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Optical conductivity of intermetallic compounds YSn_3 and $GdSn_3$

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The optical properties of binary cubic compounds YSn_3 and $GdSn_3$ were investigated by ellipsometric technique. The frequency dependences of the dielectric functions are determined in the energy range 0.083–5.64 eV. The features of the dispersion of optical conductivity in the intervals of intra- and interband light absorption are analyzed in detail. The nature of quantum light absorption in the studied materials is discussed on the basis of a comparative analysis of experimental and theoretical optical conductivity spectra. Plasma and relaxation frequencies of electrons are determined.

Keywords: intermetallic compounds, optical properties, dielectric functions, electronic structure.

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1. Introduction

Interest in binary compounds RM_3, where R — Y, Sc, rare earth metal (REM), M — p-metal, is due to the diversity of their physical properties, some of which are promising for practical use. In recent years, a large number of compounds of this series have been synthesized, and their electronic, magnetic, structural and mechanical characteristics have been studied. In intermetallic compounds $RM_3$with different crystal structures the existence of different magnetic phases, superconductivity, valence fluctuations, heavy fermions, crystal field effects, as well as features characteristic of Kondo systems were discovered [1–8]. The nature of these properties is associated with the peculiarity of the electronic structure of such compounds, namely, with the localization features $4f$-states of REM and their interaction with conduction electrons. For a number of compounds of this series the calculations of the zone spectra were carried out, in which the nature of the electronic states near the Fermi level E_F was determined, and the atomic magnetic moments were calculated.

Similar materials include intermetallic compounds YSn_3 and $GdSn_3$ with a face-centered cubic lattice of $AuCu_3$ type. Non-magnetic YSn_3 has the highest temperature of the transition to the superconducting state among compounds of this class. When studying the temperature dependences of the electrical resistance, magnetic susceptibility and electronic heat capacity of the compound, it was found [9] that the temperature of such transition is near 7 K. Experimental studies and theoretical analysis [10–13] showed that YSn_3 is a II-th type superconductor with lower and upper critical fields equal to 90 Oe and 3000 Oe, and the nature of the superconductivity appearance is associated with strong electron-phonon interaction. Also note the theoretical works related to the study of the electronic, magnetic, structural, mechanical and thermal properties of this material [14–18]. Ab initio calculations [19,20] showed that its electronic structure has a number of unusual properties with anomalies characteristic of new quantum systems — topological materials in which the rates of charge transfer on the surface and in the bulk differ significantly.

When studying the temperature dependences of magnetic susceptibility and electronic heat capacity, it was found that the compound $GdSn_3$ is an antiferromagnetic with the Néel temperature $T_N = 31$ K [21,22]. It was shown in papers [23,24] that this type of magnetic ordering arises as a result of indirect exchange interaction of localized $4f$-electrons through s, p-conduction electrons. Calculations of the electronic spectrum $GdSn_3$, carried out taking into account the effects of strong correlation of f-electrons, determined features in the structure and localization of the Gd $4f, 5d$ and Sn $5p, 5s$-states in the vicinity of the Fermi level E_F [25–29]. In these papers, calculations of phase stability, structural, electronic, optical, magnetic and mechanical properties of the compound were also carried out.

Most of the physical characteristics of both compounds, including spectral ones, predicted by theoretical calculations, require experimental confirmation. In this paper the optical properties of these materials are studied and their correspondence to previously performed calculations of electronic structures is analyzed. For this, an optical ellipsometry method covering the wide wavelength range, including the ultraviolet (UV), visible and infrared (IR) regions, is used. Experimental optical conductivity spectra of the compounds are compared with the corresponding dependences obtained from ab initio calculations of the densities of electronic states.

2. Experiment

Polycrystalline samples of compounds were prepared using the method [22] of arc melting in an argon atmosphere of high-purity Y, Gd and Sn (99.99%), taken in stoichiometric proportions. For the purpose of homogenization, the obrained ingots were annealed at a temperature of $\sim 650^\circ$C for five days. X-ray diffraction analysis of powder samples showed that both alloys crystallize in the cubic structure of $AuCu_3$ type with the lattice parameters $a = 4.66$ Å (YSn_3) and $a = 4.68$ Å ($GdSn_3$), that is close to the values obtained in papers [9,22].

The spectral properties of the compounds were studied by optical ellipsometry with a rotating analyzer, based on determining the phase difference and amplitude of light waves s- and p-polarizations reflected from the mirror surface of the sample [30]. These values, depending on the frequency of light, make it possible to calculate the real and imaginary parts of the complex dielectric permittivity $\varepsilon(E) = \varepsilon_1(E) - i\varepsilon_2(E)$ (E — light quantum energy), characterizing, respectively, the dielectric and conductive properties of the material. By values ε_1 and ε_2 the optical parameters of each compound are determined: reflectivity $R(E)$, optical conductivity $\sigma(E) = \varepsilon_2\omega/4\pi$ and characteristic electron loss function $\mathrm{Im}(-1/\varepsilon) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$. Measurements made at room temperature cover the wavelength range $\lambda = 0.22-15\,\mu$m ($E = 0.083-5.64$ eV). Mirror reflective surfaces of 14th finish class were prepared by mechanical polishing using diamond pastes of various dispersion. The error in determining the specified characteristics is 2–4%.

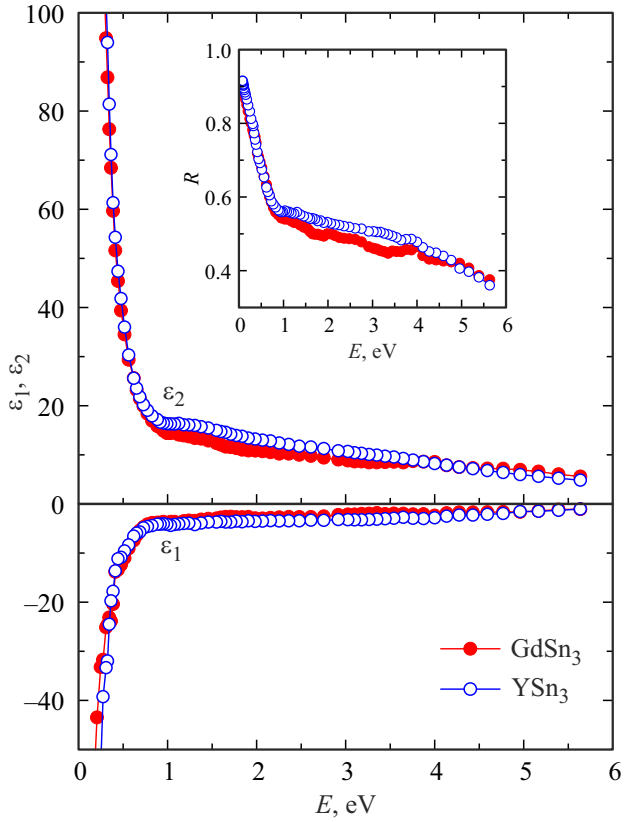

Figure 1. Real ε_1 and imaginary ε_2 components of complex dielectric permittivity and reflectivity R of compounds YSn_3 and $GdSn_3$.

3. Results and discussion

The energy dependences of the real ε_1 and imaginary ε_2 components of the dielectric permittivity of the compounds are presented in Figure 1 (the inset shows the reflectivity $R(E)$). The nature of these parameters dispersion in both alloys is typical for metallic materials. This is indicated by the fact that at all energies of light quanta the relation $\varepsilon_1 < 0$ is satisfied, and in the dependences $\varepsilon_2(E)$ and $R(E)$ in the IR range there is a sharp monotonic rise, characteristic of the occurrence of Drude light absorption mechanism. The reflectivity of both compounds is quite high, exceeding 0.9 at the low-frequency boundary of the range. In Figure 2, dark circles represent the experimental dispersion dependences of optical conductivity YSn_3 and $GdSn_3$. In contrast to static conductivity, this characteristic depends not only on the density of electronic states at the Fermi level, but also on electron densities in the entire energy range under study. In the low-energy region of the spectrum (IR range), the dispersion $\sigma(E)$ of both compounds corresponds to the Drude dependence ($\sigma \sim \omega^{-2}$, where ω — light frequency), characteristic of intraband mechanism of interaction of electrons with the electromagnetic field of the light wave. In this energy range, where the influence of interband transitions on optical properties is minimal, the kinetic characteristics of conduction electrons — plasma ω_p and relaxation γfrequencies, were calculated from the Drude relations. The parameter ω_p determines the frequency of collective oscillations of electrons, and γ — the frequency of electron collisions when taking into account all types of scattering. The numerical values of these parameters are $\omega_p = 6.8 \cdot 10^{15}\,\mathrm{s}^{-1}$, $\gamma = 4.7 \cdot 10^{14}\,\mathrm{s}^{-1}$ (YSn_3), $\omega_p = 7.4 \cdot 10^{15}\,\mathrm{s}^{-1}$, $\gamma = 5.3 \cdot 10^{14}\,\mathrm{s}^{-1}$ ($GdSn_3$). Obtained values ω_p and γ allow us to estimate the value of the Drude contribution to the optical conductivity $\sigma_D = \omega_p^2\gamma/4\pi(\omega^2 + \gamma^2)$. This contribution, calculated for each compound, is shown in Figure 2 by a thin solid line. Its value decreases in proportion to the square of the light frequency and becomes negligible at energies above ~ 2.5 eV. From the relation $n = \omega_p^2 m/4\pi e^2$ (e and m — electron charge and mass) we can calculate the values of the effective concentrations of free electrons, which are close in value for both alloys: $n = 1.05 \cdot 10^{23}\,\mathrm{cm}^{-3}$ (YSn_3), $n = 1.14 \cdot 10^{23}\,\mathrm{cm}^{-3}$ ($GdSn_3$).

Dielectric permittivities ε_1 and ε_2, obtained in the experiment, allow us to calculate the functions of volumetric characteristic losses of electron energy $\mathrm{Im}(-1/\varepsilon)$, the maximum of which occurs at $\varepsilon_1 \to 0$ and $\varepsilon_2 \ll 1$ [31]. This quantity characterizes discrete electron energy losses during the excitation of volumetric plasma oscillations. In our case,

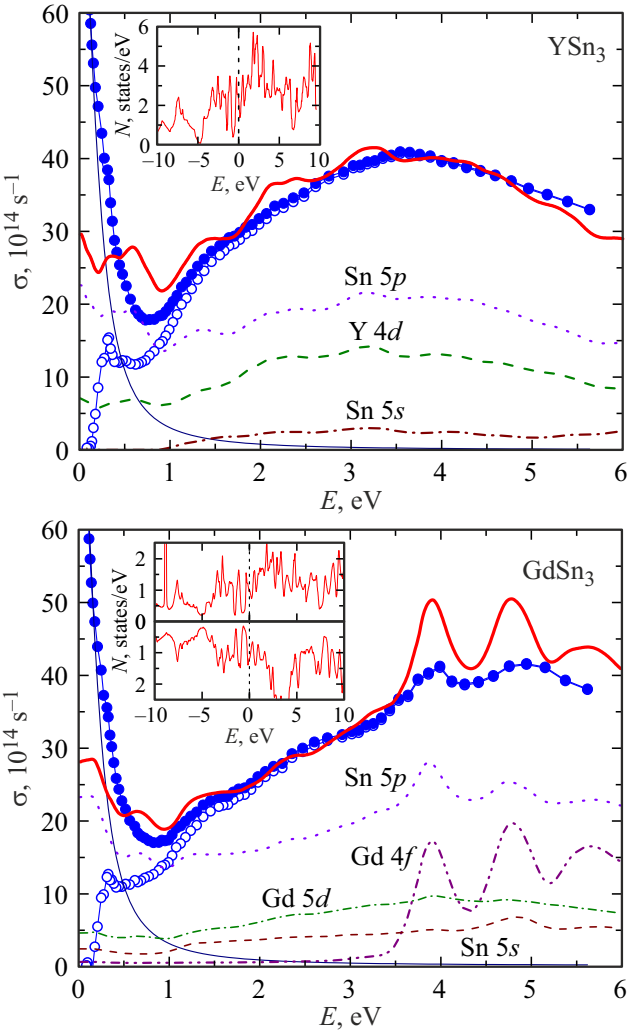

Figure 2. Experimental energy dependences of optical conductivity of the compounds YSn_3 and $GdSn_3$ (dark circles). Experimental interband (unfilled circles), calculated interband (thick solid lines), and Drude (thin solid lines) contributions. Contributions from interband transitions involving various electronic states are also presented. The inserts show the total densities of electronic states according to the data [16] (YSn_3) and [27] ($GdSn_3$).

as follows from Figure 3, the dependences $\mathrm{Im}(-1/\varepsilon)$ for both compounds show the increase over the entire energy range, without reaching the maximum value.

With photon energy increasing (visible and UV spectral regions), the formation of broad absorption bands associated with interband transitions of electrons is observed in the dependences $\sigma(E)$. By subtracting the Drude component from the experimental dependences, we can isolate the contributions of interband absorption to the optical conductivity $\sigma_{ib}(E) = \sigma(E) - \sigma_D(E)$, which are indicated in Figure 2 by unfilled circles. It is clearly seen that the shape of the absorption bands is individual for each compound. If for YSn_3 the band has a structureless dome-shaped appearance and is characterized by one maximum at an energy of 3.5 eV, then in the corresponding dependence for $GdSn_3$ two maxima appeared at 4.0 and 4.9 eV, and the center of influence of this band is shifted towards high energies. In both dependences $\sigma_{ib}(E)$ low-energy maximum appeared, localized at energy of 0.3 eV. Figure 2 shows that in a rather wide spectral region of approximately 0.2–2.5 eV, intra- and interband contributions to $\sigma(E)$ coexist.

The features of the experimental dependences of the interband components of optical conductivity can be qualitatively explained on the basis of calculations of their densities of electronic states $N(E)$ presented for YSn_3 and $GdSn_3$ in papers [16] and [27](inserts in Figure 2). Calculations showed that in the energy range $-10 < E_F < 10$ eV in the structure of the dependence $N(E)$ of the compound YSn_3 Sn $5p$, Y $4d$ and Sn $5s$ states predominate, the partial densities of which form a series of intense maxima on both sides of E_F. Again, in the density of states of magnetic-ordered $GdSn_3$, which is a superposition of two densities with different spin orientations, in the same energy range Sn $5p$, Gd $5d$ and Sn $5s$ states prevail. Narrow intense peaks associated with $4f$ electrons are localized in the spectrum $N(E)\downarrow$ near 4 eV, and in $N(E)\uparrow$ at -9 eV. It is of interest to compare the experimental spectra $\sigma_{ib}(E)$ with the theoretical dependences of this function, calculated from the densities of states of both compounds. The interband optical conductivities have been calculated similar to the method previously used in [32] based on the convolutions of full $N(E)$ below and above the Fermi level under the assumption of equal probability of all types of electronic transitions. Results of such calculations, that are of qualitative type, are shown in Figure 2 in arbitrary units by thick solid lines. It follows from the Figure, that at $E > \sim 1$ eV for both compounds there is a rather close agreement between the theoretical and experimental dependences $\sigma_{ib}(E)$. The calculated curves generally reproduce the shape of the empirical spectra and

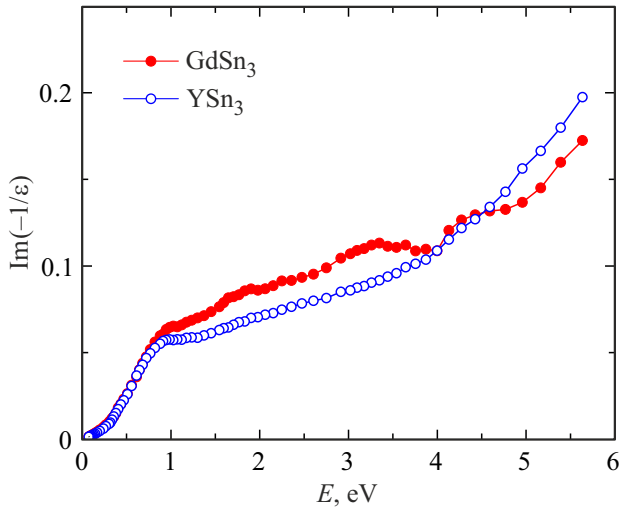

Figure 3. Volumetric characteristic electron energy loss functions of compounds YSn_3 and $GdSn_3$.

the localization of the main maxima, although a number of structural details do not completely coincide.

In accordance with the electronic structure of the compounds under study, the intense optical absorption is formed mainly due to electronic transitions between the hybridized Sn $5p, 5s$ and Y(Gd) $4d(5d)$ bands located below and above E_F. Despite the fact that their densities of states (inserts in Figure 2) demonstrate the presence of numerous maxima, the dependences $\sigma_{ib}(E)$, due to the superposition of a large number of transitions, have almost structureless appearance. Two maxima at 4.0 and 4.9 eV, observed in the experimental and theoretical dependences $\sigma_{ib}(E)$ of $GdSn_3$ compound, are identified with transitions to $4f\downarrow$ zone localized above the Fermi level. Contribution of other electronic states is minor due to their low partial densities. Figure 2 shows the most significant contributions to the interband optical conductivity associated with various electronic states. These contributions were also calculated using the method [32] and data on their partial densities given in [16,27]. When comparing, attention is drawn to the different behavior of the calculated and measured dependences $\sigma_{ib}(E)$ in the long-wave (IR) region. While the experimental curves at $E \to 0$ show a decrease, indicating a sharp decrease in the contribution from low-energy interband transitions, the calculated curves, on the contrary, show a significant increase. The abnormal increase in the intensity of such absorption, in our opinion, is associated with the approximations made in the calculations. In particular, the approximation of constancy of the matrix elements of transitions leads to some error due to the fact that transitions within one zone are assigned the probability other than zero. As a result, the calculated values $\sigma_{ib}(E)$ at low frequencies turn out to be overestimated. In general, the qualitative similarity of the experimental and theoretical spectra of interband optical conductivity YSn_3 and $GdSn_3$ indicates that the published ab initio calculations of the electronic structure provide the adequate description of their optical properties.

4. Conclusion

The results of experimental studies of the optical properties of binary intermetallic compounds YSn_3 and $GdSn_3$ in the wavelength region $0.22-15\,\mu$m are presented. The components of the complex dielectric permittivity, optical conductivities, and functions of characteristic electron energy losses were measured using the ellipsometric method. The plasma and relaxation frequencies of conduction electrons are determined. It is shown that the spectral properties of the compounds correspond to metal-type materials. The energy dependences of the optical conductivity of these intermetallic compounds in the region of interband light absorption are discussed on the basis of previously published calculations of their band structure. A satisfactory agreement between the experimental spectra of optical conductivity and the spectra calculated from the densities of electronic states is shown.

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Conflict of interest

The authors declare that they have no conflict of interest.

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