OPTICAL
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Influence of Aluminum Impurity on the Electronic Structure and Optical Properties of the TbNi$_5$ Intermetallic Compound

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Abstract—The electronic structure of the TbNi$_{5-x}$Al$_x$ intermetallic compounds ($x = 0, 1, 2$) is calculated in the local electron density approximation with the correction to strong electron correlations in $4f$ shell of terbium ions. Spectral properties of these compounds are measured by ellipsometry in a wavelength range of $0.22-16$ μm. Frequency dependences of optical conductivity in the region of interband optical absorption are interpreted based on the results of calculations of electron densities of states. The relaxation and plasma frequencies of conduction electrons are determined.

1. INTRODUCTION

Intermetallic compounds of the RNi$_5$ type (R is the rare-earth element), which possess a large variety of magnetic structures and electronic properties, are actively studied theoretically and experimentally. Interest in the investigation of these intermetallic compounds is also caused by prospects of their practical use, which are associated with their unique ability to interact reversely with atomic hydrogen. The specificity of physical properties of these alloys is largely determined by the fact that outer $5d$ electrons of rare-earth atoms occupy Ni $3d$ band, due to which the contribution of Ni atoms to spontaneous magnetic moment is insignificant. The existence of the magnetic order in RNi$_5$ is associated with an indirect exchange between $4f$ electrons through the electrons of the conduction band. The temperature of ferromagnetic ordering T_C in the TbNi$_5$ compound is close to 25 K [1].

It is found that the substitution of nickel by the metal atoms of other groups, which occurs with the conservation of stoichiometry, significantly affects many physical properties of these intermetallic compounds. For example, nonmonotonic concentration dependences of magnetic [1, 2], electronic [2, 3], crystalline [1, 4], and thermodynamic [4] characteristics are found for a system of TbNi$_{5-x}$Al$_x$ pseudobinary alloys possessing the structure of the base compound. An increase in the number of substituting atoms decreases the spontaneous magnetic moment and susceptibility as well as lowers the Curie temperature T_C [1]. It is characteristic that doping of the TbNi$_5$ binary intermetallic compound with aluminum sub-

stantially improves its electrochemical characteristics, while the unit cell of this compound is able to accept up to four hydrogen atoms at $x = 1$ [4]. Some investigations [5–8] indicate the direct correlation between anomalous behavior of various physical parameters of RNi$_5$ compounds and evolution of their electronic structure with an increase in the number of substituting aluminum atoms.

A complex investigation of the energy structure and spectral properties of compounds of this type makes it possible to get the additional information on the features of various characteristics and their variation depending on the concentration of the substituting element. In this study, in order to investigate electronic properties of the TbNi$_{5-x}$Al$_x$ system ($x = 0, 1, 2$), we use LSDA + U calculations of the band spectrum and experiments on the investigation of frequency dependences of optical absorption. The main structural features of optical conductivity dispersion curves are interpreted based on the calculated electron density of states. The calculations and the experiment allow us to evaluate quantitatively some parameters of the band spectrum of compounds and their modification with varying the number of substituting aluminum atoms. The structure of occupied energy bands at $x = 0-3$ was previously studied for this alloy family by the X-ray photoemission method [3]. It was found that the main features of photoemission spectra, which are associated with the rise in the Al content, are the shift and broadening of Ni $3d$ bands localized near the Fermi level E_F. Calculations of the energy structure performed for the TbNi$_5$ binary alloy [2, 3] showed that the main contribution to the electron density of
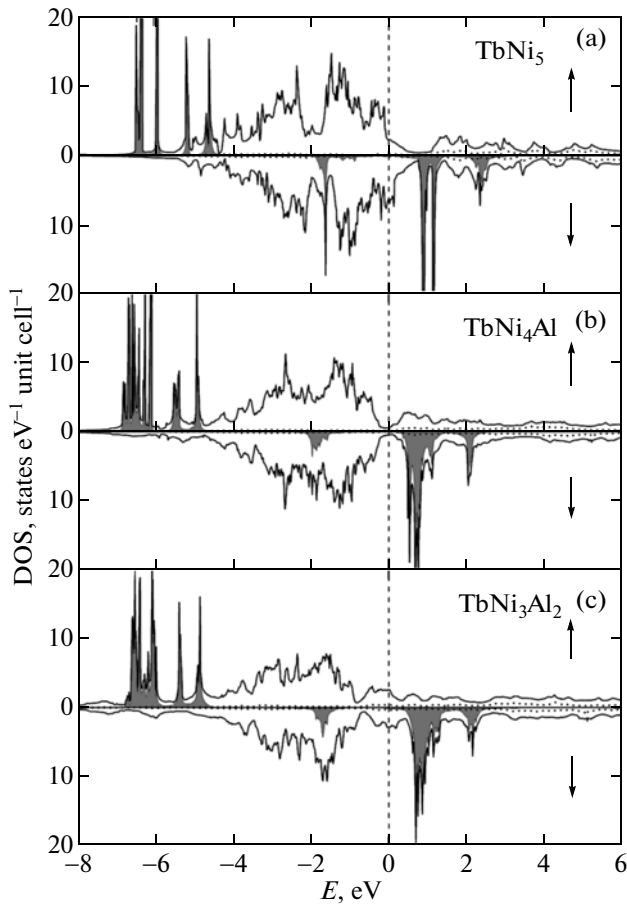
Fig. 1. Total (solid curve) and partial (Tb $4f$ states correspond to the shaded region, and Tb $5d$ states correspond to the dotted curve) electron densities of states of compounds (a) $TbNi_5$, (b) $TbNi_4Al$, and (c) $TbNi_3Al_2$. The Fermi level corresponds to zero on the energy scale.

states at energies $E_F \pm 8$ eV is caused by Tb $4f$ and Ni $3d$ bands.

2. CALCULATION OF THE ELECTRONIC STRUCTURE

The $TbNi_{5-x}Al_x$ compounds ($x = 0, 1, 2$) crystallize in the hexagonal structure of the $CaCu_5$ type (space group $P6/mmm$) with six atoms in the unit cell. Their structural parameters are presented in [1]. Two nonequivalent types of nickel atoms occupy sites Ni1 ($2c$) (1/3, 2/3, 0) and Ni2 ($3g$) (1/2, 0, 1/2) differing by symmetry, and terbium atoms are localized in crystallographic sites ($1a$) (0, 0, 0). The self-consistent calculations of the electronic structure of these intermetallic compounds are performed in the local electron spin density approximation allowing for strong electron−electron interactions between $4f$ electrons of Tb atoms (the LSDA + U method [9]). Calculations were performed using a TB-LMTO ASA program package [10] based on the method of linearized muf-

fin-tin orbitals in the approximation of atomic spheres. We used a grid of k points in the reciprocal space with a total number of $12 \times 12 \times 12 = 1728$. The orbital basis involved MT orbitals corresponding to $6s$, $6p$, $5d$, and $4f$ states of Tb as well as to $4s$, $4p$, and $3d$ states of Ni. The radius of the atomic sphere of Tb was 3.63 a.u., and for Ni1 ($2c$) and Ni2 ($3g$), it was 2.56 and 2.57 a.u., respectively. Parameters of the direct and indirect Coulomb interactions for Tb $4f$ shell were $U = 3.4$ eV and $J = 0.7$ eV. In this calculation of the electronic structure, we modeled the ferromagnetic ordering of local magnetic moments at all lattice sites. To take into account aluminum atoms, all substitution configurations of nickel atoms by aluminum atoms possible in the unit cell were considered for each value $x = 1, 2$ and averaged by the self-consistent electron densities of states. Magnetic moments are 5.8 μ_B at Tb ions for all alloys and less than 0.2 μ_B at Ni ions.

Figure 1 shows the total electron densities of states $N(E)$ of $TbNi_{5-x}Al_x$ compounds ($x = 0, 1, 2$) calculated for two opposite spin directions ($\uparrow$) and ($\downarrow$). The distribution of partial densities for Tb $4f$ and Tb $5d$ bands is also shown here. The common feature of these dependences is the fact that highest values of $N(E)$ are localized in a filled part of the valence band. The system of maxima for the $TbNi_5$ intermetallic compound, which is formed preferentially by Ni $3d$ states, is located in a range 0−4 eV below E_F, which qualitatively agrees with calculations [2, 3]. In all dependences $N(E)$, intense narrow peaks in the $\uparrow$ system, which are localized in a range of 4.5−7.0 eV below E_F, are formed by Tb $4f_\uparrow$ states. Similar strong maxima, which are formed by $4f_\downarrow$ bands, are located in the limits of 0.5−1.3 eV above E_F. In the filled part of the valence band, Ni $3d$ states dominate up to energy of ~4.5 eV being characterized by a multipeak structure, which is almost identical for two spin directions. The total width and intensity of these structures noticeably decreases as the aluminum content in the alloy decreases, while $3d$ bands themselves are displaced into a lower-energy side. The character of localization of E_F in the system of alloys substantially changes with such transformation. Namely, the Fermi level for the $TbNi_5$ compound is located at a higher-energy side of the maximum associated with the $3d$ band. On the contrary, during the substitution of nickel by aluminum, E_F initially gets into the minimum ($TbNi_4Al$) and then localizes in the region of higher values of $N(E)$ ($TbNi_3Al_2$). Structural features of $N(E)$ above E_F, which are not associated with $4f$ bands, are less pronounced being formed by the additive contribution of energy Ni $3d$ bands and Tb $5d$ bands. The calculation also showed that Al $3p$ bands introduce a small contribution to the density of states. This contribution has almost structureless shape being distributed almost uniformly over the entire energy range under study.

Electron densities of states, which are presented in Fig. 1, agree well with photoemission spectra of these compounds [3]. Localization and extension of main structural features of these spectra—the maxima formed by Tb $4f$ bands and Ni $3d$ bands—are close to the values acquired in this study. In addition, the tendency of displacing the Ni $3d$ band to the lower-energy side upon increasing the aluminum content is reproduced in the calculation.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The method of preparation of $TbNi_{5-x}Al_x$ samples ($x = 0, 1, 2$), their attestation, and magnetic properties are presented in [1]. Optical properties of compounds were studied at room temperature in wavelength range $\lambda = 0.22-16$ μm ($0.078-5.640$ eV). Fundamental spectral parameters such as refractive index $n(\lambda)$ and absorption coefficient $k(\lambda)$ are measured by ellipsometry with a rotating analyzer at incidence angles of light of $70°-80°$ with the error of $2-4\%$. Mirror surfaces of the samples were prepared by mechanical polishing on finely dispersed diamond pastes. Optical conductivity $\sigma(\omega) = nk\omega/2\pi$ (ω is the frequency of the optical wave), which is the parameter that characterizes the intensity and frequency dependence of the optical response of the reflecting medium, was calculated by the values of n and k.

Experimental spectra of optical conductivity of compounds under study are presented in Fig. 2. Characteristic features of these spectra are typical of metal-like media being determined by two types of optical absorption, namely, interband and intraband. An abrupt increase in $\sigma(\omega)$ in the lower-energy range is associated with the Drude interaction mechanism of electromagnetic waves with conduction electrons ($\sigma \sim \omega^{-2}$). As the frequency of light increases, the character of the frequency dependence of optical conductivity indicates the prevalent role of interband electron transitions. A broad band of quantum absorption appears in dispersion $\sigma(\omega)$ of all compounds at energies above ~0.7 eV; its structure varies depending on the impurity content. The spectral profile of this band substantially changes, while its "center of gravity" shifts to a higher-energy side. Since the observed modification of the $\sigma(\omega)$ spectra is associated with the change in the electronic structure of these compounds, which occurs with the substitution of nickel by aluminum, it is of interest to compare the experimental optical conductivities with those calculated from the electron densities of states (Fig. 1). The calculation of interband $\sigma(\omega)$ was made according to the method [11] based on the convolution of total $N(E)$ above and below the Fermi level under the condition of equal probability of direct and indirect electron transitions. Results of calculation are presented in Fig. 2 along with the experimental spectra in arbitrary units.
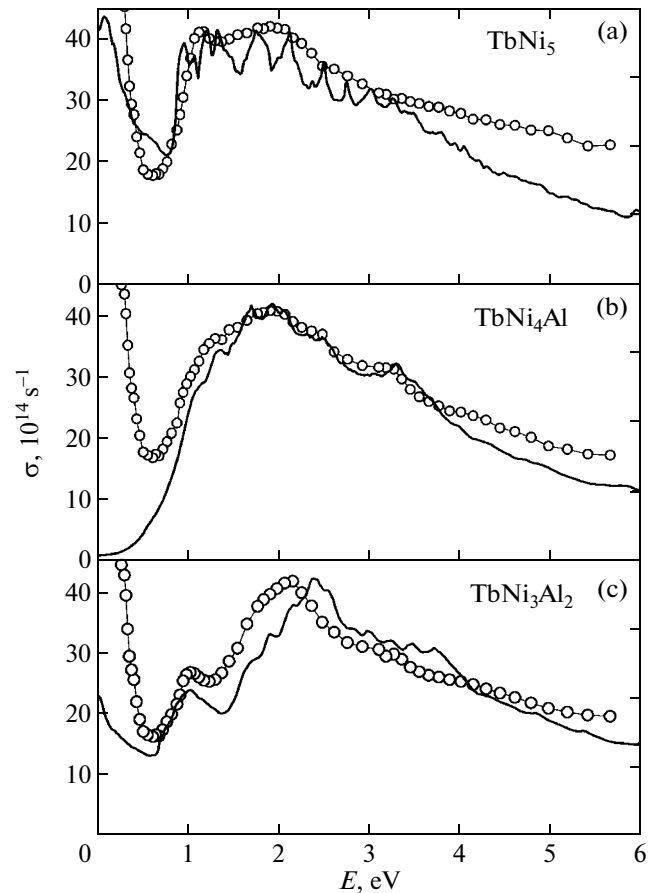
Fig. 2. Dispersion of optical conductivity for $TbNi_{5-x}Al_x$ compounds with $x =$ (a) 0, (b) 1, and (c) 2. The circles correspond to the experiment, and solid curves correspond to the calculation (in arbitrary units).

The comparison shows that interband optical conductivities, which are found theoretically from the electron densities of states, reproduce main features of experimental frequency dependences of this function. This is referred to evaluations of the lower-energy edge of electron transitions, the range of intense optical absorption, and the arrangement of main maxima and minima in spectra $\sigma(\omega)$. It should be noted that this comparison is preferentially qualitative since we did not take into account such parameters as the lifetime of the excited state and matrix elements of interband transitions, which determine their probability, in our calculations. This circumstance leads to that no correspondence is observed in details of a fine structure of the theoretical and experimental dependences, and calculated values of optical conductivity at low energies can be overestimated. This discrepancy most essentially manifested itself in the case of $TbNi_5$, where numerous peaks in curve $\sigma(\omega)$, which are found theoretically, are unobservable experimentally.

In general, both the calculation and the experiment showed that the structure of the spectrum of the interband optical conduction varies substantially depend-

ing on the aluminum impurity concentration. The profile of the calculated absorption band for aluminum-doped compounds is more smoothed than for binary $TbNi_5$, while the main maxima were shifted to higher frequencies. The nature of formation of these maxima, according to the calculations of the density of states, is associated with electron transitions between Ni $3d$ bands below E_F and hybridized $4f$ Tb bands and Ni $3d$ bands above E_F. In view of the fact that densities of Al $3p$ electron states are low and "spread" in a broad energy region, the associated structural features are not identified in the curves of interband $\sigma(\omega)$. We note that this distribution character of aluminum impurity bands lies in the basis of a significant distinction of optical spectra presented here from those found previously for $RNi_{5-x}Cu_x$ compounds [12, 13]. A more considerable reconstruction of spectrum $\sigma(\omega)$ is observed for these compounds as Ni atoms are substituted by Cu atoms, and a new intense absorption band appears near 4 eV, which is associated with interband transitions with the participation of Cu $3d$ electron states.

By the numerical values of optical constants, which are measured in the infrared spectral region of 9–16 μm, where the influence of interband transitions on the optical response is minimal (the Drude range), we determined relaxation γ and plasma ω_p frequencies of conduction electrons. Relaxation frequency $\gamma = 1/\tau$, where τ is the relaxation time, which integrally takes into account all the types of electron scattering during their excitation by the electromagnetic wave, manifests a small rise tendency with increasing content of aluminum atoms and possesses the values 2.1×10^{14} s^{-1} ($TbNi_5$), 2.4×10^{14} s^{-1} ($TbNi_4Al$), and 2.6×10^{14} s^{-1} ($TbNi_3Al_2$). The calculated magnitudes of the square of plasma frequency ω_p^2, which is the parameter proportional to the density of states at the Fermi level [14], are as follows: 34×10^{30} s^{-2} ($TbNi_5$), 21×10^{30} s^{-2} ($TbNi_4Al$), and 31×10^{30} s^{-2} ($TbNi_3Al_2$). It is noteworthy that the value of ω_p^2 for the alloy with $x = 1$ is substantially lower than the values found for two other compounds, which corresponds to the character of varying $N(E_F)$ (Fig. 1), which is predicted by the band calculation.

4. CONCLUSIONS

We investigated the evolution of the electronic structure and optical properties of $TbNi_{5-x}Al_x$ compounds ($x = 0, 1, 2$), which occurs during the substitution of nickel atoms by aluminum atoms. Energy dependences of the electron density of states, which were calculated by the LSDA + U method allowing for strong interactions in $4f$ shell of terbium ions, are presented. The nature of electron states, which form absorption spectra in the energy range of ±6 eV, is

determined. Based on found curves $N(E)$, interband optical conductivities are calculated, the behavior of which is compared with corresponding experimental dependences. It is shown that the character of the frequency dispersion of experimental curves $\sigma(\omega)$ is explained satisfactorily in the context of the performed calculation of density of states. The main features of the interband absorption of compounds under study are formed by electron transitions in the system of Ni $3d$ bands in both spin systems as well as by transitions between Ni $3d$ bands and Tb $4f$ bands in the ↓ system of electron bands. The relaxation and plasma frequencies of conduction electrons are determined from the optical data for the infrared spectral region.

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