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Optical properties of $CeNi_5$ and $CeNi_4M$ (M = Al, Cu) compounds

Yu. V. Knyazev*, Yu. I. Kuz'min, A.G. Kuchin

Institute of Metal Physics, Ural Division, RAS, 18 Kovalevskaya St., 620990 Ekaterinburg, Russia

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ABSTRACT

The experimental study of the optical properties of $CeNi_5$, $CeNi_4Cu$ and $CeNi_4Al$ compounds was carried out in the 0.083–5.64 eV energy range using the ellipsometry method. The optical constants, dielectric functions and electronic parameters (plasma and relaxation frequencies) were determined. The energy dependencies of the optical interband conductivities are discussed by using the available information on the electronic band structure of these compounds. In the ternary alloys the optical spectra show the presence of peculiarities related to effect of Cu or Al substitution at Ni sites.

1. Introduction

Intermetallic compounds of rare earth metals R with nickel attract attention from both technological applications and basic research [1–3]. In the series of RNi_5 compounds the use of Ce as the R element is especially interesting because it can lead to properties, which are typical for the correlated electron systems. In some of Ce-based intermetallics the mixed valence state of Ce ions was observed due to strong hybridization between 4*f* and conduction electrons [4–6]. The temperature dependence of the electrical resistivity of these compounds exhibited a Kondo-like effect [5,7]. The physical properties of the $CeNi_5$ display some variations with the substitution of nonmagnetic atoms for nickel. The $CeNi_5$ and ternary $CeNi_4M$ (M = Al, Cu) alloys crystallize into the hexagonal $CaCu_5$-type structure, having *P*6/*mmm* space group. These compounds are not common exchange-enhanced Pauli paramagnets and show spin-fluctuation behaviour [8,9]. The structural, magnetic and electronic properties of these compounds have been measured and analyzed [10–12]. The X-ray photoemission experiments in the valence band region have shown domination of the Ni 3*d* electronic states as well as the different localization of Cu 3*d* and Al 2*p* states below the Fermi energy E_F [7,13]. With the aim to obtain a deeper insight into electronic and magnetic properties band structure calculations were carried out for these Ce-based intermetallics [5,7,10,14,15].

The optical properties of metals and alloys depend strongly on their energy spectrum. For that reason the optical spectroscopy is rather sensitive tool for study of the electronic structure near the Fermi level. The optical response, especially in the near-infrared, visible and ultraviolet regions, involves interband transitions from occupied states below the Fermi energy to empty states above, contributing to the features in the experimental spectra. In this paper we report the optical properties of the hexagonal $CeNi_5$, $CeNi_4Cu$ and $CeNi_4Al$ compounds and interpret the behaviour of the interband conductivities using the electronic structures calculated by the band methods.

2. Experimental

The samples were prepared by the induction melting under an argon atmosphere. To obtain a single-phase state with $CaCu_5$-type structure an annealing at 1100 °C was performed for eight hours. The structure was verified by X-ray diffraction studies. The resulting lattice constants are equal $a = 4.889$ Å, $c = 4.001$ Å for $CeNi_5$, $a = 4.924$ Å, $c = 4.021$ Å for $CeNi_4Cu$ and $a = 4.951$ Å, $c = 4.087$ Å for $CeNi_4Al$. Previously on given samples were realized measurements on the structural, electronic and magnetic properties [10,11].

The studies of the optical properties were carried out at room temperature in the wavelength range $\lambda = 0.22–15$ μm (photon energies $E = 5.64–0.083$ eV). The optical constants, i.e. refractive index n and absorption coefficient k were derived from the ellipsometry measurements at the angles of incidence of 70–80° using the Beattie technique [16]. Spectroscopic ellipsometry is based on the fact that the state of polarization of incident light is changed on reflection. This change is directly related to the dielectric function of reflecting material. The samples were polished with diamond pastes until a mirrorlike surface was obtained. The values of n and k were used to calculate the real $\varepsilon_1 = n^2 - k^2$ and the imaginary $\varepsilon_2 = 2nk = 4\pi\sigma/\omega$ parts of the complex permittivity and also the reflectance $R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2]$ (ω is the cyclic frequency of the light wave and σ is the optical conductivity).

3. Results and discussion

Typical metal-like behaviour was observed in the $\varepsilon_1(E)$ and $R(E)$ dependences (Fig. 1): the ε_1 values are negative in the entire energy range under study, while R tends to unity in the low photon energy region. In the range of 0.5–2.5 eV the reflectance for ternary alloys

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* Corresponding author.
E-mail address: knyazev@imp.uran.ru (Yu.V. Knyazev).

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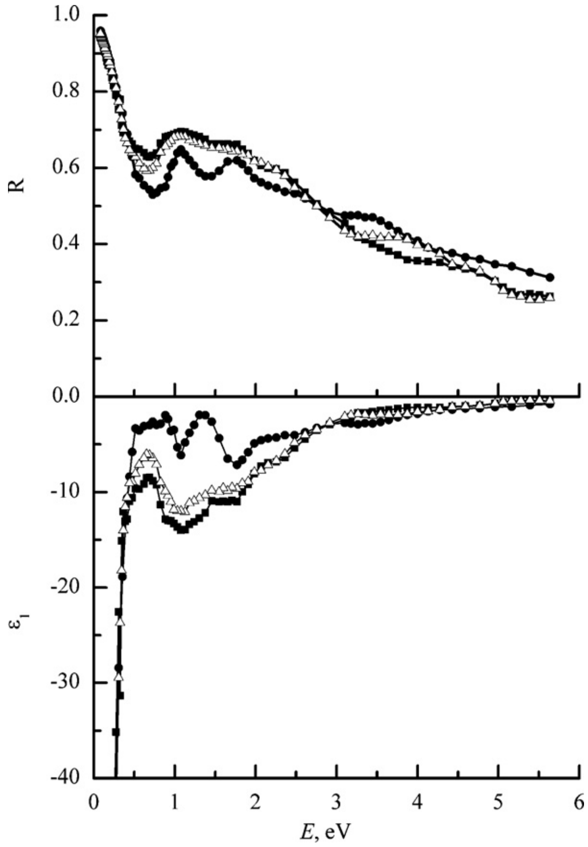

Fig. 1. Reflectance R and the real part of the complex permittivity ε_1 of the intermetallic compounds $CeNi_5$ (●), $CeNi_4Cu$ (△) and $CeNi_4Al$ (■).

exceed magnitude of R for $CeNi_5$. The low-frequency ($E < 0.5$ eV) growth of $R(E)$ and very large and negative values of ε_1 are stipulated by the intraband (Drude-type) absorption. The intraband absorption is determined by the parameters of the conduction electrons - relaxation γ and plasma Ω frequencies. The relaxation frequency $\gamma = 1/\tau = \varepsilon_2\omega/\varepsilon_1$ (τ is the relaxation time) additively take into account all types of electron scattering upon excitation by the electromagnetic field. In the limit $\omega \to 0$ the magnitude γ is determined by the static electrical resistivity. The squared plasma frequency $\Omega^2 = \omega^2({\varepsilon_1}^2 + {\varepsilon_2}^2)/\varepsilon_1$ is proportional to the Fermi velocity of electrons and their effective concentration. In the long-wavelength region $\lambda > 9\,\mu$m, γ and Ω^2 parameters are frequency-independent being stabilized at the values $\gamma = 1.5 \times 10^{14}\,s^{-1}$, $\Omega^2 = 35 \times 10^{30}\,s^{-2}$ ($CeNi_5$), $\gamma = 2.1 \times 10^{14}\,s^{-1}$, $\Omega^2 = 44 \times 10^{30}\,s^{-2}$ ($CeNi_4Cu$) and $\gamma = 2.3 \times 10^{14}\,s^{-1}$, $\Omega^2 = 45 \times 10^{30}\,s^{-2}$ ($CeNi_4Al$).

In Fig. 2 the experimental optical conductivity spectra $\sigma(E)$ of these compounds are given. In the low-energy range a monotonic growth of $\sigma(E)$ is related to the Drude-type of electron excitation $\sigma_D = \Omega^2\gamma/4\pi(\omega^2 + \gamma^2)$. As the photon energy increases the interband mechanism of light absorption dominates. The overall shape of spectra and the position of a double intensive maximum for the investigated alloys are quite similar. Nevertheless our measurements show some changes in the spectra upon substitution of Ni by atoms Cu or Al, especially at high-energy side of maximum at $E > 2$ eV. In particular the $\sigma(E)$ dependences of the ternary compounds display the intensive absorption peak at ~4 eV for the $CeNi_4Cu$ and the weak broad maximum at 2.5–3.5 eV for the $CeNi_4Al$. It is reasonable to relate the observed modification of $\sigma(E)$ spectra in the range of interband absorption to changes in electronic structure of these compounds due to such substitutions.

The theoretical calculations of the electronic structures for $CeNi_5$ [15], $CeNi_4Cu$ [14] and $CeNi_4Al$ [7] by the self-consistent TB LMTO method showed that the extended Ni 3*d* bands are localized in the range of 0–4 eV below the E_F. The appropriate total densities of electronic states $N(E)$ exhibit sets of peaks at these energies, attributed to 3*d* electrons of Ni(2*c*) and Ni(3*g*). The Fermi level is situated on the left side of the prominent 4*f*-states peak disposed at ~0.6 eV. According to the calculations [14] for the $CeNi_4Cu$ participation of the Cu atom with the 3*d* shell filled by 10 electrons is additionally and clearly evident from the separate maximum in the $N(E)$ in the region from −4.3 eV to −2.5 eV. On the contrary for the $CeNi_4Al$ compound the Al 2*p* states are hybridized with the Ni 3*d* states and exhibit in the density of states as a spread structure in the energy range of 1–6 eV below E_F [7].

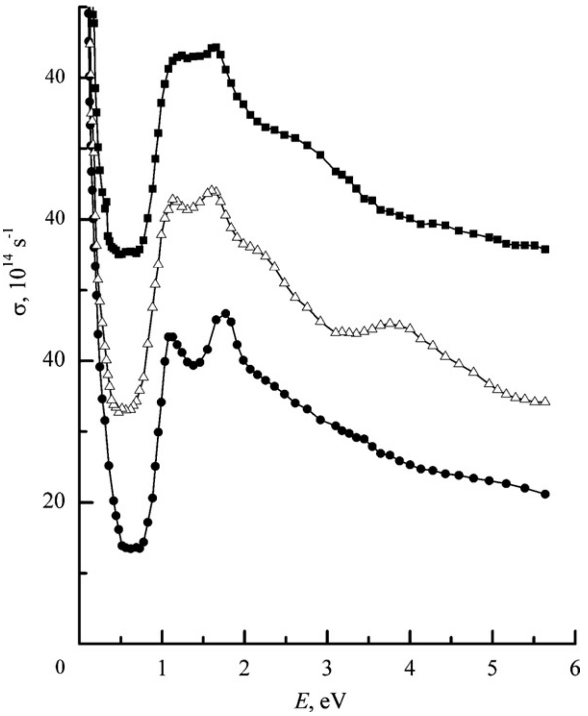

Fig. 2. Optical conductivity as a function of the photon energy for $CeNi_5$ (●), $CeNi_4Cu$ (△) and $CeNi_4Al$ (■). The two upper curves are offset upward along the axis of ordinates by 20 and 40 units, respectively.

It is of interest to compare the interband optical conductivities σ_{inter} with those calculated from the theoretical densities of states [15,14,7]. We obtained the dependences $\sigma_{inter}(E)$ for the $CeNi_5$, $CeNi_4Cu$ and $CeNi_4Al$ compounds by subtracting the Drude contributions σ_D from the experimental $\sigma(E)$ spectra (Fig. 3). The interband optical conductivities σ_{theor} calculated from the corresponding dependences $N(E)$ (shown in insets) are also given in Fig. 3 in arbitrary units. A calculation according to the scheme [17] based on the convolution of the density of states below and above E_F, makes it possible to estimate qualitatively the total contribution of all direct and indirect interband transitions to the optical conductivity, provided that they have equal probabilities. The calculations for above compounds predict the existence of a strong broad absorption band up to 6 eV in the σ_{theor} spectra, formed by electronic transitions between the states characterized by the larger values of $N(E)$. The theoretical spectra in Fig. 3 also reveal a very intense interband absorption peaks at 1–2 eV their positions are close to experimental ones. These peaks related to electron transitions from the Ni 3*d* to the Ce 4*f* states, which are represented in $N(E)$ by maxima below and above E_F. It should be noted that the minimum between two peaks at 1–2 eV in experimental spectra $\sigma(E)$ becomes more pronounced when substituting Ni by Cu or Al atoms. Also the energy shift of the second peak from 1.7 eV ($CeNi_4Cu$) to 1.8 eV ($CeNi_4Al$) is clear. As well as Cu 3*d* and

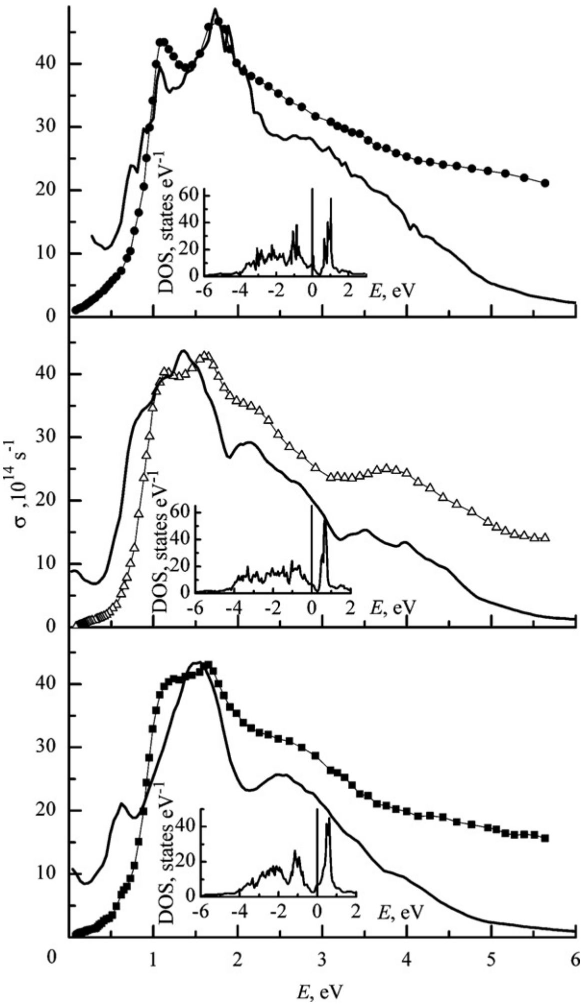

Fig. 3. Calculated (in arbitrary units) (––) and experimental dependencies of the interband optical conductivity for $CeNi_5$ (●), $CeNi_4Cu$ (△) and $CeNi_4Al$ (■). Insets show density of electronic states $N(E)$ taken from [15] ($CeNi_5$), [14] ($CeNi_4Cu$) and [7] $CeNi_4Al$ which were employed in the calculations.

Al 2*p* states are not involved in the formation of these peaks, such changes are connected with the modification of Ni 3*d* or Ce 4*f* bands under doping. As previously mentioned, the Ce ions show the intermediate valence behaviour in these systems due to hybridization between conducting electrons and Ce 4*f* electrons. The replacement of the doping component causes an alteration in the degree of hybridization and leads to changes in the structure and localization of 4*f* band. Such changes may be the main reason for observed modifications of the interband optical conductivity spectrum in the range of 1–2 eV under substitution of the Cu or Al atoms.

The theoretical and experimental dependencies of the interband optical conductivity for the $CeNi_4Cu$ have a strong peak at high-energy slope in the range of 3.3–4.8 eV. In view of calculated $N(E)$ structure of this compound [14], the formation of this maximum is due to the electron excitations from the Cu 3*d* to Ce 4*f* states. The presence of this peak in the optical spectrum $\sigma(E)$ is in reasonable agreement with the results of X-ray photoemission studies of the $CeNi_4Cu$ [13], which show that the 3*d* states of copper form rather wide (~2 eV) intensive band located at ~3 eV below the E_F in photoelectron energy. It is seen also that the interband σ_{theor} and experimental spectra for $CeNi_4Al$ at energies $E > 2$ eV are essentially differ from that observed in $CeNi_4Cu$. The nature of the broad absorption structure in the σ_{theor} of $CeNi_4Al$ alloy at 2-3 eV, in accordance to electronic spectrum [7], related to electron transitions from the hybridized *p*–*d* bands (the broad peak in the $N(E)$ at ~2 eV) to Ce 4*f* states above E_F. Owing to such hybridization this structure in the experimental $\sigma(E)$ curve observed as the smearing maximum on the high-energy slope of the absorption band. Note also that the partial deposit of the Al 2*p* electrons in the photoemission valence band spectrum of the $CuNi_4Al$ [7] was not detected because of *p*–*d* hybridization.

Summarizing, we can conclude that the energy dependence of optical conductivities for all investigated compounds is qualitatively consistent with the first-principles calculations of their band structures [7,14,15]. These calculations are capable to explain the basic features of the experimental $\sigma(E)$ spectra for given compounds: the localization of the main maxima, the width of the intense absorption region and the sharp threshold connected with the beginning of interband transitions.

4. Conclusions

The optical properties of $CeNi_5$, $CeNi_4Cu$ and $CeNi_4Al$ compounds have been measured in the range of photon energies 0.083–5.64 eV. The parameters of the charge carriers, such as plasma and relaxation frequencies, were determined. The experimental interband optical conductivity spectra qualitatively agree with the calculated values obtained from reported TB LMTO method results. The $\sigma(E)$ curves of all investigated alloys are characterized by an intense double-peak absorption band at 1–2 eV which can be related to Ni 3*d* → Ce 4*f* electron transitions. The measurements clearly show the changes in the $\sigma(E)$ spectra upon the replacement of one Ni atom by Cu or Al, especially in the range $E > 2$ eV.

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