCTION

THE electrical transport properties of semiconducting n-type $SrTiO_3$ were first investigated by Frederikse *et al.*[1] who found a band-type conduction process with an electron effective mass much greater than the free-electron mass and low-temperature mobilities greater than 1000 cm^2/V sec. Recently, other transport effects such as the piezoresistance[2] and magnetoresistance[3] effects have also been investigated but these studies have been directed toward the determination of the energy band structure rather than the carrier scattering mechanisms. The wavelength dependence of the free-carrier absorption[4] suggests that scattering by polar optical modes is dominant at room temperature but the magnitude of the measured absorption coefficient is not in agreement with theory. The electrical properties of semiconducting $KTaO_3$, which is another pseudoferroelectric having the perovskite structure, have been investigated by Wemple,[5] who finds that the temperature dependence of the electron mobility above 100°K is the same as in $SrTiO_3$. This result suggests that the scattering mechanisms are similar in these two materials. Measurements[6] of the effect of hydrostatic pressure on the electrical conductivity and dielectric constant suggest that the mobility at room temperature is limited by lattice scattering from the lowest-energy transverse optical mode in both $SrTiO_3$ and $KTaO_3$. The behavior of the electron mobility above room temperature has not been reported in either $SrTiO_3$ or $KTaO_3$.

The purpose of the present work is to make a detailed study of the electron Hall mobility in $SrTiO_3$ over a wide range of doping conditions and a wide range of temperature as a means of investigating the scattering mechanisms. The mobility has been measured from 1.5 to 550°K in niobium-doped and reduced $SrTiO_3$ samples having electron concentrations in the range from 1×10^{17} to 3×10^{19} cm^{-3}. The mobility results are compared with the behavior expected for scattering by ionized defects and polar optical lattice modes.

II. EXPERIMENTAL PROCEDURE

Single crystals of $SrTiO_3$ were obtained from the National Lead Company. The crystals were doped either by the addition of niobium during growth or by the reduction of the undoped crystals. The procedure for reducing $SrTiO_3$ has previously been described.[1,2]

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

[2] O. N. Tufte and E. L. Stelzer, Phys. Rev. **141**, 675 (1966).

[3] H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. **143**, 648 (1966).

[4] W. S. Baer, Phys. Rev. **144**, 734 (1966).

[5] S. H. Wemple, Phys. Rev. **137**, A1575 (1965).

[6] S. H. Wemple, A. Jayaraman, and M. DiDomenico, Jr., Phys. Rev. Letters **17**, 142 (1966).

TABLE I. The 300 and 2°K Hall coefficient and Hall mobility values and the 300°K electron concentrations for all of the samples investigated.

	300°K		2°K		1
Sample	R_H (cm³/C)	$\mu_H \left(\dfrac{cm^2}{V\ sec}\right)$	R_H	μ_H	$n = \dfrac{eR_H(300°K)}{(cm^{-3})}$
5	0.26	6.5	0.25	1.0×10^3	2.4×10^{19}
2	0.62	5.2	0.77	1.8	1.0×10^{19}
3	1.8	7.2	3.9	2.7	3.5×10^{18}
6	5.3	8.0	11.0	3.1	1.2×10^{18}
12	14.0	8.0			4.5×10^{17}
9	23.0	5.8			2.7×10^{17}
13(Nb)	0.22	5.5	0.22	3.3×10^3	2.8×10^{19}
8(Nb)	0.58	4.8	0.63	8.2	1.1×10^{19}
10(Nb)	3.4	6.2	3.3	12.0	1.8×10^{18}
14(Nb)	14.0	6.7	11.0	13.0	4.5×10^{17}
15(Nb)	22.0	5.4	18.0	19.0	2.8×10^{17}
11(Nb)	44.0	6.0	33.0	22.0	1.4×10^{17}

Samples were cut in the shape of rectangular bars having dimensions of the order of $1\times1\times10$ mm³. The sample surfaces were mechanically polished and electrical contacts were made by ultrasonically soldering indium or an alloy of Zn-Cd-In to the samples. Contact resistances varied from a few ohms to several hundred ohms depending on the resistivity of the sample.

A conventional dc method was used for the measurement of the resistivity and Hall coefficient. All voltages were measured with a Rubicon type-B potentiometer. A 12-in. Varian magnet capable of providing fields up

FIG. 2. The temperature dependence of the Hall coefficient in semiconducting SrTiO₃.

to 13 kG was used for all of the measurements. The Hall coefficient was found to be independent of the magnetic field strength over the range of fields investigated.

III. RESULTS

The temperature dependence of the electrical resistivity for all of the samples investigated is shown in Fig. 1. The samples that do not exhibit carrier freeze-out effects were investigated from 300 to 1.6°K. The samples in which carrier freeze-out is present were investigated only down to 77°K due to the high resistances involved at the lower temperatures. The resistivity measurements were extended to approximately 550°K for one niobium-doped sample and two reduced samples. The reduced samples begin to re-oxidize in air at temperatures above 500°K giving rise to nonreversible increases in the resistivity. However, there is no problem with high-temperature measurements in air on niobium-doped samples.

The measured Hall coefficient values at 2 and 300°K are given in Table I. The temperature dependence of the Hall coefficient for each sample is shown in Fig. 2. The Hall coefficients for the niobium-doped samples are very nearly independent of temperature and there is no evidence for the deionization of electrons to impurity sites even in the most lightly doped samples. This indicates that a majority of the niobium atoms form shallow donor centers. The large value of the dielectric

FIG. 1. The temperature dependence of the resistivity in semiconducting SrTiO₃.
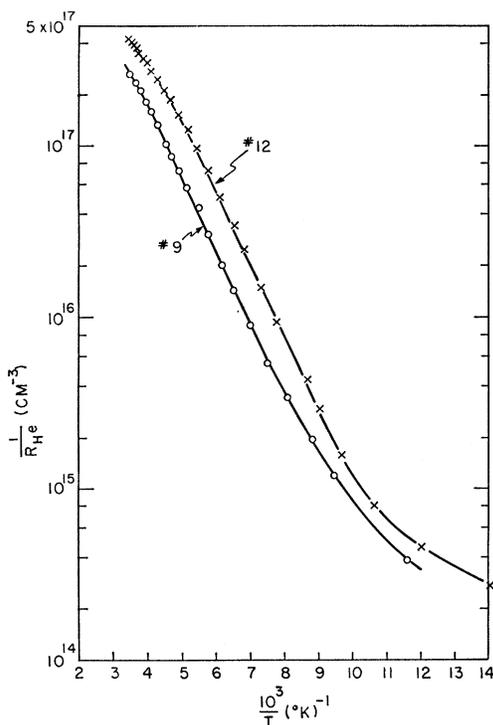
FIG. 3. The temperature dependence of the reciprocal of the Hall coefficient for the samples showing carrier deionization effects.

energy gap and a large degree of deionization occurs with decreasing temperatures.

The reciprocal of the Hall coefficient of samples 9 and 12 is replotted as a function of the reciprocal temperature in Fig. 3. The slope of the linear portion of these curves yields an activation energy ϵ of 0.08 eV, where ϵ is related to the electron concentration by $n \propto e^{-\epsilon/k_B T}$. This value is in good agreement with the activation energy that can be calculated from the data of Frederikse et al.[1] The relation between the ionization energy of the donor center and the measured activation energy depends on the degree of compensation present in the $SrTiO_3$, and cannot be uniquely determined from the present results.[9] If the samples are compensated to such an extent that the number of acceptors is greater than the electron concentration, as is probably true for the samples in Fig. 3, then the ionization energy is equal to the activation energy. For a lesser degree of compensation, the ionization energy can be up to a factor of two larger than the activation energy. In either case, the ionization energy is much too large for a hydrogenic-type donor. It should be noted that the donor center in reduced $SrTiO_3$ is quite different from reduced $KTaO_3$ where no carrier deionization has been

constant[7,8] in $SrTiO_3$ makes the activation energy of a hydrogenic-type donor small compared to $k_B T$ even at the lowest temperatures investigated so that no deionization effects should be present. In the more dilute niobium-doped samples, the Hall coefficient decreases by approximately 25% between 50 and 4°K. The resistivity also shows an abrupt decrease in these samples but only at temperatures below approximately 10°K. The origin of these effects is not understood.

In the more lightly doped reduced samples, the Hall coefficient increases rapidly with decreasing temperature indicating that carrier freeze-out effects are present. In the intermediate doping range (samples 3 and 6), the Hall coefficient increases by approximately a factor of 2 between 300 and 100°K. This suggests that an oxygen vacancy in $SrTiO_3$ forms a doubly charged donor center. In the most heavily doped samples, both of the energy levels of the donor center are in the conduction band due to overlap and screening effects, and the Hall coefficient is independent of temperature. In the intermediate doping range, the experimental results suggest that one of the levels is located in the energy gap and deionization to this level causes the increase in the Hall coefficient with decreasing temperature. In the most lightly doped samples, both of the levels are in the

FIG. 4. The temperature dependence of the Hall mobility in semiconducting $SrTiO_3$.

[7] E. Sawaguchi, A. Kikuchi, and Y. Kodera, J. Phys. Soc. Japan 17, 1666 (1962).

[8] H. E. Weaver, J. Phys. Chem. Solids 11, 274 (1959).

[9] See, for example, J. S. Blakemore, Semiconductor Statistics (Pergamon Press, Inc., New York, 1962).
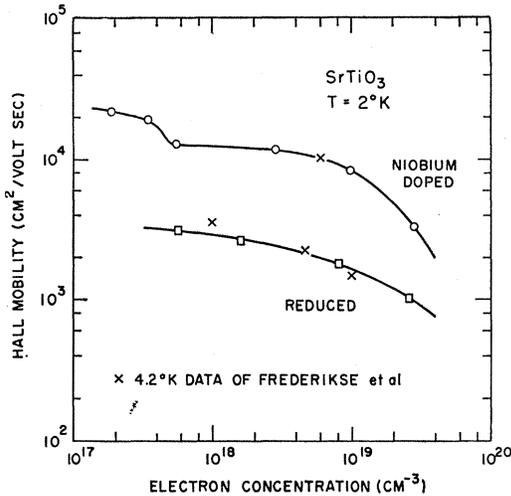
FIG. 5. The dependence of the electron mobility on the electron concentration in reduced and niobium-doped SrTiO₃ at 2°K. The 4.2°K mobility values reported by Frederikse et al. (Ref. 3) are also shown.

observed.[5] However, the detailed nature of the donor center is not presently understood in either material.

The values of the electron Hall mobility at 300 and 2°K are tabulated in Table I. The temperature dependence of the electron mobility is shown in Fig. 4. The mobility values at temperatures above 300°K, in Samples 5 and 8, were obtained by assuming the Hall coefficient is constant above 300°K. In the temperature range from 150 to 300°K, the present mobility results are in agreement with the previous results of Frederikse et al.[1] in that the mobility is very nearly independent of the electron concentration and approximates a power-law temperature dependence of the form $\mu_H = 2.9 \times 10^7 T^{-2.7}$ cm²/V sec. The mobility results for the samples exhibiting carrier freeze-out effects are the same, to within experimental error, as the other samples in the range from 300 to 100°K. Above 300°K, the mobility deviates from a power-law temperature dependence as will be discussed in detail in Sec. IV. Below 150°K, the mobility is dependent on the electron concentration, and the mobility becomes independent of temperature at low temperatures where the samples become statistically degenerate. The mobility does not exhibit any anomalies at 110°K, where a cubic to tetragonal phase transition occurs,[10] or at 40°K, where there is some indication of a ferroelectric transition in SrTiO₃.[8] The mobility in the lightly doped, niobium-doped samples exhibits a rapid increase with decreasing temperature at temperatures below approximately 10°K. A similar effect has been observed in reduced KTaO₃[5] but the origin of these effects is not understood. The concentration dependence of the mobility at 2°K is

shown in Fig. 5. The low-temperature mobility in the niobium-doped samples is approximately a factor of 4 larger than in the reduced samples at all carrier concentrations. The 4.2°K mobility values reported by Frederikse et al.[3] are also shown in Fig. 5 and are in good agreement with the present results.

IV. DISCUSSION

The large dielectric constant in SrTiO₃ at low temperatures leads to unusually large mobilities in the temperature range where ionized defect scattering is dominant because of polarization shielding of the scattering center. The potential of the charged donor can be represented by a screened Coulomb potential of the form $\phi = (Ze/\kappa)e^{-r/a}$, where Z is the charge, κ the dielectric constant,[11] and a the screening radius.[12] Using this potential and the Born approximation, the ionized impurity scattering mobility in the limit of large degeneracy is given by[13]

$$\mu = \frac{3\kappa^2 h^3 n}{16\pi^2 e^3 Z^2 N_i m^{*2} g(b)},$$ (1)

where

$$g(b) = \ln(1+b) - \frac{b}{1-b}$$

and

$$b = \frac{h^2 \kappa}{2e^2 m^*}\left(\frac{3n}{8\pi}\right)^{1/3}.$$

In this expression, m^* is the effective mass, n is the electron concentration, and N_i is the concentration of charged donor centers.

In general, the use of the Born approximation is hard to justify rigorously for scattering in semiconductors although it leads to reasonable agreement between theory and experiment in most cases if $b \gg 1$. However, in the present case the use of the Born approximation can be rigorously justified because of the weak magnitude of the scattering potential due to the large dielectric constant. The condition for the Born approximation to be valid for a screened Coulomb potential is[14]

$$Ze^2 m^*/\kappa h^2 k \ll 1,$$ (2)

where k is the wave vector of the scattered electron. In the degenerate limit, with $Z=1$, $m^*=3m_0$,[15] and $\kappa=1.8 \times 10^4$, this reduces to

$$10^4 n^{-1/3} \ll 1$$ (3)

[10] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963); K. A. Muller, Helv. Phys. Acta **31**, 173 (1958); L. Rimai and G. A. deMars, Phys. Rev. **127**, 702 (1962); E. Sawaguchi, A. Kikuchi, and Y. Kodera, J. Phys. Soc. Japan **18**, 459 (1963); F. W. Lytle, J. Appl. Phys. **35**, 2212 (1964).

[11] The use of the static dielectric constant in the scattering potential has been discussed by W. Kohn, J. Phys. Chem. Solids **8**, 45 (1959).
[12] R. B. Dingle, Phil. Mag. **46**, 831 (1955).
[13] R. Mansfield, Proc. Phys. Soc. (London) **B69**, 76 (1956).
[14] See, for example, D. Bohm, Quantum Theory (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1951), p. 552.
[15] A. S. Barker, in Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965 (North-Holland Publishing Company, Amsterdam, 1966).

for a simple parabolic band so that Eq. (1) should be valid for $n > \sim 10^{15}$ cm^{-3}.

In order to compare the theoretical mobility with the experimental results, the numerical values for the physical constants and the previously given values for the SrTiO$_3$ parameters are substituted into Eq. (1) to give

$$\mu = \frac{7.2 \times 10^6 n}{\ln(3.1 \times 10^{-4} n^{1/3}) Z^2 N_i} \text{ cm}^2/\text{V sec}, \qquad (4)$$

where the approximation of the logarithmic term is valid if $n > 10^{15}$ cm^{-3}. If we let $n = N_i$ and $Z = 1$ for the niobium donors, the calculated mobility at 2°K for a lightly doped sample (No. 11 Nb), in which $n(2°\text{K}) = 1.9 \times 10^{17}$ cm^{-3}, is 1.4×10^6 compared to the measured value of 2.2×10^4 cm^2/V sec. The calculated mobility depends on the electron concentration only through the $g(b)$ term in Eq. (1), which is a very weak dependence, so that a similar discrepancy between the calculated and measured mobilities is present at all electron concentrations investigated. The magnitude of the discrepancy is such that no reasonable change in the parameters m^* or κ can make a significant improvement.

A possible explanation for the large discrepancy between the calculated and measured mobility values is that compensation effects may be present in SrTiO$_3$ because of lattice defects in the form of interstitial atoms and vacancies which form donor and acceptor centers. Paladino et al.[16] report that unannealed SrTiO$_3$ crystals contain a high concentration of crystalline defects which tend to enhance the diffusion of oxygen. Also, the difficulty encountered in obtaining semiconducting SrTiO$_3$ having a low electron concentration suggests the presence of uncompensated acceptor sites.[1] The presence of a high concentration of compensated donor and acceptor sites would result in N_i being much greater than n in Eq. (4) and consequently a lower value for the calculated mobility. Specifically, for the most lightly doped sample (No. 11 Nb), N_i must be equal to $60n/Z^2$ to give agreement between the calculated and measured mobilities. In this case, Z refers to the charge on the donor and acceptor centers and consequently its value is not known. Such a high degree of compensation is reasonable only if the donor and acceptor centers are due to vacancies and interstitial host atoms. With this model the difference in the magnitude of the mobility between reduced and niobium-doped samples is attributed to a higher concentration of compensated centers in the reduced samples. However, the reason the difference is a factor of 4 cannot be explained without a more detailed understanding of the nature of the donor and acceptor centers. Other scattering mechanisms may be present at low temperatures because of the phase transition and domain structure in SrTiO$_3$.[10] Evidence for this is found in the results of Frederikse

et al.,[3] who report an orientation-dependent mobility in SrTiO$_3$ at 4.2°K. However, the nature of these scattering mechanisms is not presently known. It is noted that a similar discrepancy between the calculated and measured mobility also exists in KTaO$_3$ where the calculated mobility is approximately an order of magnitude larger than the experimental value.[17]

The rapid decrease in the low temperature mobility at the highest electron concentrations in Fig. 5 is also observed in KTaO$_3$[5] and has been attributed to the smallness of the scattering cross section, i.e., the scattering cross section becomes constant when it is of the same order of magnitude as the square of the lattice constant.[18] This leads to an $n^{-4/3}$ dependence of the mobility on electron concentration. In the most heavily niobium-doped sample, the scattering cross section is approximately 17 Å^2 so that this mechanism may also be important in SrTiO$_3$.

In the high-temperature region, polar optical-mode scattering would be expected to dominate in SrTiO$_3$ because of the strongly ionic nature of the lattice. The wavelength dependence of the free-carrier absorption in SrTiO$_3$ suggests[4] that scattering by polar optical modes is dominant even at room temperature. The energies of the three active longitudinal optical modes at $q = 0$ are 250, 675, and 1150°K.[19] The electron–optical-phonon coupling coefficients, usually denoted by α, have been calculated by Eagles[19] and Barker[20] and are 0.009, 0.47, and $1.83 \times (m^*/m_0)^{1/2}$ for the 250, 675, and 1150°K modes,[20] respectively, where m^* is the electron effective mass and m_0 the free-electron mass. The main problem in comparing the experimental mobility results with theory lies in the inexactness of the mobility theory in the case of moderately strong electron-phonon coupling. Low and Pines[21] and Schultz[22] have calculated expressions for the mobility for the intermediate coupling case $(1 < \alpha < 6)$. Their results are of the form

$$\mu = \frac{eg(\alpha)}{2\alpha\omega m^*}(e^{\theta/T} - 1),$$

where θ is the energy of the scattering mode in °K and $g(\alpha)$ is a numerical factor that has been tabulated[21,22] as a function of α. However, the $g(\alpha)$ values of Low and Pines are smaller than the value of Schultz and the difference increases with increasing α. Another problem is that the theory requires that $T \ll \theta$, whereas experi-

[16] A. E. Paladino, L. G. Rubin, and J. S. Waugh, J. Phys. Chem. Solids 26, 391 (1965).

[17] It was concluded in Ref. 5 that the measured low-temperature mobility is in reasonable agreement with the calculated values in KTaO$_3$. However, Eq. (5) in Ref. 5 is in error by an order of magnitude, making the calculated mobility an order of magnitude larger than the measured results.

[18] R. S. Allgaier and B. B. Houston, Jr., in Proceedings of the International Conference on the Physics of Semiconductors, Exeter (The Institute of Physics and the Physical Society, London, 1962), p. 172.

[19] D. M. Eagles, J. Phys. Chem. Solids 26, 672 (1965).

[20] A. S. Barker, Phys. Rev. 145, 391 (1966).

[21] F. E. Low and D. Pines, Phys. Rev. 98, 414 (1955).

[22] T. D. Schultz, Phys. Rev. 116, 526 (1959).

FIG. 6. The calculated mobility due to scattering by polar optical lattice modes. The dashed curves are calculated for the 675 and 1150°K modes separately and the solid curve is obtained by adding reciprocally the individual mode mobilities. The open circles are the experimental data points for sample 8.

It is noted that the temperature dependence of the calculated mobility due to scattering by the 675°K mode, in Fig. 6, is approximately the same as the measured mobility. Empirically, the high-temperature mobility data can be fitted very well by the expression $\mu = 0.83(e^{600°\text{K}/T} - 1)$ in the temperature range from 200 to 550°K as shown in Fig. 7. This exponential temperature dependence suggests that scattering by longitudinal optical modes is dominant at high temperatures in SrTiO₃ but that the mobility is limited by scattering from a 600 or 675°K optical mode. Reasonable agreement between the temperature dependence of the mobility due to scattering by a 675°K mode and the experimental results can also be obtained, but only in the temperature range from approximately 350 to 550°K. In any case, the temperature dependence of the measured mobility is not nearly large enough to be explained by scattering by the 1180°K mode.

In the intermediate temperature range $(75 < T < 300°K)$, the mobility is independent of the electron concentration indicating some form of lattice scattering. However, the magnitude and temperature dependence are too small to be explained by scattering from the 1150 or 675°K polar optical modes and the coupling coefficient for the 250°K mode[20] is too small to give the correct order of magnitude for the mobility. Recently, Wemple et al.[6] have proposed a scattering model for SrTiO₃ and other perovskites that postulates scattering by the lowest-frequency transverse optical mode at room temperature. However, the temperature dependence of this interaction has not been determined so that

mentally, this is not satisfied over the temperature range where the scattering can be attributed to optical modes. It is therefore clear that only a very qualitative comparison between the theory and the experimental mobility results can be made.

The calculated mobilities obtained from Eq. (1) by assuming an effective mass of $6m_0$ and the $g(\alpha)$ values of Schultz[22] are shown in Fig. 6. The dashed lines are calculated mobilities for each mode and the solid line is the mobility obtained by adding the reciprocals of the individual mode mobilities. The calculated mobility due to scattering from the 250°K mode is too large to be of importance. The effective-mass value of $6m$, which is approximately the value determined by susceptibility measurements,[23] was chosen to make the measured and calculated mobilities coincide at the highest temperatures. However, the calculated mobility values have a somewhat stronger temperature dependence than the measured results. If the $g(\alpha)$ behavior of Low and Pines is used, the magnitude of the calculated mobility is limited by the 1150°K mode over the entire high-temperature region so that the temperature dependence of the calculated mobility is much too large. With either theory, the calculated mobility is of the correct order of magnitude but a closer comparison is not useful due to the uncertainties in the magnitude of the calculated mobility values.

[23] H. P. R. Frederikse and G. A. Candela, Phys. Rev. 147, 583 (1966).

FIG. 7. A comparison of the temperature dependence of the experimental mobility results from sample 8 (open circles) with the calculated temperature dependence of the mobility for scattering by a 600°K polar optical mode.

it is not presently known if this mechanism can explain the temperature dependence of the mobility in the intermediate temperature range. It has also been shown theoretically[24] that scattering by a two-phonon process could give a mobility temperature dependence similar to that observed in $SrTiO_3$ in the intermediate temperature range.

V. CONCLUSION

The electron Hall mobility has been measured from 1.5 to 550°K in reduced and niobium-doped $SrTiO_3$. Niobium appears to form a simple hydrogenic-type donor center in $SrTiO_3$ and consequently has a very small activation energy. The donor formed by the oxygen vacancy is doubly charged and has an activation energy of approximately 0.08 eV at low electron concentrations. The low-temperature electron mobility in niobium-doped $SrTiO_3$ is approximately a factor of 4 larger than in reduced $SrTiO_3$ over the electron-

concentration range investigated. Low-temperature Hall mobilities as large as 2.2×10^4 cm²/V sec were measured in niobium-doped $SrTiO_3$. The measured electron mobility at low temperatures is approximately two orders of magnitude below the theoretical mobility for scattering by ionized defects. It is postulated that this discrepancy may be caused by a high concentration of compensated ionized defects. The high-temperature mobility has been analyzed in terms of scattering by polar optical lattice modes. The mobility behavior calculated from the known values of the electron-phonon coupling coefficients is not in agreement with the experimental results. However, the high-temperature mobility behavior can be approximated well by assuming scattering from a polar optical mode having a characteristic temperature of 600°K.

ACKNOWLEDGMENTS

[24] B. W. Krishnamurthy and K. P. Sinha, J. Phys. Chem. Solids **26**, 1949 (1965).

Defects in Irradiated Silicon: Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance of the Aluminum-Vacancy Pair

G. D. WATKINS

General Electric Research and Development Center, Schenectady, New York

An EPR spectrum produced in aluminum-doped silicon by 1.5-MeV electron irradiation is described. Labeled Si G9, it is identified as arising from an aluminum-vacancy pair, presumably formed when a mobile lattice vacancy is trapped by substitutional aluminum. The resonance is observed only upon illumination and is identified as a long-lived excited triplet $(S=1)$ state of the defect. The observed hyperfine interactions with Al^{27} and neighboring Si^{29} nuclei, as well as the g tensor and axial fine-structure term D, are discussed in terms of a simple model of the defect using a linear combination of atomic orbitals. No Jahn-Teller distortion is observed in this excited state, as is consistent with the predictions of the model. Preferential alignment of the aluminum-vacancy axis direction in the lattice is achieved by stressing the crystal at $\sim 200°C$. The magnitude and sense of the alignment is consistent with the prediction of the model that the ground state is a Jahn-Teller distorted state similar to the phosphorus-vacancy pair previously studied. Abnormally strong $\Delta m \neq 0$ nuclear hyperfine transitions are observed in the EPR spectrum, and the theory of this effect, found only in an even-spin system, is developed. Emission is observed for some of the lines in the spectrum similar to that reported by Tanimoto *et al.* for another photoexcited $S=1$ system. The origin of this effect is discussed in terms of the model.

I. INTRODUCTION

IN previous papers of this series,[1-5] we have shown that lattice vacancies in silicon produced by radiation damage are mobile at temperatures well below

room temperature and can be trapped by impurities to form stable electrically active impurity-vacancy pairs. Examples are the oxygen-vacancy pair[1,2] (A center, giving the Si-B1 EPR resonance) and the phosphorus-vacancy pair[3] (E center, giving the Si-G8 resonance).

[1] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

[2] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).

[3] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

[4] G. D. Watkins, in *Proceedings of the 7th International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Academic Press Inc., New York, 1965), p. 97.

[5] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).