INTRODUCTION

The terahertz (THz) range of electromagnetic waves is situated between infrared and millimeter spectral ranges, that is waves having wavelength $\lambda$ ranging from 20 $\mu$m to 0.3 mm corresponding to frequencies from 1 to 15 THz or to wavenumbers varying from 30 to 500 cm$^{-1}$ [1].

Emission (absorption) of THz electromagnetic waves accompanies many physical-chemical processes. However up to the 80-th scientists did not have rather powerful sources of THz-radiation, except for lasers functioning on water and methanol vapor generating at several widely spaced frequencies. The situation drastically changed in the middle of 80-th, when a number of free-electron lasers (FEL) capable to generate intensive monochromatic radiation with gradually tunable frequency were built and became accessible for scientific community [2].

Molecular spectroscopy came to be one of the most important applications of FEL THz radiation, because many molecular absorption lines corresponding to their vibrational and/or rotational frequencies belong to the THz spectral range. Moreover the duration of FEL's radiation pulse may be considerably less as compared with molecular relaxation time that enables scientists to control the chemical processes accompanied by definite bonds excitation with high accuracy. Use of FEL THz-radiation makes it possible to investigate chain photochemical reactions with laser radiation pumping when photo dissociation leads to formation of a large number of new molecules as well.

Molecular spectroscopy is an important division of optical spectroscopy of solids' surfaces and molecular adsorbates on them. This avenue of optical spectroscopy is important not only for solving problems of corrosion and catalysis, it is widely used in industry and laser optics, for optical control of technological and biological processes, in many other spheres of science and technique [3]. The potentialities of spectroscopy were considerably enlarged when they began to use the sample (the surface of the solid) as a part of the optical resonator where the probing radiation excites surface electromagnetic waves (SEW) [4, 5]. This technique enables scientists to obtain enhanced absorption spectra of surfaces and their transition layers as excitation of SEW is accompanied by the field’s resonance amplification lifting it up to two or even three orders of magnitude. SEW-spectroscopy falls in the category of non-destructive methods of surface characterization used not only in vacuum but under natural conditions as well. The method’s foundations were laid down in 1973, when American scientists managed to measure SEW's propagation length $L$ in infrared directly using $\mu$-laser and the two-prism technique for the SEW excitation and detection [6]. The method turned to be rather simple for realization, reliable and very effective; it gained wide recognition and was mastered in Russia as well [7].

The method of SEW-spectroscopy implies determination of the surface waves propagation length $L$ in a...
definite frequency range by measuring its field intensity not less than at two points of the track on the sample’s surface. The scheme of the set-up realizing the method is sketched in Fig. 1.

Up to the preset SEW-spectroscopy technique was practiced mainly in relatively narrow spectral regions adjacent to more intensive lines of generation of CO [8], CO2 lasers [6] as well as methanol vapor lasers [9]. As soon as FELs were built scientists could study another important feature of SEW – the dispersion in broad areas of optical frequencies ranging from plasma (~50000 cm⁻¹) to THz frequencies [10].

It was demonstrated in papers [11–13], devoted to spectroscopy and optics of SEW, that combination of bulk and surface waves has good perspectives for the spectral interferometry of metals’ surfaces and thin films on them. Use of THz-radiation produced by FEL in SEW-spectroscopy may be very fruitful for dielectric constants determination of metals themselves and those of thin films on the metals’ surfaces as well in very wide spectral range. Other well-known methods of reflectometry such as Fourier-spectroscopy and ellipsometry can not be used for this purpose due to high reflectivity of metals in the far infrared (IR) [14, 15]. But SEW-spectroscopy retains its sensitivity to the metal’s refractivity of metals in the far infrared (IR) [14, 15]. But SEW-spectroscopy may be very fruitful for dielectric constants determination of metals as well as at THz frequencies its phase velocity approaches the speed of light, the field’s penetration depth in vacuum δ increases up to centimeters, while propagation length L reaches almost 10 meters.

If we measure the real part κ’ of SEW effective refractive index along with its imaginary part κ” (which is inversely proportional to L and therefore could be determined using the two-prism technique), than it is possible to estimate the metal’s dielectric permittivity ε and its optical constants n and k.

Value of κ’ at THz frequencies could be measured using the SEW-interferometry method, which was tested in the middle infrared (~1000 cm⁻¹) on metals as well as at THz frequencies on dielectric crystals [11–13]. But under these conditions the phase shift acquired by SEW at a distance of several centimeters amounts up to 10⁻³ radians, while on metal samples at THz frequencies the shift gained by SEW at a distance of 10 cm is estimated to be 10⁻⁵–10⁻⁶ radians only. Moreover at THz frequen-

![Fig. 1. The scheme of the two-prism method for SEW propagation length measurements.](image)

The table contains values of both real – (κ’) and imaginary – (κ”) parts of SEW refractive index κ as well as those of L, calculated for the surface of evaporated aluminum (medium 2) placed in vacuum (medium 1) at different wavelengths λ using values of optical constants (the index of refraction n and the index of absorption k) taken from the handbook [15]. The fourth and the fifth Table’s columns are filled with real (ε’) and imaginary (ε”) parts of aluminum dielectric permittivity ε, which for λ = 100 μm were calculated using the Drude model (the experimental data was not found in handbooks). One can see that as the radiation wavelength increases SEW acquires more pronounced photon character, namely at THz frequencies its phase velocity approaches the speed of light, the field’s penetration depth in vacuum δ increases up to centimeters, while propagation length L reaches almost 10 meters.

<table>
<thead>
<tr>
<th>λ, μm</th>
<th>n</th>
<th>k</th>
<th>ε’₂</th>
<th>ε”₂</th>
<th>κ’</th>
<th>κ”</th>
<th>δ₁, μm</th>
<th>δ₂, μm</th>
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<tr>
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<td>7.65</td>
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<td>0.012</td>
<td>0.002</td>
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<tr>
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<td>-91.3</td>
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<td>0.001467</td>
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<td>0.016</td>
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<td>795</td>
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</table>

SEW characteristics dependencies upon the radiation wavelength calculated for aluminum–vacuum interface
cies the value of $L$ increases by two orders as compared with middle infrared range and may be as great as 10 meters. Therefore it is not an easy task to measure SEW propagation length $L$ with accuracy of at least 10% using samples of 10 cm in dimension. That is why we limited our aim in the experiments by just the fact of SEW excitation on metals at THz frequencies, detection of pronounced interferograms and determination of the real part $\kappa'$ of SEW refractive index using the interferograms.

With the aim in mind we addressed our colleagues from the Korea Atomic Energy Research Institute (KAERI) where they recently built with technical support of the Budker Institute of Nuclear Physics (Novosibirsk, Russia) the new FEL generating THz radiation in the spectral range from 60 to 100 cm$^{-1}$ [16]. The main purpose of the experiments we planned to do at KAERI was to test the applicability of SEW interferometric technique in this range for determination of complex refractive index of SEW generated on nontransparent metallic films (made of aluminum, copper and chromium) and on bulk samples (made of copper and steel).

**BRIEF THEORY AND EXPERIMENTAL SET-UP DESCRIPTION**

Surface plasmon-polaritons, that is SEW in the case of metal samples, can exist on an interface of two media only under the condition that real parts of their dielectric constants $\varepsilon_1$ and $\varepsilon_2$ have opposite signs. Then SEW dispersion equation is [4]:

$$\kappa = \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}.$$  \hspace{1cm} (1)

As the value of $\kappa'$ is larger than the refractive index of the environment $n_1 = \sqrt{\varepsilon_1}$ with dielectric constant $\varepsilon_1 > 0$ ($\varepsilon_1 = 1$ in case of air), a special coupling device is needed to excite SEW by a plane electromagnetic wave. Edge of a plate placed over the sample surface at the distance $d \sim 10 \lambda$ can be used for SEW excitation [9, 12].

The principle idea of interferometric SEW-spectroscopy was described in [11–13] and it could be realized on a modified Michelson interferometer where radiation in one of the shoulders passes a part of its path in the form of SEW. While the probing radiation exists in the form of SEW it accumulates information about the sample surface. The information is contained in the interference picture formed on the interferometer’s screen.

The scheme of the experimental set-up is presented in Fig. 2. FEL radiation is focused by the lens 1 onto the aperture 2 where it diffracts and is split into two parts, one of which is formed by a bunch of dispersing bulk waves propagating in the surrounding medium at various angles relatively to the surface of the specimen (substrate – 3, metallic film – 4) and the other part of the incident radiation is converted into SEW propagating just along the specimen surface. While SEW runs the distance $a$ to the specimen’s edge it gains phase shift $\Delta \varphi = k_0 \kappa' a$ (where $k_0 = 2\pi/\lambda$) and transforms at the edge into a bulk wave, carrying information about the surface. As these two bulk waves (the first one produced at the aperture 2 and the second – at the specimen edge) meet an interference picture 5 (interferogram), containing information about characteristics of SEW, namely about its phase velocity and attenuation, is formed. The interferogram is registered by a photo detector 6 scanned in the vertical direction at a distance $b$ from the specimen’s edge.

In our experiments FEL radiation arrived at the set-up input in the form of macro pulses with duration of 3 $\mu$s (10 W at $\lambda = 110$ $\mu$m) and repetition period of 1 s. The measured radiation intensity (normalized by independently measured beam intensity) was detected, averaged over eight sequential pulses and finally memorized by a digital oscilloscope.

Specimens were mounted as an accentual part of the SEW-interferometer onto a specially designed attachment enabling us to measure and control the distance $a$ with precision of 0.1 mm. An ordinary razor blade was used as a diffraction element for SEW excitation (the “aperture” method of excitation). The sharp edge of the
blade was placed at a distance of 2 mm over the specimen surface and remained constant and the same in all the experiments performed. FEL radiation was focused on the slit formed in this way by a polyethylene lens with the focal length of 15 cm. A Ga-doped germanium photo resistor, cooled by liquid helium and provided with 0.2 mm horizontal diaphragm on the entrance window of cryostat was used as a detector. The signal to noise ratio was on the level of 100. Distance \( b \) between the detector and the sample remained constant (200 mm) in all the experiments.

TECHNIQUE USED FOR EXECUTION OF MEASUREMENTS RESULTS

According to [12, 13], the condition for observation of the interference maximum at a point \( z \) is the following:

\[
\kappa' a + \sqrt{b^2 + (z - z_0)^2} - \sqrt{(b + a)^2 + (z - z_0)^2} = (m + \theta)\lambda,
\]

where \( z_0 \) corresponds to the zero optical paths difference between the two interfering bulk waves; \( m = 1, 2, 3 \ldots \) is an integer corresponding to the maximum order number, \( \theta \) additional phase shift undergone on the specimen’s edge as SEW transforms into a bulk wave.

This system of equations contains three unknown quantities: \( z_0 \), \( \theta \), \( \kappa' \). The authors of papers [11–13] suggested a number of graphic algorithms for \( \kappa' \) determination, which were based on an assumption that \( \theta = 0 \) and the value of \( z_0 \) corresponds to specimen surface coordinate. Such simplifications (at least the second one) are quite acceptable for the middle IR, but at THz frequencies the accuracy of maxima coordinates should be not worse than 0.01 mm that implies good knowledge of real values for \( z_0 \) (depending on distance \( a \)) and \( \theta \). In this case we can determine \( \kappa' \) with accuracy of sixth order after comma. That is why we have elaborated a new technique for \( \kappa' \) determination using interferograms obtained by the method of SEW-interferometry. This technique is an analytic one and is as follows.

The value of \( z_0 \) can be determined by the subtraction of two equations of type (2), composed for two neighboring maxima of the same interferogram:

\[
\sqrt{b^2 + (z_m - z_0)^2} - \sqrt{(b + a)^2 + (z_m - z_0)^2} = \sqrt{b^2 + (z_m + 1 + \lambda)^2} + \sqrt{(b + a)^2 + (z_m + 1 + \lambda)^2} = 0,
\]

where \( z_m = z - z_0 \) and \( z \) is the coordinate of \( m \)-th maximum. For the better precision \( z_0 \) value should be obtained for several combinations of couples of the same interferogram maxima and its averaged value of \( z_0 \) should be calculated.

It is impossible to determine the phase shift \( \theta \) using a single interferogram as the shift does not depend on the distance \( a \). But if we register several interferograms at different distances \( a \), we can get rid of \( \theta \) and determine \( \kappa' \) by the subtraction of two equations of type (2), composed for different \( a \). In case we are dealing with the same interference order \( m \) of two interferograms obtained at the same \( b \) and different distances \( a_1 \) and \( a_2 \), the subtraction brings an equation containing only one unknown quantity – desirable \( \kappa' \). Solution of this equation brings the following formula:

\[
\kappa' = \frac{\sqrt{b^2 + (z_{2m} - z_0)^2} - \sqrt{b^2 + (z_{1m} - z_0)^2} + \sqrt{(b + a_1)^2 + (z_{1m} - z_{01})^2} - \sqrt{(b + a_2)^2 + (z_{2m} - z_{02})^2}}{a_1 - a_2},
\]

where \( z_{01} \) and \( z_{02} \) are the values of \( z_0 \) obtained from the interferograms using eq.(3) at \( a_1 \) and \( a_2 \), respectively; \( z_{1m} \) and \( z_{2m} \) are the coordinates of any \( m \)-th maxima of the interferograms registered at \( a_1 \) and \( a_2 \), correspondingly.

According to [17] one can appreciate SEW absorption coefficient \( \alpha = L^{-1} \) using interferograms as well. To do this one has to solve the following equation:

\[
a \frac{2}{L} + A(z, b) = \ln \left( \frac{I_{\text{max}} + I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}} \right),
\]

where \( I_{\text{max}} \) and \( I_{\text{min}} \) are the forces of photocurrent measured at output of the photo detector, placed at neighboring extrema. \( A \) is a constant dependent upon values of \( z \) and \( b \). Having taken interferograms at different distances \( a \) and the same \( b \), one can exclude \( A \) and determine \( L \). Although it should be noted that such way for determination of the coefficient \( \alpha \) is characterized by very low accuracy as compared with the two-prism method, when they measure value of \( L \) directly.

Having determined values of \( \kappa' \) and \( L \) by the above-described way, one can evaluate values of the real \( \varepsilon_2' \) and image \( \varepsilon_2'' \) parts of the metal dielectric permittivity either using the approximate formulae [13] or by solving the equation (1) substituting the found values of \( \kappa' \) and \( \kappa'' \) (taking into account that \( \kappa'' = \lambda/(4\pi L) \)) in it.

EXPERIMENTAL RESULTS AND DISCUSSION

The experiments were performed at two frequencies of the tunable FEL radiation with wavelengths \( \lambda = 110 \) and 150 \( \mu \)m. The specimens represented themselves nontransparent mirrors with metallic layers made by
thermal evaporation on optically polished glass substrates (with dimensions \(30 \times 150 \times 5\) mm) in vacuum.

Results of the experiments obtained for specimens made of aluminum, copper and steel are presented on Fig. 3–10. We did not manage to get interferograms for the specimens with chromium coverage. To our mind, the fact may be explained by very small SEW propagation length on chromium at THz frequencies.

The interferograms registered in the experiments with \(\lambda = 110\) µm at the distance \(a = 80\) mm are presented in Fig. 3–6, while at Fig. 7 – the interferogram obtained for nontransparent copper film at \(a = 80\) mm for radiation with \(\lambda = 150\) µm. Having compared the interferograms got for evaporated copper and depicted on Fig. 4 and Fig. 7, one can state that the phase shift \(\Delta \phi\) acquired by SEW while its propagation is inversely proportional to the radiation wavelength (at the same other conditions) and its value significantly influences the form of the interferogram and number of maxima it has.

Interferograms obtained for the aluminum specimen at the both wavelengths \(\lambda\) and different distances \(a\) are presented on Fig. 8 and Fig. 9. In this case we had an opportunity to estimate the value of SEW’s effective index of refraction \(\kappa = \kappa' + j\kappa''\) following the above described execution procedure.

Using the data got for radiation with \(\lambda = 110\) µm (Fig.8) and substituting it in the equation (3) the following values of \(z_0\) were calculated: \(z_{01} = 90.887\) mm at \(a_1 = 80\) mm and \(z_{02} = 74.226\) mm at \(a_2 = 20\) mm. Afterwards using formula (4) the real part of \(\kappa\) was determined: \(\kappa' = 1 + (8.3 \times 10^{-4} \pm 50\%)\).

Analogous calculations for radiation with \(\lambda = 150\) µm (Fig.9) brought the following results: \(z_{01} = 80.548\) mm at \(a_1 = 120\) mm, \(z_{02} = 77.398\) mm at \(a_2 = 80\) mm and finally \(\kappa' = 1 + (5 \times 10^{-5} \pm 10\%)\).

Accuracy of \(\kappa'\) determination in case of radiation with longer wavelength turned to be higher as spectral width of emission line of FEL radiation at \(\lambda = 150\) µm was narrower than at \(\lambda = 110\) µm [16].
Using values of maxima and minima relative intensities of the signal (Fig. 9) and formula (5) we appreciated the SEW propagation length $L$ on aluminum for radiation with $\lambda = 150 \mu m$. The calculations indicated that in this case $L = 15 \text{ cm}$. This result contradicts the well-known condition $L_1/L_2 = \lambda_1^2/\lambda_2^2$ [4]. Really according to the calculations for aluminum (Table 1) for radiation with $\lambda = 10 \mu m - L = 3 \text{ cm}$, while for radiation with $\lambda = 150 \mu m$ SEW propagation length $L$ should be about 10 m, that is not in the accord with our appreciation that $L = 15 \text{ cm}$. Analogous discrepancy was noted by other authors as well [18] but with no comments. This fact (the discrepancy of calculated and experimental values of $L$) is worth of performing additional special experiments on determination of SEW energy loses at THz frequencies.

To test SEW interferometer sensitivity to thin films on the metal surface we registered interferograms for $\lambda = 150 \mu m$ and $a = 120 \text{ mm}$ for two aluminum specimens having silicon and germanium layers with thickness 100 nm on both of them (Fig. 10). The interferograms' displacements in comparison with clean Al surface to smaller values of $z$ take place due to the increase of $\kappa'$, which is proportional to the refractive index of the overlayer material. Both interferograms, registered for Al surface with an overlayer, are identical, what means that films' refractive indexes are practically the same. Similar effect was observed in the 10 $\mu m$ wavelength range for both Ge and Si films $n \cong 3$ [17], what was explained by conditions of films evaporation. One can see that even in the very far infrared SEW are sensitive to the presence of thin films on the guiding metallic surface.
CONCLUSION

For the first time, the interferometric studies of SEW exited by free-electron laser on surface of metals (aluminum, copper, steel) in the terahertz frequency range were made. The real part of SEW refractive index (κ') propagating along clean aluminum surface was determined at wavelengths of 110 and 150 μm. High sensitivity of SEW phase velocity to the radiation wavelength and presence of a semiconductor layer on the surface has been experimentally demonstrated. The further improvement of the experimental set-up, as well as data acquisition system and software are promising the acceptable accuracy of the both parts of the SEW complex effective index of refraction determination. Finally this will enable us to determine optical constants of clean metal surfaces and investigate absorption spectra of thin films of various natures formed on the surfaces in the terahertz spectral range.

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REFERENCES


ПЕРВЫЕ ЭКСПЕРИМЕНТЫ ПО ПРИМЕНЕНИЮ ТERAГЕРЦОВОГО ИЗЛУЧЕНИЯ ЛАЗЕРА НА СВОБОДНЫХ ЭЛЕКТРОНАХ ДЛЯ ИССЛЕДОВАНИЯ ПОВЕРХНОСТИ МЕТАЛЛОВ

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Проведены первые эксперименты по генерации поверхностных электромагнитных волн (ПЭВ) в терагерцовом диапазоне (60–100 см⁻¹) лазером на свободных электронах на поверхности металлических (алюминий, медь, сталь, хром) "глухих" зеркал оптического качества. Для алюминиевых образцов путем интерференционных измерений, выполненных по схеме асимметрического интерферометра, в одном из плеч которого излучение часть пути проходит по образцу в виде ПЭВ, определено отличие k' от единицы действительной части показателя преломления ПЭВ. Установлено, что для излучения с длинной волны λ = 150 мкм величина k' = 1 + 5 × 10⁻³, а для λ = 110 мкм k' = 1 + 8 × 10⁻⁴. Продемонстрирована высокая чувствительность ПЭВ к присутствию на поверхности алюминия 100 нанометровых пленок кремния и германия.