Emission of "hot" electrons from liquid and solid argon and xenon

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The dependence of the coefficient (probability) for emission of conduction electrons from condensed argon or xenon into the equilibrium gas on the external electric field strength and on the temperature is measured with a pulsed ionization chamber. The potential barrier at the interface is calculated by using the Lekner electron-energy distribution functions. The values obtained are 0.02, 0.065, 0.42, and 0.85 eV respectively for solid and liquid argon and for solid and liquid xenon.

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Emission of free electrons from solid argon was apparently observed back in 1948.[1] However, whereas the devices based on this phenomenon were already used in experimental physics[2,3] the emission process and the dependence of the coefficient of emission (of the escape probability) of electrons on such parameters as the temperature and the electric field strength remained practically uninvestigated. In earlier studies[4-6] it was observed that in electric fields lower than 3 kV/cm there is no emission, and above 5–7 kV/cm practically all the free electrons are emitted in the gas phase. It was concluded therefore that the emitted electrons are "hot," i.e., their energy $\varepsilon \gg kT$ exceeds the work function ε_0. An estimate of the emission time has shown that the electrons remain on the interface not more than 0.1 μsec. The results, however, were found to be contradictory and frequently were only estimates. Thus, e.g., the scatter of the results for different samples of crystalline xenon turned out to be very large, and was attributed by the authors of Ref. 5 to the difference in the quality of the grown crystals because of the different crystallization regimes. In our opinion, of much greater importance is the purity of the material, since the presence of insignificant amounts of molecular impurities lowers greatly the energy, and consequently also the probability of escape of the electrons. In that case, even if the initial gas is of the same purity, different crystallization regimes lead to different degrees of crowding out of the impurity from the crystal into the liquid in the course of the growth, and correspondingly to different purity of the produced crystal.

In this connection, using a pulsed ionization chamber described in detail in Ref. 6, we have investigated electron emission from condensed argon and xenon of extremely low (~10^{-7} vol.%) density of extraneous impurities.

EXPERIMENTAL RESULTS

Figures 1 and 2 show the emission coefficients (escape probabilities) of electrons from the condensed phase into an equilibrium gas, measured by us as functions of the electric field intensity inside the condensed phase. The emission curves have abrupt thresholds and are shifted in the case of the crystal towards lower values of E, especially in the case of argon, where the emission threshold is near 50–70 V/cm. In the crystals, furthermore, the emission coefficient was independent of the growth rate when the latter was varied from 1 to 10 mm/h.

The electric field intensities corresponding to the emission threshold varied nonmonotonically with temperature, having a maximum near 120 K (Fig. 3).

Oscillograms of the current and voltage pulses in a two-phase system offer evidence that the electron emission from liquid argon is a complicated process that proceeds in two stages. At high temperatures the electron emission is "fast," i.e., the electrons, while stopped by the interface, do not stay there more 0.1 μsec. At temperatures near the triple point, however, a "slow" component is observed. Part of the electrons is then emitted rapidly, and part stays for a relatively long time ($\gtrsim$0.1 msec) on the interface, and gradually escapes into the gas. Since the time constant RC of the employed amplifier did not exceed 400 μsec, we were unable to carry out detailed investigations of the slow component, and these have a semiquantitative character. It was observed, in particular, that with increasing electric field strength the lifetime of the slow electrons on the interface decreases rapidly, as does also the contribution of the slow component to the overall emission coefficient, until only the fast component remains, as is seen from Fig. 1. It is possible that at

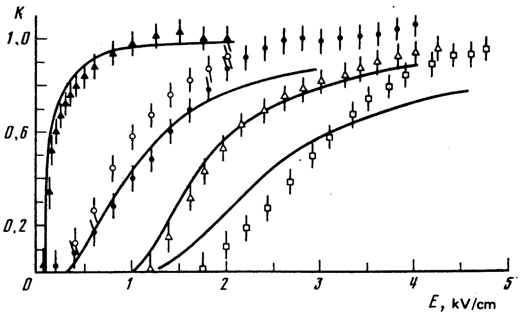

FIG. 1. Dependence of the coefficient of electron emission from solid (▲, 80 K) and liquid (●—fast component, ○—fast plus slow components, 90 K) argon, and solid (△, 160 K) and liquid (□, 165 K) xenon on the electric field intensity. Solid lines—calculations.

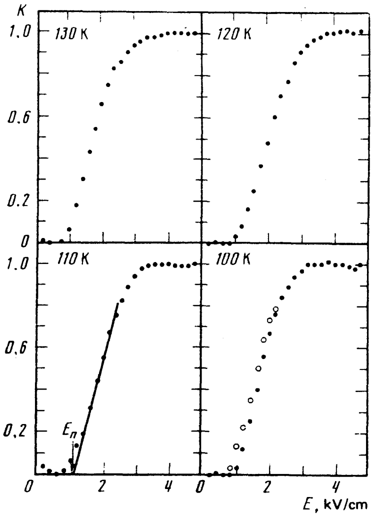

FIG. 2. Dependence of the coefficient of emission from liquid argon on the electric field intensity at various temperatures: ●—fast component, ○—fast plus slow components.

higher temperatures the lifetime of the slow electrons on the interface is so large compared with RC that the slow component is not absorbed, although it does exist. Practically all the electrons then escape into the gas even at values of E for which the measured emission coefficient pertaining to the fast component differs from unity.

The reason for the previously observed[6] influence of the emission polarization of the crystal and of the liquid in fields at which the emission coefficient has a value 0.1–0.2 is either that the lifetime of the slow electrons is too long compared with the intervals between the excitation pulses, or that some of the electrons are not emitted into the gas phase at all. Surface-charge electrons are thus gradually accumulated and lead ultimately to a complete blocking of the drift gap. It suffices, however, to turn off the external field that keeps the electrons on the surface for several seconds to restore completely the emission properties of the material.

POTENTIAL BARRIER ON THE INTERFACE

It is known that in semiconductors and dielectrics the potential barrier on the surface of the material, which prevents the escape of free electrons, is due to the force produced by polarization of the material by the departing electron. This force is equivalent to the interaction force between the electron and its dielectric image. According to the Schottky model, this barrier is equal to the work function

$$\varepsilon_0=\frac{\varepsilon_c-1}{\varepsilon_c+1}\frac{e^2}{8\pi\varepsilon_d a}, \tag{1}$$

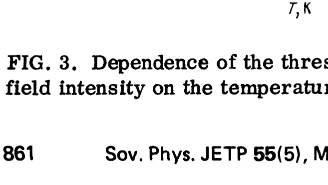

FIG. 3. Dependence of the threshold values of the electric-field intensity on the temperature in liquid argon.

where ε_c and ε_d are the dielectric constants of the material and of the vacuum, e is the electron charge, and a is a characteristic dimension of the order of the lattice constant.

When an external electric field is applied, the work function is decreased by an amount

$$\Delta\varepsilon_0=e\left(\frac{\varepsilon_c-1}{\varepsilon_c+1}\frac{eE}{4\pi\varepsilon_d}\right)^{1/2}, \tag{2}$$

where E is the electric field intensity inside the condensed phase.

Since ε_0 depends on a, Eq. (1) is only an estimate of the barrier, whereas (2) is perfectly exact in our model. In condensed argon and xenon $\varepsilon_c = 1.5–2.0$, we assume the parameter a to be equal to the lattice constant ~5 Å, so that $\varepsilon_0 \gtrsim 0.1$ eV. It is known[7] that in fields ~10^3 V/cm, which are typical for emission, the average electron energy is also ~0.1 eV and exceeds substantially the thermal energy. On the other hand, the potential barrier $\Delta\varepsilon_0$ in such fields is lowered according to (2) by 0.01 eV and is small compared with ε_0, with the possible exception of solid argon. In this case the width of the potential barrier is too large for the existence of the tunnel effect. Consequently electron emission from condensed noble gases is strictly speaking neither thermionic nor field emission, but constitutes a specific form of emission connected with the penetration of the electric field through the entire depth of the dielectric, which leads to effective "heating" of the electrons, i.e., to an increase of their energy above the thermodynamic equilibrium. In this sense the emission of electrons from condensed argon, krypton, and xenon is closer to thermionic emission, in which the role of the "heater" is assumed by the external electric field.

The emission process can then be represented in the following manner. The electrons reaching the surface of the condensed phase and having a momentum projection $p_\parallel \geqslant p_0 = (2m\varepsilon_0)^{1/2}$ along the electric field are emitted into the gas and surmount the potential barrier. The electrons whose momentum does not satisfy this condition (they include also those whose energy $\varepsilon \geqslant \varepsilon_0$) are reflected from the barrier and return to the condensed phase. If the process were to terminate at this stage, the emission coefficient for an almost spherically symmetrical distribution of the momentum direction (this is precisely the distribution assumed in elastic scattering) would not exceed 0.5, at variance with the experimental data.

It can be proposed that the electrons reflected from the barrier return after several scattering acts separated by the momentum-transfer mean free path λ_1, to the surface with a nearly spherically symmetrical distribution in the momentum direction, and the described process is repeated. It is obvious that in the course of the redistribution of the momentum direction upon reflection from the barrier the electron cannot gain energy but only lose it, and the fraction of the lost energy is $\sim(2m/M)\lambda_1/\lambda_0$ (M is the mass of the atom, λ_0 is the electron energy-transfer mean free path). At the fields typical of emission we have $\lambda_0 \sim 10^{-7}$ cm and $\lambda_1 \sim 10^{-5}$ cm (Refs. 7 and 8), so that the fraction of the lost energy is $\sim 10^{-3}$. This means that during the time of the redistribution of the momentum direction the electron hardly loses any energy. The characteristic time of the redistribution is the momentum relaxation time $\lambda_1/(2\varepsilon/m)^{1/2} \sim 10^{-12}$–$10^{-13}$ sec. Successive repetition of the "escape–reflection–redistribution–escape" process results in emission of practically all the electrons having energy $\varepsilon \geqslant (\varepsilon_0 - \Delta\varepsilon_0)$. It appears that several dozen reflections are sufficient to make the emission process practically complete, so that the characteristic emission time is $\sim 10^{-9}$–10^{-10} sec. The emission coefficient can now be expressed in terms of the electron energy distribution function $F_0(\varepsilon)$

$$K = \int_{\varepsilon_0-\Delta\varepsilon_0}^{\infty} \varepsilon^{1/2} F_0(\varepsilon)\,d\varepsilon \Big/ \int_0^{\infty} \varepsilon^{1/2} F_0(\varepsilon)\,d\varepsilon. \tag{3}$$

However, this interpretation of the emission is valid only if the barrier width is less than or of the order of the mean free path of an electron of given energy in the gas phase; in the opposite case it is necessary to take into account the energy lost to scattering in the gas. According to the Schottky model, the barrier width is $\sim 2\times 10^{-6}$ cm, and the electron mean free path is $\sim 5\times 10^{-4}$ cm (argon) and $\sim 1\times 10^{-4}$ cm (xenon) in an equilibrium gas near the triple point.[9] Thus, the influence of the gas phase on the emission can manifest itself only at a pressure higher than 20 MPa in the case of argon and 2–3 MPa in the case of xenon.

Equation (3) contains one unknown parameter—the work function ε_0. In principle ε_0 can be determined by measuring the long-wave boundary of the photoeffect, if the width of the forbidden band is known. However, both the theoretical and experimental values of ε_0 (Refs. 10–13) listed in Table I, are subject to a large scatter due (for the experimental values) apparently to the large band gap compared with ε_0 — approximately 10 eV and more. If the photoeffect boundary is measured accurate to 1%, the error in ε_0 can reach 100%. Also doubtful are the negative values (the position of the bottom of the conduction band is taken to be zero) of ε_0 in solid argon, for in this case the electron mobility ε_0 would turn out to be smaller by several orders of magnitude than the measured value because of trapping of the electrons in microscopic bubbles.[14]

It is therefore undoubtedly of interest to approach this problem from a different point of view and calculate the work function, using (3), on the basis of our measurements of the emission curves and of the Lekner distribution function.[8,15] The results of numerical integration are shown in Fig. 1 and in Table I. In the calculations, ε_0 was varied from 0 to 1 eV in steps of 0.001 eV, and the plot of the electron emission coefficient against the electric field intensity obtained for a given ε_0 was compared with the experimental plot, the criterion of agreement being the minimum of the sum of the squares of the deviation of the calculated values of K from the experimental ones, taken at the same value of E at 25 points on each pair of curves.

TABLE I.

ε_0, eV							
solid argon		liquid argon		solid xenon		liquid xenon	
exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
−0.4	−1.12	0.21	0.63	0.5	3.7	0.61	–
−0.3	−2.23	0.33	0.46	0.39	–	0.67	–
–	−0.06	0.25	–	0.49	–		
–	−2.4	0.45	–				
–	−2.25	0.2	–				
–	3.73						
–	8.1						
–	−0.35						
Our results							
0,02	–	0,065	–	0.42	–	0,85	–

For solid argon and xenon, calculation yields good agreement with the experimental curve. The calculated values of ε_0 are respectively 0.02 eV and 0.42 eV which, at least for solid xenon, agrees well with the data in Table I. For the liquid, however, the agreement between the calculated and experimental curve is somewhat worse. It appears that the mechanism of electron emission from liquid noble gases is more complicated, as is evidenced in particular by the presence of two emission components—fast and slow.

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