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Optical spectroscopy of ScNiSb and YNiSb intermetallic compounds

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Experimental studies of the optical and dielectric properties of intermetallic half-Heusler compounds ScNiSb and YNiSb have been performed. The frequency dependences of optical constants — refractive indices and absorption coefficients, were measured using an ellipsometric method in the energy range of 0.08−5.64 eV. Using these parameters, the spectra of the real and imaginary parts of the complex permittivity, optical conductivity, reflectivity, and the function of characteristic electron energy losses are calculated. Based on a comparative analysis of experimental and theoretical optical conductivity spectra, the nature of interband light absorption in both materials is discussed. The semi-metallic properties of the compounds are manifested in the anomalous behavior of spectral characteristics in the infrared region of the spectrum.

Keywords: intermetallic compounds, optical properties, permittivity, optical conductivity, electronic structure.

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1. Introduction

The triple equiatomic intermetallides ScNiSb and YNiSb belong to an extensive group of semi-Heusler alloys with the chemical formula RTX, where R is rare earth, Sc or Y, T is the transition metal, and $X-s$- or p-element. The materials of this family, which have different types of crystal structures, exhibit a variety of electronic properties due to different types of conductivity [1–3], non-trivial topological features of the electronic structure [4,5] and anomalies associated with heavy fermions [6]. The magnetic characteristics of these compounds are also characterized by a number of interesting features. They demonstrate the coexistence of magnetism and superconductivity [7], the presence of phase magnetic transitions [3,8], gigantic magnetoresistive and large magnetocaloric effects [9–11]. The prospects for the practical use of such alloys are primarily related to their unique thermoelectric properties, which make it possible to efficiently convert thermal energy into electrical energy [12,13].

ScNiSb and YNiSb compounds studied in this paper crystallize in a cubic structure of the MgAgAs type (space group $F\bar{4}3m$, №216). Both materials are paramagnets, and the behavior of the temperature dependences of the transport characteristics indicate their semiconductor properties [14–17]. Studies have shown that the thermal EMF coefficient of these alloys reaches sufficiently large values of $S = 80$ and $240\,\mu$V/K for YNiSb [15] and ScNiSb [17], respectively. At the same time, their figure of merit ZT, expressed as $\mathrm{ZT} = S^2\sigma T/\kappa$ (σ and κ is the electrical conductivity and thermal conductivity of the material, T is the temperature) can be increased by changing the concentration of dopants and sample defects [18–20]. The high values of the parameter S are associated with the main feature of the electronic structure of these compounds — the presence of energy gaps in the densities of electronic states localized at the Fermi level E_F. The nature of the formation of these anomalies, as shown in calculations of the electronic structure in Refs. [21–25] conducted within the framework of various computational schemes, is attributable to the peculiarities of the structure and hybridization of p- and d-energy bands. The width of the energy gaps, according to calculations by various authors, is in the range of 0.3 eV, which is indirectly confirmed by experimental studies of some electronic properties of these compounds [14,16,19].

The optical spectroscopy is used in this paper to study the features of the electronic structure of ScNiSb and YNiSb compounds. The energy dependences of the optical and dielectric characteristics of both materials have been studied in a wide range of wavelengths, including the ultraviolet (UV), visible, and infrared (IR) ranges. The information about the electronic structure provided by optical measurements is compared with the previously obtained theoretical data.

2. Experiment

Polycrystalline samples of ScNiSb and YNiSb compounds were prepared by arc melting from an initial mixture of high-purity ($\sim 99.99\%$) components in an atmosphere of pure argon. The technique described in Ref. [11] was used for the synthesis and subsequent annealing of the molten ingots. X-ray data obtained in K_α radiation of Cu using DRON-6 diffractometer showed the formation of a cubic structure of MgAgAs type in alloys. The values of the crystal lattice parameters are close to those previously published in Refs. [11,15,16,20] and are $a = 6.070$ Å (ScNiSb) and $a = 6.245$ Å (YNiSb).

Optical constants such as refractive index $n(E)$ and absorption coefficient $k(E)$ (E is the light wave energy) were measured using an ellipsometric method with one and two reflections from the sample plane in the wavelength range $\lambda = 0.22-15\,\mu$m ($E = 0.083-5.64$ eV). The measurement error in the entire spectral range was 2–4%. Based on the values of n and k, the real $\varepsilon_1 = n^2 - k^2$ and imaginary $\varepsilon_2 = 2nk$ parts of the complex dielectric constant, reflectivity $R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2]$ and optical conductivity $\sigma = \varepsilon_2\omega/4\pi$ (ω is the cyclic frequency of the light wave) were cflculated. The flat mirror surfaces of the samples were prepared by mechanical polishing on diamond pastes of various dispersity. The grain size at the last stage of processing was less than $1\,\mu$m.

3. Results and discussion

The experimental dependences of the functions $\varepsilon_1(E)$, $\varepsilon_2(E)$ and $R(E)$, in the structures of which there is great similarity for both compounds, are shown in Figure 1. The character of the dispersion of these spectra is typical for conductive materials in the low-energy region of photons ($E \lesssim 0.5$ eV), namely, the values of ε_2, R and $|\varepsilon_1|$ sharply increase with the increase of the wavelength because of the impact of intraband light absorption. At the same time, the absolute values of these parameters are small, significantly lower than those typical for good metals [26], indicating that the metallic properties in the studied alloys are significantly weakened. In particular, the values of reflectivity at the edge of the low-energy range (IR region) are quite low and are in the range of 0.7. At the same time, the reflection of each individual metal in the compound at these wavelengths is extremely high, approaching unity [27]. Positive values of ε_1 observed in the studied compounds in the local (0.5–1.5 eV) part of the spectrum are uncharacteristic for materials with high electrical conductivity. A number of peaks are present on the dispersion dependences $\varepsilon_2(E)$ and $R(E)$ as the light wave energy increases, the nature of which is associated with quantum light absorption. The intensity and shape of these features are usually individual for a particular material and are determined by its electronic structure. In this case, the spectral profile of dependences shown in Figure 1 indicates a great similarity of their electronic structures.

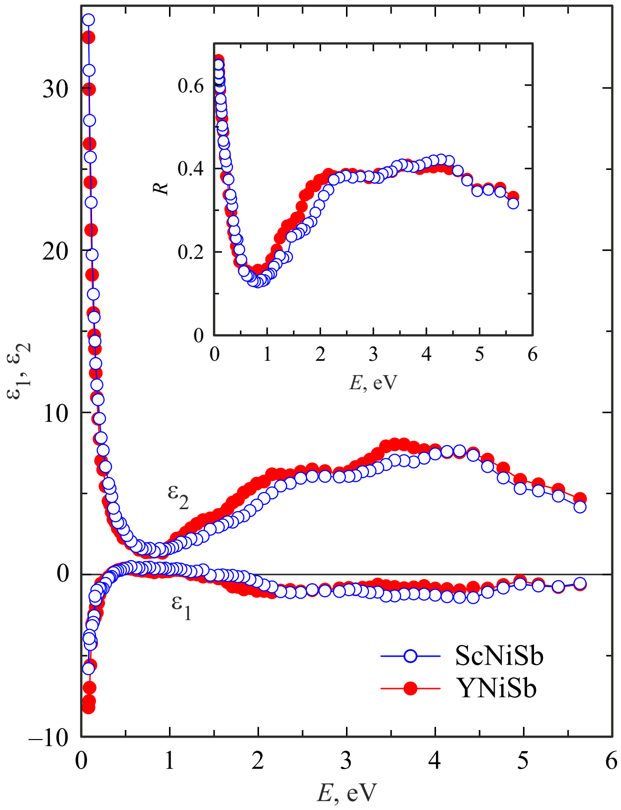

Figure 1. The reflectivity $R(E)$ and the dielectric functions $\varepsilon_1(E)$ and $\varepsilon_2(E)$ of the ScNiSb and YNiSb compounds.

The experimental optical conductivity spectra of the parameter characterizing the frequency dispersion and intensity of the spectral response of the studied compounds are represented by circles in Figure 2. This function, unlike static conduction, is determined not only by the density of electronic states at E_F, but also depends on $N(E)$ in the entire studied energy range. A common feature of the curves shown in the figure is that the values of $\sigma(E)$ are quite low in the region of $E \lesssim 1$ eV, and their significant growth begins at higher energies. At the same time, the nature of the dispersion of the optical conductivity of both materials in the low-energy range differs sharply from the Drude dependence $\sigma \sim 1/\omega^2$ characteristic of metallic materials. Previously, a similar anomalous behavior of $\sigma(E)$ was observed in a number of compounds [28–30], whose electronic structure is characterized by the presence of energy gaps or pseudogaps at the Fermi level.

The role of interband light absorption increases as the photon energy increases, which is evidenced by the shape of dependencies $\sigma(E)$ of both intermetallides. Wide absorption bands with similar profiles are located in this range of the spectrum with intensive peaks near 4.4 eV, on each side of which there are almost symmetrically located features in the form of „shoulders“. The formation of these absorption bands is associated with quantum transitions between electronic states below and above E_F and is determined by the band structure of the compound. This allows us to explain the nature of their origin taking into account previous calculations of $N(E)$. Calculations in Refs. [22,25] showed that bands Sc 3d (Y 4d), Ni 3d and Sb 5p forming intensive peaks on both sides of the Fermi level prevail in the range of $E_F \pm 6$ eV in densities of the states of the studied compounds, fragments of which are shown in the inserts of Figure 2. In this case, the bands Ni 3d and Sb 5p have high partial densities at energies below E_F, and bands Sc 3d (Y 4d) — above E_F. The main feature of

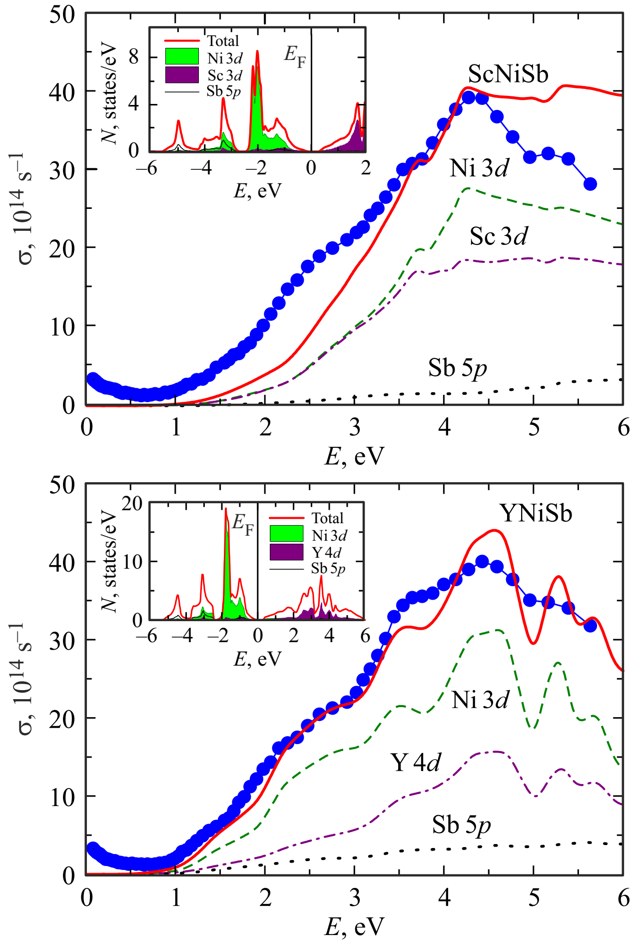

Figure 2. Experimental (circles) and calculated (solid lines) energy dependences of the optical conductivity of compounds ScNiSb and YNiSb. Partial contributions from interband transitions involving electronic states Ni,3*d*, Y,4*d*, Sc,3*d* and Sb,5*p* are also shown. The inserts show the densities of electronic states according to data from [22] (ScNiSb) and [25] (YNiSb).

the calculated dependences $N(E)$ is that the Fermi levels in both compounds are localized in the band energy gap which allows them to be classified as semiconductor materials. The comparison of the empirical dependences $\sigma(E)$ with the spectra calculated from the total densities of electronic states $N(E)$ is of interest for evaluation of the degree of correspondence between theory and experiment [22,25]. The results of such calculations are shown for both compounds in Figure 2 together with the experimental spectra. Interband $\sigma(E)$ were calculated for both compounds in accordance with the method used in Ref. [31], based on convolutions of the total densities of states above and below E_F, provided that all types of interband transitions are equally probable. The approximation used assumes a qualitative nature of the calculation, in which the dependences of the interband optical conductivity are presented in arbitrary units.

The comparison shows that the theoretical curves of the interband optical conductivities correspond fairly well to the experimental dependences. Despite a number of differences in the localization and intensity of some structural elements, the calculated spectra $\sigma(E)$ adequately describe the overall pattern of interband absorption and the location of the main maxima. The similarity of both dependencies is more complete in the YNiSb compound. The formation of the observed absorption bands, in accordance with calculations in Refs. [21–25], is associated with electronic transitions between occupied and empty energy bands of *p* and *d* type located on either side of E_F. The corresponding bands are identified with Sc 3*d* (Y 4*d*), Ni 3*d* and Sb 5*p* states associated with a number of peaks of $N(E)$ and separated by an energy gap. Figure 2 shows, together with the interband optical conductivities calculated from the total densities of states, the most significant partial contributions associated with the above-mentioned electronic states. As follows from the figure, the role of such contributions is crucial in both compounds for forming the overall pattern of interband absorption.

The low-frequency contribution to optical conductivity is due to the interaction of electromagnetic waves with electrons localized near the Fermi boundary. A complete absence of such a contribution is predicted in the calculated dependences of $\sigma(E)$ in the low-energy region $E \lesssim 1$ eV, which is explained by the presence of gaps at E_F in the electronic spectra of both compounds. Meanwhile, judging by the experimental curves $\sigma(E)$, a weak but rather noticeable level of optical light absorption is observed in this range, indicating that the anomaly in the band spectrum in the studied materials has a pseudo-gap character when the density of states at the Fermi level does not reach zero values. Formation of a pseudogap may have a different nature, for example, it can be associated with the presence of other phases, impurities, structural defects in these materials, as well as deviations from the stoichiometry.

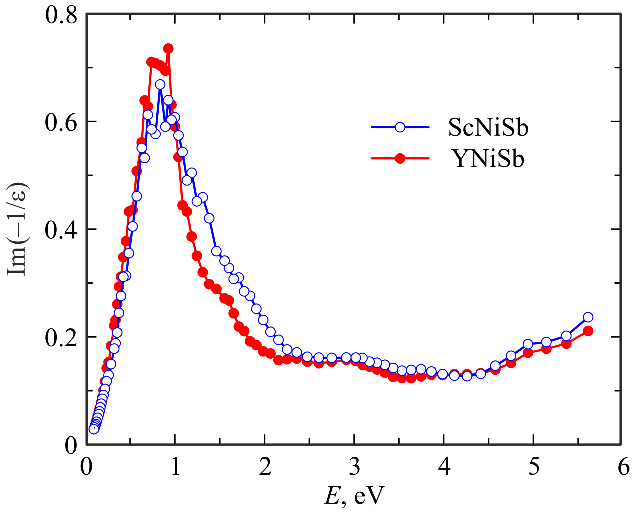

Figure 3. Functions of volumetric characteristic energy losses of electrons of compounds ScNiSb and YNiSb.

The energy dependences of the parameters n and k obtained from the experiment make it possible to estimate the probability of existence and energy of plasma fluctuations constituting collective oscillations of current carriers in a conductive medium. The values of plasma frequencies of conduction electrons ω_p of both compounds can be determined from the spectral behavior of the volume characteristic loss function of electrons, which is represented by the ratio $\mathrm{Im}\left(-1/\varepsilon(\omega)\right) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$ [32]. This function characterizes discrete losses of free electrons during the excitation of volumetric plasma oscillations and has a maximum at $\varepsilon_1 \to 0$, the localization of which is determined by the frequency ω_p. The dependences of $\mathrm{Im}\,(-1/\varepsilon)$ provided in Figure 3 show that the intense maxima in both compounds are located at close energies $\sim 0.8\,\mathrm{eV}$, which corresponds to the plasma frequency $\omega_p = 1.1 \cdot 10^{-15}\,\mathrm{s}^{-1}$.

4. Conclusion

The optical and dielectric properties of ternary intermetallic compounds ScNiSb and YNiSb belonging to the family of semi-Heusler alloys have been experimentally studied. Ellipsometric measurements of optical constants of refractive indices and absorption coefficients were performed in a wide range of wavelengths of $0.22-16\,\mu\mathrm{m}$. The energy dependences of dielectric functions, reflectivity, optical conductivities, and volumetric characteristic loss functions are calculated using these parameters. It is shown that the optical conductivity spectra of the compounds demonstrate a high level of interband absorption in the energy range above $\sim 1\,\mathrm{eV}$ and the absence of a pronounced Drude contribution below this value, which is abnormal for materials with a metallic type of conductivity. The structural features of the experimental dependences of $\sigma(E)$ are satisfactorily reproduced by calculations of this function performed taking into account the density spectra of electronic states published earlier. The weak optical absorption observed in the low-energy region of the spectrum correlates with the results of band calculations showing the presence of an energy gap at E_F in the spectra $N(E)$. At the same time, the experimental values of $\sigma(E)$ in this range do not reach the zero in both alloys, indicating the pseudo-gap nature of this feature of the electronic structure, which, as a rule, is characteristic of semi-metallic materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

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