=========== **METALS** ===========

Influence of Copper Impurities on the Evolution of the Electronic Structure and Optical Spectra of the LuNi$_5$ Compound

Yu. V. Knyazev[a, *], **A. V. Lukoyanov**[a, b], **Yu. I. Kuz'min**[a], **and A. G. Kuchin**[a]

[a] *Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences,*
ul. Sofii Kovalevskoi 18, Yekaterinburg, 620990 Russia
[b] *Ural Federal University named after the First President of Russia B. N. Yeltsin,*
ul. Mira 19, Yekaterinburg, 620002 Russia
* e-mail: knyazev@imp.uran.ru
Received November 17, 2014

Abstract—The optical properties of LuNi$_{5-x}$Cu$_x$ intermetallic compounds ($x = 0, 1, 2$) have been investigated using ellipsometry in the wavelength range of 0.22–15 μm. It has been established that the partial substitution of nickel by copper leads to substantial variations in the spectral characteristics, as well as in the plasma and relaxation frequencies of conduction electrons. Self-consistent calculations of the electronic structure of these compounds have been performed in the approximation of the local electron spin density. The experimental frequency dependences of the optical conductivity in the interband optical absorption region have been interpreted based on the calculated densities of electron states.

1. INTRODUCTION

The system of intermetallic compounds of the RNi$_5$ type (R is the rare-earth metal), which are notable for a large variety of magnetic structures and electronic properties, has attracted attention due to a wide range of practical applications. Unique physicochemical characteristics of such compounds ensure the possibilities of their application as magnetostrictive and magnetoresistive materials [1, 2] as well as materials for magnetic cooling [3, 4] and storage of atomic hydrogen [5, 6]. It is known that the partial substitution of nickel by atoms of other p and d metals in alloys of the RNi$_5$ family, which leads to a change in parameters of the electron spectrum, crystalline field, and exchange interaction, substantially affects structural, electrical, and magnetic properties. Such variation in physical characteristics of these intermetallic compounds upon introducing impurity is actively used to improve their functional properties.

One representative of the mentioned class of compounds is LuNi$_5$, certain properties of which were investigated in recent years. The literature reports the results of experimental measurements of some magnetic [7], structural, and electronic characteristics [8, 9], the distinctive features of which are in many aspects associated with the fact that the 4f shell of the rare-earth metal is filled completely while the contribution of 3d electrons of Ni in the spontaneous moment is negligible. We showed [10] that this compound is the Pauli exchange-enhanced paramagnet, where the spin paramagnetism is the determining factor. In contrast to the LuNi$_5$-base intermetallic compound, copper-doped LuNi$_{5-x}$Cu$_x$ compounds were not investigated. In order to explain the experimental results and understand the nature of observed physical properties, the information on the electronic structure of this family of intermetallic compounds is necessary. In this study, in order to investigate the features of the structure of valence bands of the LuNi$_5$ binary compound as well as their evolution upon the partial substitution of nickel by copper, we use the calculations of the electron spectrum in the local electron spin density approximation (LSDA) and optical measurements allowing us to determine the energy dependences of a number of spectral characteristics.

2. CALCULATION OF THE ELECTRONIC STRUCTURE

The LuNi$_{5-x}$Cu$_x$ compounds ($x = 0, 1, 2$) have a hexagonal structure of the CaCu$_5$ type in the space group $P6/mmm$. The Lu atoms occupy the crystallographic site 1a (0, 0, 0) in the LuNi$_5$ unit cell consisting of one formula unit, while Ni atoms are localized in two sites 2c (1/3, 2/3, 0) and 3g (1/2, 0, 1/2) nonequivalent by symmetry. We used the following experimentally measured parameters of the hexagonal lattice in calculations of the electronic structure of the LuNi$_5$ compound: $a = 4.816$ Å and $c = 3.9817$ Å. Lattice constants increase as the copper content increases and have the following values: $a = 4.8385$ Å, $c = 4.0012$ Å for LuNi$_4$Cu and $a = 4.863$ Å, $c = 4.0197$ Å for LuNi$_3$Cu$_2$.
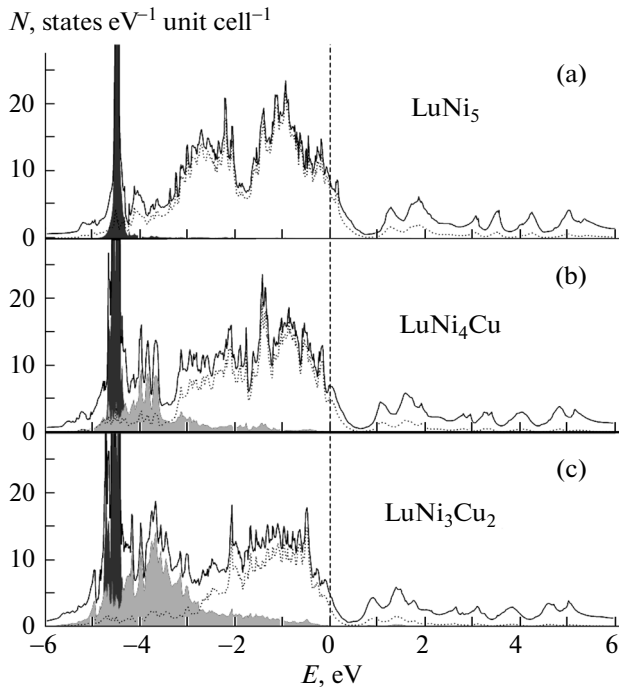
Fig. 1. Total (solid curve) and partial for Ni 3d (dotted line), Lu 4f (dark regions), and Cu 3d (gray regions) densities of electron states for compounds (a) LuNi$_5$, (b) LuNi$_4$Cu, and (c) LuNi$_3$Cu$_2$, calculated in terms of the LSDA method. The Fermi level corresponds to zero in the energy scale.

Fig. 2. Dependences of the refractive index n and absorption coefficient k for LuNi$_5$, LuNi$_4$Cu, and LuNi$_3$Cu$_2$ compounds on the wavelength of light.

Self-consistent calculations of the electronic structure in LuNi$_{5-x}$Cu$_x$ compounds ($x = 0, 1, 2$) were performed in the LSDA method in the TB–LMTO–ASA software package [11] based on the method of linearized muffin-tin orbitals in the approximation of atomic spheres. The integration was performed over the grid of k-points in the reciprocal space with total number of $10 \times 10 \times 10 = 1000$ k-points. The orbital basis included MT orbitals corresponding to 6s, 6p, 5d, and 4f states of Lu as well as 4s, 4p, and 3d states of Ni. The radius of the atomic sphere of Lu was 3.5 a.u., and radii of atomic spheres of Ni1 (2c) and Ni2 (3g) are 2.6 a.u.; the same radius of the atomic sphere was used for Cu. The electron configurations found due to the self-consistent process showed the absence of spin polarization in all lattice sites. All possible substitutional configurations of nickel atoms by copper atoms in the unit cell were considered for $x = 1, 2$; then, the self-consistent partial densities of electron states were averaged with corresponding weights.

Total densities of electron states $N(E)$ of LuNi$_{5-x}$Cu$_x$ compounds ($x = 0, 1, 2$) are presented in Fig. 1. The distribution of partial densities for 4f electrons of Lu and 3d electrons of Ni and Cu is also shown here. In all three compounds, the region of higher values of $N(E)$ is arranged in the filled part of the valence band at energies smaller than the Fermi level by the
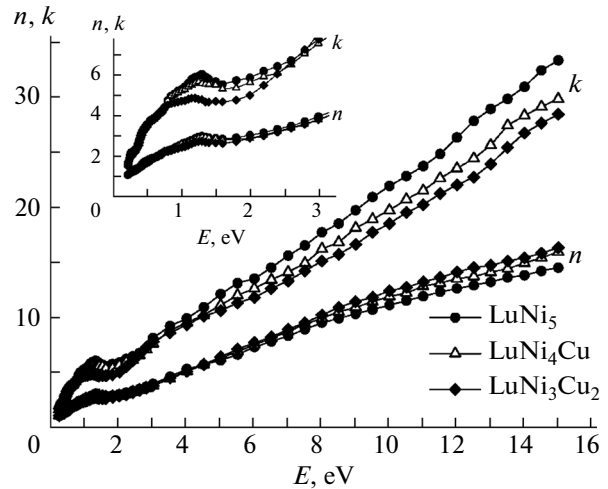
magnitude up to ~6 eV. Intense peaks localized in the energy range by 4–5 eV below E_F are caused by 4f electrons of Lu atoms. A noticeable transformation of the energy dependence of the total density of states is observed as the copper content increases ($x = 1$ and 2). A minimum at energies lying approximately by 2 eV below E_F, which occurs in the structure of $N(E)$ for the binary compound, disappears. In addition, the formation of a new structure consisting of a group of narrow maxima genetically associated with 3d electron states of Cu atoms, is observed in the range of energies below E_F by 3–5 eV. The intensity and width of these features, as it is reflected in Figs. 1b and 1c, substantially increases as the concentration of copper atoms increases. It should be noted that the localization energy of 3d zone of Cu is close to values determined previously for other compounds of this type with various rare-earth metals [12–14].

3. RESULTS AND DISCUSSION

A method for preparing compounds under study and their attestation are presented in [7]. The spectral characteristics of the samples were investigated in the wavelength range $\lambda = 0.22$–15 μm (0.083–5.64 eV). Optical constants, namely, refractive index $n(\lambda)$ and absorption coefficient $k(\lambda)$, were measured by ellipsometry with a single and double reflection of light from a mirror sample surface. A number of spectral functions, which characterize the optical response of the medium, was calculated by values of n and k. Dispersion dependences $n(\lambda)$ and $k(\lambda)$ for three compounds under study are presented in Fig. 2. Ratio $k > n$ is fulfilled overall the entire wavelength range, which is typical for the media with the metallic type of conduction. A nonmonotonic variation in these parameters at $\lambda < 2$ μm points to the manifestation of the mecha-
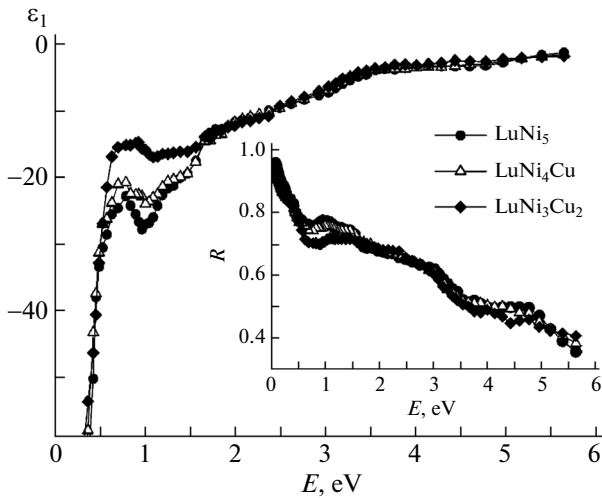
Fig. 3. Energy dependences of the real part of permittivity ε_1 and reflectivity R (inset) for $LuNi_5$, $LuNi_4Cu$, and $LuNi_3Cu_2$ compounds.

Fig. 4. Dispersion of the optical conductivity for $LuNi_5$, $LuNi_4Cu$, and $LuNi_3Cu_2$ compounds. Curves are shifted relative to each other along the ordinate axis by 10 units.

nism of the interband absorption of light, while their subsequent smooth rise with an increase in λ points to the intraband (Drude) electron excitation. The variation in optical constants in the Drude spectral range with an increase in amount of the copper impurity is directed differently: n rises while k drops. The character of the wave dependence of these parameters corresponds to the fact that the real part of permittivity ε_1 is negative, while reflectivity R increases as the energy of the optical wave decreases (Fig. 3).

Dispersion dependences of optical conductivity $\sigma(\omega) = nk\omega/2\pi$ (ω is the cyclic frequency of the optical wave) for family of $LuNi_{5-x}Cu_x$ intermetallic compounds ($x = 0, 1, 2$) are presented in Fig. 4. The behavior of $\sigma(\omega)$ for all compounds in the low-energy region to energy of ~0.7 eV is determined by an abrupt drop $\sigma \sim \omega^{-2}$, which is typical of the Drude absorption of light. The dispersion character of the optical conductivity varies abruptly as the frequency increases, which is evidenced by the appearance of maxima inherent to the manifestation of the quantum excitation mechanism. In a wide energy region, where interband electron transitions dominate, there are structures whose position and intensity substantially depend on the composition of the compound. Three broad maxima at energies near 1, 2.5, and 4.5 eV are shown up in spectrum $\sigma(\omega)$ of the $LuNi_5$ binary intermetallic compound. When substituting one nickel atom with copper ($x = 1$), mainly the profile of the first maximum varies, while the shape of two other remains almost invariable. The further increase in the copper concentration ($x = 2$) leads to the transformation of two maxima into a single extended band with a "shoulder" in the low-energy spectrum.

The observed modification of spectra $\sigma(\omega)$ in the region of quantum absorption of light is caused by the
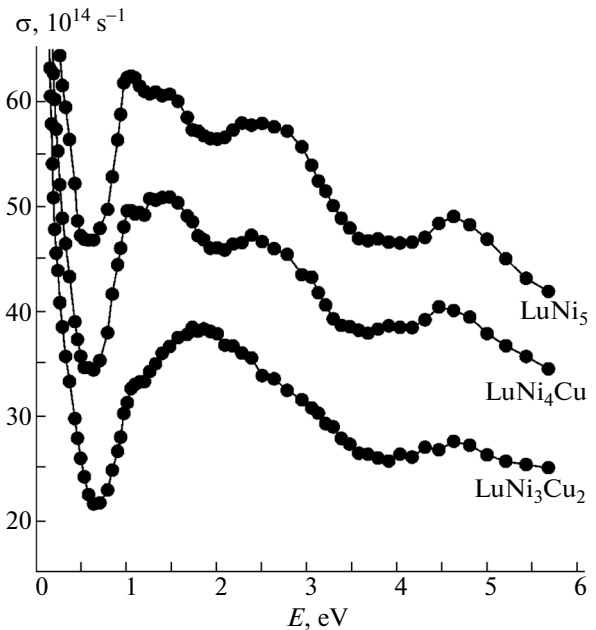
variation in the band structure of compounds during the partial substitution of nickel by copper. Therefore, it is of interest to compare the experimental interband optical conductivities $\sigma_{ib} = \sigma - \sigma_D$ (σ_D is the Drude contribution) with corresponding dependences calculated from the densities of electron states (Fig. 1). The latter were determined according to the method proposed in [15] and were expressed by integral functions based on convolutions of total densities of states below and lower the Fermi level. Dependences $\sigma_{ib}(\omega)$, which were calculated not allowing for the selection rules, are presented along with the experimental curves in Fig. 5. Partial contributions to the interband optical conductivity from quantum transitions with the participation of electrons of $4f$ band of Lu and $3d$ band of Cu are also presented in Fig. 5. The comparison shows that the frequency dependences of the curves $\sigma_{ib}(\omega)$ both for binary and ternary compounds qualitatively reproduce the main features of the experimental spectra. The character of transformation of calculated $\sigma_{ib}(\omega)$ curves with an increase in the number of substitutional atoms in general corresponds to the tendency observed experimentally. According to the calculation, the nature of maxima observed in the experimental spectra to energies of ~4 eV is preferentially associated with the interband transitions in a system of $3d$ band of Ni. A broad peak near 4 eV for all compounds is formed by transitions with the participation of $4f$ electrons of Lu. The system of $3d$ electrons of copper also introduces a small contribution to the interband optical conductivity of ternary alloys. Figures 5b and 5c show that this contribution has a form of a monotonically rising
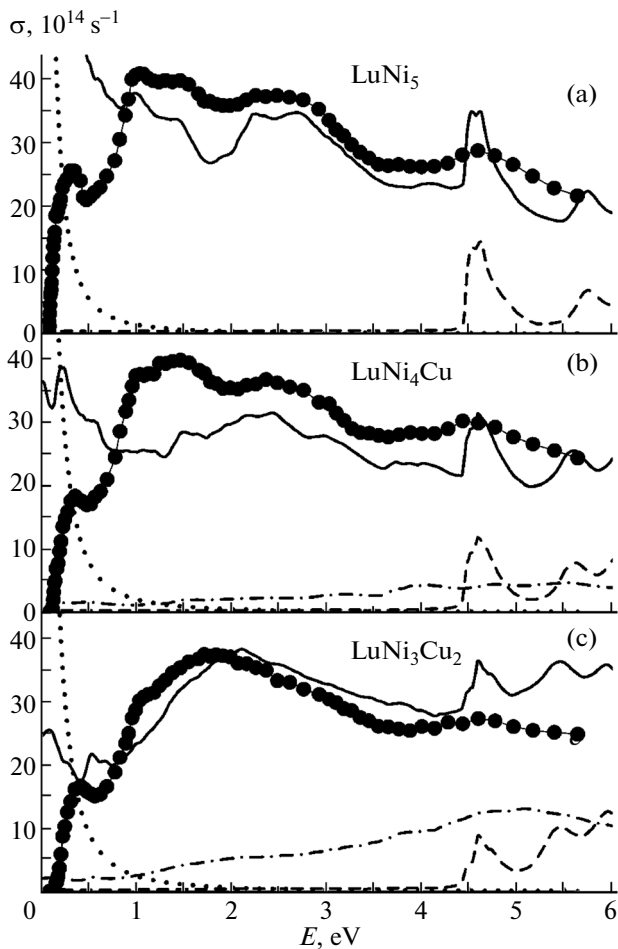
Fig. 5. Interband optical conductivity spectra for $LuNi_{5-x}Cu_x$ compounds ($x = 0, 1, 2$). Points correspond to the experiment. Solid curves correspond to the calculation from the total densities of states. The dotted line is the Drude contribution. Dash-and-dot and dashed lines correspond to the partial contributions to conductivity from transitions with the participation of $3d$ band of Cu and $4f$ band of Lu, respectively.

carriers. Relaxation γ and plasma ω_p frequencies of conduction electrons for the corresponding wavelength range (10–15 μm) are determined using the Drude relations. It is established that the relaxation frequency, which additively takes into account all scattering types of electrons during their interaction with the electromagnetic wave, substantially increases with the partial substitution of nickel by copper and have the following values 1.5×10^{14} s^{-1} (LuNi$_5$), 1.9×10^{14} s^{-1} (LuNi$_4$Cu), and 2.2×10^{14} s^{-1} (LuNi$_3$Cu$_2$).

The square of plasma frequency ω_p^2—the parameter, which depends on the local structure of the electron spectrum in the near-Fermi region and electron–electron correlation effects—manifests a weak tendency to rise [16]: 31.2×10^{30} s^{-2} (LuNi$_5$), 32.3×10^{30} s^{-2} (LuNi$_4$Cu), and 33.5×10^{30} s^{-2} (LuNi$_3$Cu$_2$). The found values of γ and ω_p^2 were used to calculate the Drude contributions to optical conductivities of alloys under study (Fig. 5).

4. CONCLUSIONS

The electronic structure and optical properties of $LuNi_{5-x}Cu_x$ intermetallic compounds ($x = 0, 1, 2$) as well as their variations occurring during the partial substitution of nickel by copper were investigated. Energy dependences of total and partial densities of electron states, which were calculated using the LSDA method, were presented. The nature of electron states participating in the formation of the interband optical absorption spectrum was identified. It was shown that the character of the frequency dependences of optical conductivities in the region of quantum electron transitions as well as their transformation with the variation in the impurity content find a satisfactory explanation in terms of the presented calculations of the densities of states. The relaxation and plasma frequencies of conduction electrons were determined from the optical data in the low-energy spectral region.

extended band with a broad maximum near 5 eV. It should be noted that the correspondence of the structural features of experimental and theoretical dependences $\sigma_{ib}(\omega)$ is affected by the qualitative character of calculations performed not allowing for probabilities of interband transitions and lifetimes of excited states. For example, the magnitude of theoretical $\sigma_{ib}(\omega)$ dependence in the low-energy region to ~1 eV for compounds with $x = 0, 1$ (Figs. 5a, 5b) turned out substantially higher than the corresponding values in the same range found experimentally.

The dispersion of optical conductivity in the low-energy spectral range, where the intraband electron excitation mechanism dominates during the absorption of light, while the influence of interband transitions is insignificant, the dispersion of optical conductivity is determined by microcharacteristics of charge

REFERENCES

1. K. A. Gschneidner, Jr, V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
2. *Concise Encyclopedia of Magnetic and Superconducting Materials*, Ed. by K. H. J. Buschow (Elsevier, Amsterdam, 2005).
3. P. J. von Ranke, M. A. Mota, D. F. Grangeia, A. Magnus, G. Carvalho, F. C. G. Gandra, A. A. Coelho,

A. Caldas, N. A. de Oliveira, and S. Gama, Phys. Rev. B: Condens. Matter **70**, 134428 (2004).

4. D. L. Rocco, J. S. Amaral, J. V. Leitão, V. S. Amaral, M. S. Reis, S. Das, R. P. Fernandes, J. P. Arau'jo, A. M. Pereira, P. B. Tavares, N. V. Martins, and A. A. Coelho, J. Phys. D: Appl. Phys. **42**, 055002 (2009).

5. H. Senoh, N. Takeichi, H. T. Takeshita, H. Tanaka, T. Kiyobayashi, and N. Kuriyama, Mater. Sci. Eng., B **108**, 96 (2004).

6. X. Zhao and L. Ma, Int. J. Hydrogen Energy **34**, 4788 (2009).

7. A. G. Kuchin, A. S. Ermolenko, Yu. A. Kulikov, V. I. Khrabrov, E. V. Rosenfeld, G. M. Makarova, T. P. Lapina, and Ye. V. Belozerov, J. Magn. Magn. Mater. **303**, 119 (2006).

8. L. Romaka, V. Romaka, and Yu. Stadnyk, Chem. Met. Alloys **4**, 89 (2011).

9. L. Guénée, and K. Yvon, J. Alloys Compd. **356–357**, 114 (2003).

10. K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1977).

11. O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

12. A. Bajorek, G. Chełkowska, and B. Andrzejewski, J. Alloys Compd. **509**, 578 (2011).

13. Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuz'min, and A. G. Kuchin, J. Alloys Compd. **509**, 5238 (2011).

14. Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuz'min, and A. G. Kuchin, Phys. Status Solidi B **249**, 824 (2012).

15. C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964).

16. M. I. Kaganov and V. V. Slezov, Sov. Phys. JETP **5**, 1216 (1957).

Translated by N. Korovin