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Effect of quasi-stationary electric field on charge transfer in poly(phenylene oxide) based composites

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Abstract. The article explores the processes of charge transfer in the samples of polymeric composites based on poly(phenylene oxide) with fullerene and endometalfullerene in the electric field of low frequencies ($f = 10^{-1}$ Hz). The article identifies transfer processes connected with intramolecular and intermolecular conductivity. It is found that conductive channels are formed in a polymeric matrix at high concentrations of fullerene, thus, the type of conductivity changes from semiconductor to metallic. The embedding of iron into the fullerene frame molecule leads to the appearance of metallic conductivity of the composite in some temperature range.

Keywords: dielectric relaxation, charge transfer, polymeric composites.

Introduction

In recent years, research has been focusing on the development of polymeric composite materials (PCM) with high dielectric permittivity. These materials have large potential for application in various industrial technologies, namely electronics and automobile manufacturing (Cha, Kim, Hwang et al. 2012). Polyphenylene oxide (PPO) is considered to be one of the most promising polymers in the synthesis of composites. When modified, PPO changes its electrophysical properties significantly. Currently, fullerene (C_{60}) and endohedral carbon clusters, i.e., fullerenes with atoms of metals and nonmetals embedded into their cavity, have attracted considerable interest as polymer modifiers. Our prior research was limited to the analysis of photoluminescence spectra, IR absorption spectra and gas diffusion through films of fullerene-containing polyphenylene oxide (Polotskaya, Penkova, Toikka et al. 2007). The purpose of this research is to determine an effect of quasi-stationary electric field (low frequencies) on the charge transfer in the polyphenyleneoxide based composites with fullerene as a filler.

Experimental methods

The composites were obtained by mixing solutions of PPO in chloroform (concentration 2 wt.%) and fullerene C_{60} or endofullerene Fe@C₆₀ in toluene (concentration 0.14 wt.%) in the amounts that provide

the desired content of fillers. Thus obtained, the solution was left for 3–4 days to achieve the interaction between the polymer and the fullerene molecules. Then, the solution of the composite was processed with ultrasound for 40 min. and filtered through the Shot's filter to remove dust impurities. The films were obtained by casting 2 wt.% polymer solutions on a cellophane surface with subsequent solvent evaporation at 313K and drying in vacuum at 313K up to constant weight (Biryulin, Melenevskaya, Mikov et al. 2003).

The surface morphology and composition of the samples was studied by scanning electron microscopy EVO 40. The scan of the surface of $PPO/C_{60(4\%)}$ sample is shown in Figure 1.

The measurement of the dielectric spectra was carried out on the spectrometer "Concept 81" (NO-VOCONTROL Technologies GmbH) with the automatic ALPHA-ANB high performance frequency analyzer. The samples were films of a thickness of 60–125 μ m and of a diameter of 20 mm. Temperature dependences of the real part of the complex conductivity σ' were obtained for samples of PPO/C_{60(4%)}, PPO/C_{60(1%)}, and pure PPO in the temperature range between 173 K and 523 K at 10⁻¹ Hz and at applied voltage 1.0 V.



Fig. 1. Scan of a slice of the $\text{PPO/C}_{_{60(4\%)}}$ sample at a resolution of 20 μm

Results and discussion

Specific conductivity or its reciprocal value—the specific electrical resistance of polymers—is conditioned by the existence of free charges (electrons and ions) that are characterized by mobility. Polymer chains themselves do not contribute to the transfer of electric charges. Free charges that are not chemically bound to the macromolecules are probably due to low molecular weight ionic impurities whose mobility is limited by the high viscosity of the environment. Therefore, the electrical conductivity of polymers is extremely low, and the electrical resistance is very high (Polotskaya, Lebedev, Gofman, Vinogradova 2017).

To estimate the activation energy of conductivity, temperature dependences of natural logarithm of the real part of the complex conductivity σ' at 10⁻¹ Hz for PPO/C_{60(3%)}, PPO/C_{60(1%)}, and pure PPO were plotted and presented in Figures 2, 3, and 4 respectively. These dependences show two temperature ranges which can be approximated by straight lines corresponding to the Arrhenius equation (Jonscher 1996):

$$\sigma' = \sigma'_0 \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where σ'_0 —pre-exponential factor,

*E*_-conductivity activation energy.

The values of the activation energy and the pre-exponential factor for the two ranges on the curves of temperature dependence σ ' that were measured using the formula (1) are presented in Table for all measured samples. The error in the activation energy values assessment does not exceed 4.5%.

We can assume that low and high temperature ranges corresponding to different activation energy values could be attributed to the existence of intermolecular and intramolecular types of conductivity respectively.

When transferred intramolecularly, the electrons can "jump" from atom to atom, provided these atoms have electron orbitals with equal energy values. If the molecules overlap, the electrons move from

Samples	E _{al} , eV	E _{all} , eV	σ_{01} , Ohm ⁻¹ cm ⁻¹	$\sigma_{_{0II}}$, Ohm ⁻¹ cm ⁻¹
РРО	0.09	0.75	$6.6^{*}10^{-15}$	$4.12^{*}10^{-6}$
PPO/ _{C60(1%)}	0.08	1.37	$3.1^{*}10^{-16}$	$4.88^{*}10^{-1}$
PPO/ _{C60(4%)}	0.23	1.19	$7.2^{*}10^{-13}$	1.04^*10^{-1}
PPO/ _{C60(8%)}	0.28	1.17	9.6*10 ⁻¹²	5.70*10-2

Table. Parameters of electrical conductivity of investigated samples at $f = 10^{-1}$ Hz

macromolecule to macromolecule. The first conductivity stage with lower activation energy values is specific for the intermolecular charge transfer (range II), while higher activation energy values correspond to intramolecular charge transfer (range I).

Figure 2 shows that for temperatures 333–403 K the specific conductivity for PPO/ $C_{_{60(8\%)}}$ (the highest concentration of $C_{_{60}}$ in composite) increases when temperature decreases. This picture is typical of metallic conductivity. It can be assumed that at high concentrations of fullerene in the polymer matrix, $C_{_{60}}$ molecules form conductive channels, which changes the type of conductivity from semiconductor to metallic. Figure 1 clearly shows fullerene regions—the black areas are clusters of $C_{_{60}}$ molecules. With a further increase in temperature (above 403 K), the conductivity behavior is dielectric again: with temperature increasing, the electrical conductivity increases too. This may be the result of the destruction of conductive channels by increased temperatures.



Fig. 2. Electron energy loss spectra for Mg. $E_p = 100$ eV. $\phi = 80^{\circ}$. Emergent angles α are specified near the curves

Moreover, the region of metallic conductivity is observed in the samples of fullerene PPO/Fe@C_{60(1%)} with embedded iron atoms (Figure 3) at temperatures below 60°C, which is due to clearly displayed metallic properties of iron. The samples which do not contain iron in the fullerene frame, like PPO/C_{60(1%)} (Figure 3) and the pure PPO (Figure 4), are only characterized by the semiconductor type of conductivity in the temperature range t = 173—523 K. At temperatures above 443 K, the conductivity dependences for the samples with endometallofullerene and fullerene are very similar. At low temperatures the conductivity of samples with embedded iron begins to increase, while the conductivity of iron-free samples continues to decrease. The metallic type of conductivity in PPO/Fe@C₆₀ samples is the result of the growing concentration of conduction electrons with the increase of endofullerene content in the polymer matrix. An iron atom encapsulated in a fullerene molecule becomes an electric donor. The metal atoms transfer their valence electrons to the external surface of the fullerene frame, increasing the conductivity of the samples.



Fig. 3. Temperature dependence of specific conductivity at f = 10^{-1} Hz for PPO/Fe@C60(1%) (\Box), PPO/C60(1%) (\circ) samples



Fig. 4. Temperature dependence of specific conductivity at $f = 10^{-1}$ Hz for pure PPO

Conclusion

The article focuses on the processes of electric charge transfer in quasi-stationary electric field (in the low-frequency range) in the samples of fullerene-containing polyphenylene oxide. The research has revealed two logarithmic dependences of conductivity on the inverse temperature. Each of them corresponds to one of the two conductivity stages. The first conductivity stage with a lower activation energy characterizes intermolecular charge transfer, while the second stage (with a higher activation energy) corresponds to intramolecular transfer. The existence of temperature regions of metallic conductivity was found in composites with endometallofullerene and with high concentration of fullerene (8% C_{co}).

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Impulse and DC breakdown strength of polypropylene thin film

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Abstract. The paper presents the results of a study of the electric strength of a polypropylene film with a thickness of 2 µm. The breakdown voltage of the film was determined under the influence of electric pulses and with a slowly increasing voltage. The rate of increase in voltage at the pulse front varied from 1.8 to 78 GV/s, and with a slowly increasing voltage it varied from 28 to 1100 V/s. A statistical analysis of the breakdown voltage data was performed. For both modes of electrical testing and at all rates of voltage increase, the most probable breakdown voltages $F_{br.exp}$ were calculated. The effect of the voltage rise rate on the value of $F_{br.exp}$ was not detected. The obtained values $F_{br.exp}$ were approximately the same for both test modes and amounted to 550 MV/m for DC and 570 MV/m for pulses.

Keywords: breakdown, polymers, films, polypropylene, impulse, DC, Weibull distribution.

Introduction

The electrical strength of polymer dielectric materials has been studied for many decades. However, due to the great scientific and practical importance of the phenomenon of electrical destruction and breakdown of dielectrics, studies on the electrical strength of polymers remain relevant.

Numerous experiments have shown that the electrical destruction of polymer dielectrics is not a critical event that occurs when a certain field strength is reached. The lifetime of dielectrics in an electric field (durability) τ decreases exponentially with increasing field strength. The kinetic nature of electrical strength of polymers is due to the gradual accumulation of various kinds of damage of macro-molecules in them, which is initiated by an electric field. The rate of damage accumulation depends on the electric field strength *F* (Li, Yin, Wang et al. 2003; Liufu, Wang, Tu et al. 1998; Zakrevskii, Sudar, Zaopo, Dubitsky 2003).

Thus, when determining the electrical strength characteristics of polymer dielectrics it is necessary to take into account the peculiarities of the electric test mode, i.e. to take into account the dependence $\tau(F)$ when the polymer is exposed to a constant electric field, or the dependence of the breakdown intensity F_{br} on the rate of electric field strength increase dF/dt. Here F = U/d, where U is the stress on the sample, d is its thickness, t is time. The F_{br} value is determined by the voltage on the sample at the time of breakdown.

As a result of the kinetic nature of electrical destruction of polymers, the F_{br} values of polymer materials measured at different values of dF/dt may differ significantly (Zakrevskii, Sudar 1996). Therefore,

the electrical strength of different polymers may only be compared by comparing the F_{br} dependencies on dF/dt established for these polymers.

Difficulties also occur when comparing impulse breakdown strength and breakdown strength determined in a slowly increasing electric field (quasi-constant electric field) for the same polymer dielectric.

The known data on the pulse electrical strength of polymers are quite contradictory. For example, prior research (Watson 1971; Watson 1972) on the impulse breakdown of polymethylmethacrylate

has established the existence of a maximum on the $F_{br}(dF/dt)$ dependence. By contrast, the minimum breakdown voltage on $F_{br}(dF/dt)$ is set for polymers such as PET, PTFE and polyimide (Vazhov, Moldobaev 2009). The authors of (Krivko, Lekht 1970; Zakrevskii, Pakhotin, Sudar 2018) recorded only the increase of F_{br} for polyethylene terephthalate when the edge steepness of the pulse increases.

At the same time, a number of works show a decrease in the breakdown voltage of polymers on impulses in comparison with F_{br} value at slow (100–1000V/s) increasing voltage (Artbauer, Griač 1965; Cooper, Rowson, Watson 1963; Watson 1971). It should be noted here that the F_{br} values obtained by the authors of these works may have statistical variation. Therefore, conclusions about the difference in the electrical strength of polymers in the pulsed and quasi-permanent electric fields should be statistically justified; however, in the cited publications there is no statistical analysis of the results. Thus, the indicated difference in F_{br} values cannot be considered conclusively proven.

The purpose of the present work was to determine the value of the impulse breakdown strength of polypropylene (PP) film and F_{br} values of this film in the quasi-static mode of electrical influence at different rates of voltage rise on the sample, as well as provide comparison and statistical substantiation of the obtained results.



Fig. 1. Oscillogram of the signal recorded at the breakdown of PP film

Experiment design

The object of investigation was an oriented industrially produced PP film with the thickness of $d = 2 \mu m$. It was fixed in a special mandrel between two steel electrodes and placed in capacitor oil, which prevented the occurrence of edge and surface discharges. One of the electrodes (flat) was under the ground potential. The second spherical (6 mm in diameter) electrode was supplied with either a high voltage pulse of negative polarity with duration of ~10 µs or an increasing negative voltage. Both at impulse and quasi-stationary electric influence on film samples, the voltage increased by exponential law, $U(t) = U_{max} [1 - \exp(-t/\tau)]$, where $U_{max} = 2000$ V, and τ is the time constant, varied in the experiments. The value of U_{max} was chosen so that the breakdown of the polymeric film occurred at a single exposure of a sample to an electrical pulse. It was usually observed at the pulse front.

It should also be noted that with exponentially rapid voltage rise, the rate of voltage growth on the sample decreases as the voltage increases. Therefore, further on, when comparing the experimental data, the largest value dF/dt was used, which was defined at t = 0 and equal to $U_{max}/(\tau d)$.

The moment of the polymer film breakdown was recorded by a digital oscilloscope fixing the high voltage on the sample at any given time. High voltage was supplied to the oscilloscope input via a TT-HV-250 1:100 voltage divider with a 300 MHz band and a maximum operating voltage of 2500 V. When determining F_{br} the oscilloscope "Velleman" PCS-500 was used in the quasi-stationary mode, and the oscilloscope "Aktakom" ASD-2332 was used in the pulse mode.

A typical oscillogram of the impulse breakdown development in the investigated film is presented in Fig. 1. The moment of breakdown corresponds to the moment when oscillations arise.

Experiment results and discussion

The breakdown voltage values U_{br} , experimentally determined in both electrical test modes, demonstrated statistical variance. So, with each fixed value of dF/dt, 55 breakdowns were made in different areas of the polymer film. On the basis of the obtained U_{br} values, the breakdown voltage distribution function (DF) f(U) was calculated, defined as

$$f\left(U\right) = \frac{n}{N},\tag{1}$$

where *N* is the number of tests performed (N = 55) and *n* is the number of samples that broke through when the voltage *U* was reached. Thus, the DF shows the probability that the U_{br} value does not exceed the specified *U* value.

For approximation of the empirical DFs calculated by equation (1), we used the Weibull distribution (Weibull 1951):

$$f(U) = 1 - \exp\left[-\left(\frac{U}{U_0}\right)^m\right],\tag{2}$$

where *m* is a form parameter and U_0 is a scale parameter. Fig. 2 presents typical empirical DFs obtained from impulse electrical breakdown for $dF/dt = 2.7 \cdot 10^{15}$ V/(m·s) (line *1*) and quasi-stationary breakdown $dE/dt = 3.4 \cdot 10^7$ V/(m·s) (line 2) on the Weibull probability paper. In the coordinates under consideration, they can be approximated by straight lines whose parameters are determined using the least squares method. Based on the values of the angular coefficient and the initial ordinate of these lines, the values of the form and scale parameters were calculated. Their values are presented in the Table. It should be noted that in all cases the correlation coefficient of approximating lines was no less than 0.9, which indicates the validity of the Weibull distribution.



Fig. 2. Linearized DFs for the breakdown stresses of PP film at different values of field strength increase rate: $1 - 2.7 \cdot 10^{15} \text{ V/(m \cdot s)}; 2 - 3.4 \cdot 10^{7} \text{ V/(m \cdot s)}$

Quasi-stationary testing mode			Pulse testing mode		
dF/dt, V/(m·s)	m	U ₀ , V	dF/dt, V/(m·s)	m	U ₀ , V
5.6.108	2.7	1300	3.9.1016	2.9	1010
4.2.108	2.5	1050	1.2.1016	2.3	1160
1.6.108	2.7	1260	4.6.1015	3.1	1260
6.8.107	2.0	1150	2.7.1015	2.3	980
3.4.107	3.1	1410	1.9.1015	2.0	1290
1.4.107	1.9	1560	9.0.1014	1.8	940

Table. Values of the scale and form parameters of DF for different values of dF/dt

The values *m* and U_o were used to calculate the mathematical expectation of the breakdown voltage U_{brexp} and the variance σ , defined as follows

 $U_{br.exp} = U_0 \Gamma \left(1 + \frac{1}{m} \right) \tag{3}$

and

$$\sigma^2 = U_0^2 \left[\Gamma \left(1 + \frac{2}{m} \right) - \Gamma^2 \left(1 + \frac{1}{m} \right) \right]. \tag{4}$$

Fig. 3 presents the dependence of the most probable breakdown strength $F_{br.exp}$ on the electric field intensity increase rate. We can see that the values $F_{br.exp}$ determined in quasi-stationary and impulse modes of electrical tests are close in value, but are characterized by a significant variation. The rate of the voltage increase does not affect the value of $F_{br.exp}$. It should be noted that the fact that there is no dependence for the PP film at a slowly increasing voltage is well-known (Zakrevskii, Sudar 1996) and is believed to result from the peculiarities of bulk charge accumulation in the PP film.



Fig. 3. A plot of the most probable breakdown strength of the PP film vs the electric field strength increase rate, established in quasi-stationary and impulse modes of electrical testing

Conclusion

In the present paper, experimental data on the values of breakdown strength of thin film of PP at various modes of electrical tests, namely pulse and quasi-stationary modes, were obtained. Grounds for applying Weibull distribution for the analysis of the received values of breakdown voltage of a film were established. The statistical analysis of the results of electrical tests performed in the paper allowed comparison between the values of the most probable breakdown strength determined in various modes of electrical tests. The results do not indicate a difference in the electric strength of the investigated film in various test modes.

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Electronic exchange between centres of iron in the vitreous arsenic selenide

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Abstract. Iron atoms in vitreous arsenic selenide films form single electron donor centres, while the Fermi level shifts from the middle of the band gap to the bottom of the conduction band with an increase in the iron concentration due to the filling of single electron states of the acceptor type located below the Fermi level. The Mössbauer spectroscopy method was used to study the electronic exchange between ionised and neutral centres of iron in the glassy selenide of arsenic.

Keywords: chalcogenide glass, dopant iron atoms, electron exchange, Mössbauer spectroscopy.

Introduction

The fundamental property of the electrical inactivity of impurity atoms in chalcogenide glassy semiconductors is well-known (Marchenko, Nasredinov, Seregin 2018), although exceptions are known for some impurities. In particular, the electrical activity of iron impurity atoms was discovered in glassy films of arsenic selenide back in 1990 (Turaev, Seregin, Nasredinov 1990). Later, we undertook studies of both the nature of the electrical activity of iron (Marchenko, Luzhkov, Rasnyuk et al. 2017; Marchenko, Terukov, Egorova et al. 2017) and the mechanism of electrical activity of the different states of iron in As₂Se₃ (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015; Marchenko, Rabchanova, Seregin et al. 2016). In this paper, we consider all the results we obtained (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015; Marchenko, Rabchanova, Seregin et al. 2017, Marchenko, Luzhkov, Rasnyuk et al. 2017, Marchenko, Terukov, Egorova et al. 2017; Marchenko, Nasredinov, Seregin 2018; Turaev, Seregin, Nasredinov 1990) from a single perspective.

Experiment design

The modification was carried out by a high-frequency ion plasma sputtering of arsenic selenides and metal iron (enriched by ⁵⁷Fe isotope to 92% with the summary content of impurities < 10^{-4} at.%) in an argon atmosphere at a pressure of 10^{-2} Torr at a frequency of 13.6 MHz with the subsequent annealing of the films at 150°C for 30 min, in order to stabilise their properties. The iron concentration, $N_{\rm Fe}$, varied from 0.5 to 4.0 at.% and was controlled by the method of X-ray fluorescent analysis with an error of ±0.1 at.%. The amorphism of the films was checked by the X-ray phase analysis. The ⁵⁷Fe Mössbauer spectra in the range of temperatures from 80 to 400 K were recorded using a ⁵⁷Co radiation

source in a palladium matrix. The electro conductance temperature dependence and the Seebeck coefficient sign were measured using standard methods. The error in determining the electro conductance activation energy E_{σ} amounted to ±0.05 eV (Marchenko, Terukov, Egorova et al. 2017). The position of the optical absorption edge for pure and doped As₂Se₃ glass was determined in the range of 600–2500 µm at 20°C; the error in determining the optical absorption edge was ±0.02 eV. Since for chalcogenide glass an exponential dependence of the absorption coefficient α on the light frequency ω is typical in the region of the absorption (Urbach) edge, a linear dependence ($\alpha\hbar\omega$)^{1/2} = $f(\hbar\omega)$ was built and its extrapolation on ($\alpha\hbar\omega$)^{1/2} = 0 was made (here α is the absorption coefficient, and \hbar is the Planck constant), in order to measure the value of the optical band gap width $E_{\alpha\nu}$.

Results and discussion

Electrical activity of iron atoms

According to the Seebeck coefficient, the As_2Se_3 films, which do not contain iron, possess a hole type of conductivity, while their modification results in an electron type of conductivity (at $N_{Fe} > 0.5$ at.%) (Marchenko, Terukov, Egorova et al. 2017). The introduction of iron leads to a substantial increase in the conductance σ (Fig. 1); the conductance activation energy E_{σ} decreases tending to a limiting value of 0.24 eV at $N_{Fe} = 4$ at.% (Fig. 2). The optical band gap for the films E_{opt} decreases with the growth of the iron concentration (Fig. 3), but not as sharply as E_{σ} (Fig. 2) (Marchenko, Rabchanova, Seregin et al. 2016).

The ⁵⁷Fe Mössbauer spectra in the modified As_2Se_3 films are shown in Figs. 4, 5. When $N_{Fe} \le 2$ at.%, the spectra at 295 K represent quadrupole doublets (the isomeric shift $IS = 0.22 \pm 0.02$ mm/s, quadrupole splitting $\Delta = 0.64 \pm 0.03$ mm/s, and the spectral line width at half height $G = 0.31 \pm 0.03$ mm/s; these values weakly depend on the iron concentration), which correspond to iron atoms Fe³⁺ in a distorted tetrahedral environment of selenium atoms (Fig. 4) (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015). When $N_{Fe} > 2$ at.%, the Mössbauer spectra are a superposition of a quadrupole doublet referring to the already described state Fe³⁺ and a quadrupole doublet ($IS = 0.82 \pm 0.02$ mm/s, $\Delta = 1.82 \pm 0.03$ mm/s, and $G = 0.31 \pm 0.03$ mm/s; these values weakly depend on the iron concentration) corresponding to the iron atoms Fe²⁺ in a distorted tetrahedral environment of selenium atoms (Fig. 4). The fraction of iron atoms Fe²⁺ in creases with the growth of the total iron concentration in the films (Fig. 6) (Marchenko, Rabchanova, Seregin et al. 2016).

Thus, an introduction of iron into vitreous arsenic selenide leads to a shift of the Fermi level from the band gap middle (for undoped glass) to the conduction band bottom (for doped glass). For undoped glass $E_{opt} \approx 2E_{\sigma}$ and the current transfer, according to the sign of Seebeck coefficient, is realised by holes. The introduction of iron into glass leads to a change in the sign of the current carriers (the current transfer, according to the seebeck coefficient, is realised by electrons) and to a decrease in the electro conductance activation energy (Marchenko, Rabchanova, Seregin et al. 2016).

Figure 7 presents the dependence of the shift of the Fermi level from the middle of the band gap $\delta E = (E_{opt})/2 - E_{\sigma}$ on the iron concentration. As can be seen from the figure, when the iron concentration increases, the Fermi level smoothly approaches its limiting position, which is distant from the middle of the band gap by a value of 0.57 ± 0.03 eV (Marchenko, Rabchanova, Seregin et al. 2016).



Fig. 1. Electroconductance temperature dependences for As₂Se₂ films and As₂Se₂ films modified with iron



Fig. 2. Dependence of the electroconductance activation energy $E_{\sigma}(1)$ and the optical band gap $E_{opt}(2)$ of modified As₂Se₃ films on the iron concentration



Fig. 3. Optical absorption edge of iron films



Fig. 4. Mössbauer spectra for ⁵⁷Fe atoms in modified As_2Se_3 films at room temperature in the range of concentrations of 0.5–4.0 at. % Fe. The decomposition of the experimental spectra into two quadrupole doublets is shown, which correspond to the Fe³⁺ and Fe²⁺ states



Fig. 5. Mössbauer spectra for ⁵⁷Fe atoms in modified As_2Se_3 films at 80 and 440 K at concentration of 2 and 3 at. % Fe. The decomposition of the experimental spectra into two quadrupole doublets is shown, which correspond to the Fe³⁺ and Fe²⁺ states



Fig. 6. Dependence of the Fe³⁺ fraction on the total iron concentration in the ⁵⁷Fe Mössbauer spectra of As₂Se₃



Fig. 7. Dependence of the shift of the Fermi level from the middle of the band gap $\delta E = (E_{out})/2 - E_{\sigma}$ on the iron concentration

In order to explain the experimental data, we should assume that the iron atoms form a single-electron level of a donor type in the band gap. In other words, when an iron atom penetrates into a glass structural network, it forms chemical bonds with the chalcogen atoms using two valence 4s electrons coupled by the spin (i.e., the state Fe^{2+} of iron oxidation is formed), while one uncoupled valence 3d electron of an iron atom plays the role of a donor electron with an ionization energy of 0.24 ± 0.03 eV (the energy is counted from the bottom of the conduction band) (Fig. 2). If $N_{Fe} \le 2$ at.%, then all the donor iron centres are ionised and only the iron Fe^{2+} state is observed in the 57 Fe Mössbauer spectra (Fig.4) (Marchenko, Rabchanova, Seregin et al. 2016). The fraction of the Fe^{2+} ions can be calculated using the following equation:

$$p = \frac{S_n^{80}}{S_n^{80} + S_i^{80}},\tag{1}$$

where S_n^{80} and S_i^{80} are the areas under the Mössbauer spectra recorded at 80 K and corresponding to the Fe²⁺ and Fe³⁺ ions, respectively. In other words, under the conditions of film preparation, the concentration of acceptor type intrinsic defects in glass, which compensate the donor iron centres by transferring them from the Fe²⁺ state into the Fe³⁺ state, amounts to less than 2 at.%. However, these electrons do not enter into the conduction band; instead, they fill local states having a continuous energy distribution from the top of the valence band to the bottom of the conduction band. This results in the shift of the Fermi level from the middle of the band gap to the bottom of the conduction band; the higher the iron concentration, the larger this shift (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

Naturally, when the Fermi level reaches an iron donor level (this happens at $N_{\rm Fe} \sim 2$ at.%), then a part of the iron centres turns out to be in a nonionised state, and the component corresponding to Fe²⁺ appears in the ⁵⁷Fe Mössbauer spectrum. The iron Fe²⁺ fraction at $N_{\rm Fe} > 2$ at.% will increase with the iron concentration growth, which is observed in the Mössbauer spectra (Figs. 4, 5) (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

The maximum shift in the Fermi level (~0.57 eV) corresponds to the energy position of the level of the iron donor to the middle of the band gap. The monotonic decrease in the conductance activation energy of the iron As_2Se_3 films by the increase of the iron concentration is explained by the shift of the Fermi level described above.

A small decrease in the optical width of the band gap for As_2Se_3 arsenic selenide modified with iron is explained by the formation of a solid solution in glass based on arsenic selenides and iron selenides with one of the solid solution components (iron selenide) being a narrow band gap semiconductor (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

Electronic exchange between centres of iron

It is obvious that when the Fermi level is close to the level of iron, the electron exchange between the two oxidation states of iron (Fe^{2+} and Fe^{3+}) is possible, which should give rise to the convergence of the central shift values of the Mössbauer spectra of the Fe^{2+} and Fe^{3+} sites. In the limit of fast electron exchange, when the lifetimes of the Fe^{2+} and Fe^{3+} states are much shorter than the lifetime of the ^{57}mFe nuclear isomer ($\sim 10^{-7}$ s), the Mössbauer spectrum of the averaged state of iron with the following central shift should be (Marchenko, Luzhkov, Rasnyuk et al. 2017):

$$S = \frac{S_{\rm i}^{\rm 80} + PS_{\rm n}^{\rm 80}}{P+1},\tag{2}$$

where

$$P = \frac{N_{\rm Fe^{2+}}}{N_{\rm Fe^{3+}}} \le 1,$$
(3)

 S_n^{80} and S_i^{80} are the central shifts of the Mössbauer spectra recorded at 80 K and corresponding to the Fe²⁺ and Fe³⁺ sites, respectively.

The temperature dependences of the central shifts of the Mössbauer spectra of Fe³⁺ and Fe²⁺ sites at NFe = 2 at.% (when P \approx 0) and NFe = 4 at.% (when P \approx 1) are shown in Fig. 8 (Marchenko, Luzhkov, Rasnyuk et al. 2017)

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For the case when $P \approx 0$, only the quadrupole doublet corresponding to the Fe³⁺ ion is present in the Mössbauer spectrum, the central shift of which in the range of temperatures from 80 to 440 K only slightly decreases with an increase in the temperature, which can be explained by the manifestation of the transverse Doppler effect. In most cases, the central shift *S* of the Mössbauer spectra is determined by the isomeric shift δ and the squared Doppler shift *D*.

$$S = \delta + D, \tag{4}$$

and the temperature dependence of the central shift is determined by the temperature dependence of the D value, which looks as follows in the Debye approximation:

$$D = -\frac{3}{2}E_0 \frac{k\Delta T}{Mc^2} f\left(\frac{\Delta T}{\theta}\right), \tag{5}$$

where E_0 is the energy of the isomeric transition for the ^{57m}Fe isotope, k is the Boltzmann constant, M is the mass of the irradiating ⁵⁷Fe atom, c is the speed of light in vacuum, θ is the Debye temperature of the investigated material, $f\left(\frac{\Delta T}{\theta}\right)$ is the Debye function, and ΔT is the difference between the temperatures at which the Mössbauer spectra of the sample are recorded (Marchenko, Luzhkov, Rasnyuk et al. 2017).

The theoretical temperature dependences of the squared Doppler shift of the Mössbauer spectrum of the ⁵⁷Fe isotope (the used Debye temperatures are 120 and 200 K) and the experimental temperature dependence of the central shift of the Mössbauer spectrum of the Fe³⁺ sites at P \approx 0 are shown in Fig. 9. As seen from the plots, there is satisfactory agreement between the theoretical and experimental dependences.

For the case when $P \approx 1$, two quadrupole doublets corresponding to the Fe³⁺ and Fe²⁺ sites are present in the Mössbauer spectrum, the central shifts of which become close to each other with an increase in the temperature (see Fig. 8), the spectral lines are broadened (Fig. 10), and the relative area under the spectrum corresponding to Fe²⁺ sites is decreased (Fig. 11) (Marchenko, Luzhkov, Rasnyuk et al. 2017).



Fig. 8. Temperature dependences of the central shifts of the Mössbauer spectra of Fe³⁺ sites in As₂Se₃ films for an iron concentration of (1) 2 and (2) 4 at.%, and (3) of Fe²⁺ sites for an iron concentration of 4 at.%; the dashed lines correspond to the temperature dependences of the central shifts of the Mössbauer spectra of the (I) Fe³⁺ and (II) Fe²⁺ sites, which are determined from the temperature dependences of the squared Doppler shifts in the ⁵⁷Fe Mössbauer spectra



Fig. 9. Theoretical temperature dependences (solid lines) of the Doppler shift of the Mössbauer spectrum on the 57 Fe isotope for Debye temperatures of (1) 120 and (2) 200 K and the experimental temperature dependence of the central shift of the Mössbauer spectrum of the Fe³⁺ sites in As₂Se₃ films for an iron concentration of 2 at.%



Fig. 10. Temperature dependences of the spectral line widths of the Mössbauer spectra of Fe³⁺ sites in As₂Se₃ films for an iron concentration of (1) 2 and (2) 4 at.%, and (3) of Fe²⁺ sites for an iron concentration of 4 at.%



Fig. 11. Temperature dependence of the fraction of Fe^2+ sites in the Mössbauer spectra of As_2Se_3: 57Fe at $N_{\rm Fe}$ = 4 at.%

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The spectra in Fig. 5 and results of their processing in Fig. 8 and Fig. 10 illustrate the typical pattern of the electron exchange between the two iron oxidation states, Fe^2 + and Fe^{3+} . A decrease in the relative area under the spectrum corresponding to Fe^{2+} sites does not indicate a decrease in the concentration of Fe^{2+} sites with an increase in the temperature, but a more distinct dependence of the Mössbauer coefficient on the temperature for the compounds of doubly charged iron in comparison with the compounds of Fe^{3+} (Marchenko, Luzhkov, Rasnyuk et al. 2017).

Considering that the local symmetry of Fe^{2+} and Fe^{3+} sites is lower than cubic symmetry, it is reasonable to expect the electron exchange to be accompanied by a change in the tensor of the electric field gradient (EFG); i.e., the quadrupole splittings of the Fe^{2+} and Fe^{3+} Mössbauer spectra should change with an increase in the temperature.

In fact, if the local symmetry of the ^{57m}Fe Mössbauer probe is lower than its cubic symmetry, then the energy level of the ^{57m}Fe nucleus decomposes into two sublevels as a result of the interaction of the quadrupole moment Q of the iron nucleus with the EFG tensor on it, and the quadrupole splitting of the Mössbauer spectrum arises (Marchenko, Luzhkov, Rasnyuk et al. 2017). The Laplace equation U_{xx} + U_{yy} + U_{zz} = 0 is applicable for a diagonalised EFG tensor, and this EFG tensor is determined by the following two parameters: the main component U_{zz} of the EFG tensor and the asymmetry parameter $U_{ux} - U_{ux}$

 $\eta = \frac{U_{xx} - U_{yy}}{U_{zx}}$ (here *x*, *y*, and *z* are the main axes of the EFG tensor, which are chosen based on the inequality $|U_{xx}| \le |U_{yy}| \le |U_{zz}|$). The Mössbauer spectrum is represented by a doublet with the following distances between the components:

$$\Delta = \frac{1}{2} e Q U_{zz} \left(1 + \frac{\eta^2}{3} \right)^{1/2}.$$
 (6)

In general, there are the following two EFG sources on the atomic nuclei: the ions of the structural lattice of glass (they produce crystalline EFG) and no spherical valence electrons of the Mössbauer atom (they produce valence EFG). Accordingly,

$$U_{zz} = (1 - \gamma)V_{zz} + (1 - R_o)W_{zz}, \qquad \eta = \frac{(1 - \gamma)V_{zz}\eta_{cr} + (1 - R_o)W_{zz}\eta_{val}}{U_{zz}}, \qquad (7)$$

where U_{zz} , V_{zz} , and W_{zz} are the main components of the total, crystalline, and valence EFG tensors, respectively; η , and η_{cr} , η_{val} are the asymmetry parameters of these tensors; γ and R_0 are the Sternheimer coefficients (they take into account the shielding and deshielding of EFG produced by the external charges and by the internal electron shells of the probe atom).

If the valence shells of the Mössbauer atom are completely or half-filled (the Fe³⁺ ion is a typical example), then only the charges of neighbour atoms should be taken into account for such an atom upon the calculations of EFG; the Δ value in this case is insignificant, and its temperature dependence is determined by the temperature dependences of the interatomic distances in the crystal and in the structural lattice of glass, and this dependence is, as a rule, very weak. However, if the valence shells of the Mössbauer atom are filled only partially (Fe²⁺ is a typical example), then the valence electrons are the main source of EFG; therefore, the Δ value is significantly increased, and it noticeably decreases upon an increase in the temperature (Marchenko, Luzhkov, Rasnyuk et al. 2017).

The temperature dependences of the quadrupole splittings of the ⁵⁷Fe Mössbauer spectra corresponding to the Fe²⁺ and Fe³⁺ sites are shown in Fig. 12. It is seen that a small value of the quadrupole splitting Δ_i and its insignificant decrease with an increase in the temperature are observed in the range of temperatures from 80 to 400 K for the case with an iron concentration of less than 2 at.% (iron is stabilised only in the Fe³⁺ state), as expected for the triply-charged Fe³⁺ state of iron. In the case with an iron concentration of 4 at.% (iron is stabilised in the two equally populated Fe²⁺ and Fe³⁺ states), small values of the quadrupole splitting Δ_i and their decrease with an increase in the temperature are observed in the Mössbauer spectra of the Fe³⁺ sites in the range of temperatures from 80 to 350 K, whereas the Δ_i value starts to increase anomalously upon a further increase in the temperature. For the spectra of Fe²⁺ sites, the quadrupole splitting value Δ_n for the same samples is significantly larger, and the rate of its decrease upon an increase in the temperature has the following two areas: the area at the temperatures ranging from 80 to 350 K, in which the quadrupole splitting considerably decreases, and the area at T > 350 K, in which this decrease becomes more rapid.

Thus, the quadrupole splitting values of the Mössbauer spectra of the Fe³⁺ and Fe²⁺ sites in the films of arsenic selenide glass approach each other upon an increase in the temperature, which indicates that the EFG tensor parameters produced on the atomic nuclei of the neutral and ionised iron donor centres become closer.



Fig. 12. Temperature dependences of the quadrupole splitting of the Mössbauer spectra of Fe^{3+} sites in As_2Se_3 films for an iron concentration of (1) 2 and (2) 4 at. %, and (3) of Fe^{2+} sites for an iron concentration of 4 at.% (3)

Conclusion

In glass films of arsenic selenide modified by iron, the Fe^{2+} and Fe^{3+} sites corresponding to the neutral and ionised states of the one-electron donor iron centre are detected. Both the central shift and quadrupole splitting values of the Mössbauer spectra of the Fe^{3+} and Fe^{2+} sites become closer upon an increase in the temperature, which indicates that the electronic densities and EFG tensor parameters on the atomic nuclei of the neutral and ionised iron donor centres are equalised.

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Fluorescence of $Pb_{1-x}Cd_xSe$ nanocrystal films

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Abstract. The interest in lead chalcogenide structures is driven by the possibilities of using nanocrystal lead selenide films, for example $Pb_{1-x}Cd_xSe$, as fast and compact sources of infrared range with low energy consumption. Besides, PbSe films oxidised in the atmosphere of oxygen can serve as optical light receivers of infrared range in gas sensors.

Keywords: fluorescence, nanocrystalline films, semiconductor compounds, solid solutions, quantum dots, surface morphology, luminescence spectrum, band gap.

Introduction

The fluorescence of thin $Pb_{1-x}Cd_xSe$ films obtained by vacuum deposition is well-known (Yunovich, Averyushkin, Drozd, Ogneva 1979; Nepomnyaschij, Pashkevich, Shelekhin, Dijkov 1984). For instance, fluorescence may be observed during optical excitation of films heat-treated in the atmosphere of oxygen. The interest in $Pb_{1-x}Cd_xSe$ films fluorescence is driven by the possibility of using them in optics as a fast and compact light source with low energy consumption. For example, light sources based on $Pb_{1-x}Cd_xSe$ (Nepomnjashchij, Pogodina, Shelekhin, Maksjutenko 2003) are widely used in gas analyzers in the spectral range of 2–5 µm to address greenhouse gases (Gamarts, Moshnikov, Chesnokova 2006).

Besides, semiconducting compounds PbSe and CdSe form $Pb_{1-x}Cd_xSe$ solid solutions, where the width of the band gap increases as x rises. This makes it possible to move spectral characteristics of photoconductivity and photoluminescence to short-wave spectrum area compared to lead selenite.

Current LEDs based on inter-band transitions in narrow-band-gap semiconductors such as InAsSb have fundamental defects, such as challenging production technology, low light intensity, low radiation stability, etc.

Significant progress has been recently made in the study of fluorescent characteristics of $Pb_{1-x}Cd_xSe$ solid solutions due to the technological possibilities of building quantum dots in these materials. It is expected that in quantum dots, non-radiation dissipation of electron excitation energy may be significantly reduced due to the low electron-phonon interaction, which in turn will increase the emitting power of the infrared source.

Materials and methods

Fluorescence spectra of PbSe and $Pb_{1-x}Cd_xSe$ polycrystalline films have been investigated. X-ray phase analysis data showed the lead selenide precursor being stoichiometry; the x composition of $Pb_{1-x}Cd_xSe$ solid solution varied within x = (0.1 ÷ 0.2).

The films were obtained by thermal deposition on $20 \times 20 \text{ mm}^2 \text{ C}$ -29 glass substrates. The thickness of PbSe and Pb_{1-x} Cd_xSe films amounted to $2 \div 2,5 \mu \text{m}$. As a source for film deposition, we used compressed tablets of corresponding precursors on the basis of binary compound of lead selenide and lead selenide solid solution—cadmium selenide pre-treated thermally in dynamic vacuum by the procedure described in (Henry 1993; Bestaev, Makhin, Moshnikov, Tomaev 2000). To augment the uniformity of film thickness during application, a template-rotating device was used. The distance between the vapour source and the templates and their design ensured the consistency of layer thickness; the dispersion was no more than 0.05 μ m. The temperature of the template and the vapour source was monitored by chromel-alumel thermocouples. The condensation rate value was selected by trial and error and was estimated based on the evaporation time of the material. During the diffusion of precursor tablets the temperature of the templates' temperature varied from 250 to 280°C.

To obtain the needlelike structure, the surface of the glass templates was exposed to chemical etching in a weak hydrofluoric acid solution. The needles with an average size of $1-2 \mu m$, which formed on the surface of the glass template, acted as film crystallization centres. Changes in the resistance of polycrystalline films and compressed tablets in the 298–498 K temperature range in dry and argon ambient have been investigated.

It has been shown that the characteristics of temperature resistance relationships in PbCdSe oxidised samples may be related to their micro-structure and the state of the environment. It has been found that at temperatures higher than room temperatures but lower than 100°C all samples that had been pre-oxidised in the air showed an anomalous change in resistance.

We used electronic microscopy, X-ray diffractometry and thermal conductivity study methods to analyze oxidation mechanisms of semiconductor structures with varying levels of structural perfection and differing geometric structures. The following results were obtained:

external shell of PbSe structures exists in room temperatures and upwards and relates to PbSeO₃phase, volume of PbSeO₃ oxide phase on the surface of PbCdSe increases with the temperature growth, in the structures investigated in the specified temperature range phases other than PbSe and PbSeO₃ were not detected.

The surfaces and chips of original (Fig. 1a) and oxidised films (Fig. 1b) were investigated by scanning electron microscopy.

Figs. 1a and 1b present micrographs of $Pb_{1-x}Cd_xSe$ films before and after heat treatment in the oxygen atmosphere. It is quite clear that the template morphology modifies the original unoxidised surface; on oxidised surface larger crystals are evident, resulting from thermal recrystallization of the original crystals and oxidation processes. The thickness of the film may vary from 500 nm to 2500 nm.

Spectral luminescence measurements were performed using fluorimeter SHIMADSU. An example of the resultant spectrum is shown in Fig. 2.





a

Fig. 1. Morphology of $Pb_{1-x}Cd_xSe$ film surface before (a) and after (b) temperature treatment

Results and discussion

Spectrum of luminescence of $Pb_{1-x}Cd_x$ Se polycrystalline films generated by light with wavelength $\lambda \approx 900$ nm is presented in Fig. 2. The resulting spectrum is well described by the formula of W. van Roosbroeck and W. Shockley (Tomaev 2009) for inter-band electron-hole recombination. Spectral dependency of radiative recombination speed $F(\omega)$ is related to dependency of absorption coefficient k_{ω} . With no degeneration or if $\omega \approx kT$ this dependency can be recorded in a more convenient way:

$$F(\omega) = B^{2}(\omega)k_{\omega}\exp(-\frac{\hbar\omega - E_{0}}{kT})$$
⁽¹⁾

where $B(\omega)$ is directly related to the band gap E_o and to solid solution compounds used for film deposition. The position of the luminescence spectral maximum depends on the Cd concentration, and it moves to the short-wave area with increasing Cd concentration.

Fig. 3 presents spectra of luminescence registered for different $Pb_{1-x}Cd_xSe$ polycrystalline films. Curves N^0 1, 2, 3, 4 correspond to four different samples of polycrystalline films made under similar conditions.

To reduce the reflection of each layer of film, an immersion layer is applied to it. In addition, the immersion layer provides better temperature stability of the spectrum of luminescence, because it works like a thermal insulator protecting the film from overheating.

To reduce losses from film-air surface, the immersion layer is formed from a material with a refraction coefficient between those of semiconductor film and air. Typically, AsSSe chalcogenide glass is used for this purpose. This increases the output intensity of luminescence by 15–20%. Spectra 1, 2, 3, 4 in Fig. 3 show that despite the unavoidable changes in film parameters which occur during the deposition process (influence of template surface structure, deposited film thickness errors, chemical composition of Pb_{1-x}Cd_xSe solid solution), basic spectral parameters of fluorescence, such as line width and maximum position, are easily reproducible. Deposition of several Pb_{1-x}Cd_xSe films with different thickness and chemical composition allows for controlling spectral width of luminescence. This is illustrated by curve 5 in Fig. 3.



Fig. 2. $Pb_{1-x}Cd_xSe$ film luminescence spectrum ($\lambda_{ex} = 900 \text{ nm}$)



Fig. 3. PbCdSe film luminescence spectrum by number of layers

To reduce the absorption of light from low-lying films in multi-layer structures, the thickness of each subsequent layer shall be reduced by 20–25% compared to that of the previous layer. To reduce the mixing between $Pb_{1-x}Cd_xSe$ layers, a 5 nm thick SiO₂ dielectric layer was applied, which was transparent to both excitation and infrared radiation of luminescence.

In the standard operational temperature range. i.e. between -20 and $+40^{\circ}$ C, maximum luminescent spectrum shift from temperature is linear with the slope coefficient 4,48 $10^{-3} \,\mu m/^{\circ}$ K, which is obviously related to the temperature dependency of the band gap width of PbSe p-n-junction (Fig. 4).



Fig. 4. Width of the band gap of PbSe p-n-junction by temperature

Findings

- 1. $Pb_{1-x}Cd_xSe$ polycrystalline film luminescence spectra are presented.
- 2. Luminescence efficiency for Pb_{1,x}Cd_ySe film at λ_{ex} = 900 nm is about 1% of pumping power.

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Condensed Matter Physics. Physics of Thermoelectric Phenomena

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Thermoelectric phenomena and thermodynamic laws

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Abstract. The paper deals with thermoelectric phenomena from the standpoint of nonequilibrium thermodynamics of irreversible processes. The consideration is based on the fact that thermoelectric effects can occur if there is electrical and thermal contact of electrically conductive media. The necessary condition for the effect is the subsystems' different ordering degree of charge and heat carriers or different entropy and heat capacity per each carrier particle. The presented approach gives the possibility to understand physics of thermoelectric phenomena deeply. Its development can help to establish the theoretical limits of the efficiency of thermoelectric energy conversion imposed by fundamental physical laws.

Keywords: nonequilibrium thermodynamics, thermoelectricity, Seebeck effect, Peltier effect, entropy, heat capacity, heat transfer, order, disorder.

Introduction

Today we can see that thermoelectric phenomena and laws are attracting researchers because of their wide use in the field of small energy, electric power generation, or forced heat removal (thermoelectric cooling) from space and defense technology to household medicine. So it is very important to increase the efficiency of the developed thermoelectric energy converters and to develop the new thermoelectric materials with a high value of the thermoelectric efficiency parameter $Z = (\alpha^2 \sigma / \kappa)$ (Gross 1961; Ioffe 1960), which includes material parameters α —thermoelectric coefficient (Seebeck), σ —electrical conductivity coefficient, κ —coefficient of specific thermal conductivity. Today, the best thermoelectric materials are characterized by the values of the dimensionless efficiency parameter ZT \approx 1.5–1.8, as can be seen from Fig. 1.

Today, there are no studies that would allow us to conclude that there are fundamental limitations on the possibility to increase the ZT of thermoelectric materials. The authors believe that the thermoelectric phenomena analysis based on the fundamental laws of modern thermodynamics will help find ways to increase the ZT parameter of thermoelectric materials or to establish natural limitations of its magnitude. Significant progress in the analysis of thermoelectric phenomena can be achieved with the help of the following sections of modern physics: the fundamental laws of physical kinetics (Anselm 1978; Askerov 1985), the thermodynamics of irreversible processes, and the symmetry principle of the Onsager kinetic coefficients. The main issues of these sections are systematically presented by A.I. Anselm (Anselm 1973).

The initial system for describing thermoelectric phenomena in electrically conductive media based on the thermodynamics of irreversible processes and physical kinetics (Anselm 1973; 1978; Askerov 1985) usually has the following system of equations for electric charge flux density (j_{α}) and heat (j_{α}) :

$$j_{q} = \sigma E - \alpha \sigma gradT$$

$$j_{Q} = -kgradT + \pi j_{q}$$
(1)

Moreover, the symmetry condition for kinetic coefficients implies the Thomson relation between the Peltier coefficient (π) and the Seebeck coefficient (α): $\pi = \alpha T$.



Fig. 1. State-of-the-art comparison of ZT in conventional bulk materials and nanostructured composite materials (Szczech, Higgins, Jin 2011). LAST (lead antimony silver telluride): $Ag_{1-x}Pb_{18}SbTe_{20}$ HMS (higher manganese silicides): MnSi_{1.7}.

Thermoelectric phenomena in general thermodynamics

Let us see the Peltier effect on the contact of two different conductors (1) and (2) under the isothermal conditions gradT = 0. A continuous electric current with the density $(\mathbf{j}_q)_1 = (\mathbf{j}_q)_2 = (\mathbf{j}_q)$ runs through the contact.

The corresponding heat fluxes will be different $(j_Q)_1 = \pi_1(j_q), (j_Q)_2 = \pi_2(j_q)$ and Peltier heat will be generated or absorbed at the contact, depending on the electric current direction:

$$\frac{dQ}{dt} = (\pi_1 - \pi_2)(j_q).$$
⁽²⁾

In the calculation of the transition through the contact of one electron, Peltier heat will be released or absorbed

$$\frac{dQe}{dt} = (\pi_1 - \pi_2)e. \tag{3}$$

On the other hand, the amount of heat can be expressed through the entropy Q = TS. When one electron passes through the contact, heat equal to the difference in the entropy transferred by the electron will be released or absorbed.

$$\frac{dQe}{dt} = \left(s_1 - s_2\right)T \ . \tag{4}$$

Comparison of (3) and (4) leads to the following relations for each conductor: $\pi_i e = s_i T$, or, $s_i = \frac{\pi_i e}{T}$, taking into account the Thomson relation $\pi = \alpha T$, which leads us to the relation $s_i = \alpha_i e$. Let us take into account that entropy is related to the heat capacity (c_{ei}) per charge carrier as

$$s_i = \int_0^T \left(\frac{c_{ei}}{T}\right) dT \, .$$

Thus, the difference between the magnitude of the thermoelectric coefficients of two contacting conductors is determined by the difference in the entropy or heat capacity per charge carrier. The analysis shows that the Peltier effect can be considered similar to magnetic cooling—the method of getting low temperatures by adiabatic demagnetization of paramagnetic substances. In this case, heat transfer is carried out by changing the entropy and heat capacity, which is carried out by applying and removing an external magnetic field to the system of paramagnetic ions (Anselm 1973).

The method analysis to change conductor's entropy value or heat capacity gives the possibility to determine the limits in changes conductor's value of thermoelectric parameters in the of electrically conducting media.

On the other hand, the analysis of heat transfer processes from the standpoint of Peltier effect theory allows, in some cases, to deepen the physical understanding of the essence of heat transfer processes. Let's discuss, for example, the bipolar mechanism of heat transfer in intrinsic semiconductors in the presence of two sign charge carriers—electrons and holes. For the thermal conductivity due to bipolar diffusion of charge carriers $(k \pm)$, the solution of the kinetic equation leads to the expression (Askerov 1985):

$$k^{\pm} = \frac{\sigma^+ \sigma^-}{\sigma^+ + \sigma^-} T \left(\alpha^+ - \alpha^- \right)^2.$$
⁽⁵⁾

The thermoelectric field is formed in the semiconductor with charge carriers of the same sign, if there is the temperature gradient and the electric current density of zero, this field prevents diffusion of charge carriers from a warmer to a less heated face, which limits the thermal conductivity of charge carriers. If there are charge carriers of two signs, electrons in the conduction band and holes in the valence band, the total electric current is zero, but there is an electric current carried by the electrons in the conduction band $j_q^- = \sigma^- \alpha^- gradT$ and holes in the valence band $j_q^+ = \sigma^+ \alpha^+ gradT$ for $j_q^- = -j_q^+$ The created partial electric currents are equivalent to the closed electric current in the sample.

And the current direction in the conduction band coincides with the temperature gradient direction, and in the valence band it is opposite to it.

Based on the solution of the kinetic equation (Askerov 1985), one can obtain the expression for this closed electric current:

$$j_{q}^{\pm} = j_{q}^{+} = -j_{q}^{-} = -\frac{\sigma^{+}\sigma^{-}}{\sigma^{+} + \sigma^{-}} (\alpha^{+} - \alpha^{-}) gradT.$$
 (6)

In this case, on the verge with a higher temperature, when an electron transfers from the valence band to the conduction band (the creation of an electron-hole pair), heat will be absorbed, and on the verge with a lower temperature when the electron transfers from the conduction band to the valence band (electron-hole pair recombinations) the heat of a peculiar "interband Peltier effect" $\frac{dQ}{dt} = (\pi^+ - \pi^-) j_q^{\pm}$ will be released.

Taking into account the relation for the partial kinetic coefficients $\pi^{\pm} = \alpha^{\pm}T$, we obtain:

$$j_{\underline{\varrho}} = \left(\alpha^{+} - \alpha^{-}\right)Tj_{q}^{\pm} = -\frac{\sigma^{+}\sigma^{-}}{\sigma^{+} + \sigma^{-}}T\left(\alpha^{+} - \alpha^{-}\right)^{2}gradT.$$
(7)

Bipolar thermal conductivity in intrinsic semiconductors can also be given a different physical interpretation. This interpretation is based on the action of the so-called heat pipe, in which heat of phase transition (heat of evaporation) is absorbed on the face with high temperature, and heat of condensation is released on the face with low temperature. For such consideration, the heat of formation of an electronhole pair and the heat of recombination of an electron-hole pair must be represented as the heat of some phase transition.

Conclusions

From the standpoint of modern thermodynamics, thermoelectric phenomena manifest themselves when charge carriers pass through the boundary of systems with different degrees of ordering, different entropy, and specific heat per each charge carrier.

This approach in combination with the traditional interpretation gives the possibility to understand deeply the physics of thermoelectric phenomena, which provides more opportunities for analyzing the prospects for increasing the efficiency of thermoelectric energy conversion and for determining the possible limits and restrictions on these processes imposed by fundamental physical laws.

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Theoretical Physics. Quantum Mechanics

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Characteristics of high-frequency emission of an electron in graphene in a constant electric field

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Abstract. The article describes the photon emission of the low-energy electron of a graphene monolayer in a constant electric field that exists during a macroscopic time period. We work in the Fock space representation of the Dirac model, which takes exact account of the effects of vacuum instability caused by an electric field, and in which the interaction between electrons and photons is taken into account in the first-order approximation. We find the main contribution to the total probability of a high-frequency photon emission of the electron and analise angular distribution of the emission.

Keywords: graphene monolayer, Fock space representation, high-frequency photon emission.

Introduction

Low-energy single-electron dynamics in graphene monolayers at the charge neutrality point is described by the Dirac model, being a 2+1 dimensional version of massless quantum electrodynamisc (QED) with the Fermi velocity $v_F \simeq 10^6 \text{ m/s}$ playing the role of the speed of light in relativistic particle dynamics. This area is currently under intense development, see the reviews (Sarma, Adam, Hwang, Rossi 2011; Vafek, Vishwanath 2014). In particular, the effect of particle production from vacuum due to a low-frequency electric field is crucial for understanding the conductivity of graphene, especially in the so-called nonlinear regime; e.g., see Ref. (Gavrilov, Gitman, Yokomizo 2012) for the review. Electron-hole pair production at the charge neutrality point (which is an analog of the electron-positron pair production from the vacuum) was recently observed in graphene by its indirect influence on the graphene conductivity, see Ref. (Vandecasteele, Barreiro, Lazzeri et al. 2010).

In this article we consider an infinite flat graphene sample on which a uniform electric field is applied, directed along the axis x on the plane of the sample. We assume that the applied field is a constant electric field that exists during a macroscopically large time period T (we call it as the *T*-constant) compared to the characteristic time scale $\Delta t_{st} = (e|E| v_F/\hbar)^{-1/2} \gg 0.24$ fst specific to graphene, $10^{-12} \text{ s} || T > \Delta t_{st}$; see Ref. (Gavrilov, Gitman, Yokomizo 2012) for details. This field turns on to E at $-T/2 = t_{in}$ and turns off to 0 at. $T/2 = t_{out}$.

The electromagnetic field is not confined to the graphene surface, z = 0, but rather propagates (with the speed of light *c*) in the ambient 3+1 dimensional space-time, where *z* is the coordinate of the axis normal to the graphene plane. The article focuses on the characteristics of high-frequency emission

 $(\omega \gg T^{-1})$ of an electron graphene in a constant electric field. Note that such an emission could be observable which makes it highly interesting. Taking into account that a low-frequency external electric field requires a non-perturbative treatment of massless carriers, we use non-perturbative methods of the strong-field QED with unstable vacuum, see Ref. (Fradkin, Gitman, Shvartsman 1991). We work in the Fock space representation of the Dirac model, which takes exact account of the effects of vacuum instability caused by external electric fields, and in which the interaction between electrons and photons is taken into account perturbatively in the first-order approximation, following the general theory (the generalized Furry representation), see Ref. (Fradkin, Gitman, Shvartsman 1991).We use the representation of the Dirac model in the Fock space adjusted for the interaction of photons with Dirac fermions, Ref. (Gavrilov, Gitman 2017). Applying this representation we find the main contribution to the total probability of a high-frequency photon emission by an electron in graphene and analise angular distribution of the emission.

The total probability of a photon emission

In what follows, we use boldface symbols for three-dimensional vectors and symbols with arrows for in-plane comonents, for example, $\tilde{r} = (x, y)$. The Dirac equation in an external field that couples minimally to the electrons on the graphene plane is

$$i\hbar \partial_t \psi(t, \bar{r}) = H^{\text{ext}} \psi(t, \bar{r}),$$

$$H^{\text{ext}} = v_F \gamma^0 \bar{\gamma} \cdot \left(\bar{p} - \frac{e}{c} \bar{A}^{\text{ext}}(t, \mathbf{r}) \right), \quad p^j = -i\hbar \partial_j,$$
(1)

where $\psi(t, \bar{r})$ is a two-component spinorial field, $\bar{\gamma} \cdot \bar{p} = \gamma^1 p_x + \gamma^2 p_{y_y}$, the γ -matrices satisfy the standard anti-comutation relations, $\{\gamma^{\mu}, \gamma^{\nu}\} = 2\eta^{\mu\nu}$, $\eta_{\mu\nu} = \text{diag}(+1-1,-1)$, $\mu,\nu = 0,1,2$, and e is the charge of the electron, e = -|e|. The algebra of γ -matrices has two inequivalent representations in 2+1-dimensions, and a distinct (pseudo spin) representation is associated with each Dirac point,

$$\gamma^{0} = \sigma^{3}, \quad \gamma^{1} = i\sigma^{2}, \quad \gamma^{2} = -i\zeta\sigma^{1}, \quad (2)$$

where the σ^{i} are Pauli matrices, and $\zeta = \pm 1$ labels inequivalent representations.

In the usual dipole approximation, *z*-dependence of the QED Hamiltonian can be integrated out. Then the Hamiltonian of the electron-photon interaction is

$$\hat{\mathcal{H}}_{int} \approx -\int \overline{\tilde{y}}_{in}(t,\bar{r}) \cdot \overline{\hat{A}}(t,\mathbf{r}) \Big|_{z=0} d\bar{r},$$

$$\bar{j}_{in}(t,\bar{r}) = \frac{ev_F}{2c} \Big[\hat{\Psi}^{\dagger}(t,\bar{r}), \gamma^0 \overline{\tilde{\gamma}} \hat{\Psi}(t,\bar{r}) \Big]_{-},$$
(3)

where quantum fields $\hat{\mathcal{O}}(t,\bar{r})$ and $\hat{\mathcal{O}}^{\dagger}(t,\bar{r})$ obey both the Dirac equation with the potential $\bar{A}^{\text{ext}}(t,\bar{r})$ and the standard equal time anticommutation relations. We decomposed quantum electromagnetic field in the interaction representation into terms of the annihilation and creation operators of photons, C_{kg} and C_{kg}^{\dagger} :

$$\hat{\mathbf{A}}(t,\mathbf{r}) = c \sum_{\mathbf{k},\vartheta} \sqrt{\frac{2\pi\hbar}{\varepsilon V \omega}} \mathring{a}_{\mathbf{k}\vartheta} \Big[C_{\mathbf{k}\vartheta} \ \mathrm{e}^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + C^{\dagger}_{\mathbf{k}\vartheta} \ \mathrm{e}^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \Big], \tag{4}$$

where $\vartheta = 1,2$ is a polarization index, the $\varepsilon_{k\vartheta}$ are unit polarization vectors transversal to each other and to the wavevector **k**, $\omega = ck$, $k = |\mathbf{k}|$, *V* is the volume of the box regularization, and ε is the relative permittivity ($\varepsilon = 1$ for graphene suspended in vacuum).

The in - and out - operators of creation and annihilation of electrons (a_n^{\dagger}, a_n) and holes (b_n^{\dagger}, b_n) are defined by the two representations of the quantum Dirac field $\hat{\Psi}(t, \bar{r})$ as

$$\hat{\Psi}(t,\bar{r}) = \sum_{n} \left[a_{n}(\operatorname{in})_{+}\psi_{n}(t,\bar{r}) + b_{n}^{\dagger}(\operatorname{in})_{-}\psi_{n}(t,\bar{r}) \right]$$

$$= \sum_{n} \left[a_{n}(\operatorname{out})^{+}\psi_{n}(t,\bar{r}) + b_{n}^{\dagger}(\operatorname{out}))^{-}\psi_{n}(t,\bar{r}) \right],$$
(5)

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where $_{\zeta}\psi_n(t,\bar{r})$ and $^{\zeta}\psi_n(t,\bar{r})$ are in - and out -solutions of the Dirac equation with the potential $\bar{A}^{\text{ext}}(t,\bar{r})$ for given quantum numbers *n* and well-defined sign of the frequency ζ either before the turnon or after the turn-off of the field, respectively. They are related by a linear transformation, i.e. a linear canonical transformation (the Bogoliubov transformation) between in - and out - operators; see (Fradkin, Gitman, Shvartsman 1991) for details.

The initial and final states with definite numbers of charged particles and photons can be generally written in the following way:

$$|\operatorname{in}\rangle = C^{\dagger} \dots b^{\dagger}(\operatorname{in}) \dots a^{\dagger}(\operatorname{in}) \dots |0, \operatorname{in}\rangle,$$
$$|\operatorname{out}\rangle = C^{\dagger} \dots b^{\dagger}(\operatorname{out}) \dots a^{\dagger}(\operatorname{out}) \dots |0, \operatorname{out}\rangle.$$

The S -matrix or the scattering operator in the first-order approximation with respect of electronphoton interaction (it is exact with respect of an interaction with an external field) is

$$\mathcal{S} \approx 1 + i \mathbf{Y}^{(1)}, \quad \mathbf{Y}^{(1)} = -\frac{1}{\hbar} \int_{-\infty}^{\infty} \hat{\mathcal{H}}_{int} dt$$
 (6)

In general, the emission of a single photon by an electron is accompanied by the creation of a number of electron-hole pairs from the vacuum by the quasiconstant electric field. We are interested in the probability of transition from the single-electron state characterized by the quantum numbers l with the emission of one photon with given \mathbf{k} , ϑ and the production of arbitrary number of pairs from the vacuum, that is, the total probability of the emission of the given photon from the single-electron state, $\mathcal{P}(\mathbf{k}\mathcal{G}|l)$. This probability can be presented as the average number of photon emitted

$$\mathcal{P}\left(\mathbf{k}\boldsymbol{\vartheta}\big|^{\dagger}\right) = 0, \text{in}\left|a_{n}\left(\text{in}\right)\boldsymbol{\mathcal{S}}^{\dagger}\boldsymbol{C}_{\mathbf{k}\boldsymbol{\vartheta}}^{\dagger}\boldsymbol{\mathcal{C}}_{\mathbf{k}\boldsymbol{\vartheta}}\boldsymbol{\mathcal{S}}\boldsymbol{a}_{l}^{\dagger}\left(\text{in}\right)\right|0, \text{in}\rangle.$$
(7)

It is convenient to represent Eq. (7) as

$$\mathcal{P}\left(\mathbf{k}\mathcal{S}|\stackrel{*}{l}\right) = \sum_{n} \left| w_{in}^{(1)} \left(\stackrel{*}{n}; \mathbf{k}\mathcal{S}|\stackrel{*}{l}\right) \right|^{2},$$

$$w_{in}^{(1)} \left(\stackrel{*}{n}; \mathbf{k}\mathcal{S}|\stackrel{*}{l}\right) = 0, \text{in} \left| a_{n}(\text{in}) C_{\mathbf{k}\mathcal{S}} i \mathbf{Y}^{(1)} a_{l}^{\dagger}(\text{in}) \right| 0, \text{in} \rangle.$$
(8)

Note that to calculate the amplitude $w_{in}^{(1)} \left(\stackrel{+}{n}; \mathbf{k} \boldsymbol{\beta} \middle| \stackrel{+}{l} \right)$ we need only initial electron states.

The case of a constant electric field

Let us calculate the total probability for emission, given by Eq. (8), in a near constant electric field that is realised as the *T*-constant electric field (Gavrilov, Gitman 2017). We consider the case of the field described by a vector potential with only one nonzero component $A_1^{ext}(t)$ ($A_{\mu}^{ext}(t) = 0$, $\mu \neq 1$),

$$A_{\rm I}^{ext}(t) = cE \begin{cases} t_1 & t \in {\rm I} = (-\infty, t_{in}), \ t_1 = -T/2 \\ t, & t \in {\rm Int} = [t_1, t_1], \\ t_2, & t \in {\rm II} = (t_2, \infty), \ t_2 = T/2 \end{cases}$$

such that the electric field $\mathbf{E}(t)$ also has only one nonzero component, which is nonzero for $t \in \text{Int}$, i.e.,

$$E^{1}(t) = E, t \in \text{Int}; E^{1}(t) = 0, t \in I \cup \text{II}.$$

To simplify notation, it is convenient to let E < 0, so that eE > 0. We are only interested in the case of a slowly varying homogeneous electric field E which remains constant for a macroscopically large time period T,

$$T / \Delta t_{st} \gg 1.$$
 (9)

The time scale Δt_{st} plays the role of the stabilization time in the sense that the differential mean numbers of created pairs have the form

$$N_n \simeq e^{-\pi\lambda}, \quad \lambda = \frac{v_F p_y^2}{eE\hbar},$$
 (10)

which is the same for the case of the constant electric field in a finite momentum range.

The solutions of the Dirac equation (1) in the *T*-constant field are studied in details in Ref. (Gavrilov, Gitman 2017). It was demonstrated that the *in*-set $\{ \zeta \Psi_n(t, \bar{r}) \}$ of these solutions can be taken in the form

$${}_{\pm}\psi_{\vec{p}}\left(t,\bar{r}\right) = \left(i\hbar \ \partial_{t} + H^{ext}\right) {}_{\pm}\phi_{\vec{p},\mp 1}\left(t,\bar{r}\right),$$
$${}_{\pm}\phi_{\vec{p},\mp 1}\left(t,\bar{r}\right) = e^{i\vec{p}\cdot\vec{r}/\hbar} {}_{\pm}\phi_{\vec{p},\mp 1}\left(t\right)U_{\mp 1},$$
(11)

where U_{s} are the constant orthonormalized spinors

$$U_{+1} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \qquad U_{-1} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}.$$

In a finite momentum range, the functions ${}_{\pm}\varphi_{\bar{p},s}(t)$ take the form of the following Weber parabolic cylinder (WPC) functions (Bateman 1953):

with the normalization constant

$$C = \left(2eE\hbar v_F S\right)^{-1/2} \exp\left(-\pi\lambda/8\right),\tag{13}$$

where *S* is the graphene area. An in-state $_{\pm}\psi_{\bar{p}}(t,\bar{r})$ describes a particle/hole with a well-defined energy in the distant past. In such a description, the probability of an emission of a given photon in the *T*-constant electric field for $t \in$ Int is indistinguishable from the effect produced by a constant field $(T \rightarrow \infty)$. Then, in what follows, we assume that $T \rightarrow \infty$.

It is useful to define an orthonormal triple

$$\mathbf{k} / k = (\sin\theta\cos\phi, \ \sin\theta\sin\phi, \ \cos\theta),$$

$$\mathbf{a}_{\mathbf{k}1} = \mathbf{e}_{z} \times \mathbf{k} / |\mathbf{e}_{z} \times \mathbf{k}|, \quad \mathbf{a}_{\mathbf{k}2} = \mathbf{k} \times \mathbf{a}_{\mathbf{k}1} / |\mathbf{k} \times \mathbf{a}_{\mathbf{k}1}|.$$
(14)

where

$$\dot{a}_{k1} = (-\sin\phi, \cos\phi, 0),$$
$$\dot{a}_{k2} = (-\cos\theta\cos\phi, -\cos\theta\sin\phi, \sin\theta)$$

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for **k** in the upper spatial region, $k_z \ge 0$. Using the parametrization, $d\mathbf{k} = c^{-3} \omega^2 d\omega d\Omega$, we find that the probability of the emission per unit frequency and solid angle $d\Omega$ is

$$\frac{d\mathcal{P}\left(\mathbf{k}\mathcal{G}\big|\tilde{p}\right)}{d\omega d\dot{\mathbf{U}}} = \frac{\alpha}{\varepsilon} \left(\frac{v_{F}}{c}\right)^{2} \frac{\omega \ddot{\mathbf{A}} t_{st}^{2}}{\left(2\pi\right)^{2}} \left|M_{\vec{p}^{'}\vec{p}}^{+}\right|^{2} \Big|_{\vec{p}^{'}=\vec{p}-\hbar\vec{k}},$$

$$M_{\vec{p}^{'}\vec{p}}^{+} = v_{F}^{2}SC'Cexp\left(-i\omega\frac{p_{x}+p_{x}^{'}}{2eE}\right)\sqrt{\frac{\hbar}{v_{F}eE}}$$

$$\times \left\{p_{y}^{'}p_{y}\chi_{\mathcal{G}}^{1,1}Y_{11} + 2\frac{eE\hbar}{v_{F}}\chi_{\mathcal{G}}^{0,0}Y_{00}$$

$$+ \sqrt{\frac{eE\hbar}{v_{F}}}\zeta\left[\left(1-i\right)p_{y}^{'}\chi_{\mathcal{G}}^{1,0}Y_{10} + \left(1+i\right)p_{y}\chi_{\mathcal{G}}^{0,1}Y_{01}\right]\right\},$$
(15)

where $\alpha = e^2 / c \ddot{y}$ is the fine structure constant, $C' = C \Big|_{p_y \to p_y'}$, and

$$\chi_{g}^{(1+s')/2,(1+s)/2} = U_{s'}^{\dagger} \gamma^{0} \dot{\gamma} \cdot \vec{\varepsilon}_{kg} U_{s},$$

$$\chi_{1}^{0,0} = -\chi_{1}^{1,1} = \sin\phi, \quad \chi_{1}^{1,0} = -\chi_{1}^{0,1} = i\zeta \cos\phi;$$

$$\chi_{2}^{0,0} = -\chi_{2}^{1,1} = \cos\theta \cos\phi, \quad \chi_{2}^{1,0} = -\chi_{2}^{0,1} = -i\zeta \cos\theta \sin\phi.$$
(16)

In the case of a high frequency of interest, $Y_{j'j}(\rho)$ can be approximated as the following Fourier transformation of the product of the WPC functions

$$Y_{j'j}(\rho) \approx \int_{-\infty}^{+\infty} D_{-\nu'-j'} \left[-(1+i)u \right] D_{\nu-j} \left[-(1-i)u \right] e^{i\rho u} du,$$

$$v = \frac{i\lambda}{2}, \quad \nu' = \frac{i\lambda'}{2}, \quad \lambda' = \lambda \Big|_{p_y \to p_y'}, \quad \rho \approx \Delta t_{st} \omega.$$
(17)

The integrals of the type (17) have been studied in Ref. (Nikishov 1970). Similarly, one can find that

$$Y_{j'j}(\rho) = \sqrt{\frac{2}{\pi}} \sinh\left(\frac{\pi\lambda}{2}\right) \Gamma\left(i\frac{\lambda}{2} - j\right)$$

$$\times \exp\left[-\frac{\pi\lambda'}{4} + i\frac{\pi}{2}(j'+2j-1)\right] I_{j'j}(\rho), \qquad (18)$$

$$I_{j'j}(\rho) = I(\rho)\Big|_{\nu' \to \nu'+j'}^{\nu \to \nu+1-j},$$

where

$$I(\rho) = \sqrt{\pi} \exp\left[-i\frac{\pi}{4} + i\frac{\rho^{2}}{4} + i\frac{\pi}{4}(\nu' - \nu) + (\nu - \nu')\ln(\rho/\sqrt{2})\right] \times \Psi(\nu, 1 + \nu - \nu'; -i\rho^{2}/2)$$
(19)

is expressed via the confluent hypergeometric function Ψ and the gamma function Γ .

Characteristics of high-frequency emission

Assuming typical values of an electric field we obtain the following frequency scale

$$E = aE_0, \quad E_0 = 1 \times 10^6 \,\mathrm{V/m}, \quad 7 \times 10^{-4} \ll a \ll 8,$$

$$\omega_{sc} = \Delta t_{st}^{-1} \approx \sqrt{a} \times 0.38 \times 10^{14} \,\mathrm{s}^{-1}.$$
(20)

At high frequencies, $\rho \gg 1$, we can use the asymptotic behavior of the function Ψ , given by Eq. (6.13.1.(1)) in (Bateman 1953),

$$\Psi(a,c;-i\rho^2/2) = e^{i\frac{\pi}{2}a} \left(\rho^2/2\right)^{-a} \left[1 + O(\rho^{-2})\right].$$
(21)

The term $\left|M_{\vec{p}|\vec{p}}^{+}\right|^{2}$, given in Eq. (15), is Gaussian function of λ '. It is exponentially small for $\lambda' > 1$ and whatever λ ,

$$\left|M_{\vec{p}'\vec{p}}^{+}\right|^{2} \sim e^{-\pi\lambda'} \sinh\left(\frac{\pi\lambda}{2}\right) \exp\left(-\frac{\pi\lambda}{2}\right).$$
(22)

Then, in what follows, of interest is the case of small $\lambda > 1$ only. It implies an approximate conservation law,

$$v_F k_y \omega_{sc}^{-1} \sim \operatorname{sign}(p_y) \sqrt{\lambda}.$$
 (23)

Under this condition it can be shown that the leading contribution to the probability (15) is from terms with Y_{00} and Y_{01} ,

$$Y_{00}(\rho) \approx f\tilde{A}\left(i\frac{\lambda}{2}\right)e^{-i\pi/2}\left(\frac{\rho}{\sqrt{2}}\right)^{-(\nu'+\nu+1)},$$

$$Y_{01}(\rho) \approx f\tilde{A}\left(i\frac{\lambda}{2}-1\right)e^{i\pi/4}\left(\frac{\rho}{\sqrt{2}}\right)^{-(\nu'+\nu)},$$

$$f = \sqrt{2}\sinh\left(\frac{\pi\lambda}{2}\right)\exp\left[i\frac{\rho^{2}}{4}-\frac{3\pi\lambda'}{8}-\frac{\pi\lambda}{8}\right].$$
(24)

Thus, we obtain that

$$\left| M_{\vec{p}'\vec{p}}^{+} \right|^{2} \approx \frac{\hbar}{v_{F} eE} \frac{2\pi}{\lambda} \sinh\left(\frac{\pi\lambda}{2}\right) \exp\left[-\pi\left(\lambda' + \lambda/2\right)\right] \\ \times \left| \chi_{g}^{0,0} \frac{2}{\rho} - \zeta \operatorname{sign}\left(p_{y}\right) \chi_{g}^{0,1} \frac{\operatorname{sign}\left(p_{y}\right) \sqrt{\lambda}}{i\frac{\lambda}{2} - 1} \right|^{2}.$$

$$(25)$$

Unlike the example considered in Ref. (Gavrilov, Gitman 2017) under condition $|\lambda - \lambda\rangle| < 1$ the expression given by Eq. (25) is valid at whatever λ and λ . At small $\sqrt{\lambda} < 2/\rho$ the term with $\chi_{g}^{0,0}$ in Eq. (25) is leading. In this case $\left|M_{\vec{p}'\vec{p}}^{+}\right|^{2} \sim \rho^{-2}$ is rather

small.

The main contribution to Eq. (25) is due to the term with $\chi^{0,1}_{g}$ when $ho \gg 1/\sqrt{\lambda}$,

$$\left|M_{\bar{p}'\bar{p}}^{+}\right|^{2} \approx \frac{\hbar}{v_{F}eE} \frac{2\pi}{\left(\lambda/2\right)^{2}+1} \sinh\left(\frac{\pi\lambda}{2}\right) \exp\left[-\pi\left(\lambda'+\lambda/2\right)\right] \left|\chi_{g}^{0,1}\right|^{2}.$$
(26)

We see that the probability of the emission (15) where the factor $\left|M_{\vec{p}'\vec{p}}^{+}\right|^{2}$ is given by Eq. (26) has naximum at $\lambda \sim 1$. a maximum at $\lambda \sim 1$.

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In this case, taking into account Eq. (23), we can estimate k_{z} component as $k_{y} \sim \omega_{sc} / v_{F}$. An angular distribution for the emission is determined by the factor $|\chi_{g}^{0,1}|^{2}$ given by Eq. (16). We finally find the emission with a polarization index $\vartheta = 1$ tends to its maximum at $\phi \to 0, \pi$, when $|k_{x}/k_{y}| \gg 1$ and whatever k_{z} . That is, the maximum of the emission is near plane y = 0. The emission with a polarization index $\vartheta = 2$ tends to its maximum at $\phi \to \pm \pi/2$ and $\theta \to 0$, when $k_{z}^{2} \gg k_{x}^{2} + k_{y}^{2}$ and $|k_{y}/k_{x}| \gg 1$. That is, this emission is directed near plane x = 0 and concentrated near axis z.

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