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Optical and dielectric properties of LuSb and LuBi semimetallic compounds

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In the energy range of 0.077−5.64 eV, the refractive indices and absorption coefficients of LuSb and LuBi semimetallic compounds were measured using an ellipsometric method. The spectra of dielectric constant, optical conductivity, reflectivity, and the function of characteristic electron energy losses were obtained. The features of interband light absorption in both materials are interpreted on the basis of a comparative analysis of experimental and theoretical optical conductivity spectra. It has been established that the optical characteristics of compounds in the infrared region of the spectrum exhibit abnormal behavior due to their semi-metallic nature.

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

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1. Introduction

Binary intermetallic compounds of scandium, yttrium and lanthanides with nitrogen subgroup elements (monopnictides) have been actively researched in the recent years. These materials have various, in some cases unique electric, magnetic and structural properties, some of which being promising for practical use. Physical characteristics of these compounds may vary in the wide range from semiconductor to metallic ones. Different types of magnetic ordering have been found therein [1–3], and crystalline and electron parameters depend on stoichiometry [4], pressure [5,6], admixtures of other elements [7,8]. Practical application capabilities of these materials are based on such properties as superconductivity [9,10], giant magnetoresistance [11,12], high thermoelectric [13,14], magnetocaloric [15] and magnetooptic [16] effects.

The specified family of intermetallic compounds includes binary compounds LuSb and LuBi with a cubic crystalline lattice of NaCl type. At high pressures 24 (LuSb) and 32 GPa (LuBi) this lattice is transformed into tetragonal structure of CsCl type with a volume collapse close to 5 and 7 % accordingly [17–19]. Predicted changes in electron, phonon, mechanical and thermodynamic properties taking place in such transition are discussed in theoretical papers [20–23]. Experimental studies conducted on these compounds are scarce. Based on the interpretation of results from the study of Hall and de Haas-van Alphen effects, the conclusion was made that both compounds are compensated half-metals with equal number of electrons and holes [24,25]. Besides, their temperature dependences of electrical resistance correspond to metal type, and extremely high magnetoresistance in magnetic field 9 T reaches values of around 10^4 % [25,26]. In LuBi an intermittent transition to a superconducting state was found, which is induced by high pressure [27].

Using various computing methods for these compounds the first-principles calculations of a band structure were performed to define the nature and features of electron states near Fermi energy E_F [18,20,24,28–30]. With qualitative similarity of the results obtained in the cited papers, all of them show the presence of strong abnormalities in electron spectra, namely wide energy gaps localized in E_F. As shown in these studies, the presence of such features causes half-metal nature of conductivity in the compounds, contributes to manifestation of high thermoelectric properties. The unique property of electron structure of the studied materials obtained in some calculations is the prediction of topological features in them, indicating a substantial difference in the speeds of charge transfer on the surface and volume. Such properties, promising for development of the systems of superfast electronics, have been experimentally found previously in tantalum and niobium arsenides.

In this paper the method of optical ellipsometry is used to obtain information about electron properties of LuSb and LuBi compounds. The energy dependences of the optical and dielectric characteristics of both materials have been studied in a wide range of wavelengths, including the UV, visible, and IR ranges. Experimental optical conductivity spectra are compared with the corresponding spectra obtained on the basis of previously calculated densities of electron states.

2. Experiment

Polycrystalline specimens LuSb and LuBi, studied in this paper, were prepared by arc melting of highly pure metals ($\sim$ 99.99 %), taken in stoichiometric proportions,

in the atmosphere of pure argon. The arc-melted ingots were annealed for 10 hours in vacuum 10^{-5} mm · Hg at temperature $\sim 800^{\circ}$C with the purpose of homogenization. X-ray data obtained in CuK_α radiation using DRON-6 diffractometer confirmed the formation of a cubic structure of NaCl type in alloys. The values of the compound crystal lattice parameters are close to those previously published in papers [1,17,19] and are 6.065 Å (LuSb) and 6.140 Å (LuBi). The mirror reflecting surface of the specimens of 14 finish class were prepared by mechanical polishing on diamond pastes of various dispersity.

Optical constants of compounds — refractive indices $n(\lambda)$ and absorption coefficients $k(\lambda)$, were measured at room temperature by Beattie's ellipsometric method in the wavelength interval of $\lambda = 0.22-16\,\mu$m (energy range $E = 0.077-5.64$ eV). This method is based on definition of amplitudes and phase shifts of reflected from a specimen light waves of s- and p-polarizations. The measurement accuracy was 2–4 %. Experiments were performed at single and double reflection of light from the specimens in the interval of incident angles 70–80° on the setups designed on the basis of applied spectrometers Spectromom-204 (visible and UV areas of the spectrum) and IKS-12 (IR range). Using the values of optical constants, some spectral parameters were calculated, which characterize the interaction of light with the reflecting medium: real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ parts of complex dielectric permittivity, reflectivity $R(E)$ and optical conductivities $\sigma = \varepsilon_2\omega/4\pi$ (ω — light frequency). Depth of light penetration in the studied materials $\delta = c/\omega k$ (c — light velocity) captures from several dozens (near UV) to several hundreds (IR area) atomic layers, which makes it possible to interpret the optical characteristics as volume properties of the substance.

3. Results and discussion

Energy dependences $\varepsilon_1(E)$, $\varepsilon_2(E)$ and $R(E)$, obtained for compounds LuSb and LuBi, are presented in Figure 1. The features of their behavior with the change of light frequency are in general typical for metal materials. This is indicated by negative values ε_1 in the entire wavelength range, and division of spectra into two areas where intra- and interband light absorption dominates, which is specific to the conducting media. In the presented dependences the intraband absorption is associated with sharp rises in the curves $|\varepsilon_1|$, ε_2 and R in the low-energy range at $E \leq 0.5$ eV, and the interband one — with the structural features at higher energies. It should be noted that the value of reflectivity and real part of dielectric permittivity for both compounds in the IR area are low, which indicates the weakening of their metallic properties compared to good metals, where R approaches one, and absolute values $|\varepsilon_1|$ are two–three orders higher [31].

Spectra of optical conductivity $\sigma(E)$ of the studied compounds — a parameter characterizing the intensity and frequency dependence of the optical response of the reflective medium, are shown with dots in Figure 2.

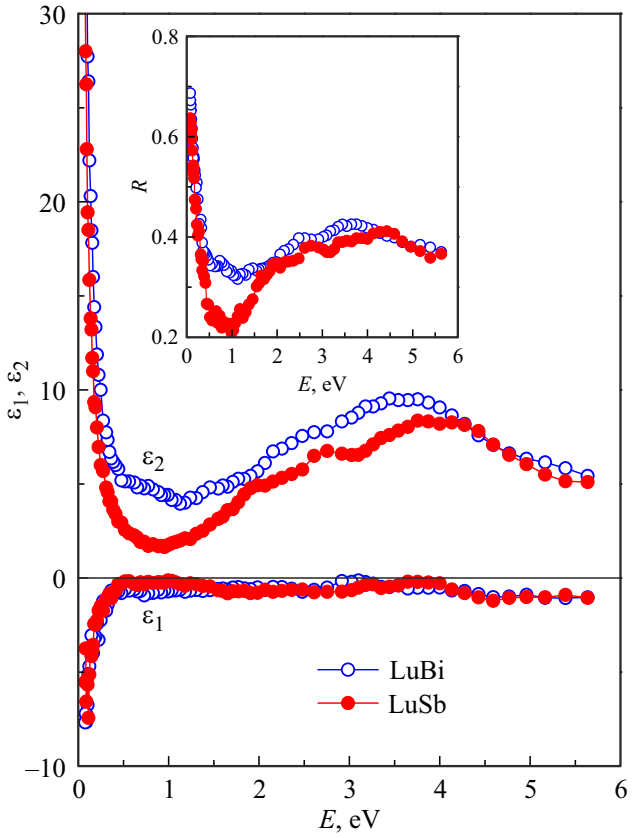

Figure 1. Reflectivity $R(E)$ (on the insert) and dielectric functions of $\varepsilon_1(E)$ and $\varepsilon_2(E)$ of compounds LuSb and LuBi.

As quantum energy increases, substantial growth $\sigma(E)$ occurs, which is related to domination of interband light absorption. Both materials demonstrate formation of wide intense absorption bands of nearly the same profile with the maxima located near 4 eV. In the long-wave area of the spectrum the $\sigma(E)$ values are rather low, and their weak growth is only traced in the interval of up to ~ 0.3 eV. Such behavior of optical conductivity in this range differs drastically from the Drude behavior $\sigma \sim \omega^{-2}$ specific to metals and usually occurring below ~ 1 eV [31]. It should be noted that such dependence $\sigma(E)$ in the IR interval of wavelengths characterized by low values and abnormal dispersion for the metals,was observed previously in the compounds, whose feature is low density of states at Fermi level [32,33].

The shape of spectra $\sigma(E)$ in the area of interband light absorption is determined by electron structure of these compounds, and the nature of the formation of absorption features may be explained qualitatively on the basis of band calculations [18], in general complying with the results of papers [20,24,28–30]. The calculations have shown that in the energy interval $-6 < E_F < 6$ eV in density of electronic states $N(E)$ compounds, which are shown with inserts in Figure 2, Lu $5d$ and Sb $5p$ (Bi $6p$) bands prevail, forming some minima and maxima at both sides of Fermi level. Besides, d-bands of lutetium have high partial

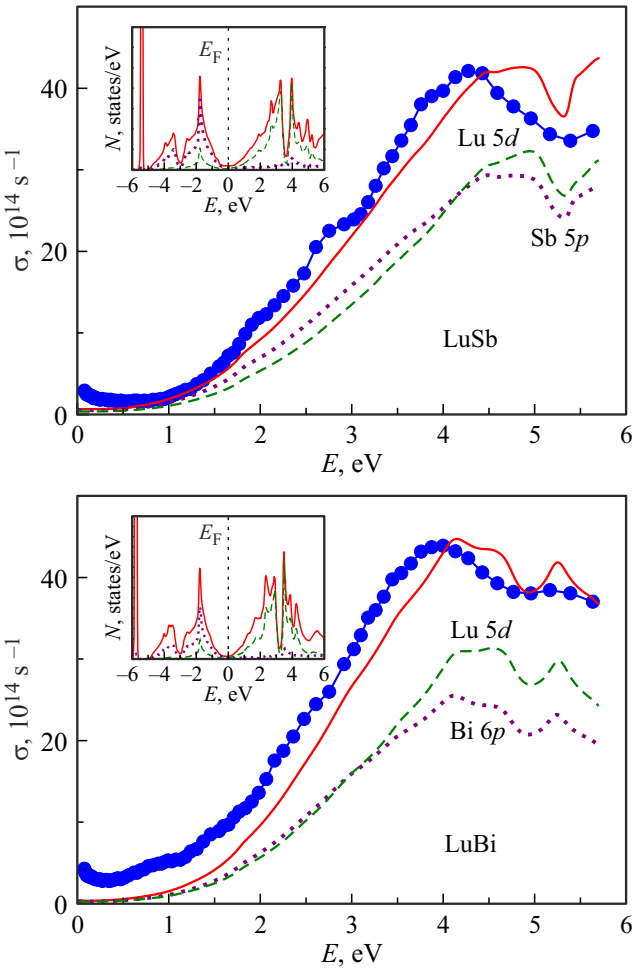

Figure 2. Experimental (circles) and calculated (bold solid lines) energy dependences of the optical conductivity of compounds LuSb and LuBi. Partial contributions from interband transitions with participation of Lu 5*d* and Sb 5*p* (Bi 6*p*) electron states are also shown.

densities at energies above E_F, and *p*-bands of antimony and bismuth — below E_F. The specified partial contributions in this energy interval by intensity substantially exceed the contributions formed by *s*-electron states. The main feature of the spectra $N(E)$ of both compounds consists in the fact that the Fermi levels are located in the center of deep dips, which explains low concentration of conductivity electrons and high electrical resistance of these materials. Abnormally small values of the experimental $\sigma(E)$ observed in the low-energy spectrum range also correspond to $N(E)$ structure shown in [18] and indicate substantial degradation of metallic properties in the studied compounds.

Figure 2 also presents curves of theoretical dependences of interband optical conductivities calculated from the spectra of total densities of states published in [18]. Calculations made using method [34] based on convolutions of full $N(E)$ below and above E_F make it possible to assess the total contribution of direct and indirect transitions in the assumption of their equal probability. Such approximation assumes a qualitative nature of the calculation, in which the dependences of the interband $\sigma(E)$ are presented in arbitrary units. The comparison shows that despite certain relative shifts of experimental and theoretical curves, their profiles are quite well compliant with each other. The calculation describes adequately the width of the absorption bands and localization of maxima near 4 eV. The nature of occurrence of these bands, as it follows from the structure of the density of states [18], is related to the quantum transitions between the filled and free hybridized energy bands Lu 5*d* and Sb 5*p* (Bi 6*p*). The corresponding bands are identified with the high value ranges of $N(E)$ at both sides of the Fermi level that have various structures and are separated from each other by a deep dip. Figure 2 shows, together with interband $\sigma(E)$ calculated from total densities of states, the most significant contributions associated with various electron states. In both compounds, as it follows from the figures, the main contributions to the formation of absorption bands are made by electronic transitions with participation of bands Lu 5*d* and Sb 5*p* (Bi 6*p*). Therefore, the main features of the spectra of optical conductivity of both compounds consists in the presence of abnormally low interband absorption in the range of up to ~ 1.5 eV and its drastic amplification in the energy range above the specified value. The structure of spectra $\sigma(E)$ is qualitatively interpreted on the basis of calculations presented in [18] for the densities of electron states of these materials, indicating their half-metal nature and having predicted the wide gaps at Fermi level.

Using values of real ε_1 and imaginary ε_2 parts of the complex dielectric permittivity, functions of volume characteristic energy losses of electrons were calculated for both compounds presented by the following ratio: $\mathrm{Im}\,(-1/\varepsilon) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$ [35]. This function, the maximum of which occurs at $\varepsilon_1 \to 0$, characterizes the discrete losses of free electrons upon excitation of volume plasma oscillations, and values of plasma frequencies ω_p may be

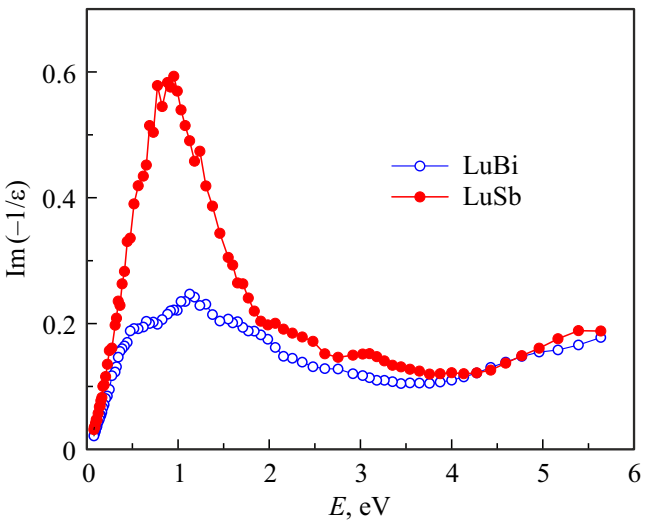

Figure 3. Functions of volumetric characteristic energy losses of electrons of compounds LuSb and LuBi.

determined using localization of the maxima on the energy scale. Energy dependences shown in Figure 3 $\mathrm{Im}(-1/\varepsilon)$ show that such maxima of various intensity are located near 0.9 eV (LuSb) and 1.2 eV (LuBi), which corresponds to values $\omega_p = 1.2 \cdot 10^{15}\,\mathrm{s}^{-1}$ and $\omega_p = 1.5 \cdot 10^{15}\,\mathrm{s}^{-1}$.

4. Conclusion

The paper studied the optical and dielectric properties of binary intermetallic compounds LuSb and LuBi. In the wide interval of wavelengths $0.22-16\,\mu$m the ellipsometric method was used to measure the refractive indices and absorption coefficients, energy dependences of which were used to calculate dielectric functions, reflectivities, optical conductivities and functions of volume characteristic losses. The features of the spectra of optical conductivity of both materials in the area of interband light absorption are satisfactorily interepreted on the basis of previously published first principles calculations of density of electron states. It is shown that in the low-energy area of the spectrum the experimental values $\sigma(E)$ are abnormally low, which corresponds to the conclusions of paper [18] on the presence of deep minima $N(E)$ near the Fermi level. In general the completed optical studies confirm the half-metal nature of conductivity in these compounds predicted previously by the calculations of the electron structure.

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Conflict of interest

The authors declare no conflict of interest.

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