On the possibility to supercool molecular hydrogen down to superfluid transition

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Recent calculations by Vorobev and Malyshenko (JETP Letters, 71, 39, 2000) show that molecular hydrogen may stay liquid and superfluid in strong electric fields of the order of $4 \times 10^7 V/cm$. I demonstrate that strong local electric fields of similar magnitude exist beneath a two-dimensional layer of electrons localized in the image potential above the surface of solid hydrogen. Even stronger local fields exist around charged particles (ions or electrons) if surface or bulk of a solid hydrogen crystal is statically charged. Measurements of the frequency shift of the $1 \rightarrow 2$ photoresonance transition in the spectrum of two-dimensional layer of electrons above positively or negatively charged solid hydrogen surface performed in the temperature range 7 - 13.8 K support the prediction of electric field induced surface melting. The range of surface charge density necessary to stabilize the liquid phase of molecular hydrogen at the temperature of superfluid transition is estimated.

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The prediction by Ginzburg and Sobyanin [1] that sufficiently supercooled liquid molecular hydrogen may undergo transition to a superfluid state attracts much current attention. Recent theoretical calculations [2,3] show that such a transition may occur around 1.1 - 1.2 K. On the experimental side, a lot of work has been done on molecular hydrogen in porous vycor glass [4,5] and on the thin hydrogen films adsorbed on different substrates [6]. Although some supercooling of liquid hydrogen was indeed observed in the experiment, the temperatures achieved were not sufficiently low to induce superfluid transition.

Very recently a new possibility to produce a strongly supercooled molecular hydrogen state has been suggested on the basis of thermodynamic functions calculation of the molecular hydrogen in both the stable and metastable regions [7]. It has been proposed to expose a two-phase system of solid and liquid hydrogen to the effect of strong external electric field. According to [7], the condition of phase equilibrium in this case may be written as

$$\mu_1(p) - \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_T = \mu_2(p) - \left(\frac{\partial \mu_2}{\partial \rho_2}\right)_T,$$

(1)

where $\mu_1(p)$ and $\mu_2(p)$ are the chemical potentials of the solid (1) and liquid (2) hydrogen phases at pressure $p$, $E$ is the electric field intensity, $\epsilon$ is the dielectric constant, and $\rho$ is the density. The plus sign corresponds to the case when the field is generated by constant charges, and the minus sign corresponds to the field created by constant potential. The action of electric field on the two-phase system may be understood in terms of creation of "different pressures" in the phases. As a result, the liquid and solid hydrogen phases which normally can not coexist at any positive pressure around 1 - 2 K, may coexist in equilibrium with each other around the temperature of superfluid transition at small positive pressures. Unfortunately, the electric field necessary for this to occur is quite large due to the small difference in $\epsilon$ for liquid and solid hydrogen. The result obtained in [7] for the case of field generated by constant potentials and the field lines parallel to the phase boundary looks like

$$E = \left(\frac{24\pi(\mu_1(0) - \mu_2(0))\rho_1\rho_2}{(\epsilon_1^2 + 4\epsilon_1 - 2 - 3\epsilon_2)(\rho_1 - \rho_2)}\right)^{1/2} = 4 \times 10^7 V/cm,$$

(2)

where Clausius-Mosotti relation was used to get the value of $(\partial \epsilon / \partial \rho)_T$, and the following values of dielectric constant and density were accepted: $\epsilon_1 = 1.3$, $\epsilon_2 = 1.25$, $\rho_1 = 0.087 g/cm^3$, and $\rho_2 = 0.078 g/cm^3$. About the same value of the electric field may be obtained for the cases of field created by constant charges and/or field lines perpendicular to the phase boundary. It was unclear for the authors of [7] if such strong fields can be created in solid hydrogen because of dielectric breakdown and other experimental difficulties.

In this Letter I am going to show that strong local electric fields of similar magnitude exist in some real physical systems created in the lab, namely, beneath a two-dimensional layer of electrons localized in the image potential above the surface of solid hydrogen [8]. Even stronger local fields exist around charged particles (ions or electrons) if surface or bulk of a solid hydrogen crystal is statically charged. I am going to present the data of measurements of the frequency shift of the $1 \rightarrow 2$ photoresonance transition in the spectrum of such two-dimensional layer of electrons above positively or negatively charged solid hydrogen surface performed in the temperature range 7 - 13.8 K. These previously unpublished data obtained in [8] strongly support the prediction [7] of electric field induced melting of solid hydrogen. I am also going to estimate the range of surface charge density necessary to stabilize the liquid phase of molecular hydrogen at the temperature of superfluid transition.

Most of the experimental and theoretical work on two-dimensional surface image states above the dielectric sur-
faces with \((\epsilon - 1) < 1\) has been done for the case of liquid helium \([10]\). In the simplest model, the interaction potential \(\phi\) for an electron near the surface of such a dielectric depends only on the electrostatic image force, and on the external electric field \(E\), which is normal to the surface and is necessary for the electron confinement near the surface:

\[
\phi(z) = -e^2(\epsilon - 1)/(4\ell z (\epsilon + 1)) + eEz = -Qe^2/\ell z + eEz
\]

(3)

for \(z > 0\), and \(\phi(z) = V_0\) for \(z < 0\), where the \(z\) axis is normal to the surface, and \(V_0\) is the surface potential barrier. If \(V_0 \to \infty\) one obtains the electron energy spectrum

\[
E_n = -Q^2me^4/(2\hbar^2 n^2) + eE < z_n > + p^2/(2m)
\]

(4)

The first term in this expression gives the exact solution for \(E = 0\). The second term is the first-order correction for a non-zero confining field, where the average distance of electrons from the surface in the \(n\)th energy level is \(< z_n > = 3n^2\hbar^2/(2me^2Q)\). This correction provides an extremely convenient way of fine-tuning the energy spectrum. The last term corresponds to free electron’s motion parallel to the surface. It is important to mention that at sufficiently high electron density individual electrons in these surface states are no longer free. When the average electrostatic potential energy per electron exceeds about \(100k_BT\) the electron layer undergoes transition into the two-dimensional Vigner crystal state \([8]\) with the parallel motion of individual electrons substantially restricted by other electrons in the lattice of the Vigner crystal.

Similar two-dimensional electron layers have been observed on the surface of liquid and solid hydrogen. Resonance absorption of light for \(1 \to 2\) and \(1 \to 3\) transitions in the spectrum of electrons levitating above the surface of solid hydrogen has been reported and the frequencies of these transitions were measured as a function of the confining electric field \([\overline{3}]\). While general agreement with the spectrum (4) within 30% has been observed, quite a few important questions have been raised by these experiments which have not yet found satisfactory answers. The most striking feature of this system is a very strong dependence of the photoresonance frequencies on the hydrogen temperature (or vapor pressure). The frequency of \(1 \to 2\) transition in zero confining field grew by 20% on the cooling down from 13.6 K to 7 K. In the absence of any other competing theory at the time of the measurements, this effect was interpreted in terms of quantum refraction \([\overline{13}]\) due to the presence of hydrogen vapor molecules around the levitating electrons. For this explanation to be true, the scattering length value for the scattering of an electron by a hydrogen molecule has to be equal to \(L = -1.4\AA\), contrary to the currently accepted value of \(L = +0.672\AA\) \([12]\). On the other hand, if spectral changes are completely attributed to the increase in the value of \(Q = (\epsilon - 1)/(4(\epsilon + 1))\), the frequency shift may be interpreted as a gradual freezing of the supercooled liquid hydrogen film on top of the hydrogen crystal (with an increase of the dielectric constant of the thin surface layer from the liquid hydrogen value of 1.25 to the solid hydrogen value of 1.3). This consideration raises an important question: how strong is the electric field on the surface of the solid hydrogen just below an electron in the ground surface state? Can it cause a substantial supercooling of the liquid molecular hydrogen phase on the surface?

If we imagine for a moment that the electron is not moving parallel to the surface, the answer is very easy to get. We may forget about small contribution from the electron’s image and write the average value of the local field as \(< E_L > = e/\ell z^2 > = 9e/(2 < z_1 >^2)\), where we have used the ground state wave function for an idealized potential (3) with an infinite potential barrier. Taking into account the experimentally observed value of \(< z_1 > = 20\AA\) \([\overline{3}]\), we obtain \(< E_L > = 1.6 \times 10^7V/cm\). This field is of the same order of magnitude as the field that is (according to \([\overline{3}]\)) sufficient to stabilize superfluid liquid hydrogen phase.

Unfortunately, free electrons rapidly move around the surface and every region of solid hydrogen surface experiences this strong electric field for very brief periods of time. This situation changes at sufficiently high electron density and low temperature when the electron layer undergoes transition into the Vigner crystal state. In this state the motion of each individual electron is substantially restricted to a small area around electron’s equilibrium position in the Vigner crystal lattice by electrostatic interaction with other electrons in the lattice. Let us estimate the size of this area for the parameters of the electron system typically observed in the experiment.

The density of electrons on the solid hydrogen surface is determined by the external confining field: \(n \leq E/(4\pi\varepsilon)\) \([\overline{6}]\). Density values of the order of \(3 \times 10^{10} - 10^{11}cm^{-2}\) were routinely observed. At \(n = 10^{11}cm^{-2}\) an electrostatic potential energy per electron is of the order of \(e^2/2 = 540k_B \times 1K\). Thus, at \(T = 1K\) such an electron system will be in two-dimensional Vigner crystal state. Classically allowed area of electron’s motion around its equilibrium state in the lattice may be estimated by taking into account only the nearest neighbors located at a distance \(d\) from each other. For the potential energy we may write approximately

\[
V = e^2/(d - x) + e^2/(d + x) = 2e^2/d + 2e^2x^2/d^3
\]

(5)

where \(x\) is the displacement towards the nearest neighbor. Immediately we obtain an estimate for the radius of the allowed area as \(x = n^{-1/2}(k_BT/(e^2n^{1/2}))^{1/2}\). At \(T = 1K\) and \(n = 10^{11}cm^{-2}\) this radius is approximately 10\AA. Thus, an electron stays over the same region of the hydrogen surface. We may now conclude that at the above mentioned parameters of the electron system and at the temperatures near the temperature of suspected
superfluid transition a substantial portion of the solid hydrogen surface under the electrons will experience strong electric fields of the order of the field necessary to induce the superfluid transition. Taking into account that the maximum density of surface electrons may be substantially increased with respect to the values observed in [8], this system looks extremely promising for observation of superfluid transition of the supercooled molecular hydrogen.

Another evident way to create even stronger local electric fields inside a solid hydrogen crystal is accumulation of static electric charge in the form of positive or negative ions and bound electrons on the surface or in the bulk of hydrogen crystal. Such an accumulation of negative and positive static charge was a routine problem in our spectroscopic experiments. The detection of static charge has been discussed in detail in [8]. The results of these experiments published so far were carefully selected to avoid any influence of static charges which were considered to be a problem. Nevertheless, the influence of negative and positive static charge of the hydrogen surface on the frequency and the linewidth of photoresonance $1 \rightarrow 2$ transitions was carefully measured and reported in [8]. Because of the recent appearance of paper [7] and considering the arguments above, I feel necessary to make physical community aware of these results.

The most careful measurements of the influence of negative static surface charge on the frequency and linewidth of $1 \rightarrow 2$ transitions were performed at a fixed temperature $T=13.4K$ ($P=40$ Torr), just below the triple point of hydrogen. The negative surface charge was formed by energetic electrons which were not stopped by the surface potential barrier $V_0$ upon the deposition of free electrons on the solid hydrogen surface. Fig.1 reproduces the data of these measurements as they were presented in [8]. Both the frequency shift and the line broadening was measured at a fixed wavelength of excitation light by tuning the confining field $E$. The negative frequency shift and the line broadening were measured at fixed wavelengths of excitation light ($79 \mu m$ and $84.3 \mu m$) by tuning the confining electric field $E$. Energy spectrum (4) must be used to convert these data into the units of frequency. The dashed line has a slope of $2\pi$.

Similar negative frequency shift was observed also in the case of positive static surface charge, although detailed measurements of the frequency shift and line broadening were not conducted in this case. It was possible to create a two-dimensional electron layer on the surface of positively charged hydrogen crystal (in zero or even repulsive external electric field $E$). Both positive ions charging the surface and free electrons were deposited in turn on the surface of hydrogen crystal at $P=5$ Torr hydrogen vapor pressure from the gas discharge created in the experimental chamber. The life time of free electrons in such a system was longer than an hour which allowed us to perform spectroscopic measurements shown in Fig.2. Photoresonance $1 \rightarrow 2$ transition has been detected in such a system at $\lambda = 118.6 \mu m$ wavelength of excitation light at $N \sim 10^{10} cm^{-2}$ density of positive ions deposited onto the hydrogen crystal surface. This corresponds to the frequency of $1 \rightarrow 2$ transition substantially below the frequencies of $1 \rightarrow 2$ transitions in zero confining field observed in surface electron layers in the absence of static charge in all the temperature range studied (7-13.8 K). The fact that negative frequency shift is observed both for positive and negative static surface charge is a strong argument in favor of electric field induced liquid hydrogen supercooling phenomenon.
FIG. 2. Photoresonance 1 → 2 transition detected at λ = 118.6 μm wavelength of excitation light in the two-dimensional electron layer levitating above the surface of positively charged ∼ 0.5 mm thick solid hydrogen crystal. The signal (b) proportional to the derivative of the optical absorption was recorded while scanning the potential of the electrode located below the hydrogen crystal (note that the external field applied to the electrode is repulsive for the surface electrons). The upper curve (a) show the non resonant radio frequency absorption of the electron layer used to characterize the electron density [8]. Positive ions charge the hydrogen surface at point (1) when gas discharge was created in the experimental chamber. When the potential of the electrode was reversed, the gas discharge appeared again at point (2) leading to the appearance of free electrons on the hydrogen surface. The curve (b) was measured on the way from (2) to (3). At point (3) free electrons started to leave the hydrogen surface. They completely disappeared at point (4).

Although the physical location of static charges with respect to the hydrogen surface is not as clear as in the case of free electrons (and, hence, the sample is not as well characterized) our data show that the charged solid hydrogen phase is easily accessible to experiments, and it is a very interesting physical object from the point of view of superfluid molecular hydrogen observation. If $E_λ$ is a field necessary for supercooled liquid hydrogen at the temperature of superfluid transition occur naturally in such existing physical systems as electrons levitating above the surface of solid hydrogen and statically charged hydrogen crystals. The results of photoresonance measurements performed on the system of levitating electrons with and without static surface charge strongly indicate the possibility of liquid hydrogen supercooling in these systems. It would be extremely interesting to study the behavior of charged solid hydrogen at temperatures around T=1 K with the goal of the observation of supercooled superfluid hydrogen phase.

[1] V.L. Ginzburg and A.A. Sobyanin, JETP Lett. 15, 242 (1972).
[2] M.C. Gordillo and D.M. Ceperley, Phys.Rev.Lett. 79, 3010 (1997).
[3] S.M. Apenko, Phys.Rev.B 60, 3052 (1999).
[4] M. Schindler, Y. Kondo, and F. Pobell, J.Low Temp.Phys. 110, 549 (1998).
[5] D.F. Brewer, J.C.N. Rajendra, and A.L. Thomson, J.Low Temp.Phys. 101, 317 (1995).
[6] M.D. Evans and N.S. Sullivan, J.Low Temp. Phys. 100, 535 (1995).
[7] V.S. Vorobev and S.P. Malyshenko, JETP Lett. 71, 39 (2000).
[8] V.V. Zavyalov and I.I. Smolyaninov, JETP 65, 194 (1987).
[9] I.I. Smolyaninov, Ph.D. Thesis, Kapitza Institute for Physical Problems, Moscow, Russia, 1990 (In Russian).
[10] V.S. Edelman, Sov.Phys.Usp. 23, 227 (1980).
[11] E.P. Bashkin, JETP 55, 1076 (1982).
[12] R.W. Crompton and M.A. Morrison, Phys.Rev.A 26, 3695 (1982).
[13] V.V. Zavyalov and I.I. Smolyaninov, JETP 67, 171 (1988).