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Effect of Cu-doping on the electronic structure and optical properties of $LaNi_5$

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ABSTRACT

Optical properties of intermetallic isostructural compounds $LaNi_{5-x}Cu_x$ ($x = 0, 0.6, 1, 1.2$) have been studied in the spectral range from 0.22 to 15 μm using the ellipsometry method. It was found that the substitution of copper for nickel leads to local changes in the optical conductivity spectra. Theoretical calculations of the electronic structure and interband optical conductivity of $LaNi_{5-x}Cu_x$ compounds with $x = 0, 1, 2, 3$ were performed in the generalized gradient approximation within the pseudopotential plane-wave method PWSCF. Both the optical spectroscopic measurements and theoretical calculations demonstrate the presence of a broad absorption band around 4 eV associated with the Cu 3d → Ni 3d electron transitions and increasing with the growth of copper content.

1. Introduction

The RNi_5 intermetallic compounds, where R is a rare earth or yttrium, have been the subject of a large number of investigations [1–3]. These compounds are known to show diverse magnetic and transport properties associated with both localized moments of R atoms and itinerant electrons of the Ni atoms. Also the $LaNi_5$-type alloys attract considerable interest to their electronic properties due to the high capacity for hydrogen absorption [4–6].

In this context, substitutions at the La and Ni sites by atoms of p- or d-elements (with $CaCu_5$-type crystal structure of alloys remaining the same) were extensively used to improve the hydrogen storage capacity and achieve desirable electrochemical properties. For such ternary alloys $LaNi_{5-x}M_x$ dependences of some magnetic properties, electron specific heat and resistivity on x concentration were experimentally examined. Different ranges of paramagnetic solid solutions for $LaNi_{5-x}Cu_x$ alloys were reported in the literature, covering the composition range from $x = 0$ to 5. A number of studies of these compounds revealed a direct correlation between physical parameters and electronic structure evolutions with the change of the copper content [7–10]. On the theoretical side, band structure results were reported for $LaNi_5$ [11–13] and its hydrides [14–16]. The X-ray photoemission study of these alloys showed the presence of the Cu 3d band, which is located almost 2 eV below the center of the Ni 3d band and is weakly hybridized with the latter one [7]. To explain these experimental data, one needs more detailed investigations on the electronic structure of $LaNi_{5-x}Cu_x$ series for different x.

In this paper we report the investigations of the electronic structure of $LaNi_{5-x}Cu_x$ isostructural alloy series with $x = 0, 1, 2, 3$ using self-consistent *ab initio* calculations. Based on the calculated DOS the interband contribution to the optical conductivity was determined and analyzed. These theoretical results were found in qualitative agreement with the optical conductivity obtained from the ellipsometric studies of $LaNi_{5-x}Cu_x$ ($x = 0, 0.6, 1, 1.2$).

2. Calculation of the electronic structure

The $LaNi_5$ compound crystallizes in a hexagonal structure of $CaCu_5$ type with a space group $P6/mmm$. The nickel has two inequivalent crystallographic positions Ni1(2c) (1/3 2/3 0) and Ni2(3g) (1/2 0 1/2), La has a position (1a) (0 0 0). Electronic structure calculations without spin polarization were performed within the pseudopotential planewave method PWSCF, as implemented in the Quantum ESPRESSO package [17]. We used the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof version [18] for the exchange-correlation potential in the Rappe–Rabe–Kaxiras–Joannopoulos form [19]. The Brillouin zone integration was performed with a $10 \times 10 \times 10$ k-point grid. A kinetic energy cutoff of 45 Ry was employed for the plane-wave expansion of the electronic states. To account for Cu atoms, for each x value ($x = 1, 2, 3$) we considered all possible configurations of Cu atoms substitutions for Ni and averaged over the self-consistent density of states.

The total density of states (DOS), as well as partial Cu 3d DOS, for $LaNi_{5-x}Cu_x$ compounds with $x = 0, 1, 2, 3$ are plotted in Fig. 1. Although there are some general similarities, the structures of total DOS for x differ from each other. More intense maxima are located below the Fermi level which is situated on the top of bonding part of DOS. For parent $LaNi_5$ system narrow intensive peaks formed

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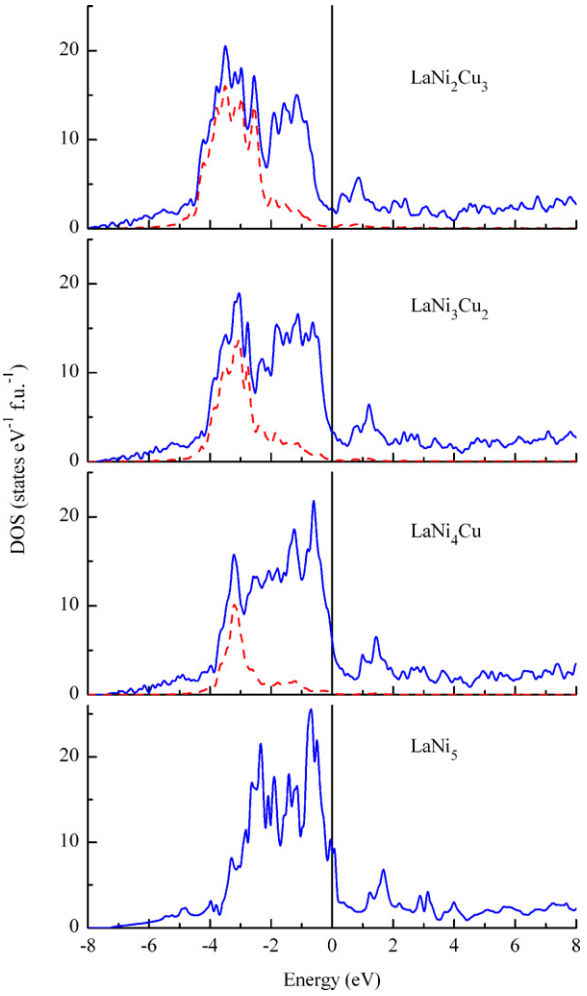

Fig. 1. Calculated total DOS for $LaNi_{5-x}Cu_x$ compounds with $x = 0, 1, 2, 3$. Dashed lines represent the partial contribution of the Cu 3d states. The Fermi level corresponds to zero.

mainly by the Ni 3d states are found in the range of 0–4 eV below the Fermi energy (E_F). These DOS for $LaNi_5$ are in good agreement with the reported results obtained in the other approaches [5–7]. Replacement of Ni atoms by Cu results in a rather independent Cu 3d band centered at approx. −3.3 eV for the compounds with $x = 1, 2, 3$. Its band width is considerably smaller with respect to the Ni 3d states. The total DOS width becomes larger after Cu substitution as compared with that in $LaNi_5$ and depends on the copper content. The spectral weight of DOS is transfered to the lower energies with doping. Simultaneously, a relative intensity and the width of the Cu 3d band around 3 eV increase. The density of states at the Fermi level is gradually reduced with the increase of Cu concentration. These results correlate with the X-ray photoelectron spectroscopy data [7] where both valence band and core level spectra of $LaNi_{5-x}Cu_x$ system were analyzed. The computed DOS value at E_F follow the same trend as the low-temperature magnetic susceptibility and heat capacity of these compounds [7,10].

The calculated DOS of $LaNi_{5-x}Cu_x$ ($x = 0, 1, 2, 3$) were used to interpret experimental optical data. In order to calculate theoretical interband optical conductivity σ_{theor} we applied a rather simplified approximation technique [20] assuming that the direct and indirect (involving phonons) interband transitions are equally probable. Namely, we computed σ_{theor} as an integral function based on the convolution of the density of states located both below and above E_F. The low-energy interval of DOS $E_F \pm 0.2$ eV was excluded from the calculations because of prevailing Drude absorption and

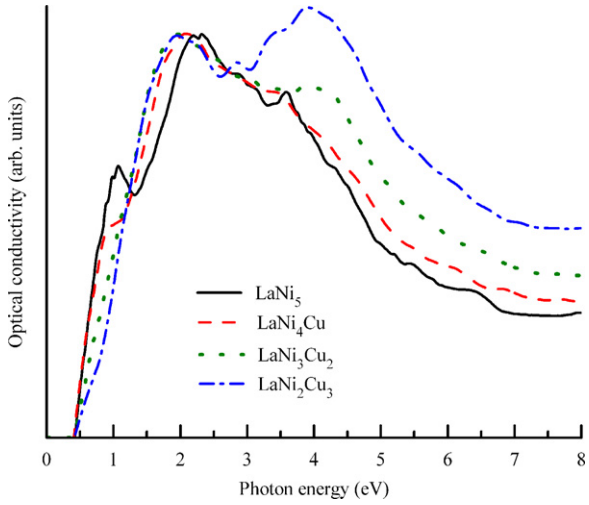

Fig. 2. Interband optical conductivities for $LaNi_{5-x}Cu_x$ calculated from the total DOS (in arbitrary units).

insignificant probabilities of the interband transitions in this region. The results of these calculations are shown in Fig. 2. The significant peak at ~2 eV is the most pronounced feature in σ_{theor} typical for all alloys. The intensity of another maximum at ~4 eV drastically increases with increasing Cu concentration ($x = 2, 3$). For $LaNi_2Cu_3$ the intensity of this feature is the largest one and comparable with that of the peak at 2 eV.

3. Optical conductivity results and discussion

The studies of optical properties were carried out at room temperature in the wavelength range 0.22–15 μm (photon energy

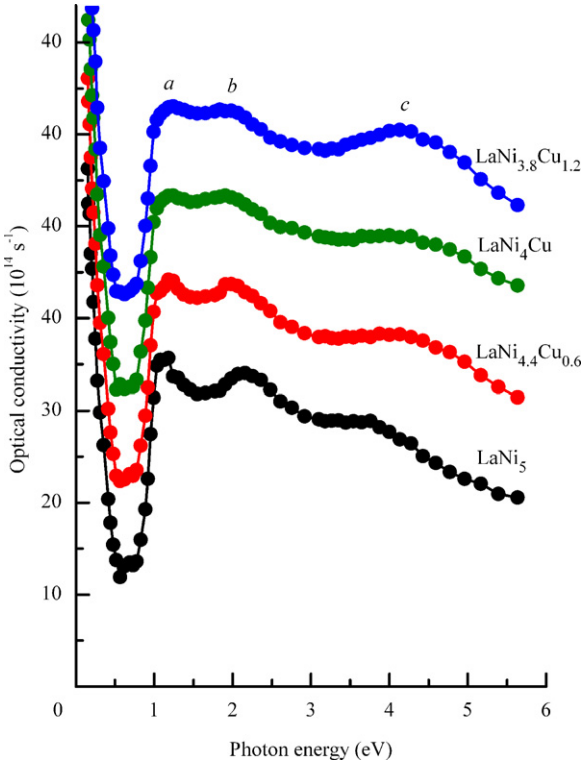

Fig. 3. Energy dependences of the optical conductivity spectra of $LaNi_{5-x}Cu_x$ with $x = 0, 0.6, 1, 1.2$. The curves are shifted upward with respect to each other along the ordinate axis by 10 units.

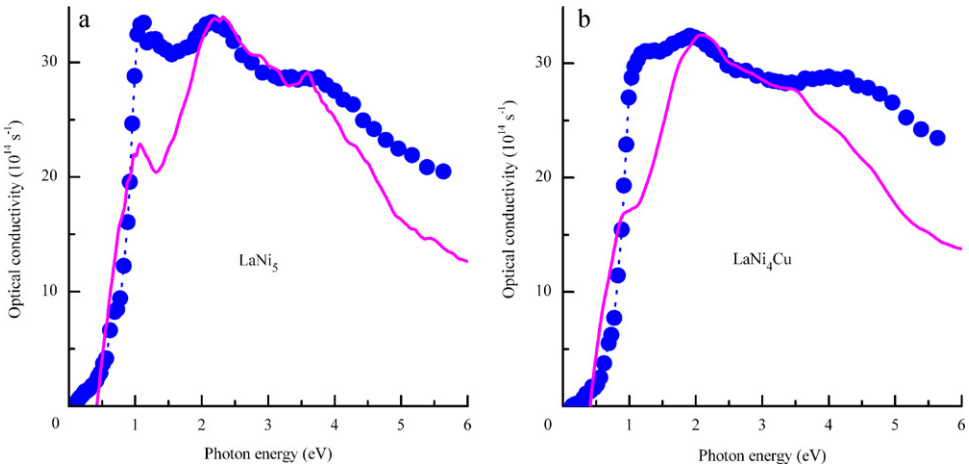

Fig. 4. Comparison of the measured (circles) and calculated (solid lines in arbitrary units) interband contributions to the optical conductivity spectra of $LaNi_5$ (a) and $LaNi_4Cu$ (b).

$E = 5.64–0.083$ eV). The optical constants, refractive index n and absorption coefficient k, were measured ellipsometrically using the Beattie technique. 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 functions of the reflecting material. Smooth surfaces of the samples were obtained by means of mechanical polishing with diamond pastes. The values of n and k were used to calculate the optical conductivity $\sigma = nk\omega/2\pi$, ω is the frequency of the light wave.

The samples $LaNi_{5-x}Cu_x$ ($x = 0$, 0.6, 1, 1.2) 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. Both a and c lattice parameters increase with the growth of copper content. The resulting lattice constants are $a = 5.007$ Å, $c = 3.981$ Å for $LaNi_5$, $a = 5.026$ Å, $c = 3.998$ Å for $LaNi_{4.4}Cu_{0.6}$, $a = 5.032$ Å, $c = 4.008$ Å for $LaNi_4Cu$ and $a = 5.040$ Å, $c = 4.014$ Å for $LaNi_{3.8}Cu_{1.2}$.

In Fig. 3 the experimental spectra of optical conductivity for the $LaNi_{5-x}Cu_x$ ($x = 0$, 0.6, 1, 1.2) system are presented. (Note that the curves are shifted with respect to each other along the ordinate axis by 10 units.) In the energy region below ~0.5 eV (infrared spectral range) the behaviour of $\sigma(\omega)$ for compounds with all concentration is determined by the sharp Drude growth, which is proportional to ω^{-2} and determined by the intraband mechanism of electron excitations by electromagnetic field of light wave. Above ~0.7 eV the shape of $\sigma(\omega)$ dispersion indicates the dominant role of interband absorption. The broad absorption region is characterized by structures whose intensity and localization depend on the compound composition. The optical conductivity of the $LaNi_5$ binary alloy (lower curve) has two peaks (a and b) at photon energies 1.1 and 2.2 eV, respectively, and a broad peak located at 3.7 eV. With the increase of the Cu content ($x = 0.6$, 1, 1.2) one can note that minimum between structures a and b becomes less pronounced and a broad absorption band c arises gradually at energies 3.5–4.5 eV.

It is reasonable to suppose that the formation of the feature c is related to substantial change in the energy spectrum of $LaNi_{5-x}Cu_x$ upon substitution of copper for nickel atoms. The position of the maximum c in the experimental $\sigma(\omega)$ and the dependence of its intensity on the Cu content correlate qualitatively with the theoretical DOS in Fig. 2. Note, that the analogous maximum in optical conductivities was also found at ~4 eV and interpreted as Cu 3d → Ni 3d transitions in $TbNi_{5-x}Cu_x$ [21] and $GdNi_{5-x}Cu_x$ [22] compounds, despite the fact that magnetic properties of these systems are different and were theoretically obtained from LSDA + U method accounting for strong electron correlations in 4f shell of the rear-earth element and magnetic ordering. The formation of the maximum c in $\sigma(\omega)$ of $LaNi_{5-x}Cu_x$ systems is likely to be determined by a similar type of quantum absorption.

A comparison between the calculated σ_{theor} and experimental σ_{ib} interband optical conductivities for the $LaNi_5$ and $LaNi_4Cu$ alloys is given in Fig. 4. The contribution in absorption from bound electrons was obtained by the subtraction of the Drude parts from experimental dependences, i.e. $\sigma_{ib} = \sigma(\omega) - \sigma_D(\omega)$. In both curves there are two maxima in the region of 1–2.5 eV originating mainly from electronic transitions between filled Ni 3d-bands located in DOS at 0.7 and 1.3 eV below E_F and empty Ni 3d-bands above E_F, see Fig. 1. The positions of maxima σ_{theor} at ~2 eV in both alloys coincide with the optical experiment. In contrast, the peaks at 1.1 eV in σ_{ib} are not so well reflected in the corresponding theoretical dependencies. Near this energy for $LaNi_5$ and $LaNi_4Cu$ σ_{theor} curves have a small maximum and weak shoulder. While for $LaNi_4Cu$ the correspondence between theory and experiment is not good in the energy region around a peak at 4 eV, interpreted as Cu 3d → Ni 3d transitions, in general the results of optical convolution qualitatively reproduce the basic features of the experimental $\sigma(\omega)$ spectra for these compounds. Namely, the sharp threshold associated with the beginning of interband transitions, the width of the intense absorption interval, and the smooth decreasing of the high-energy slope are in good agreement with experimental data.

4. Conclusions

To study effects of Ni by Cu substitution in $LaNi_{5-x}Cu_x$ systems, we have performed theoretical calculations of the electronic structure and optical conductivity for $x = 0$, 1, 2, 3. The main spectral weight for all DOS is located below the Fermi level, and we observed its monotonic decreasing at E_F with the Cu content growth. For $x = 0$, 1, 2, 3 total DOS at energies 2–4.5 eV below E_F substantially differ due to the Cu 3d states. Based on the calculated total DOS, the interband optical conductivities σ_{theor} were determined with intense maxima at ~2 eV (Ni 3d → Ni 3d transitions), and ~4 eV (Cu 3d → Ni 3d transitions). The optical measurements of $LaNi_{5-x}Cu_x$ ($x = 0$–1.2) were found in qualitative agreement with the calculated optical conductivities for $x = 0$ and 1. Namely, both theoretical and experimental optical conductivities demonstrate that the substitution of Cu for Ni results in the drastic increase of the maximum at 4 eV due to the growing contribution of the Cu 3d states and simultaneous decrease of the peak at ~1 eV due to the modification of the energy spectrum.

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