Electron Cavity Formation in Solid Helium*

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In this paper we consider a trapping mechanism for excess electrons in solid helium. Structural modifications are energetically favored in this system resulting in the localization of the excess electron in an expanded cavity of a radius of ~9 Å. The optical and the transport properties of this trapping center are qualitatively examined. A pressure induced transition from the localized to the delocalized state of the excess electron is considered.

Recent experimental work[1,2] on the motion of charge carriers in solid helium reveals the following surprising features: (a) The electron mobility (as roughly deduced from the current measurements) is low, being of the same order of magnitude as in liquid helium[1] ($\mu \sim 10^{-2}$ cm^2 V^{-1} sec^{-1}).[3] (b) The temperature coefficient of the mobility is positive.[2] These features radically differ from the properties of excess electrons in other solid rare gases (e.g., Ar, Kr, and Xe)[4] where extremely high electron mobilities ($\mu = 1000 - 4000$ cm^2 V^{-1} sec^{-1}) were recorded, and where the temperature coefficient of the mobility is negative,[4] as expected for a quasifree electron in a conduction band. These experimental data lead us to propose that a stable localized state of the excess electron is formed in solid helium. In view of the strong short-range electron-helium atom repulsion, and the weak long-range polarization interactions in solid helium, the quasifree electron state is energetically unstable. Structural changes are favored in the solid resulting in the localization of the excess electron in a cavity. This picture provides us with a mechanism of electron trapping which is unique in a solid, but which is analogous to the bubble model for electron localization in liquid helium[5-10] and liquid hydrogen,[11] and for positronium localization in liquid He,[12] H_2, Ne, and Ar.[13]

Our general physical arguments will be presented as follows: We shall first estimate the ground-state energy of the quasifree electron state in solid helium by the Wigner-Seitz method. Subsequently, we shall demonstrate that a stable configuration of the localized state of the excess electron in the solid is achieved which is characterized by a lower free energy than the quasifree electron state.

The energy V_0 of the quasifree state is estimated from the relation[8,10]

$$V_0 = \hbar^2 k_0^2/2m, \tag{1}$$

where the wave vector k_0 is determined from the appropriate boundary conditions in the form

$$\tan k_0(r_S - a) = k_0 r_S, \tag{2}$$

where $a = 1.13$ a.u. is the electron-helium atom scattering length[10] and $r_S = [(3/4\pi)\rho_0]^{1/3}$ is the Wigner-Seitz radius. Taking[14] for the density $\rho_0 = 0.2$ gm/cm^{-3} (at 1°K and 30 atm), we get $V_0 = +1.6$ eV for ground-state energy of the quasifree electron in solid helium.

We assume the electron to be localized within a spherical cavity of a radius R_0. The total energy of the localized state is taken to be[8,10]

$$E_t = E_e + E_s + E_{pv}. \tag{3}$$

The electronic energy E_e is given by[10]

$$E_e = X^2 V_0, \tag{4}$$

where the parameter X is obtained from the relation[10]

$$\cot(X k_0 R_0) = (1 - X^2)^{1/2}/X. \tag{5}$$

The pressure-volume energy is expressed in terms of the external pressure p:

$$E_{pv} = (4\pi/3) p R_0^3. \tag{6}$$

Finally, the interfacial energy E_S required to form the cavity in the solid, will be assumed to be given in the form

$$E_s = B R_0^2. \tag{7}$$

The following avowedly oversimplified estimates of this last term will be adequate for our purpose. Consider a cavity of radius R_0 formed in the solid by transferring atoms from the bulk to the surface. The surface energy associated with the formation of the cavity is $E_S = 4\pi R_0^2 F_S$, where F_S is the specific surface free energy of the solid.[15-17] Now, in the liquid the surface free energy F_l is equal to the surface tension γ.[18] The theoretical esti-

mates of Hiroke *et al.*[9] demonstrated that the surface energy in the liquid varies approximately as ρ_0^2. The theoretical value derived by Hiroke *et al.* for liquid helium at $T=0$ and at $p=0$ is γ (theory) $=0.53$ dyn cm^{-1}, which is somewhat higher than the experimental value[9] γ(exp.) $=0.36$ dyn cm^{-1}. It was pointed out by us[10] that the experimental surface tension along the liquid vapor interface provides only a lower limit for the estimate of the surface work expanded in the formation of the microscopic bubble in the liquid, because electron-atom repulsions tighten the surface, increasing the kinetic-energy contribution. In view of this inherent difficulty, we have concluded that the estimate $F_l=\gamma$(theory) is adequate[10] for estimates of the bubble free energy and the bubble radius in liquid helium at zero pressure. At $p=20$ atm the estimate $F_l=1.97\pm0.39$ dyn cm^{-1} is consistent with the experimental bubble radius.[10] Now, because of the large contributions from zero-point energy oscillations, the radial distribution function for the helium crystal will not appreciably differ from that in the liquid state. To obtain an estimate of the surface energy in the solid we follow Hiroke's work[9] and set $F_S=F_l(\rho_0 \text{ solid})^2/(\rho_0 \text{ liquid})^2$. Taking $\rho_0=0.20$ gm cm^{-3} for the solid at $p=30$ atm and utilizing the F_l value for the liquid at $p=20$ atm, we get $B\approx 30$ dyn cm^{-1}.

Finally, we should inquire what is the effect of the volume shear stress in the solid on the cavity energy. A simple argument may be provided to illustrate that the energy changes associated with this effect are small. The cavity of radius R_0 may not represent the energetically stable configuration of the system, as elastic shear effects may change the cavity radius from R_0 to R_1. Treating the solid as an isotropic elastic medium strained by inserting a rigid sphere of radius R_1 into a cavity of radius R_0 (where $R_1>R_0$), the corresponding energy change is[19]

$$e(R_1,R_0)=8\pi G R_0(R_1-R_0)^2\ , \tag{8}$$

where G is the elastic constant. Equation (8) gives an upper limit for the strain energy because the cavity is not rigid as assumed. An upper limit is sufficient for our purposes since we show below this term to be unimportant. Now the total energy of the system is given by

$$E_t(R_0,R_1)=E_e(R_1)+(4\pi/3)pR_1^3 +4\pi F_s R_1^2+e(R_1,R_0). \tag{9}$$

Hence the total energy depends parametrically both on R_0 and R_1. Assuming that the dependence of F_S on R_0 is weak, the minimum condition $\partial E_t/\partial R_0=0$ immediately implies that $R_0=R_1$, and Eq. (9) is reduced to the simple form

$$E_t(R_0)=E_e(R_0)+4\pi F_s R_0^2+\frac{4\pi}{3}pR_0^3. \tag{10}$$

Simple numerical calculations for electron trapping in solid helium (taking $B=30$ dyn cm^{-1} and $p=30$ atm) lead to the following results: $E_t=+0.5$ eV and $R_0=9$ Å. As $E_t<V_0$ the stability criterion for the localization of an excess electron in solid helium is satisfied.

It should be noted that it is the low value of E_S which makes the electron localization energetically feasible in solid helium. Simple scaling laws[15-17,20] for molecular solids relate the solid surface free energy with the heat of vaporization H_v. Thus, for example, for closed packed molecular solids the following relation[15,16] was proposed: $F_S=KH_v/a_0^2$, where K is a numerical constant and a_0 corresponds to a characteristic interatomic distance. Although such relations are not applicable to solid helium, where the contribution of zero-point vibrations cannot be neglected, they are sufficient to indicate qualitatively that the low heat of sublimation of solid helium results in a low contribution for the surface-energy term. On the other hand the F_S values for other rare-gas solids are expected to be higher by one order of magnitude than the corresponding value for solid helium.[15,16]

We conclude with the following comments and predictions:

(a) The ground-state energy of an excess electron in solid helium at moderate pressures involves a localized electron state in a cavity. This situation differs from the anion-vacancy F center and from Landau's strong-coupled polaron model, where no structural changes are encountered. Even for the case of $(\text{halogen})_2^-$ formation by hole trapping in alkali halides, the structural changes are only on the few-atom scale.

(b) At high pressures the localized state will collapse (due to the positive contribution of the E_{pv} term) and the quasifree electron state will be energetically favored. Rough estimates, using methods previously developed by us,[11] indicate that this transition will take place when $(p/\text{atm}) > 10^3(V_0/\text{eV})^{5/2}$. Hence the transition from the localized to the delocalized state in solid helium will take place as $p\gtrsim 4000$ atm. Mobility data in the solid can experimentally establish this spectacular transition.

(c) The electron localization mechanism, which is accompanied by drastic structural modifications in the solid, is a unique feature of solid He^3 and He^4. In liquid H_2 and D_2, theory and experiment demonstrate that the excess electron is localized[11] and the same situation may also prevail for liquid Ne,[11] however in the corresponding solids the increased positive contribution of the E_S term[15,16] will make the localized state unstable. Hence in all molecular crystals except solid He, where no

stable atomic or molecular negative ions can exist, quasifree electron states will be energetically favored.

(d) The following estimates can be given for the frequencies[21] of the breathing mode $\nu \sim 2 \times 10^{11}$ sec^{-1} and of the quadrupole distortion mode $\nu \sim 10^{12}$ sec^{-1} of the localized electron center in solid helium. Raman scattering experiments can be applied for the identification of the symmetric mode,[22] while microwave absorption experiments will monitor the assymmetric mode.[10,21]

(e) Optical absorption experiments will monitor[8,22] the energy levels of the trapping center. The lowest $1s \rightarrow 1p$ excitation in the solid should be observed at $h\nu \sim 0.5$ eV and is expected to be very intense ($f \sim 0.9$). The second $1s \rightarrow 2p$ transition is expected to result in a metastable state which will autoinize into the continuum.

(f) Photoionization experiments of the localized electron center will provide information concerning the location of the conduction band. The threshold ionization energy in solid helium is predicted to be located at $I = 1.1$ eV. Similar experiments were performed in liquid helium.[23]

(g) Some speculative comments on the electron mobility mechanism in solid helium are in order. Over the temperature range 1.5°K–0.8°K (at $p = 40$ atm) the temperature dependence of the mobility reveals the features of an activated transport process.[2] This behavior can be rationalized in terms of surface diffusion of the helium atoms into the electron cavity boundaries. In the temperature range below 0.7°K the (negative ion) current-temperature curve flattens off[2], so that the electron mobility seems to be practically temperature independent. In this low-temperature region a tunneling process of the helium atoms into the cavity region will account for the rather low electron mobility in the solid. The atom tunneling mechanism implies an appreciable mass effect on the electron mobility in solid He^3 as compared to solid He^4 at temperatures below 0.7°K. Finally, in the temperature region above 1.5°K the electron mobility reveals again only a very weak temperature dependence.[2] In this temperature region anharmonicity effects in the helium crystals are of considerable importance. However, the rather abrupt onset of this weak temperature dependence strongly suggests that at temperatures close to the solidification temperature premelting at the cavity surface occurs, whereupon the electron mobility mechanism in this temperature region will be apparently similar to that in the liquid state. This last conclusion concurs with the analysis of Ifft *et al.*[2]

(h) It has not escaped our attention that the same model as employed herein for electron localization predicts positronium localization in an expanded cavity in solid helium. Positronium annihilation experiments in this system were recently performed by Stewart,[24] and the results are consistent with this theoretical prediction. At high pressures, a pressure-induced transition from the localized to the delocalized state of positronium in solid helium should take place. The nature of this transition is analogous to that discussed in Sec. (b) for the excess electron in this system.

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[18]To specify the cavity surface energy in a solid, we use the concept of (specific) surface free energy F rather than the surface tension γ. These are related by

$$\gamma = d(AF)/dA = F + AdF/dA,$$

where A corresponds to the surface area. For a one-component liquid $\gamma = F$. On the other hand, in the solid one has to carefully specify the conditions of measurement and usually $dF/dA \neq 0$ that that $\gamma \neq F$ (see Refs. 17 and 18). The energy required to form a surface is obviously $\int F dA$.

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Transverse Plasma-Wave Echoes

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The concept of plasma-wave echoes, introduced by Gould, Malmberg, O'Neil, and Wharton for the case of longitudinal, electrostatic waves, is here extended to the case where one of the excitations is a transverse electromagnetic wave propagating parallel to an external magnetic field, and the echo is of the same character. (If both excitations are transverse and $k_\perp = 0$, there is no transverse echo in lowest order.) A transverse electromagnetic signal of frequency ω_1 is excited at $z = 0$, and a longitudinal electrostatic signal of frequency ω_2 is excited at $z = L$. A transverse echo with frequency $\omega_1 \pm \omega_2$ then appears at $z_0 = \omega_2 L[\omega_2 \pm (\omega_1 + \Omega_C)]^{-1}$, where Ω_C is the signed cyclotron frequency of the species involved, and ω_1 is positive for right-hand polarization of the transverse excitation, negative for left-hand polarization. The expression for the echo location is correct for both $z_0 > L$ and $z_0 < 0$. The echo in the latter case arises from particles which have $v_z < 0$, and hence see the longitudinal excitation first, followed by the transverse excitation. In contrast to the purely longitudinal case, the echo frequency may either be the sum or difference of the excitation frequencies. Echoes due to a given species and given circular polarization for the transverse excitation may have either right- or left-handed polarization, depending on the values of ω_1 and ω_2; echoes due to a given species (e.g., electrons and ions) occur at different locations and, in some cases, with different frequencies; and echoes arise for all values of ω_1 and ω_2, although the analysis is simple only if the waves associated with the excitations decay (due to Landau or cyclotron damping) in a distance less than L. A perturbation, Vlasov analysis, which takes into account all collective effects gives an expression for the echo shape in terms of a one-dimensional integral over v_z.

The plasma-wave echoes predicted theoretically by Gould *et al.*[1] and observed experimentally[2] involve only longitudinal waves (Langmuir oscillations or ion acoustic waves), but the mechanism can easily be generalized to include other waves as well. This extension appears worthwhile, not