Drift of electrons in condensed argon

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The drift velocities of electrons in condensed argon have been measured in the temperature region from 70 to 110 K and electric field strength 0.8–8.5 kV/cm. The results are satisfactorily described by means of the Davydov electron energy distribution function. On the basis of the experimental results the average energy and diffusion coefficient of the electrons in condensed argon for fields less than 10^4 V/cm are calculated.

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INTRODUCTION

The development of radiation detectors employing condensed noble gases as the working material requires a knowledge of the behavior of the charge carriers in these materials. In particular, the most important characteristic of the material for coordinate detectors is the electron drift velocity. Investigation of this characteristic is extremely attractive also from the point of view of solid-state physics, since the relative simplicity of the structure of condensed noble gases and the possibility of obtaining very pure samples and of easy introduction of the necessary impurities provide the possibility of checking various theoretical models with relatively small effort.

The material which has been most investigated is condensed argon.[1-9] Unfortunately the experimental data on the drift velocities are contradictory, as can be seen from Fig. 1, where we have shown the results of various experiments.[1-9] In addition to the dependence of the drift velocity on electric field, in Refs. 5–8 studies have also been made of the dependence of the drift velocity on temperature in fields less than 200 V/cm: in liquid argon in the region 85–145 K and in crystalline argon in the region 65–82 K.

We present below our measurements of the electron drift velocity in pure condensed argon and their description by means of a Davydov distribution. On the basis of this distribution we have calculated such characteristics as the average electron energy, the electron range and diffusion coefficient, and also the spatial resolution of a coordinate detector based on condensed argon.

EFFECT OF IMPURITIES ON THE ELECTRON DRIFT VELOCITY

The dynamics of an electron in ideally pure crystalline argon is determined by the interaction with acoustic phonons. One can expect that near the triple point in liquid argon there will be no catastrophic destruction of the band structure[10] and the behavior of the electron in the liquid will be similar to its behavior in the crystal.

The presence of impurities in a real crystal has a strong influence on the value of the drift velocity. First of all the presence of any molecular impurity leads to inelastic scattering of the electron by the impurity, i.e., to a decrease of the average electron energy and consequently to a change of the drift velocity. An electronegative impurity which captures electrons, while not influencing the energy distribution of the electrons, can also lead to a distortion of the experimental results the distortion being due to the technique of measurement of the drift velocity.

It is easy to evaluate the concentration of a molecular impurity whose presence does not affect the dynamics of the electron in the crystal. For this purpose it is necessary that the energy loss of the electron per unit drift length be determined only by elastic collisions (i.e., scattering by phonons), i.e.,

$$(m/M)\bar{\varepsilon}/\Lambda_0 \gg \Delta W p \sigma_v,$$

where $(m/M)\bar{\varepsilon}$ is the average energy lost in the collision, $\bar{\varepsilon}$ is the average energy of the electron, ΔW and σ_v are respectively the excitation energy of a vibrational level and the cross section for its excitation, Λ_0 is the mean free path of the electron for energy transfer, and p is the absolute concentration of the impurity. For the most likely impurities—hydrogen and nitrogen—$\Delta W \sim 0.1$ eV and $\sigma_v \sim 10^{-16}$ cm^2. The corresponding concentration is $p = 10$ ppm (1 ppm $= 10^{-4}\%$ by volume).

Measurement of the electron drift velocity, as a rule, is carried out by measuring the rise time of the electron component of the voltage pulse in a two-electrode ionization chamber. Excess carriers are produced near one of the electrodes by irradiation with a pulsed beam of electrons[5,8] or α particles.[1-4] The depth of penetration of the radiation in condensed argon is 20–50 μm and for a distance between electrodes $d \geq 1$ mm the size of the region of excitation can be neglected and the excitation assumed to be of a point nature.

Then, if the number of electrons does not change during the time of drift, the rise time of the voltage pulse t_r coincides with the drift time $t_0 = d/V$, where V is the drift velocity.

The presence of an electronegative impurity leads to a change of the number of electrons $n(t)$ forming the pulse, in proportion to the amount of drift,

$$n(t) = n_0 \exp[-Vt/D],$$

where D is the average displacement of an electron before capture. In liquid argon this quantity is determined by the relation[11]

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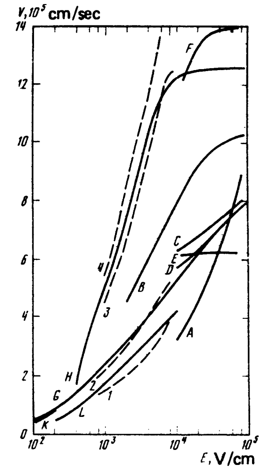

FIG. 1. Drift velocity of electrons in condensed argon as a function of electric field strength. Liquid argon: *A*—Ref. 1, *B*—Ref. 2, 90 K; *C*—Ref. 3, 90 K; *D*—Ref. 3, after passage of the argon through a trap cooled to 77 K; *E*—Ref. 4, 87 K; *G*—Ref. 5, high-purity argon, 85 K; *K*—Refs. 6–8, measurements of the temperature dependence of the mobility in fields 100–200 V/cm; *L*—Ref. 9, further purification, 97 K. Solid argon: *F*—Ref. 4, 80 K; *H*—Ref. 5 82 K. Dashed lines—results of the present work: 1—110 K, 2—90 K, 3—80 K, 4—70 K.

$$D=0.14E/p.$$

It can be shown that for measurement of the voltage pulse at a level, say, 0.95 of the maximum height the rise time will be

$$t_r'=(D/V)\ln[1/0.95\exp(-d/D)+0.05]<t_r.$$

Thus, the occurrence of capture leads to an error in determination of the drift velocity. In order for the difference between the rise time and the drift time to be less than 10% it is necessary that $D\geqslant d$, which leads to a permissible concentration of an electronegative impurity less than 1 ppm even for $d=1$ mm in fields $E>10^3$ V/cm.

Decrease of the distance between electrodes in turn produces the appearance of an error due to the finite size of the excitation region. Consequently a measurement of the electron drift velocity in condensed argon requires careful preparation of the experiment, including outgassing of the experimental apparatus, use of oil-free vacuum pumps, and additional purification of industrial argon, even of the "specially pure" type which contains ~10–100 ppm of various impurities. This fact obviously has not been taken into account in most of the studies mentioned, which have used argon of industrial purity with unknown impurity content; this fact is responsible for such a large spread of the experimental results. References 3 and 9, where further purification of the argon was carried out, are an exception.

EXPERIMENTAL RESULTS

The considerations given above were taken into account in our measurement of the electron drift velocity in condensed argon. To reduce to a minimum the effect of electronegative impurities, the experimental apparatus was made of materials with low gas evolution and before each experiment was evacuated by zeolite (molecular sieve) and magnetic discharge ion pumps to ~10^{-6} Torr with simultaneous heating to 100 °C for 12 hours. Gaseous argon of "specially pure" grade was subjected to further purification in a titanium getter at a temperature 1000 °C, which assured a guaranteed content of nitrogen and oxygen no greater than 0.1 ppm.

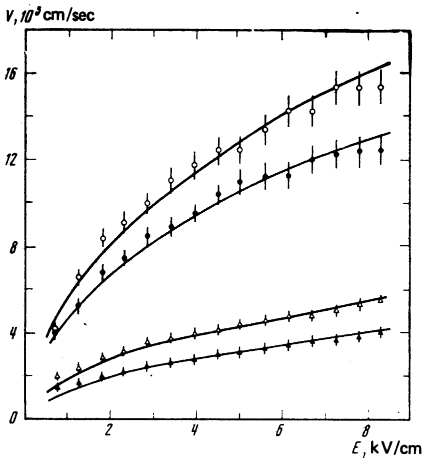

FIG. 2. Drift velocity of electrons in condensed argon as a function of electric field strength. The solid lines are the theory. Equilibrium pressure. The experimental points are as follows: ○—70 K, ●—80 K, △—90 K, ▲—110 K.

Measurement of the drift velocity and monitoring of the purity of the condensed argon were carried out in a two-electrode ionization chamber by the pulsed x-ray technique described by us previously.[12] The measured average displacement of the electron before capture in liquid argon was at least 5 cm in an electric field ~10^3 V/cm, which corresponded to an impurity concentration less than 0.03 ppm and permitted reliable operation with a drift gap of 1 cm. Measurements were made in the temperature range from 70 to 110 K. The accuracy in measurement of the temperature was ~0.5 K, and the accuracy of the stabilization was ~0.1 K.

The experimental results are shown in Figs. 1–3. It can be seen from Fig. 1 that the values of electron

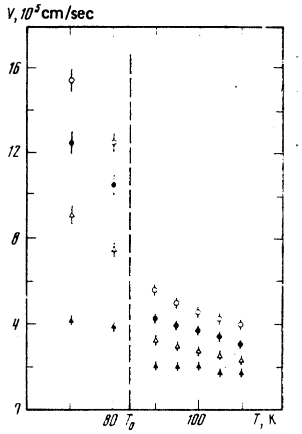

FIG. 3. Drift velocity of electrons in condensed argon as a function of the temperature. T_0 is the triple point. ○ corresponds to 8.3 kV/cm, ●—4.5 kV/cm, △—2.3 kV/cm, ▲—0.7 kV/cm.

drift velocity measured by us are in good agreement with the results of Ref. 5, where high-purity argon with oxygen content less than 1–2 ppm, nitrogen content less than 5–10 ppm, and hydrogen content less than 1 ppm was used but the drift gap was 100–300 μm.

The temperature dependence of the drift velocity (Fig. 3) is satisfactorily described by a power law T^{-n} with an exponent $n=1.4\pm0.2$ for solid argon and $n=1.65\pm0.25$ for liquid argon. This result agrees with the value $n=1.5$ obtained in Ref. 5 for solid argon near the triple point and is characteristic of the interaction of electrons with acoustic phonons.

AVERAGE ENERGY AND DIFFUSION OF ELECTRONS IN CONDENSED ARGON

An analysis of the measured drift velocities in condensed argon on the basis of the Shockley model[13] is given in Refs. 5 and 14. In terms of this model it is assumed that the electrons have a Maxwellian distribution with some effective electron temperature. The behavior of the drift velocity in various regions of electric field is explained by the authors as due to a change of electron temperature and effective mass. Use of this model appears to us to be legitimate only for the region of intermediate electric fields, where the electron energy is greatly different from thermal. At the same time it has been shown[15,16] that in electric fields above 10^3 V/cm the average energy of the electron already considerably exceeds the thermal energy.

A more general approach is given in Refs. 15 and 17, where the Boltzmann equation was solved for electrons in liquid argon with inclusion of a structure factor. The results are in good agreement with experiment in the region of electric fields less than 10^5 V/cm. The electron mean free path for momentum transfer, which was calculated by these authors over a wide range of fields, does not depend on the electric field, and this permits description of the electron dynamics by the Davydov[18] distribution, use of which is more convenient for calculations:

$$F(\varepsilon, b)=(\varepsilon/kT+b)^b e^{-\varepsilon/kT};\qquad b=(E/E_0)^2,\quad E_0=(6m^*u^2kT/e^2\Lambda^2)^{1/2}, \tag{1}$$

where e, ε, and m^* are the charge, energy, and effective mass of the electron, u is the velocity of sound, Λ is the mean free path for momentum transfer (which does not depend on ε), and k is the Boltzmann constant.

Using the general expression for the drift velocity[19]

$$V=\frac{eE}{3}\left(\frac{2}{m}\right)^{1/2}\frac{1}{N}\int_0^\infty \frac{\varepsilon}{\sigma(\varepsilon)}\frac{\partial}{\partial\varepsilon}F(\varepsilon, b)\,d\varepsilon,$$

we obtain, taking into account that $\Lambda=1/N\sigma$,

$$V=\left(\frac{4}{3}\right)^{1/2} ub^{1/2}\int_0^\infty x^2(x+b)^{b-1}e^{-x}\,dx\Big/\int_0^\infty x^{1/2}(x+b)^b e^{-x}\,dx. \tag{2}$$

The drift velocities calculated for various temperatures by means of Eq. (2) with substitution of a selected value of the parameter E_0 are given in Fig. 2. The drift velocities vary with electric field according to an $E^{1/2}$ law as in Ref. 5. The calculated curves are in good agreement with the experimental results.

Using the distribution (1) and the values obtained in E_0, it is easy to calculate the average electron energy in various electric fields:

$$\bar{\varepsilon}=kT\int_0^\infty x^{3/2}(x+b)^b e^{-x}\,dx\Big/\int_0^\infty x^{1/2}(x+b)^b e^{-x}\,dx.$$

The calculated dependences are shown in Fig. 4. In the limit of strong electric fields in the Davydov distribution function goes over to the Druyvesteyn distribution function,[20] for which analytical integration is easily carried out and

$$\bar{\varepsilon}=0.427Ee\Lambda(kT/mu^2)^{1/2}. \tag{3}$$

Thus, the region of strong electric fields begins at $E=10^3$ V/cm for the liquid and at $E=400$ V/cm for the crystal. For the liquid the electron energy does not depend on temperature in this region, apparently as a result of the mutual compensation of the temperature dependence of the terms Λ, $T^{1/2}$, and u in Eq. (3). In crystalline argon the dependence of the velocity of sound on temperature is weaker, which leads to a rise of $\bar{\varepsilon}$ with temperature.

The behavior of the drift velocity as a function of the electric field in mixtures of argon with hydrogen, nitrogen, and hydrocarbons at high electric fields should be determined by inelastic scattering on these impurities. The excitation energies of the first vibrational level of these materials are respectively 0.5, 0.3, and ~0.02–0.04 eV and deviations from the behavior in pure argon should set in at electric fields of 2×10^4, 10^4, and 4×10^2–10^3 V/cm, respectively. This is in excellent agreement with the results of Refs. 3, 9, and 16. In addition, the deviation from the $V\propto E$ dependence characteristic of a Maxwellian distribution occurs at an electric field 2×10^2 V/cm[5]. Accordingly at these values of electric field strength the electron energy begins to exceed the thermal equilibrium energy (Fig. 4).

The dependence of the electron effective mass on energy in condensed noble gases is unknown, but for an electron at the lower boundary of the conduction band in liquid argon[21] $m^*=0.43m_e$, where m_e is the mass of the free electron. Assuming $m^*=0.5m_e$, we obtained a

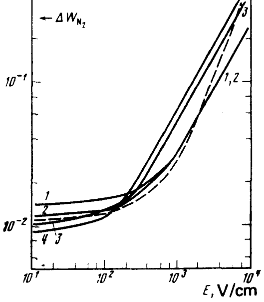

FIG. 4. Average energy of electrons in condensed argon as a function of electric field strength at various temperatures. The dashed curve is the result of Ref. 15 at 85 K; curves 1, 2, 3, and 4 correspond to 110, 90, 80, and 70 K.

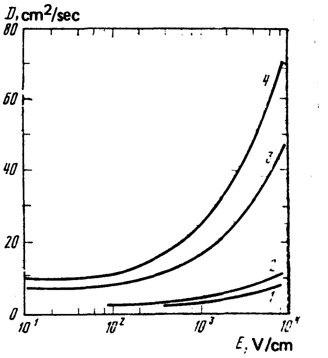

FIG. 5. Isotropic diffusion coefficient in liquid argon (1, 2) and solid argon (3, 4) as a function of electric field strength. Curves 1, 2, 3, and 4 correspond to 110, 90, 80, and 70 K.

mean free path for momentum transfer 4×10^{-6}, 3×10^{-6}, 1×10^{-6}, and 0.7×10^{-6} cm at temperatures 70 and 80 K in solid argon and 90 and 110 K in liquid argon. According to the data of Refs. 16 and 17 we have respectively in liquid argon $\Lambda = 1.36\times10^{-6}$ cm and $\Lambda = 1.54\times10^{-6}$ cm with no dependence on energy for $E < 10^4$ V/cm. Thus, use of the Davydov distribution function (1) for description of the dynamics of electrons in condensed argon in electric fields of the order of or less than 10^3 V/cm can be considered justified.

A quantity which is important from the practical point of view is the isotropic diffusion coefficient

$$D=\left(\frac{4}{3}\right)^{1/2} kT\frac{ub^{1/2}}{eE}\int\limits_0^\infty x(x+b)^b e^{-x}\,dx\Big/\int\limits_0^\infty x^{1/2}(x+b)^b e^{-x}\,dx. \qquad (4)$$

Calculated values of the diffusion coefficient are given in Fig. 5. It can be seen that the isotropic diffusion coefficient has very small values ~1–10 cm²/sec in condensed argon in comparison with $D \gtrsim 100$ cm²/sec in gaseous argon under normal conditions. This fact may have important practical application in coordinate detectors for elementary particles—drift chambers.

EFFECT OF DIFFUSION ON THE SPATIAL RESOLUTION OF COORDINATE DETECTORS

The accuracy of localization of the place of passage of a particle through a coordinate detector is to a considerable extent determined by the diffusion broadening of the particle track caused by drift of the electrons in the detector. Here one must consider that the diffusion of the electrons in an electric field is no longer isotropic and the diffusion along the field differs from the transverse diffusion. The latter is determined by Eq. (4). The ratio of longitudinal and transverse diffusion for the case of elastic scattering is given[22] by the expression

$$D_L/D=\partial(\ln V)/\partial[\ln(E/N)],$$

where D_L is the longitudinal diffusion coefficient.

For condensed argon in the range of fields investigated we have $V\sim E^{1/2}$, and therefore $D_L/D = 0.5$. For the gas[19] $D_L/D = 0.14$. The diffusion broadening, which is determined by the formula $\sigma_d = (2D_Lt)^{1/2}$, for gaseous argon under normal conditions leads to a limiting resolution ~100 μm. In Fig. 6 we have shown calculated values of σ_d for liquid, solid and gaseous argon (at a pressure 100 atm). It can be seen that liquid argon permits a resolution better than 50 μm to be obtained.

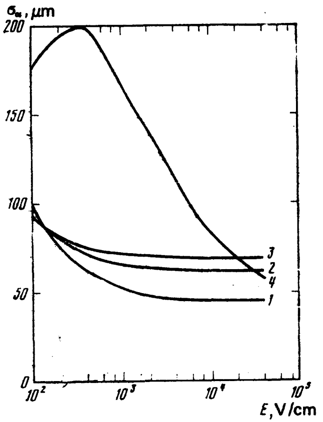

FIG. 6. Longitudinal diffusion broadening in liquid argon (1), solid argon (2, 3), and gaseous argon at 100 atm (4) as a function of electric field strength. Curves 1, 2, and 3 correspond to 90, 80, and 70 K.

If we use the technique of matching to the center of gravity of the electron cloud for recording the tracks, then the accuracy of localization at the track is improved[23]:

$$\sigma=\sigma_d/n_e^{1/2},$$

where n_e is the number of electrons in the cloud. For a relativistic particle in 1 cm of path $n_e = 1.4\times10^5$ in liquid argon and $n_e = 0.17\times10^5$ in gaseous argon at 100 atm, which gives limiting accuracies $\sigma = 0.12$ μm and $\sigma = 0.46$ μm, respectively.

Thus, the use of condensed argon to record the tracks of elementary particles permits a record accuracy of localization to be achieved.

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Role of anharmonic dynamics in vibrational relaxation of impurity molecules in solids

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A new method is proposed for calculating the rate of multiphonon relaxation of vibrational excitation of an impurity molecule, with account taken of the exact anharmonic dynamics of a multidimensional system. The method consists of searching for the optimal classical tunnel trajectory of the system that determines the probability of the quantum process. It is shown that the probabilities of the vibrational relaxation (VR) differ from the results obtained on the basis of harmonic dynamics by many orders of magnitude; the difference increases sharply with increasing vibrational quantum. The accuracy of the pair-collision approximation, which is effective for the VR, is analyzed.

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1. INTRODUCTION

The vibration relaxation (VR) of impurity molecules in solids and liquids, as shown in many experimental and theoretical studies (for a detailed bibliography see the reviews[1-3] and later papers[4-7]), is a rather slow process because of the need for exchanging the energy of the intramolecular quantum $\hbar\omega$ for a large number $N=\omega/\Omega$ of the phonons of the solid. The description of the VR, i.e., of the population relaxation as contrasted to the phase relaxation[1,4] is based on the theory of multiphonon processes[8-11] initially developed for electronic transitions.[12,13] However, whereas in the excited electronic state the causes of the electronic transitions are the shifts of the equilibrium positions (and of the frequencies) of the phonon oscillators, in vibrational excitation of an impurity molecule (IM) these shifts are too small, and the multiphonon transition is caused by anharmonic interaction with the nearest neighbors.[10,11] The method of calculating the probability in Refs. 10 and 11 takes into account the anharmonicity of the interaction that causes the transition, but the lattice dynamics remains harmonic in each of the states participating in the transition. A contrary approach[14] is based, just as in a gas phase, on the concept of individual collisions of the molecule with the atoms of the solid, but does not account in any way for the influence of the properties of the solid on the probability of the required high-energy pair collision. It is necessary therefore to develop an approach that reflects both the anharmonicity of the motion of the nearest neighbors and the specifics of their interaction with the rest of the lattice. For the VR of a classical oscillator in a classical medium, substantial progress was made possible by the method of generalized Langevin equations (GLE)[15,7] and its numerical realization, wherein the dynamics of several nearest neighbors was trajectorywise calculated with account taken of the damping and of the fluctuation forces introduced by the remaining (harmonic) lattice.

In the present paper we formulate an approach to the solution of the classical and quantum multiphonon VR problems with account taken of the exact anharmonic dynamics of the nearest atoms of the lattice, which exerts, as will be made clear, a substantial influence on the VR probability. (This corresponds to a large role of the anharmonicity in the electronic nonradiative transitions.[17-19]) At $N \gg 1$ the probability of the VR is determined by the complex (tunnel) classical trajectory that corresponds to one optimal realization of the fluctuation force $R(t)$, whereas in Ref. 7 $R(t)$ is a random process, calling for a laborious averaging over its realizations. Moreover, whereas at $N \gg 1$ the exponentially increasing VR time leads in the GLE to the need for increasing correspondingly the time and accuracy of the trajectory transitions, in our method, which yields also the quantum probability, the time of integration of the multidimensional tunnel trajectory does not depend on N and is of the order of the characteristic period of the lattice vibrations.

2. FORMULATION OF THE QUANTUM AND CLASSICAL PROBLEMS

We describe the system of an impurity diatomic molecule (AB) in a solid by the paired potential of the interaction between all the atoms and retain the complete anharmonic potential only for the interaction $U_{Ai}(x_i - x_A)$ and $U_{Bi}(x_i - x_B)$ of the atoms A and B with several nearest atoms of the lattice. Here $x_i(x=1,\ldots), x_A$ and x_B are the displacements of the atoms, and x_0 is the dis-