Surface-State Electrons on a Hydrogen Film. 1. Annealing of the Film

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We have investigated the surface of thin films (thickness ~2 μm) of solid H_2 between 1.5 and 4.2 K by measuring the ac conductivity of surface-state electrons (SSE). The films were prepared on a glass substrate by quench condensation at 1.5 K and were therefore initially strongly disordered. In fact the surface of the virgin films before any heat treatment was so rough that no current due to SSE could be observed. Annealing the films decreased the surface roughness and gave rise to a thermal-activation-type temperature dependence of the SSE conductivity. By proper heat treatment up to 8 K the activation energy could be reduced to $10k_B$.

1. INTRODUCTION

Surface-state electrons (SSE) on a solid hydrogen surface have attracted much attention recently[1-6] as an alternative system to SSE on liquid helium, which have been studied over the last two decades as an example of a particularly clean and well-defined two-dimensional electron system. One of the motivations for studying SSE on the surface of solid hydrogen is to increase the electron density beyond the limit of $n_c = 2 \times 10^9$ cm^{-2}, which exists for the liquid helium substrate due to its surface instability.[7-10] It would be extremely interesting to have an SSE system available with electron densities several orders of magnitude higher and thus comparable to those of MOSFET systems, since a variety of phenomena (quantum electron-solid, highly correlated quantum liquid, etc.) are to be expected in such a system. The surface of solid hydrogen is one of the most promising candidates for

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this purpose, because an electrohydrodynamic instability as is found for the liquid helium surface does not occur in this case, and the SSE mobility can be fairly high.[2] In order to reach a high electron density n_s, the hydrogen substrate should not be too thick—preferentially forming only a *thin film*— since the maximum electron density is proportional to the applied electric field and hence is inversely proportional to the film thickness that separates the SSE from the electrode underneath them.

In addition to possible applications as a substrate for SSE, quench condensed films are of importance also in their own right. Due to the rapid cooling during preparation, quench-condensed films are usually strongly disordered. The structure and excitations of such systems are a topic of current interest.[11,12]

In consideration of these facts, an attempt to develop a hydrogen film by quench condensation on a cold substrate at 1.5 K was made in this work. The film surface was investigated by means of ac SSE conductivity measurements between 1.5 and 4.2 K over a frequency range from 10 to 100 kHz. We found that annealing of the film increased the SSE conductivity drastically, implying a considerable improvement of the surface quality. The results show that the temperature dependence of the SSE conductivity follows a behavior expected from a thermally activated process and that the activation energy is reduced by the annealing procedure.

In Sec. 2, the basic aspects of SSE will be treated. Section 3 describes the experimental method: experimental apparatus, preparation of the hydrogen film, and conductivity measurements. The experimental results will be presented in Sec. 4 and discussed in relation to former work on quench condensed films.[11,12]

2. GROUND STATE OF SURFACE STATE ELECTRONS

The potential energy of electrons in the presence of an insulating surface having a double-layer structure, as shown in Fig. 1, can be approximated by the expression[13]

$$V(z) = \begin{cases} -\dfrac{\lambda_1 e^2}{z} - \dfrac{\lambda_2 e^2}{z+d}, & z > 0 \\ +\infty, & z \leq 0, \end{cases} \qquad (1)$$

$$\lambda_1 = \frac{\varepsilon_1 - 1}{4(\varepsilon_1 + 1)}, \qquad \lambda_2 = \frac{\varepsilon_1(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_1 + 1)^2(\varepsilon_2 + \varepsilon_1)}$$

Here $-e$ is the electronic charge, ε_1 and ε_2 are dielectric constants of materials I and II, respectively, d is the thickness of the material I, and z is the distance of the electrons from the surface of the material I.
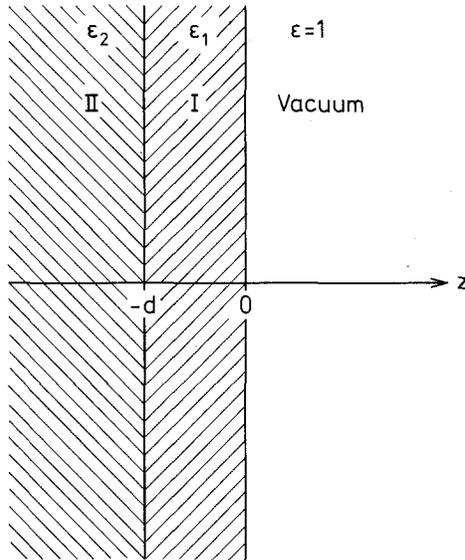
Fig. 1. Schematic drawing of the double-layered structure. ε, ε_1, and ε_2 denote the dielectric constants of vacuum, material I, and material II, respectively. Electrons are supposed to be on the vacuum side.

In case $d \to \infty$, Eq. (1) retains a simple form, and the ground state electron wavefunction in the z direction is

$$\psi_0(z) = 2\gamma_0^{3/2} z e^{-\gamma_0 z}$$

$$\gamma_0 = \lambda_1 / a_B$$

(2)

where a_B is the Bohr radius and λ_1 was defined in Eq. (1). The effective Bohr radius is defined as $a_{EB} = a_B / \lambda_1 = \gamma_0^{-1}$. In the x, y-direction, the wavefunction is taken to be a plane wave. If we consider a solid hydrogen substrate, the dielectric constant is about 1.29, and the value of a_{EB} approximately 1.67 nm; for the case of liquid helium, which will also be discussed as a substrate below, we have the dielectric constant and effective Bohr radius being 1.057 and 7.6 nm, respectively. The binding energy of electrons in the ground state $|E_0|$ is given by $\lambda_1^2 R_\infty$, where R_∞ is the Rydberg constant (13.6 eV.) E_0 is -160 K for the solid hydrogen case and -7.6 K for liduid helium.

When the thickness d is finite, the problem may be solved by employing the variational method. The test wavefunction is the same as in Eq. (2), with γ_0 being taken as a variational parameter. Figure 2 shows the d dependence of a_{EB}, where it is supposed that the material I is solid hydrogen
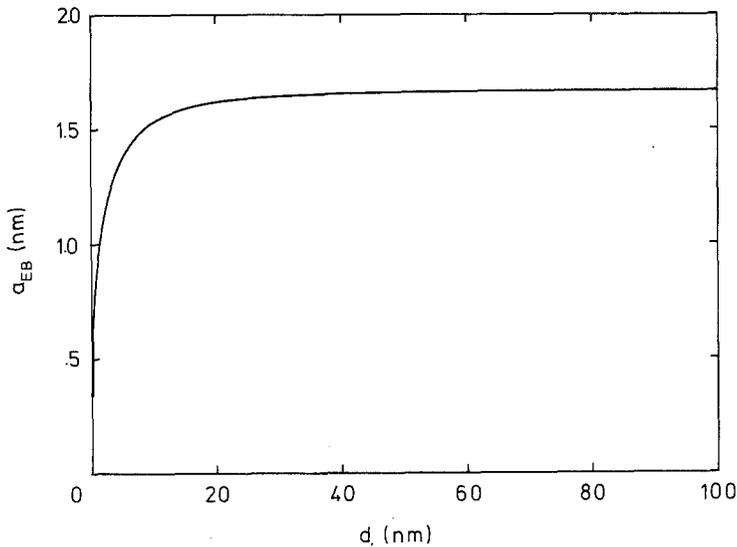
Fig. 2. Effective Bohr radius a_{EB} of surface state electrons vs. the thickness d of the material I. The material I and II are taken to be solid hydrogen ($\varepsilon_1 = 1.29$) and a glass ($\varepsilon_2 = 4.5$), respectively.

and II is a glass plate with $\varepsilon_2 = 4.5$. From this figure, it can be seen that the contribution from material II diminishes very quickly as d increases. On a hydrogen film thicker than 20 nm, the surface state is only marginally affected by the substrate material II. In this work, we have used hydrogen films with a thickness of 2 μm, so that the electronic state is considered almost the same as for the bulk-hydrogen case.

3. EXPERIMENTAL

The hydrogen films were quench-condensed onto a cold glass substrate. Figure 3 shows a schematic drawing of the sample cell.

The hydrogen inlet consisted of a thin-walled, stainless steel tube thermally isolated from the other parts of the sample cell in order to prevent it from freezing. A heater and a thermometer were attached to the inlet, and its temperature was stabilized around 30 K during film growth.

The substrate for the hydrogen film was a float-glass plate of 0.2 mm thickness. In order to clean its surface, the glass was soaked in a chromic acid mixture for 30 min. Then it was attached to two concentric copper electrodes, which were used to measure the SSE conductivity. The electrodes were thermally anchored to but electrically insulated from the bottom of the cell. In order to establish the proper temperature distribution, the bottom was equipped with a copper tail. During the growth of the hydrogen film,
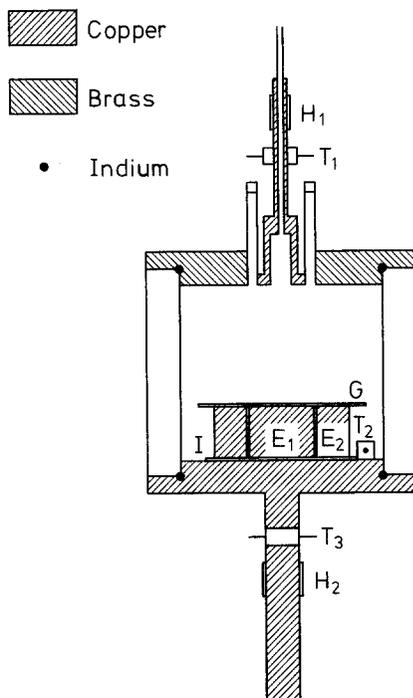
Fig. 3. Schematic drawing of the experimental cell. E_1 and E_2 are concentric electrodes. G is the glass substrate and I is an insulating sheet. H_1 and H_2 are manganin heaters and T_1, T_2, and T_3 are carbon resistors. Hydrogen enters the cell from the top through a capillary.

the cell position was adjusted such that only the tail was immersed in liquid helium. In this way the bottom plate was the coldest part inside the cell.

The heat of sublimation for hydrogen is 1.03 kJ/mol.[14] During the quench condensation, this energy is released when the hydrogen molecule accommodates to the surface. It was found that in order to obtain a smooth growth of the film, the heat of condensation has to be removed quickly. A shiny surface of the film was observed only in the region where the glass plate was in thermal contact with the copper electrodes, whereas in the peripheral region outside, the surface became milky. Since good thermal conductivity thus appears to be essential, an improvement might be expected by using substrate materials like silicon or sapphire as compared to the glass plate of this work.

The hydrogen gas used for the film preparation was of commercial grade and cleaned by passing it through a charcoal trap. It was fed into the cell at a rate of about 10^{-8} mol sec^{-1}, which led to a film of 2 μm thickness after one to two hours. The film thickness was measured by interferometry. Figure 4 shows an example of the film profile, obtained
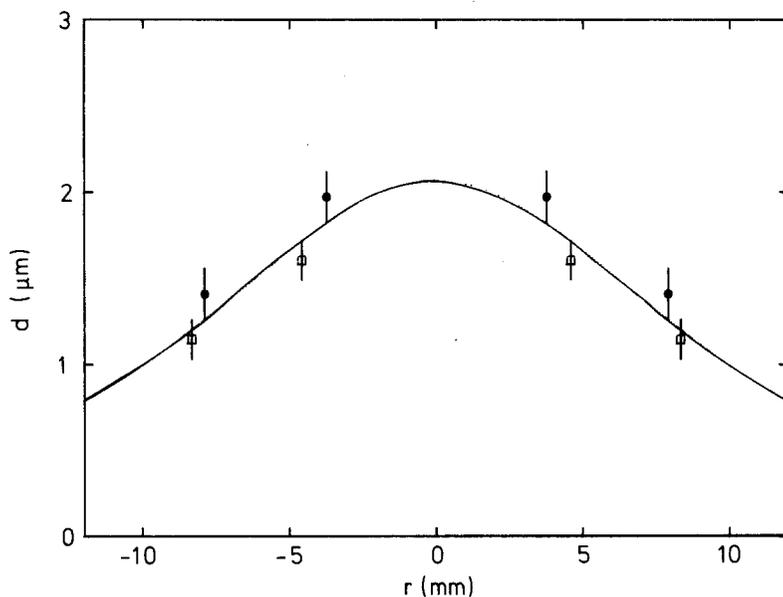
Fig. 4. Thickness profile of the hydrogen film. Solid circles are obtained from fringes of 633 nm light, whereas open squares are from those of 515 nm light. A solid line is a fit of the data using a formula $d = BVl/(l^2 + r^2)^{3/2}$, where B is the total hydrogen flux, v is molar volume of solid hydrogen (23 cm^3/mol), and l is a distance between the hydrogen source (which is assumed to be pointlike) and the substrate. Fitting parameters are B and l, which are 1.43×10^{-5} mol/sterradian and 1.26 cm, respectively.

from interference fringes produced by the film at two different laser wavelengths. The profile is bell shaped with maximum thickness in the center, a distribution resulting from the solid angle which is covered by the hydrogen source. The amount of H_2 adsorbed on the glass plate was found to be about a factor of two smaller than the total amount of H_2 admitted to the cell. From this we conclude that the sticking coefficient of H_2 molecules at a cold substrate is about 0.5 for the conditions of our experiments.

After preparation of the hydrogen film, a small amount of helium gas was fed into the sample cell. Then the hydrogen surface was charged with electrons emitted from a heated thin tungsten filament. The helium atoms served to reduce the mean free path of the electrons and thus to prevent them from picking up too much energy in the externally applied electric field. The electrons could therefore not overcome the energy barrier at the hydrogen surface and were collected as surface-state electrons. The maximum density of the SSE is expected to be $n_s = C_\square V_{dc}/e$, where $C_\square$ is the sheet capacitance of the SSE and V_{dc} is the applied dc voltage. It turned out that for our set-up this was correct only for voltage V_{dc} higher than

about 10 V. For lower voltages, stray fields in the cell gave rise to an additional charging of the film, and about 4×10^8 electrons/cm^2 were accumulated even for $V_{dc} = 0$, as determined from magneto-resistance measurement. One could still reduce this amount of charge, however, by applying a negative voltage to the lower electrodes.

Experimental methods for measuring the SSE conductivity have already been described in several articles.[15-18] In the present work, we have employed the Sommer-Tanner method,[15] for which Merohtra[19] carried out a detailed analysis. Since Merohtra's analysis is also applicable here the details of the calculation will not be described.

The electrodes were arranged in the Corbino geometry, i.e., an inner disk and an outer ring, separated concentrically by a narrow gap of about 0.2 mm. The outer diameter of the electrode system was 2.0 cm, and the diameter of the inner electrode was 1.0 cm. The glass substrate was attached to these electrodes, as described above. With the detecting circuit as shown in Fig. 5 and with the Corbino geometry, the following relation is expected between the output voltage induced on the outer electrode and the input voltage applied on the inner electrode

$$\frac{V_{\text{out}}}{V_{\text{in}}} = \pi^2 r_1^2 \left(\frac{C_\square}{C_0}\right) \left(\frac{J_0(\zeta r_1)}{J_0(\zeta r_0)}\right) (N_0(\zeta r_0)J_0(\zeta r_1) - J_0(\zeta r_0)N_0(\zeta r_1)) \tag{3}$$

$$\zeta = (-iR_\square C_\square \omega)^{1/2}$$

Here r_0 is the radius of the outer electrode ($r_0 = 1.0$ cm), r_1 that of the inner electrode ($r_1 = 0.5$ cm), $C_\square$ and $R_\square$ are the sheet capacitance and resistivity of the SSE, respectively, ω is the frequency of the applied ac voltage, C_0
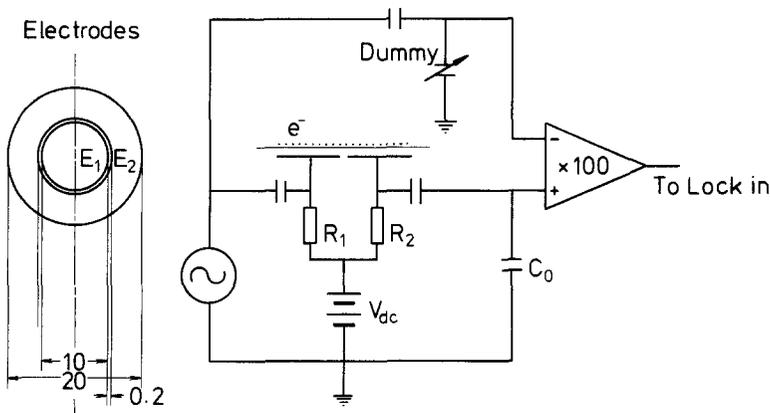

Fig. 5. Block diagram of the conductivity measurement system and the electrode assembly.

the input capacitance of the detecting circuit, and J_0 and N_0 are the Bessel and Neumann functions.

4. RESULTS AND DISCUSSION

After charging the surface, the conductivity $\sigma_\square\ (=R_\square^{-1})$ due to the SSE was measured as a function of temperature, with a sweep rate of about 2 K/hour. It turned out that the behavior of $\sigma_\square$ depended strongly on the history of the sample, as described below. A typical trace for the conductivity of SSE on a freshly prepared hydrogen film is shown in Fig. 6.

Starting at temperature of 1.5 K, the conductivity is rather high. This is not a measure of the mobility of SSE on the bare hydrogen film, however, because the hydrogen surface was covered with a saturated liquid He film of about 30 nm thickness due to the amount of He in the cell. The mobility on such a thick He film is close to the mobility on bulk helium. Upon heating, the conductivity decreases abruptly at a certain temperature, which in Fig. 6, for example, is approximately 1.65 K. We denote this temperature by T_0, hereafter. The sudden drop in $\sigma_\square$ reflects a rapid thinning of the helium film, occurring at T_0, which depends on the amount of helium in the cell. For $T > T_0$, nearly all the helium is in the gas phase (apart from
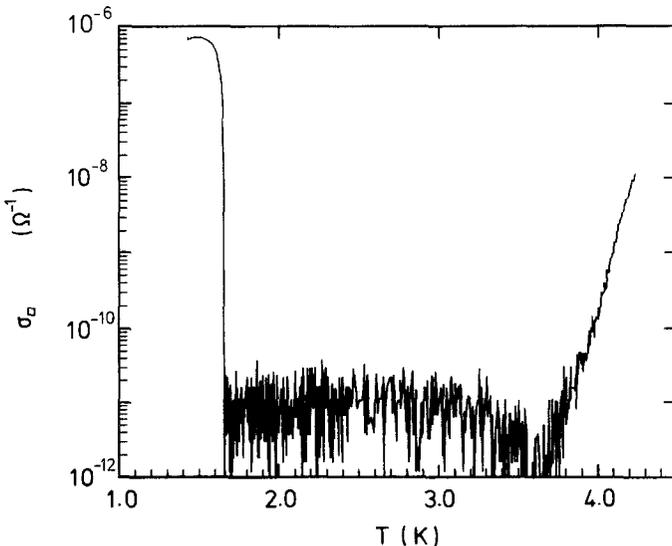

Fig. 6. Behavior of the conductivity for the first warming up. The conductivity measurement was done under the following conditions in the present work, unless otherwise specified: The driving frequency was 10 kHz, driving voltage amplitude 20 m V_{p-p}. The holding field V_{dc} was 1.0 V.

a few monolayers,) so that the data there represent the mobility on essentially the bare hydrogen surface. In the following we will concentrate on this temperature range where the electrons probe the properties of the hydrogen film. The mobility of SSE on helium films supported by a hydrogen substrate, i.e., the range $T < T_0$, will be the subject of part 2 of this work.[20]

As is seen from Fig. 6, the conductivity on the as-prepared H_2 film is extremely low (actually, below our sensitivity threshold of $10^{-11}\Omega^{-1}$) up to about 3.5 K. For higher T, $\sigma_\square$ begins to grow gradually. Qualitatively the same behavior was observed also for all the other runs (cf. Fig. 7a).

The observed variation of $\sigma_\square$ with temperature appears to be caused by two effects: (i) A thermally activated motion of the electrons, which at low temperatures are trapped at surface irregularities; (ii) gradual annealing of the surface at higher temperatures, which partly removes these irregularities and gives rise to a lowering of the typical trapping energies.

As a result the SSE conductivity on the hydrogen film improves as the annealing process is further pursued. Figure 7 shows a series of data taken from another H_2 film at different annealing steps. Figure 7a is the first warming-up period, which displays essentially the same behavior as in Fig. 6. Figure 7b is the second temperature sweep, after the hydrogen film has experienced the temperature excursion to 4.2 K. The improvement of the surface quality is evident. Comparing Fig. 7a with 7b, it can be seen that the effect of annealing during the first temperature sweep up to 4.2 K was so large that the SSE conductivity changed even in the region where the hydrogen film was covered by the saturated helium film ($T < 1.9$ K, in this case.)

A qualitative difference is observed between the first step of annealing, Fig. 7a, and the subsequent annealing cycles. While the trace in Fig. 7a can obviously be obtained only during warming-up, because irreversible processes occurring between 3.5 and 4.2 K change the surface structure on the time scale of the experiment, the trace in 7b, c, and d were reversible for warming and cooling on a scale of one hour. Figures 7c and 7d display the improvement upon further annealing.

Figure 7c was taken after the sample was left at 4.2 K for 12 hours, and Fig. 7d shows the result after the sample temperature had been increased to 8 K for a time of 1 h. The conductivity increase after each of these steps is most pronounced in the vicinity of the minimum near 2.1 K, where it amounts to almost two orders of magnitude on going from Fig. 7b to 7d. It appears interesting to note that below $T_0 = 1.9$ K there is *no* difference between the data in Figs. 7b, c, and d. Hence we conclude that the changes of the surface on annealing are so small that they do not affect the electrons over a distance roughly given by the thickness of the saturated helium film.
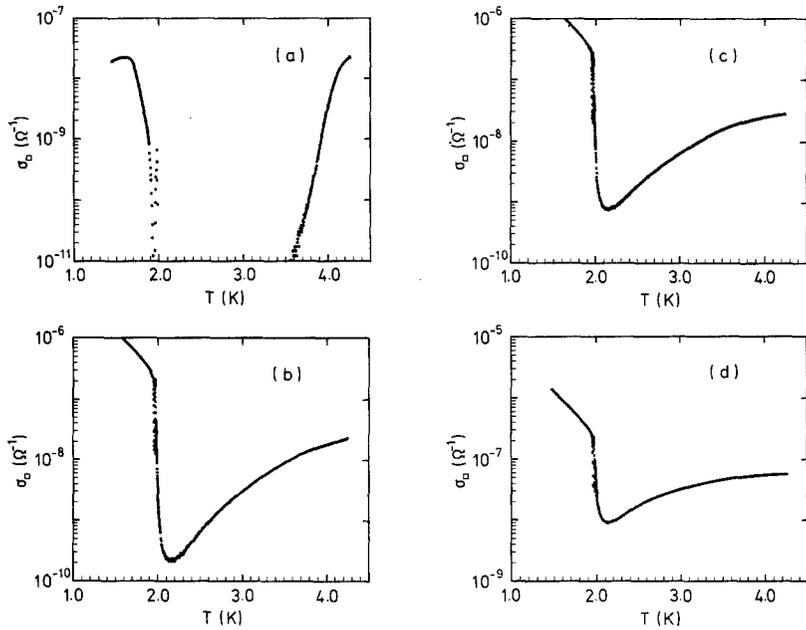
Fig. 7. Series of the conductivity data corresponding to different annealing stages: (a) the first warming up, (b) cooling down again from 4.2 K, (c) after leaving the film at 4.2 K for 12 hours, and (d) after annealing at 8 K for 1 h. Only the degree of annealing was changed among (a)-(d); the other experimental conditions, especially, the amount of the helium gas inside the cell and the electron density were kept unchanged. The electron density was 3.1×10^8 cm^{-2}, which was modified from the initially accumulated amount by applying the negative V_{dc} momentarily, and determined by measuring magnetoresistance at low temperature.

In order to elucidate the nature of the processes which determine the electron mobility on the hydrogen films, we have redrawn the data of Fig. 7 in an Arrhenius plot (Fig. 8.) In the region of interest here ($T > T_0$, where the electrons are residing on the nearly bare hydrogen surface) the conductivity can approximately be represented in this plot by straight lines. This indicates a temperature dependence

$$\sigma_\square = \sigma_0 \, e^{-\Delta E / k_B T}$$

and thus an electric conductivity governed by thermal activation. The activation energies ΔE obtained for the various annealing steps are summarized in Table I. Apparently ΔE is gradually reduced by the annealing process. The lowest activation energy obtained in this run was 10 K, more than an order of magnitude smaller than the binding energy of the electrons to the hydrogen surface.
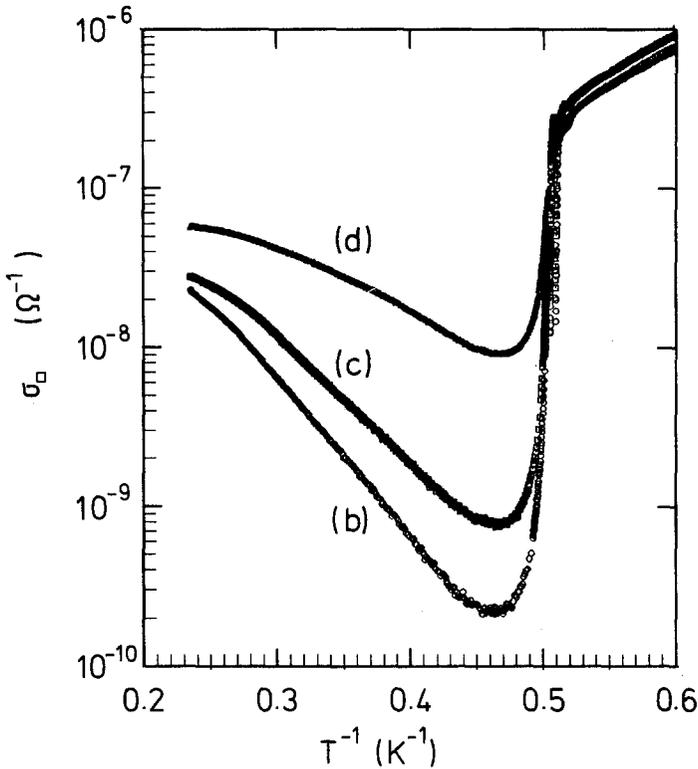
Fig. 8. Arrhenius plots of Figs. 7b, 7c, and 7d.

The rough surface structure of the quench-condensed films observed here is in accord with results for hydrogen and rare-gas solid films reported by other authors. Klitzner and Pohl,[11] for example, have investigated hydrogen films condensed onto silicon at temperature of 1 K. Phonon scattering was used to determine the surface roughness. The strongest scattering was found to occur at a phonon wavelength of about 200 nm, which reflects the characteristic length scale of the roughness.

TABLE I

Annealing conditions	ΔE	Figure
Virgin	—	7a
4.2 K	22 K	7b
4.2 K for 12 h	18 K	7c
8 K	10 K	7d

Strong disorder has also been reported for quench-condensed films of Xe by Steinmetz *et al.*[12] Using X-ray diffraction, these authors found that the films consists of very small crystallites with a lattice constant smaller than that of bulk Xe. Contrasting this to the observed macroscopic density deficit, they suggested that such films have an open structure with many voids and internal surface. The annealing behavior of the films as obtained from specific heat measurements was also interesting. For films condensed at 6 K ($=0.037T_m$, where $T_m = 160$ K is the triple-point temperature) the specific heat displayed a pronounced contribution in excess to the bulk value, which was partly assigned to surface modes. Annealing of the films reduced the excess part, observable already for an annealing temperature of less than $0.1 T_m$, and the bulk value of the specific heat was attained after annealing at $0.34T_m$. Although these results differ somewhat from our observation for the H_2 films (there the annealing effect became observable at $0.25 T_m$, and a certain amount of roughness remained even after annealing at $0.57 T_m$,) the difference is not too surprising considering the fact that the specific heat is not as sensitive to the surface morphology as the surface-state electrons. Besides, quantum effects might influence the scaling of the temperature in the case of hydrogen.

As shown in Fig. 8 and Table I, the temperature dependence of the SSE conductivity is of the thermal-activation type. We assign the activation energy to surface roughness. In order to obtain an estimate of the roughness in a first-order perturbation, we follow Shikin and Monarkha,[13] who have derived the perturbation Hamiltonian for SSE due to fluctuations of the surface. This Hamiltonian was used to calculate the ripplon-limited mobility of the SSE on liquid helium[21] and proved its validity. Applying this Hamiltonian to the solid hydrogen case, we can estimate the local change of the ground-state binding energy of the SSE due to deviations of the surface from a plane. The first-order perturbation gives the following results for the peak to peak change ΔE of the binding energy E_0,

$$\Delta E = \frac{2k}{\gamma_0}(ak)\left(1+\log\frac{k}{4\gamma_0}\right)+2eEa \qquad (4)$$

where the surface displacement $u(r)$ is supposed to be $u(r) = a \cos kr$ and E is an external electric field, which is $2\pi e n_s$ under the saturated condition. If we employ the results of Ref. 11, namely, $k \sim 2\pi/200$ nm^{-1}, we obtain a roughness amplitude of about 10 nm in order to reproduce the observed activation energy of the order of 10 K. Obviously the application of Eq. (4) is only qualitative, since there should be a wide distribution of the localized levels. In this sense, ΔE is to be taken as some average of such distributions.

According to Eq. (4) ΔE should increase as the applied voltage V_{dc} is raised, because, qualitatively speaking, the electrons are pulled more

strongly into the troughs of the surface deformation. As Fig. 9 shows, such a behavior is observed indeed. Correlation effects between the electrons, which are known to become important below about 1 K for the charge densities investigated here, should not be essential in the present temperature range $T \geq 2$ K.

Finally, we would like to refer to the conductivity oscillations observed by Paalanen and Iye[2] and Cieslikowski, Dahm, and Leiderer[4] upon condensation of the first few monolayers of helium on solid H_2. Here we have not observed such oscillations, which we attribute to the higher temperature range of our experiment and the corresponding smearing out of the oscillations by thermal fluctuations.
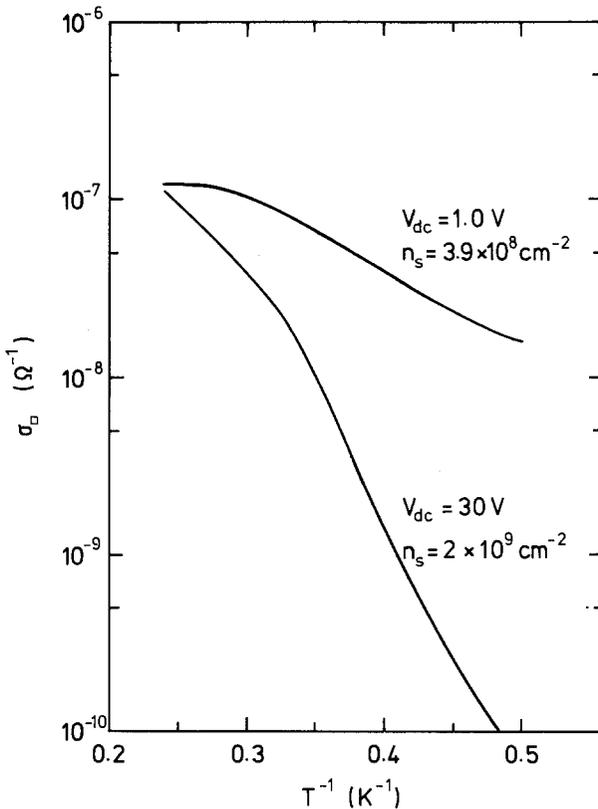

Fig. 9. n_s dependence of the thermal-activation type conductivity. For the sample of $n_s = 3.9 \times 10^8$ cm^{-2}, the applied dc voltage was $V_{dc} = 1.0$ V, the density was determined by a magnetoresistance measurement. For the other sample, $V_{dc} = 30$ V, the density was estimated by using the relation $n_s = C_\square V_{dc}/e$.

5. SUMMARY

In conclusion, we have measured the conductivity of surface-state electrons (SSE) on a quench-condensed hydrogen film. Although the surface was so rough just after the quench condensation that the SSE conductivity was unobservably small, annealing of the hydrogen film improved the surface quality considerably. The temperature dependence of the SSE conductivity after annealing was found to be of thermal-activation type. This fact suggests that the electrons are trapped in random potentials. The activation energy is lowered, as the annealing stage advances.

Although the surface quality of the H_2 films investigated here—measured in terms of the mobility of SSE—was not as high as for the surface of bulk hydrogen, the film system appears to be very interesting for further studies of 2D electrons. It might be expected that optimizing the annealing conditions could lead to further improvements of the surface. Moreover, the solid hydrogen films can be used as a substrate for He films carrying SSE, a subject which is treated in part 2.

ACKNOWLEDGMENTS

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