# Surface Transport Phenomena in PbSe Epitaxial Films

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We examine the effect of ambients on the electrical properties of a number of PbSe epitaxial films. These properties are compared with the calculations based on existing theoretical models. We conclude that the existing surface-mobility calculations for degenerate semiconductors are inadequate. The most important result is that the scattering of carriers at the surface appears to be completely specular in character.

## I. INTRODUCTION

E PITAXIAL films of PbS, PbSe, PbTe, and SnTe have been produced possessing essentially bulkhave been produced possessing essentially bulklike properties.<sup>1-4</sup> These films were found to have a wide variety of defects some of which affect the electrical properties.<sup>5,6</sup> Evidence for bulk electrical phenomena in the films was obtained by ZJS. No direct observation of surface effects on these films has been presented, though Skalski has observed some field-effect processes on PbTe.7 Measurements at this laboratory have indicated that the surfaces of epitaxial films of the lead salts are very stable. The conductivity and Hall coefficient of a number of PbS films were remeasured after a two-year exposure to laboratory ambient gases and were found to be essentially unchanged. This is in marked contrast to the known sensitivity of polycrystalline films to laboratory ambients. It was established many years ago that adsorbed oxygen plays a key part in the photoconductivity of lead-salt films.<sup>8-10</sup>

In the work on photoconductive films, it was found that oxygen could be added or removed from the surface by pumping.8 Quantitative measurements on the adsorption of oxygen on these materials were not carried out at that time. In the last two years, two studies of the adsorption of oxygen have been conducted on PbS and PbTe.11,12 This work indicates that at room temperature, the adsorption of oxygen is very slow and that the sticking coefficient is very small  $(\sim 10^{-9})$ . Except for a small initial fraction of the coverage, the binding energy is quite low.

A330 (1965). Hereafter referred to as ZJS.
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152, 1350 (1963) [English transl.: Soviet Phys.—Doklady 8, 960

- <sup>10</sup> R. L. Petritz, Phys. Rev. 104, 1508 (1956)

One important characteristic of the lead salts is that they are nonstoichiometric solids. As a result, the carrier concentrations are fairly high. Generally speaking, surface research tends to be divided between low-carrier-concentration materials  $(n < 10^{15}/\text{cm}^3)$  or metals. Bismuth has been a major exception.<sup>13,14</sup> There has been no work reported on the surface dependence of the electrical properties of heavily doped semiconductors or semimetals. This is due in part to the difficulties in preparing sufficiently thin samples suitable for transport measurements. Epitaxial films have provided the preparation technique needed to permit the study of the surface electrical properties of these materials.

The theoretical situation for high-carrier-concentration materials is not very satisfactory. Siewatz and Green have calculated the general dependence of surface charge on surface potential for a fermion sea.<sup>15</sup> However, the mobility for such a system has not been calculated. The closest approach has been the work of Greene et al.<sup>16,17</sup> Their calculations are based on nondegenerate statistics. Whether such an approach is appropriate is open to some doubt.

In this paper, we examine the effect of a few ambient gases on the electrical properties of a number of PbSe epitaxial films. These properties are then compared to the calculations based on existing theoretical models. The general conclusions arrived at are: The existing surface mobility calculations based on diffuse surface scattering are inadequate; the surface appears quite specular; nonparabolicity of the energy surfaces plays an important part in the surface dependence of the mobility.

#### **II. EXPERIMENTAL DETAILS**

Five PbSe films were deposited on heated NaCl single crystals.<sup>1</sup> Thicknesses ranging from 0.03 to  $1.3 \mu$ were obtained. Both n- and p-type materials were grown. A conventional bridge was scribed on the film in order

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<sup>&</sup>lt;sup>5</sup> J. W. Matthews, Phil. Mag. **76**, 1347 (1961); **8**, 711 (1963). <sup>6</sup> A. D. Wilson, R. C. Newman, and R. Bullough, Phil. Mag. **8**,

<sup>&</sup>lt;sup>7</sup> J. Skalski, Trans. IEEE **53**, 1792 (1965). <sup>8</sup> D. Bode and H. Levinstein, Phys. Rev. **96**, 259 (1954). <sup>9</sup> J. N. Humphrey and W. W. Scanlon, Phys. Rev. **105**, 1192 (1957).

<sup>&</sup>lt;sup>11</sup> L. J. Hillenbrand, J. Chem. Phys. 41, 3971 (1964). <sup>12</sup> M. J. Lee and Mino Green, J. Phys. Chem. Solids 27, 797 (1966).

<sup>&</sup>lt;sup>13</sup> A. N. Friedman and S. H. Koenig, IBM J. Res. Develop. 4, 158 (1960).

<sup>&</sup>lt;sup>14</sup> J. E. Aubrey, C. James, and J. E. Parrott, in *Proceedings of the International Conference on the Physics of Semiconductors*, Paris, 1964 (Dunod Cie, Paris, 1964), p. 689. <sup>15</sup> R. Siewatz and M. Green, J. Appl. Phys. 29, 1034 (1958).

<sup>&</sup>lt;sup>16</sup> Y. Goldstein, N. B. Grover, A. Many, and R. F. Greene, J. Appl. Phys. **32**, 2540 (1961). <sup>17</sup> R. F. Greene, D. R. Frankl, and J. N. Zemel, Phys. Rev. **118**,

<sup>967 (1960).</sup> 



FIG. 1. Hall mobility as a function of the total film resistivity for these *p*-type films.  $\bigcirc$  is used for PbSe 8*a*,  $\ominus$  for PbSe 8*b*, and  $\oplus$  for PbSe 9. Thickness is approximately 1000 Å.

to carry out the electrical measurements.18 Using a constant current source, the resistivity and Hall voltages were measured using conventional dc techniques. A Hewlett-Packard 425A high-impedance microvoltmeter, which has a  $\pm 3\%$  accuracy, was used to measure the Hall voltage. Resistivity voltages were read with a millivolt potentiometer and were accurate to  $\pm 0.1\%$ . The constant current source was stable to within its  $\pm 0.1\%$  specifications. Major errors were introduced by the magnetic field and the dimensions of the specimen. The magnetic field had an estimated error of  $\pm 5\%$  while the length-to-width ratio had an error of  $\pm 4\%$ . Far and away the greatest error was due to the thickness. This thickness error was largest for the thinnest films. While the carrier density and resistivity are dependent on the thickness, the mobility is not. No magnetoresistances were observed during these measurements up to field of 4 kOe. Contact to the films were made with silver paste as described by ZJS.

The films were mounted in the same apparatus used



FIG. 2. Hall coefficient as a function of the total film resistivity for three *p*-type films.  $\bigcirc$  is used for PbSe 8a,  $\bigcirc$  for PbSe 8b, and  $\oplus$  for PbSe 9. Thickness is approximately 1000 Å.



FIG. 3. Hall mobility as a function of the total film resistivity for an *n*-type film, PbSe 5. Thickness is  $1.3 \mu$ .

in ZJS. Measurements were conducted at atmospheric pressure and during the evacuation of the system. Slow changes in the electrical properties occurred during the initial pumpdown. The changes were markedly faster when the ionization gauge was turned on. In the system employed, it was impossible for ions to diffuse to the specimen. It was assumed, therefore, that the ion gauge generated some gaseous species which was effective in removing oxygen from the surface of PbSe. A likely candidate is atomic hydrogen generated by the decomposition of  $H_2O$  in the ion gauge. Without a mass-spectrometric analysis of the residual gases, it is impossible to unambiguously establish the cause of the shift.

## **III. MEASUREMENTS**

In Fig. 1, the mobility of PbSe 8a, 8b, and 9, all p type films, are shown as a functions of the resistivity. The Hall coefficient is plotted against the resistivity in Fig. 2. Considering the enormous change in the number of carriers, the variation of mobility is surprisingly small. The thickness of all these films was approximately 1000 Å. The agreement between the electrical properties for these films is extremely good. Two different pieces of the same film, 8a and 8b, were studied and the agreement between them is poorer than between 8b and 9. A very thin p-type film, PbSe 28, was also



RESISTIVITY (10<sup>-3</sup> OHM CM)

FIG. 4. Hall coefficient as a function of the total film resistivity for an *n*-type film, PbSe 5. Thickness is  $1.3 \mu$ .

<sup>&</sup>lt;sup>18</sup> E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths Scientific Publishers, Inc., Ltd., London, 1960).



FIG. 5. Hall mobility as a function of the total film resistivity for a high-carrierconcentration p-type film, PbSe 28. Thickness is estimated to be 300 Å.

examined and the results are shown in Figs. 3 and 4. Since it was desirable to see if the variation with ambient gas was the same for *n*-type material, the same galvanomagnetic measurements were performed on PbSe 5 and the results are shown in Figs. 5 and 6. All in all, the general behavior with ambient gas was quite independent of the bulk carrier type. The temperature dependence of the low-carrier-concentration mobility was obtained for two films. PbSe 8*a* and 28. These are shown in Fig. 7. The Hall coefficient versus temperature is shown in Fig. 8.



FIG. 6. Hall coefficient as a function of the total film resistivity for a high-carrier-concentration p-type film, PbSe 28. Thickness is estimated to be 300 Å.

RESISTIVITY (10-3 OHM CM)

A detailed examination of ambient gas effects was carried out on PbSe 8*a*. After evacuation to a pressure near  $2 \times 10^{-5}$  Torr, the electrical properties stabilized. The Hall coefficient and resistivity were both maxima at this point while the mobility had decreased after an initial maximum. The same low-pressure values were obtained after repeated cycling to atmospheric pressure and then repumping. Exposure to dry N<sub>2</sub> and He had virtually no effect on the electrical properties. Admitting O<sub>2</sub> was equivalent to exposing the film to air. An attempt to examine the behavior of the film in a wet He ambient led to the destruction of the film. No further experiments in wet ambient gases were conducted.



FIG. 7. Hall mobility as a function of absolute temperature for PbSe 8*a* and PbSe 28.

#### IV. THEORY

Unlike other substances whose surface electrical properties have been previously considered, the films are degenerate at room temperature. The minimum carrier concentration observed was estimated to be approximately 10<sup>18</sup>/cm<sup>3</sup>. Following Siewatz and Green,<sup>15</sup> we obtain an expression for the dependence of the Fermi energy on the carrier concentration.

$$p_{b} = 4\pi \left(\frac{2m^{*}kT}{h^{2}}\right)^{3/2} F_{1/2}(W_{vF}), \qquad (1)$$

where  $m^*$  is the effective mass of the carriers, T is the absolute temperature, k is the Boltzmann constant, h is Planck's constant, and  $W_{vF}$  is defined through the general relationship

$$V_{ij} = (E_i - E_j)/kT, \qquad (2)$$

in which *i* and *j* stand for any of the subscripts defined below.  $E_v$  is the bulk valence-band-edge energy and  $E_F$ 



is the Fermi energy. The quantity  $F_{1/2}(W_{vF})$  is defined as

$$F_{1/2}(W_{vF}) = \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1 + \exp(\epsilon + W_{vF})} \,. \tag{3}$$

Siewatz and Green have derived an expression for the surface charge on a strongly degenerate p-type bulk material and obtain<sup>15</sup>

$$Q_{s} = 2qL_{D}(\gamma n_{i})^{1/2} \left\{ \frac{N_{A}}{\gamma} \ln \frac{1 + \frac{1}{2} \exp(-W_{ts})}{1 + \frac{1}{2} \exp(-W_{tv})} + \frac{2}{3} \left[ F_{3/2}(W_{sF}) - F_{3/2}(W_{vF}) \right] \right\}^{1/2}$$
(4)

$$\gamma = 4\pi \left(\frac{2m^*kT}{h^2}\right)^{3/2}.$$
 (5)

 $L_D$  is the Debye length

$$L_D = \left(\frac{\epsilon \epsilon_0 kT}{2q^2 n_i}\right)^{1/2},\tag{6}$$

where  $n_i$  is the intrinsic carrier concentration,  $\epsilon$  is the

(8)

static dielectric constant, q is the electronic charge, and  $\epsilon_0$  is the permittivity of free space. Referring again to Eq. (4),  $N_a$  is the density of bulk acceptors,  $E_t$  is the energy of the bulk acceptors, and  $E_s$  is the energy of the valence-band edge at the surface. Assuming that  $m^*=0.08m_e$ , then at room temperature  $\gamma$  has a value of  $6.15 \times 10^{17}/\text{cm}^3$ . The intrinsic carrier concentration is

$$n_i = \gamma F_{1/2}(W_{vc}/2).$$
 (7)

For PbSe,  $|W_{vc}|$  at room temperature is 10.8 according to ZJS.  $n_i$  can then be calculated using the tables of McDougall and Stoner.<sup>19</sup> A value of  $1.5 \times 10^{15}/\text{cm}^3$  is obtained.  $L_D$  can then be calculated using 250 for the static dielectric constant, and is found to be  $3.48 \times 10^{-5}$  cm.<sup>20</sup> The position of the Fermi level in the bulk can be obtained from Eq. (1) if the bulk carrier density is known. For convenience, we let  $p_b = 1.23 \times 10^{18}/\text{cm}^3$  which leads to a value of  $W_{vF} = 1.58$ , i.e., the Fermi level is 1.58 kT into the valence band at room temperature. The position of the various energy levels is shown in Fig. 9.

The excess surface charge can now be calculated from Eq. (4) as a function of the surface potential  $W_{sv}$ . This is plotted in Fig. 10. The surface mobility  $\mu_{ps}$  can be obtained from the work of Goldstein *et al.*<sup>16</sup> This work is an extension of the theory of Greene, Frankl, and Zemel.<sup>17</sup> The theory assumes that the surface are diffusely scattered and that they obey nondegenerate statistics. There are no estimates for the effect of degeneracy on the surface mobility. Lacking a better theory, we will make use of the nondegenerate calculation.<sup>16</sup> The values for the surface mobility depend critically on the ratio of the mean free path  $\lambda$  to extrinsic Debye length L, where

and

$$L = \left[\frac{\epsilon\epsilon_0 kT}{q^2(n_b + p_b)}\right]^{1/2} \simeq \left(\frac{\epsilon\epsilon_0 kT}{q^2 p_b}\right)^{1/2}; \quad p_b \gg n_b. \tag{9}$$

 $\mu_b$  in Eq. (8) is the bulk mobility. Assuming that  $\mu_b$ 

 $\lambda = \frac{\mu_b h}{2a} \left( \frac{3p_b}{-} \right)^{1/3}$ 



<sup>&</sup>lt;sup>19</sup> J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) A237, 67 (1938).



FIG. 10. Surface potential dependence of the charge in the surface space-charge region. The surface mobility for a mean free path to extrinsic Debye length ratio of 0.1 and the ratio of total film resistivity to bulk resistivity when the thickness of the film is 1000 Å.

for the better films is of the order of 750 cm<sup>2</sup>/volt sec, and using  $p_b = 1.23 \times 10^{18}$ /cm<sup>3</sup>, we obtain  $\lambda = 1.6 \times 10^{-6}$ cm and  $L = 1.7 \times 10^{-6}$  cm. In other words,  $\lambda/L$  is of the order of unity. A plot of the ratio of the surface mobility to bulk mobility as a function of surface potential is given in Fig. 10. These surface mobilities, it should be noted, are drift mobilities.

The Hall mobility has been only partially treated in the literature.<sup>21,22</sup> Our treatment will follow the effective mobility formation of Petritz.<sup>23</sup> The conductivity is

$$\sigma d = \sigma_b d + q \mu_{ps} \Delta P , \qquad (10)$$

where d is the thickness of the sample,  $\sigma_b$  is the flat band conductivity,  $\Delta P$  is the excess surface charge, and  $\mu_{ps}$  is the mobility of the excess surface charge. For accumulation layers in degenerate materials

$$Q_s = q \Delta P. \tag{11}$$

In the effective mobility formalism, the Hall mobility is

$$\mu_H = R\sigma = \frac{p_{b\mu}b^2 d + \Delta P \mu_{ps}^2}{P_{b\mu}b d + \Delta P \mu_{ps}},$$
(12)

where R is the Hall coefficient and  $\mu_b$  is the bulk mobility. It is a simple matter to show that

$$R = \frac{1}{qp_b} \frac{1 + (\Delta P/p_b d) (\mu_{ps}/\mu_{pb})^2}{(1 + (\Delta P/p_b d) (\mu_{ps}/\mu_{pb}))^2} = \frac{1}{qp}, \quad (13)$$

where p is the apparent carrier concentration in the film. The resistivity can be easily calculated from Eq. (10):

$$p = \frac{\rho_0}{1 + (\Delta P/p_b d)g_s},\tag{14}$$

<sup>21</sup> J. N. Zemel, Phys. Rev. 112, 762 (1958).

- <sup>22</sup> A. Amith, J. Phys. Chem. Solids 14, 271 (1960).
- <sup>23</sup> R. L. Petritz, Phys. Rev. 110, 1254 (1958).

<sup>&</sup>lt;sup>20</sup> J. N. Zemél, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1964), p. 1061.

where

$$\rho_0 = 1/q p_{b\mu b},$$

$$g_s = \mu p s/\mu p b.$$
(15)

Then it follows

$$R = \frac{\rho}{\rho_0} \left( g_s + (1 - g_s) \frac{\rho}{\rho_0} \right). \tag{16}$$

 $\rho/\rho_0$  is plotted as a function of  $W_{sv}$  in Fig. 10 to complete the comparison of the relevant quantities. In Fig. 11, R is plotted as a function of  $\rho/\rho_0$  for a 1000-Å-thick film having a bulk carrier concentration of 10<sup>18</sup> carriers/cm<sup>3</sup>.

## V. DISCUSSION

A comparison of Fig. 11 against Fig. 2 establishes that the diffuse-scattering model is very bad. If we assume that  $g_s$  is unity, i.e., independent of surface potential, the agreement is much better. This is also shown in Fig. 11. Because  $g_s$  is independent of  $W_{sv}$ , the Hall mobility is independent of resistivity. The fact that there is a variation does not automatically imply a measure of scattering. The valence band of the lead salts is known to be complicated.

In the lead salts the band gap is direct and occurs at the L point. There are other extrema which are located at other points in k space, some of which are separated from the band-gap extrema by relatively small energies.<sup>24</sup> Riedl has obtained absorption data on p-type lead telluride that indicates a second conduction or valence band about 0.18 eV from the band gap.<sup>25</sup> Data of Allgaier on the temperature dependence of the Hall coefficient support the presence of a second nearby valence band.<sup>26,27</sup> In PbSe, a second valence band would be ex-



FIG. 11. Hall coefficient as a function of the ratio of the total film resistivity to bulk resistivity when the thickness of the film is 1000 Å Two cases are treated: Diffuse scattering based on the mobility in Fig. 10 and specular scattering where  $\mu_s/\mu_b = 1$ .

<sup>24</sup> L. Kleinman and P. J. Lin, in Proceedings of the International <sup>24</sup> L. Kleinman and P. J. Lin, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1964), p. 63; G. W. Pratt and L. G. Ferreira, *ibid.*, p. 69; J. O. Dimmock and G. B. Wright, *ibid.*, p. 77.
<sup>25</sup> H. R. Riedl, Phys. Rev. 127, 162 (1962).
<sup>26</sup> R. S. Allgaier, J. Appl. Phys. Suppl. 32, 2185 (1961).
<sup>27</sup> R. S. Allgaier and B. Houston, in Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962 (The Institute of Physics and The Physical Society, London, 1962), p. 172

pected to be split off even further.<sup>24</sup> Therefore, it does not seem too likely that the decreasing mobility with increasing surface potential is due to interaction with a second band in PbSe. This mechanism should apply to PbTe and could be a direct test of the importance of a second valence band to the conduction process.

On the other hand, Palik, Mitchell, and Zemel<sup>28</sup> have shown that there is an appreciable nonparabolicity in the reduced effective mass. Because of the symmetry of the valence and conduction bands, this nonparabolicity should occur in both bands. Because of the degeneracy of the system, the mobility will depend on the effective mass at the Fermi energy. This mass increases with energy causing the mobility of the excess carriers to decrease as the surface potential increases in magnitude. In many important respects, the behavior of the mobility when the mass varies with position conforms to the effective mobility model of Petritz.<sup>23</sup> Neglecting the energy dependence of the relaxation time,  $\tau$ , we get

$$\sigma d = \int_0^d q^2 n(z) \frac{\tau}{m(z)} dz, \qquad (17)$$

where

$$m^*(z) = m^* [W_{vF}(z)],$$

i.e., the magnitude of the Fermi level in the space-charge region is a function of position. Nonlocal processes would not affect the z dependence of the Fermi energy. Using the data of Palik, Mitchell, and Zemel, we have calculated mobilities for the excess charge.<sup>28</sup> We have used two extremely crude assumptions to calculate the Hall coefficient as a function of resistivity ratio. The first assumption is that all of the excess charge has a mobility based on an effective mass

$$m^* = m^* (W_{fv} = W_{sv}).$$
 (18)

This means that we are allowing all of the excess charge to have a mass given by Eq. (18). The second assumption is

$$m^* = m^* (W_{fv} = \frac{1}{2} W_{sv}). \tag{19}$$

The first assumption greatly overestimates the energy dependence of the effective mass. The variation of the Hall coefficient with resistivity for this case is shown as curve c in Fig. 12. The second assumption is more realistic since the number of carriers with low effective mass contribute more to the average mobility than do those with large mass. The Hall coefficient-versusresistivity ratio for this is shown as curve b in Fig. 12. Curve a is the Hall coefficient variation for parabolic bands. The behavior of curve b is more in keeping with the observations of Fig. 2. The effect of nonparabolic

p. 172.

<sup>&</sup>lt;sup>28</sup> E. D. Palik, D. L. Mitchell, and J. N. Zemel, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1964), p. 325.

FIG. 12. Hall coefficient as a function of the ratio of total film resistivity to bulk resistivity when the thickness of the film is 1000 Å. Three cases are treated for the effect of nonparabolicity of the valence band: (a) effective mass at the surface potential energy, (b) effective mass at 0.5 surface potential energy, (c) effective mass independent of energy.



energy surfaces on surface phenomena in these lead salts should be of some interest.

There is supporting evidence for a specular-surfacescattering hypothesis in the temperature dependence of the mobility. This can be seen in Fig. 8. Film 28 has an estimated thickness of 300 Å. If surface scattering was important, the limiting mean free path would be the thickness.<sup>29</sup> At liquid-nitrogen temperatures, film 28 has a mobility of approximately  $1100 \text{ cm}^2/\text{V}$  sec. Because of the very high carrier concentration, this corresponds to a mean free path of 660 Å. The important point is that the mobility has not leveled off as yet and could be expected to rise another factor of 2. In the case of 8a where the thickness is known more accurately, the mean free path at 77°K is 650 Å. This is almost equal to the thickness of the film, 1000 Å. From the way the mobility is increasing, a final residual mobility of 5-10 000 cm/V sec would be possible. This would lead to a mean free path of over 2000 Å. Therefore, it can be concluded that the lead salts are the first semiconducting materials to show a significant deviation from diffuse surface scattering.

A reasonable objection to the room-temperature argument is that nondegenerate statistics were used to calculate the surface mobilities employed. This is a valid objection but in the absence of suitable calculations, we have employed what is available. The calculation of surface mobilities for a degenerate system is urgently needed to resolve this question.

The low-temperature argument cannot be faulted on those grounds, however, and two interesting points are raised by these results. First, bulk carrier concentrations can be made sufficiently large so that anomalous and extreme anomalous skin-effect measurements can be made. A comparison of dc and high-frequency surface-scattering results would be of interest. The second point deals with the very high surface charge densities induced by the oxygen. A surface charge of  $2-5 \times 10^{13}$ carriers/cm<sup>2</sup> generates fields of up to 10<sup>5</sup> V/cm.<sup>15</sup> The effective screening length is  $1.85 \times 10^{-6}$  for a carrier concentration of  $10^{18}$ /cm<sup>3</sup>. The change in energy over a screening length is 0.27 eV, a value greater than the band gap. This suggests that reflectivity data in the visible range could be distorted by the presence of these extremely high surface fields. No systematic data on this question have been obtained. It represents an interesting problem. Some brief mention should be made about the surface state resopnsible for the surface charge. We assume that the near flat-band condition occurs in the low-pressure regime. This is based on the known response of the lead salts to oxygen adsorption.8,9 Furthermore, Juhasz has observed a marked p-type shift when freshly deposited epitaxial PbTe films are exposed to O<sub>2</sub>.<sup>30</sup> These increases in surface charge must be due to a surface state located well below the valenceband edge. Charging of this surface state will cause an increase hole density in the space-charge region. Using the maximum induced charge, we obtain a surface potential of at least 9kT at room temperature. This implies that the energy of the surface state is at least 9kT below the valence-band edge. So far as we know, this is the first evidence for a surface state located that far below a valence-band edge (or correspondingly above the conduction band for electrons).

## VI. CONCLUSIONS

Based on surface-transport measurements it appears that surface scattering in PbSe is specular. Extremely high surface charge densities are observed for films exposed to normal laboratory ambient gases. The theoretical description of the surface fields in a degenerate semiconductor appears adequate but the nondegenerate calculation of surface mobilities does not apply to these materials. Comparison of skin-effect measurements to the dc measurements should provide useful information concerning the scattering process.

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<sup>&</sup>lt;sup>29</sup> E. H. Sondheimer, Advan. Phys. 1, 1 (1952).

<sup>&</sup>lt;sup>30</sup> C. Juhasz (private communication).