Some optical properties of CeNi$_5$ thin films

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Single-phased CeNi$_5$ thin films were obtained using pulsed laser vaporization with deposition on a quartz substrate. The thickness of the layers was determined by optical absorption. The spectral dependence of the refraction index and dispersion coefficient was computed in the domain 1-10 eV for thicknesses up to 50 nm using the reflection spectra and the Kramers-Kronig formalism for a broad range of the wavelengths.

1. Introduction

The study of the physical properties of the inter-metallic compounds of rare earths with 3d transition elements as thin layers is of particular interest from both a theoretical and a technological point of view due to the high number of applications for this class of materials [1].

2. Method and samples

The CeNi$_5$ thin films were deposited on glass or quartz substrate using pulsed laser vaporization with electro-optical tuning of the quality factor. The structure and the composition of the thin films were studied using X-ray diffraction. As a result, single-phased thin films were obtained.

The thickness of CeNi$_5$ layers was determined by optical absorption at specific wavelengths and extrapolated down to nanometres according to the number of impulses of the laser radiation. A linear dependence of the layer thickness on the number of laser impulses used to obtain the thin films was observed. The layers of small thicknesses displayed a discontinuous structure and had an insular shape.

3. Results and discussion

3.1 The reflection spectra $R(\hbar\omega)$

The reflection spectra $R(\hbar\omega)$ for the CeNi$_5$ thin film with a thickness of $d = 6\ nm$ has a band structure with energies of *2.7 eV*, *3.5 eV*, *4.8 eV*, *5.5 eV* and *6.3 eV*. The reduction of the reflection coefficient, evident in the domain of photonic energies lower than *2.1 eV,* is characteristic to dielectric materials and semiconductors. Here the photonic energies converge to the width of the energy gap. One can assume that the free charge carriers are confined to the surface states. For low thicknesses of
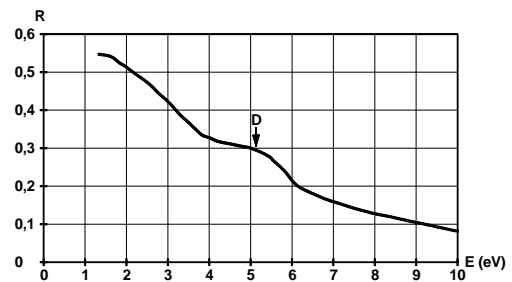
the CeNi$_5$ film, the shape of the reflection spectrum is determined by transitions between the bands which are completely occupied and those only partially occupied.

(a)
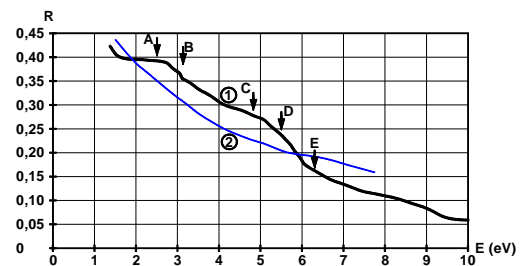
(b)

(c)

Fig. 1. Reflection spectrum of the CeNi$_5$ layer on glass substrate with thicknesses of (a) d = 6 nm, (b) d = 27 nm and (c) d = 35 nm.

The optical transitions are both between the split bands (which result from the spin-orbit interaction) and the special points of the inferior band for which the following condition holds:

$$\frac{\partial E}{\partial k} = 0$$

Usually, these points correspond to different values in the Brillouin zone. When the CeNi₅ layer thickness is *27 nm*, the characteristic feature with the energy of *6.3 eV* disappears completely.

The reflection spectra of the layers of nanometric thicknesses (*d ≤ 10 nm*) have a band structure localized in the $\hbar\omega < 2$ *eV*. The rapid increase of the reflectance in this domain is determined by the interaction of the photons with the free charge carriers from within the thin layer. In this case, the Fermi level E_F shifts toward the bottom of the valence band owing to the capture of the free charge carriers from the surface states, in contrast with the bulk sample, where the contribution of the surface states is negligible. The maximum of the reflection bands appear as a result of the optical transitions of electrons from the surface states and the occupied states at the bottom of the valence band to the free levels immediately near the Fermi level.

3.2 The spectral dependence of the refraction index

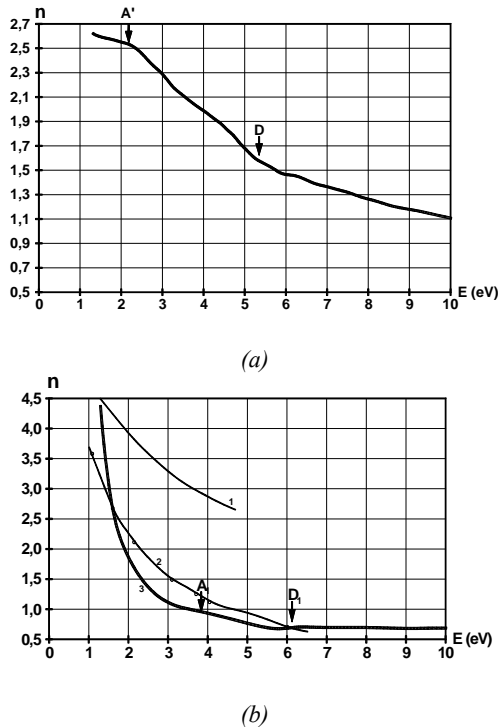In Fig. 2 one can observe the descending tendency of the refraction *n(ℏω)* index at higher photonic wavelengths.

The relatively low values of *n* on the whole domain indicate again that the photons interact with tightly bound electrons, as in dielectric substances. The features at *2.7 eV* and *5.5 eV* are still present in the case of the reflection spectrum of the thin film with *d = 6 nm*. These are probably determined by the high number of states around the said values. The sudden increase of *n*, which can be noticed for values of $\hbar\omega < 2$ *eV* and the layer thickness of *d = 35nm*, indicates that the concentration of free electrons in this thin film is much higher than that of the capturing centres. For $\hbar\omega > 5$ *eV* there is practically no dependence of the refraction index on photonic energies; only two weak features remain at around *4 eV* and *6.1 eV*. The curves 1 and 2 from Figure 2b are theoretical ones. A much higher increase rate of the refraction index on photonic energy can be observed in our experimental data than for the theoretical models.

3.3 The dispersion of the absorption coefficient

The curve of *k(ℏω)* for a thickness of *d = 6 nm* shows the characteristics of materials with thermally excited conductibility. The charge carriers are located in the band which is completely occupied and in a free band. This result clearly indicates that the very thin layer has an insular shape. The dependence for $\hbar\omega \leq 4$ *eV* can be interpreted as the absorption of the photons resulting in optical transitions of the electrons between two energy bands separated by a band gap *ΔE*. The approximate width of the gap was obtained extrapolating *k(ℏω)* in the domain $\hbar\omega < 3$ *eV* down to *k = 0*, and is approximately equal to *1 eV*. The decreasing tendency of the absorption index for $\hbar\omega > 6$ *eV* can be determined by the decrease of the density of states in the fully occupied band.
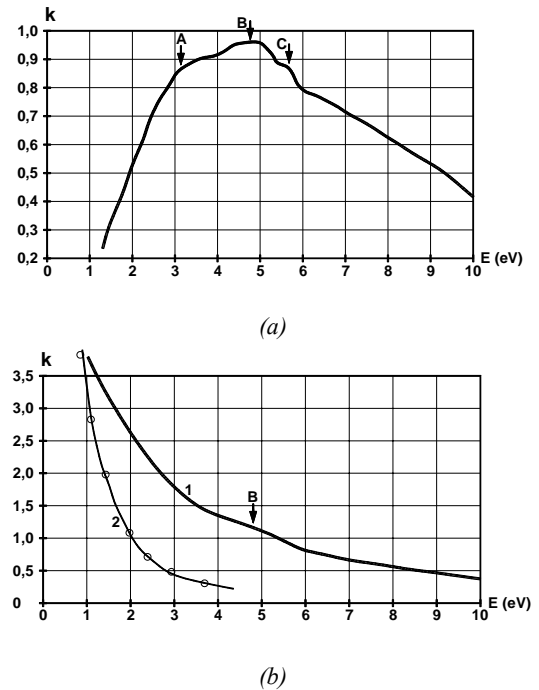

(a)

(b)

Fig. 2. The dependence of n(ℏω) for the CeNi₅ thin layer on glass substrate with thicknesses of a) d = 6 nm and b) d = 35 nm (1 – real, for the substrate, 2 – theoretical, based on the Drude model, 3 – experimental).

(a)

(b)

Fig. 3. (a) The dispersion of the absorption coefficient k(ℏω) for the CeNi₅ layer on glass substrate for thickness d = 6 nm; (b) the XPS spectrum for the valence band of CeNi₅ in the same case.

The shape of $k(\hbar\omega)$ in the range of *3-6 eV* has characteristic features at $\hbar\omega$ = *3.4 eV*, $\hbar\omega$ = *4.6 eV* and $\hbar\omega$ = *5.5 eV*, indicating a higher density of states around these values. If we admit that the optical transitions causing this dependence have the source in a single band and the transition probabilities are all equal, then the shape of the absorption coefficient vs. energy can represent the distribution of the states in the energy band.

It is important to notice the very good correlation between the shapes of the $k(\hbar\omega)$ and the XPS spectrum of the valence band for this compound. Once again, one can see the complementarities and the precision of these two methods, namely the optical measurements followed by the computation of the optical functions based on the Kramers-Kronig [2] and the X-ray photoelectron spectroscopy [3-7].
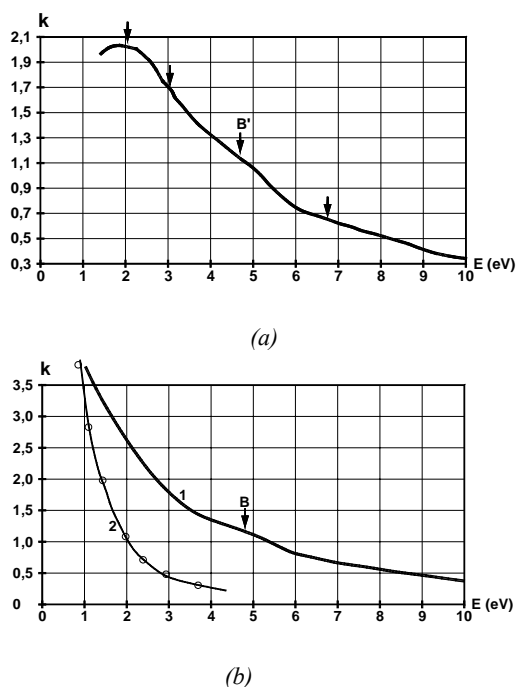

(a)

(b)

Fig. 4. The dispersion of the absorption coefficient $k(\hbar\omega)$ for the CeNi$_5$ layer on glass substrate for thicknesses of (a) d = 27 nm, (b) d = 45 nm (1 – experimental, 2 – theoretical).

If the layer thickness increases to *27 nm*, the shape of $k(\hbar\omega)$ undergoes significant changes. The values of k increase with the wavelength if its value is higher than *250 nm*. In the domain *5-10 eV* there is no dependence of k on the layer thickness; thus, we can admit that the optical functions for CeNi$_5$ are determined here by tightly bound electrons.

For the layers with thicknesses of *27 nm* and *45 nm*, the absorption coefficient $k(\hbar\omega)$ increases as the photonic energies decrease. This kind of behaviour can be determined by the increase in the density of states when approaching the Fermi level E_F. The feature at *5 eV* can be explained by electronic transitions from the lower bands and is predominant for a film thickness of *d = 6 nm*.

The theoretical curve, which describes the absorption

taking place in the interaction between photons and free charge carriers, can be observed in Figure 4 (b) marked as line 2, and is obtained using the Drude model; consequently, one can deduce that free charge carriers influence the dispersion of $k(\hbar\omega)$ in the near-IR domain. The behaviour in the visible and UV spectra is determined by the bound states as in the very thin CeNi$_5$ films. To overcome the differences between the theoretical and experimental results it would be necessary to resort to a bi-dimensional model for the computation of the energy bands applied to very thin metallic films [8].

4. Conclusions

In the present paper, the energy band structures for CeNi$_5$ thin films obtained experimentally were investigated using the following optical functions: the reflection coefficient $R(\hbar\omega)$, the refraction index $n(\hbar\omega)$, and the absorption coefficient $k(\hbar\omega)$. The thin layers were produced using pulsed laser deposition on quartz or glass substrate; single-phased thin films were obtained.

The reflection spectra for the nanometric layers ($d \leq$ *10 nm*) have a band structure localized in the domain $\hbar\omega <$ *2 eV*. In this case, the Fermi energy is shifted towards the lower edge of the valence band caused by the trapping of free charge carriers. The peaks in the reflection bands appear as a result of the optical transitions of the electrons from the surface states and the occupied states from the bottom of the valence band to the free levels in the immediate vicinity of the Fermi energy. As the thickness of the film increases to tens of nanometres, the concentration of the free charge carriers increases in comparison to the number of the surface states, and the reflection spectra gains the characteristic shape of the spectrum obtained for bulk metals. Here, for the whole domain of *1-10 eV*, the reflection spectra are determined by the interaction of light with the free electrons. The resonant feature when $\hbar\omega$ = *5 eV* and thicknesses are higher than *20 nm* is shown as a threshold on the reflection curve where all the free carriers participate.

The shape of the absorption coefficient $k(\hbar\omega)$ when the thickness of the film is of a few tens of lattice constants is specific for a discontinuous layer. At higher thicknesses of the films, both $k(\hbar\omega)$ and $n(\hbar\omega)$ increase with the wavelength of the incident light. The slopes of increase for $\hbar\omega <$ *2 eV* are much higher than those given by the free charge carrier mechanism and is in agreement with the XPS spectrum in this energy interval.

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