PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Effect of Pressure on the Electron Mobility in Solid Helium†

V. E. Dionne,* R. A. Young,‡ and C. T. Tomizuka
Department of Physics, University of Arizona, Tucson, Arizona 85721
(Received 28 September 1971)

The effect of pressure on the mobility of the cavity-localized electron in solid helium has been studied to a pressure of 6660 atm. No delocalized electron state has been detected at this pressure below the melting point of the solid. It is shown that the results are consistent with the presence of electron bubbles at the highest pressures investigated. The nature of possible charge-trapping mechanisms that might account for the results is discussed.

INTRODUCTION

The study of properties of excess electrons in liquid[1-3] and gaseous[4,5] helium has received much attention during the past decade. The localized nature of the excess electron has been demonstrated both experimentally and theoretically. Its configuration as a bubble has been well established. With several exceptions, relatively little has been investigated in solid helium in which the electron is also localized. Keshishev, Mezhov-Deglin, and Shal'nikov[6] made preliminary measurements which have established a lower limit for the mobility of electrons in ^{4}He crystals. Cohen and Jortner[7] have extended theoretical considerations initially made for the liquid and gas phases to the problem of excess electrons in solid helium.

Within a broad range of helium densities the excess electron is self-trapped in a cavity whose radius is several times the interatomic distance. The cavity is the minimum free-energy configuration in helium associated with a weakly attractive long-range electron–helium-atom polarization potential and a strong short-range electron-atom re-

TABLE I. Electron mobility in four rare-gas solids. T_c is the critical temperature and T is the temperature at which the measurement was made. Pressure was 1 atm, except for helium which was measured at 38 atm.

Species	T_c(°K)	T/T_c	μ (cm^2/V sec)
Xe[a]	289.8	0.54	4.5×10^3
Kr[a]	209.4	0.54	3.7×10^3
Ar[a]	150.7	0.54	1.0×10^3
He^4[b]	5.20	0.47	$\geq10^{-5}$

[a]Reference 9. [b]Reference 6.

pulsion.[8] Among solids, this mode of electron localization is unique to helium. In a comparison of the electron mobility in solid helium to other rare-gas solids, the cavity-localized electron of helium is at least 10^5 times less mobile than the free electrons of argon, krypton, or xenon (Table I).

In their theoretical treatment of the localized electron in solid helium, Cohen and Jortner[7] proposed an experiment to increase the helium density in an attempt to raise the localized electron energy level above that of a free-electron state. The energetically favored delocalized electrons would be expected to behave in a manner similar to electrons in other rare-gas solids. In particular, their mobility should increase several orders of magnitude. This transition is expected to take place at about 4000 atm according to their calculation. This paper reports on the search for the delocalized electron state in helium.

EXPERIMENTAL METHOD

The experiment consists of a series of electron-mobility measurements at low temperatures and high pressures. A null current method, after Cunsolo,[10] is used to monitor any pressure-induced mobility change. A glass or other nonconducting sample vessel has an extremely limited capacity for pressure containment and is not suitable for the present purpose. A fully hardened beryllium-copper vessel is used. The simple linear array of electrodes commonly used with the null current measurement of carrier mobility is not practical with a metal vessel. A cylindrical electrode configuration in which the pressure vessel becomes a guard electrode is successfully employed.

The gas pressure generating apparatus of the pressure system, similar to that of Goldsmith and Heard,[11] is separated by a high-pressure valve from the sample vessel and pressure gauge (Fig. 1). A 100 000 lb/in.^{2} Heise gauge with rated accuracy of ±100 lb/in.^{2} is used to measure pressure. The sample vessel, constructed of hardened beryllium copper, (Berylco 25 alloy, The Beryllium Corp., Reading, Pa.) is sealed at its closure plug with a brass Bridgman extrusion ring. The mobility probe is mounted directly on the closure plug. The high-pressure solid-helium sample is frozen isochorically from pressurized helium gas generated at room temperature. At the highest working pressures less than 10% of the generated pressure is lost in lowering the vessel temperature from 300 to 4.2 °K.

A thin cone of EC 2850 GT Epoxy (Emerson and Cuming, Inc., Canton, Mass.) is used in place of the standard pipestone or lavite cone for electrical lead insulation. This substitution allows all the insulated electrical leads to be sealed in a single cone. No detectable leak is present when the system is isolated by the valve and the vessel is filled with solid helium.

The current probe (Fig. 2) consists of three concentric cylindrical electrodes, the source, grid, and collector. These are mounted concentric with the pressure vessel cavity. The vessel serves as a guard electrode. The electrodes are separated by supports made of Hysol CP2-4289 Epoxy (Hysol Corp., Olean, N. Y.). Both Epoxy insulating materials are chosen for their high volume resistivity. (Hysol CP2-4289: 6×10^{14} ohm cm at 298 °K; EC 2850 GT: 5×10^{16} ohm cm at 298 °K.) The collector electrode is gold-plated copper. The grid and source electrodes are made of brass and copper, respectively. Connections to the electrodes and the entire electrical network are made with low-thermal solder.

The flux of excess electrons is provided by ionization of helium atoms in the vicinity of the source electrode by α-particle radiation from 10 μCi of polonium 210 plated on the source electrode. In solid and liquid helium the range of the 5.30-Mev α particles is less than 0.3 mm.[1] This ensures

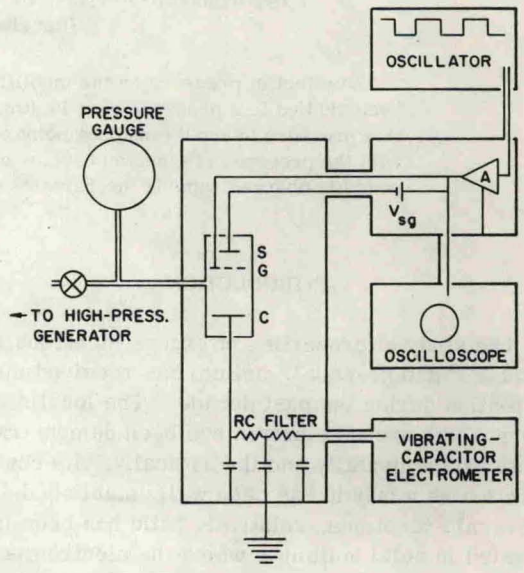

FIG. 1. Schematic diagram of the apparatus.

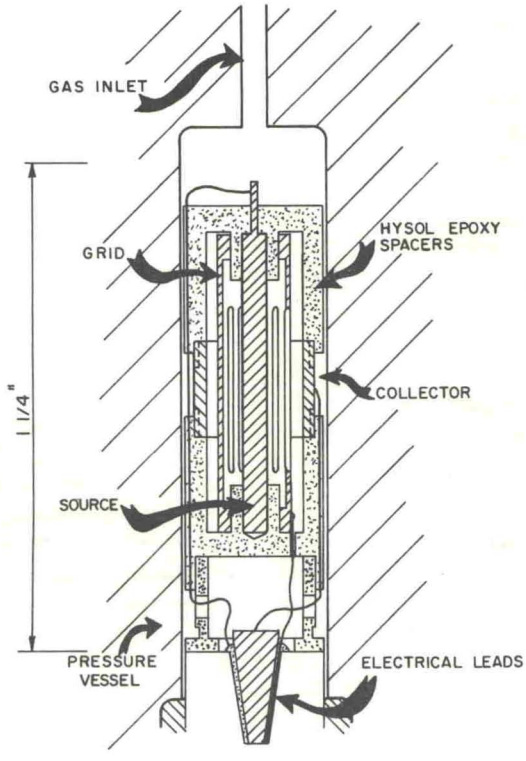

FIG. 2. Cross-sectional view of assembled probe.

that free electrons are not created in the drift space between the grid and collector. Both positive and negative ions can be extracted to the grid depending on the field polarity applied to them.

Temperature is maintained by immersing the high-pressure vessel in a pumped bath of liquid helium which is kept stable to within 0.05 °K during measurement. Temperature regulation is provided simply by controlling the bath vapor pressure with the pumping speed. A calibrated germanium resistance thermometer is used to measure bath temperatures which can be varied between 1.2 and 4.2 °K.

SAMPLE PURITY

The problem of sample purification in this type of measurement has received extensive consideration by many investigators.[9,12] The operation of the gas high-pressure-generating apparatus inevitably introduces impurities and one cannot obtain helium purity as high as that attainable in low-pressure measurements. Precautions are taken to minimize oxygen contamination of the system, primarily by keeping an overpressure of high-purity argon or helium in it at all times. The solid helium is frozen from 99.9999%-pure helium gas as purchased from Matheson Gas Products (East Rutherford, N. J.). To purge contaminants from the pressure system it is alternately filled to tank pressure and bled back to 50–100 lb/in.^{2} six times before it is pumped to working pressure. In the high-pressure runs the gas is pressurized at room temperature and the pressure vessel and gauge are isolated from the rest of the system by the line valve before cooling. Before the sample is cooled to solidification, an electric field of reverse polarity is applied between the source and grid electrodes. This procedure removes charged impurities, such as oxygen molecules which capture electrons, and it generally results in significantly lower background-current levels.

PROBE CALIBRATION

Accurate determination of the electron mobility requires evaluation of the effective probe dimensions as well as determination of the carrier transit time T_0 between the grid and collector in a known field E_g. To maximize the probe sensitivity, the grid-collector separation is minimized. Of the two radii (i.e., grid and collector) which characterize the drift space, only the collector radius r_c can be determined directly. The grid is a thin-walled cylinder with slots along its length; the effective grid radius lies within the thickness of its walls. Two grids have been built and used successfully. The most sensitive probe incorporates a grid whose wall thickness is 0.010 cm. A thinner wall does not offer sufficient structural rigidity. The grid is calibrated by comparing the pressure dependence of the mobility of both positive and negative ions in liquid helium with known results[6] at 4.2 °K. Calibration results for this grid are shown in Fig. 3. With a cylindrical electrode probe the mobility of an ion is given by

$$\mu = \frac{1}{2T_0 V_g}\,(r_c^2 - r_g^2)\ln\left(\frac{r_c}{r_g}\right).$$

This expression can be used to determine r_g and the sensitivity of the equipment. The effective grid radius is determined to be

$$r_g = 0.303 \pm 0.001 \text{ cm}.$$

This gives a drift distance

$$d = 0.015 \pm 0.002 \text{ cm}.$$

In performing the probe-calibration experiments in liquid helium satisfactory pressure can be generated by the helium supply tank. In these experiments the pressure generating equipment is bypassed and the helium tank is connected to the high-pressure gas line entering the vessel. For work in the liquid, the apparatus is limited to detection of transit time T_0 below 0.25 sec by the output RC-filter network and the power supplies. The response time with this equipment configuration is less than 1 min. Alterations to the RC-filter network to increase

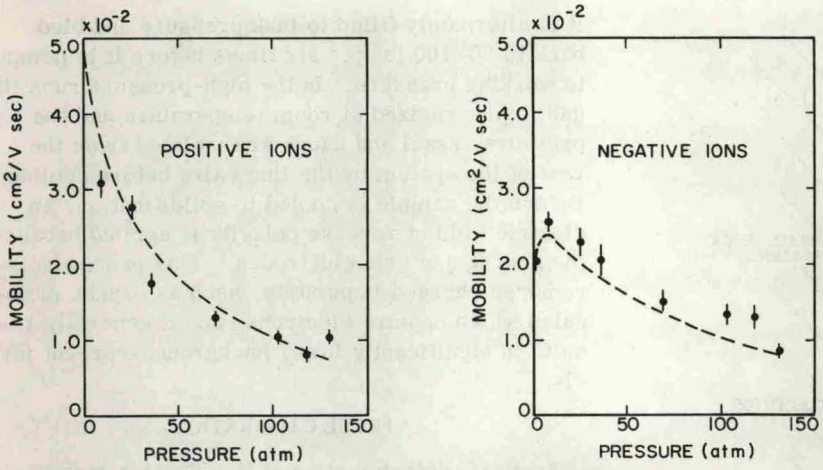

FIG. 3. Calibration results for the most sensitive probe. Ion mobility vs pressure, 4.2 °K. Dashed curves from Keshishev, Mezhov-Deglin, and Shal'nikov (Ref. 6).

the transit-time-detection limit to a maximum of 2.5 sec have resulted in a response time of nearly 30 min. This latter arrangement has been tested in liquid helium to confirm its accuracy and is used in solid helium only with the most sensitive probe.

EXPERIMENTAL RESULTS

Electron-mobility measurements in high-density helium at low temperatures have been performed over a wide pressure range. The measurements in solid helium are supplemented by isolated measurements in the liquid at very low temperatures and in the dense gas at a temperature of approximately 80 °K.

In solid helium the probe sensitivity was 1.6×10^{-6} cm^2/V sec. At 4.2 °K no charge transport was observed at pressures up to 6400 atm in a maximum field of 3300 V/cm. Similar measurements at 1.2 °K and 32 atm yielded the same result. Two experimental runs were performed at high pressure in which the temperature of the helium sample was allowed to rise above the melting temperature from 4.2 °K. In both cases fast probe response was needed to follow the warm-up, thus necessitating use of probe sensitivities an order of magnitude poorer than that attainable with the slow probe. The first run terminated with a pressure of 6270 atm at the melting point of 45 °K, and the second sample melted at 48 °K with a pressure of 6660 atm. Electronic charge transport was not observed in these runs at any temperature below the melting point. The present results, in spite of comparable probe sensitivity, do not agree with the results obtained by Keshishev *et al.*[6] who report the negative-ion mobility value of 9.7×10^{-6} cm^2/V sec in a field of 1.52×10^4 V/cm at 1.96 °K and 38 atm.

Measurements in liquid helium at temperatures below 4.2 °K are in satisfactory agreement with work published by other experimenters. These results are reproducible when the sample phase is cycled from liquid to solid and back to liquid, indicating that no damage has been sustained by the probe during the phase changes.

The results of mobility measurements made in the dense gas at 6760 atm and 80 ± 10 °K of both the positive and negative charge carriers are given below:

$$\mu_- = (3.1 \pm 0.5)\times10^{-3}\ cm^2/V\ sec\ ,$$

$$\mu_+ = (4.9 \pm 0.6)\times10^{-3}\ cm^2/V\ sec\ .$$

The large uncertainty in the temperature results from a lack of sensitivity in the germanium resistance thermometer in this temperature range and from lack of provision for thermal stabilization above liquid-helium bath temperatures.

DISCUSSION

Two explanations may account for the results of the present experiments. First, the localized electron state may not collapse at or below the applied pressure. Second, the electrons may be trapped by imperfections in the solid phase whether they are cavity localized or quasifree.

Let us first assume that no ion-trapping mechanisms of sufficient strength or number are present in the solid-helium sample. Earlier work has confirmed the presence of cavity-localized electrons in the solid phase at low pressures.[6,7] The existence of localized electron states at the maximum pressure applied is indicated by both direct and indirect experimental results. Primary evidence is given by the fact that no high-mobility ion was detected in the solid below its melting temperature. Indirect evidence comes from analysis of the present results in the dense gas. It is shown below that electron bubbles with a radius of approximately 6 Å exist in the gas at densities similar to that in 4000-atm solid helium. Thus, to the extent

that electron localization is independent of the degree of order in solid or gaseous He, the experimental results conclusively show that the electron state is localized in the solid up to pressures of 4000 atm. Furthermore, since helium does not undergo a large volume change on melting (< 5%) it is most probable that similar sized bubbles exist in the solid near the melting point at 6760 atm. Thus the present observations are consistent with the presence of cavity-localized electrons in the solid at the highest experimental pressure which is approximately 60% larger than the 4000 atm estimated by Cohen and Jortner.[7]

The size of the negative ion in the dense gas can be estimated in the following manner. Stokes's Law gives a classical hydrodynamic expression for the mobility of a charged solid sphere in a viscous fluid[13]:

$$\mu = e/6\pi\eta R ,$$

where e is the electronic charge, η is the viscosity of the fluid, and R is the radius of the sphere. One can determine the viscosity of the dense gas by using the measured value of μ for the positive ions and a theoretical value of the positive ion radius. This radius is calculated using Atkins's model[14] for positive ions in liquid helium which takes into account the effect of electrostriction on the effective mass of the ion. Accordingly, the ion radius is given by

$$R_+ = \left(\frac{N\alpha e^2}{2V_M \epsilon_0^2 (p_s - p)}\right)^{1/4} ,$$

where $N\alpha$ is the molar polarizability, p_s is the solidification pressure, p is the external pressure, V_m is the molar volume, and ϵ_0 is the permittivity of vacuum. The polarizability is $N\alpha/V = 6\times10^{-3}$ C^2 sec^2/g cm^3.[13] This gives

$$R_+ = 3.9\times10^{-8} \text{ cm.}$$

This leads to a calculated viscosity of the dense helium gas near 80 °K of

$$\eta = 4.4\times10^{-4} \text{ P.}$$

From the measurement of μ_- at this pressure and temperature and the above estimate of η one can obtain the electron-bubble radius

$$R_- = 6.2\times10^{-8} \text{ cm.}$$

This estimate of the bubble radius is consistent with the measurements of Triftshäuser *et al.*,[15] who find $R_- \approx 8$ Å at 170 atm in solid helium.

The density of the helium gas has been estimated by scaling the reduced molar volume as a function of the reduced temperature. The molar volume measurements of Bridgman[16] in helium gas at 65 °C and the PVT data of Dugdale[17] were used to obtain the value $V_M = 9.1$ cm^3/mole. The corresponding density is $\rho = 0.44$ g/cm^3 which is similar to that in solid helium at 4000 atm.

To summarize, we have assumed that the effect of trapping is negligible in the solid-helium sample and shown as a result that cavity-localized electrons persist to pressures of 6400 atm and all temperatures below the melting point of the solid. This pressure is well in excess of the minimum collapse pressure of 4000 atm calculated by Cohen and Jortner.

Let us now reexamine their solution to the problem of excess electrons in solid helium to see if a more accurate critical pressure can be calculated using the present results. Following Cohen and Jortner[7] the energy of the cavity-localized electron can be written

$$E_t = X V_0 + \tfrac{4}{3}\pi R_0^3 p + 4\pi R_0^2 F_s .$$

These terms account for the increased electron energy due to confinement in the cavity, work done against pressure to create the cavity, and work done against the surface stress, respectively. V_0 represents the energy of a quasifree electron, estimated by a Wigner-Seitz calculation, and X is a parameter related to the cavity-edge boundary conditions.[18] R_0 is the cavity radius and p is the external pressure. F_s is the surface free energy of the cavity. In their work, Cohen and Jortner used the low-energy electron–helium-atom scattering length $a = 1.13$ a.u. $= 0.60$ Å as the radius of a hard sphere which was their model of the electron-helium potential used in the Wigner-Seitz calculation.[19] However, in the present case the increased pressure leads to a significant decrease in the Wigner-Seitz radius. The resulting Bloch wave function corresponding to $\vec{k} = 0$ will now contain a significant amount of high-energy plane-wave components. The presence of these high-energy components implies that the simple low-energy constant scattering length approximation is no longer quantitatively correct and the complete energy-dependent nonlocal electron-helium pseudopotential[8] must be used to determine V_0 by the Wigner-Seitz method.

It is not the purpose of the present work to perform such a calculation. We can, however, obtain a qualitative understanding of how inclusion of the complete pseudopotential will affect V_0 by simply allowing the scattering length to be a function of energy. Let us estimate the energy values for the highest non-negligible components of the $\vec{k} = 0$ Wigner-Seitz wave function by

$$E = \hbar^2 k^2/2m ,$$

where

$$k \approx \pi/r_s ,$$

and r_s is the Wigner-Seitz radius. This gives

$$E \approx 10 - 14 \text{ eV.}$$

The effective s-wave core radius can be estimated from calculations of the electron-helium atom cross section.[20] One obtains

$$0.46 \leq \alpha(E) \leq 0.54 \text{ Å} .$$

Recalling that the total electron energy must be less than V_0 if the electron is to be localized in the cavity, we have calculated the pressure dependence of V_0 for three values of the helium-atom model-potential radius α. This is shown in Fig. 4 and demonstrates the strong dependence of V_0 at any pressure on this parameter. At sufficient pressure, E_t must exceed V_0 regardless of the value of α and the nonlocalized electron state will be favored. The pressure-induced collapse criterion for the cavity-localized electron state can be written[7] as

$$p \gtrsim \frac{3}{4\pi}(1 - X^2)\frac{V_0}{R_0^3} .$$

When one adopts a reasonable bubble radius in the range of 4 – 7 Å and appropriate values for X this expression reduces to

$$p \gtrsim 720\ V_0^{5/2} ,$$

where p is expressed in atmospheres and V_0 in electron volts. Using values of V_0 from Fig. 4 for $\alpha = 0.60$ Å, we find that the bubble does not collapse at any pressure. However, application of suitably high pressures for

$$0.46 \leq \alpha \leq 0.54 \text{ Å}$$

will result in collapse of the electron cavity. We estimate critical pressures of

$$p \gtrsim 20 \times 10^3 \text{ atm} \quad (a = 0.54 \text{ Å}) ,$$

$$p \gtrsim 3 \times 10^3 \text{ atm} \quad (a = 0.46 \text{ Å}) .$$

The strong dependence of the critical pressure on the core size makes it very difficult to establish reasonable estimates for this quantity. In view of the large uncertainty associated with the estimation of collapse pressure, the results presented here are understandable. Although we have applied pressure 60% in excess of the minimum predicted for collapse of the cavity-localized electron state by Cohen and Jortner,[7] and have failed to see the collapse, it is certainly possible that a 500% excess may be needed.

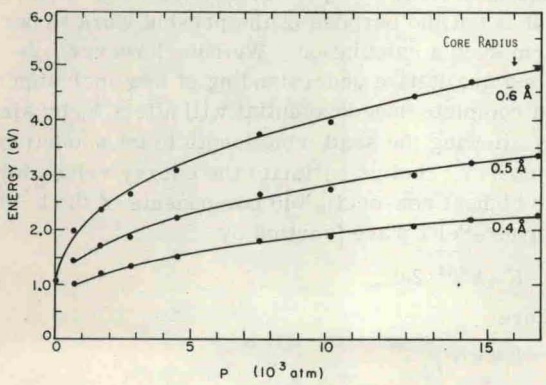

FIG. 4. Pressure dependence of Wigner-Seitz energy calculation of V_0.

The likelihood that the cavity-localized electron states in solid helium have not collapsed at the pressures applied is consistent with the observation that there is no high-mobility charge carrier in the solid at these pressures. However, it fails to account for the fact that within the sensitivity of the instrument the charge carriers are not detected at all in the solid. The possible causes for this apparent total immobility are insufficient instrument sensitivity, actual immobility of the localized electrons, and trapping of the electron. The last possibility is consistent with either a localized or delocalized electron, and both must be considered, although we have shown the probable existence of the cavity-localized electron at all experimental pressures of the present work. Neither insufficient sensitivity nor actual bubble immobility alone are complete explanations of these data. The work of Keshishev *et al.*[6] at higher electric fields and at low pressure indicates that both current and mobility sensitivity are satisfactory in the present work, and that, at least in very high electric fields, the localized electrons are mobile enough to have measurable speed under optimum crystal conditions. It is therefore probable that some type of trapping is effective for the excess electrons.

Structural faults such as vacancies and crystal grain boundaries can exist in the solid as well as charged and uncharged impurities. In addition, trapping at the interface between the electrodes and the solid helium is a possible mechanism that would be highly effective for the electrons. A high density of voids in the solid is a possible source of traps in the vicinity of the source electrode where they could be created by radiation damage from the polonium 210. Trapping on the crystal grain boundaries in the solid is also a possible mechanism. The effectiveness of both the void and grain-boundary traps should be strongly temperature dependent, and both should be effective for localized and quasifree electrons. Considering the wide range of temperature employed for the present work, one should have been able to observe some charge release from the traps at temperatures approaching the melting point. This would be especially so for normally quasifree electrons. Impurities as traps may be discounted since they should be nearly as effective in the liquid as in the solid. Finally, we must consider the trapping mechanism operating at the grid–solid-helium interface.

The electrons are created between the source

and grid of the probe and pass through the grid with a forward electric field into the drift space. If we assume an appreciable decrease in density in the solid helium wherever it is in contact with a surface, then such a density fluctuation would serve as a very effective trap for electrons near the grid. Thus, even with a forward electric field between the grid and collector the electrons would remain trapped at the grid, enter the grid-source circuit, and go undetected at the collector. At the present time we know of no evidence for the existence (nor of the absence) of the necessary density variation to account for this trap. This type of trapping mechanism is, however, consistent with the conclusion of Keshishev *et al.*[6] that one must minimize the number of grids present in order to obtain satisfactory mobility measurements.

Strictly speaking, mobility is only defined in the limit as the electric field strength approaches zero. Although Keshishev *et al.*[6] have "measured" the electron mobility in electric fields of 15 200 V/cm, they have established only a lower value for the zero-field mobility. It is desirable to make measurements at lower fields to determine the field dependence. Considering the problems in the present experiment which are associated with the presence of the grid and the use of polonium 210, one can suggest an alternate method to measure the cavity-localized electron mobility. It would use a two-electrode probe with a tritium-impregnated–titanium beta source. This would ensure creation of the electrons in the bulk of the drift space (their energy being large enough to escape any traps at the source electrode) and minimize the probability of radiation damage to the solid helium. The disadvantage of such a probe is the necessity to account for the effective region in which the cavity-localized electron is created.[21]

---

†Research supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-1041. Work performed in partial fulfillment of the requirement for the degree of Doctor of Philosophy for V. E. D.

*Present address: Department of Physiology and Biophysics, School of Medicine, University of Washington.

‡Alfred P. Sloan Research Fellow.

[1]F. Reif and L. Meyer, Phys. Rev. 119, 1164 (1960).

[2]W. T. Sommer, Phys. Rev. Letters 12, 271 (1964).

[3]M. A. Woolf and G. W. Rayfield, Phys. Rev. Letters 15, 235 (1965).

[4]H. R. Harrison, thesis (University of Michigan, 1971) (unpublished).

[5]J. L. Levine and T. M. Saunders, Phys. Rev. 154, 138 (1967).

[6]K. O. Keshishev, L. P. Mezhov-Deglin, and A. I. Shal'nikov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 12, 234 (1970) [Sov. Phys. JETP Letters 12, 160 (1971)].

[7]M. H. Cohen and J. Jortner, Phys. Rev. 180, 238 (1969).

[8]J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, J. Chem. Phys. 43, 2614 (1965).

[9]L. S. Miller, S. Howe, and W. E. Spear, Phys. Rev. 166, 871 (1968).

[10]S. Cunsolo, Nuovo Cimento 21, 76 (1961).

[11]J. R. Goldsmith and H. C. Heard, J. Geol. 69, 45 (1961).

[12]H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. 150, 127 (1966).

[13]R. G. Arkhipov, Usp. Fiz. Nauk 88, 185 (1966) [Sov. Phys. Usp. 9, 174 (1966)].

[14]K. R. Atkins, Phys. Rev. 116, 1339 (1959). In using the macroscopic Atkins model for the positive ion we are neglecting the possibility that the positive-ion mobility may be that of a stable He_2^+ molecule interacting with its surroundings. The Atkins model may therefore only be expected to yield order of magnitude effects.

[15]W. Triftshäuser, J. Legg, A. T. Stewart, and C. V. Briscoe, in *Proceedings of the Eleventh International Conference on Low Temperature Physics* (St. Andrews Printing Department, University of St. Andrews, St. Andrews, Scotland, 1968), p. 304.

[16]P. W. Bridgman, *The Physics of High Pressure* (Bell, London, 1958).

[17]J. S. Dugdale, Nuovo Cimento Suppl. 9, 27 (1958).

[18]B. E. Springett, M. H. Cohen, and J. Jortner, Phys. Rev. 159, 183 (1967).

[19]J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, *Modern Quantum Chemistry, Istanbul Lectures*, edited by O. Sinanoğlu (Academic, New York, 1966), p. 129.

[20]R. W. LaBahn and J. Callaway, Phys. Rev. 135, A1539 (1964).

[21]R. L. Williams, Can. J. Phys. 35, 157 (1957).