OPTICAL AND ELECTRONIC PROPERTIES OF METALLIC COBALT IN VARIOUS STRUCTURAL STATES

V.S. STASHCHUK, O.P. POLJANSKA, S.I. STASHENKO

Taras Shevchenko National University of Kyiv, Faculty of Physics
(64, Volodymyrs'ka Str., Kyiv 01601, Ukraine)

PACS 42.25.Ja, 78.20.-e,
71.23.-k,Dq, 75.50.

We have measured the refractive and absorption indices of thin films of amorphous and crystalline cobalt in the spectral region 0.25–17.0 μm (0.07–4.96 eV) at room temperature. On the basis of these data, we have calculated the optical conductivity which is related to interband transitions. It is shown that, at structural transformations "amorphous state–crystalline state", the optical properties of metallic cobalt are determined, in the first turn, by the nearest neighborhood, and the electronic structure is not subjected to significant modifications.

1. Introduction

Optical properties of polycrystalline cobalt are studied completely and in various aspects [1–4]. The performed theoretical calculations of the energy band structure of cobalt [5, 6] allowed one to identify the experimentally observed absorption bands with the interband transitions of electrons.

But the question about the influence of structural transformations on optical and electronic properties of ferromagnetic cobalt which is widely used in technique due to its exceptional magnetic properties remains else unstudied. In particular, the magnetic recording of information is directly related to the use of the surface of such materials. Therefore, the goal of the present work is the investigation of optical properties of cobalt films in the amorphous and crystalline states in a wide spectral range.

2. Method of Experiments

Optical properties of cobalt are studied at room temperature on film specimens 40 μm in thickness obtained by the method of magnetron sputtering on leucosapphire substrates cooled by liquid helium. Due to a high cooling rate ($\sim 10^5$ K/s), the amorphous structure of films was formed, and this metastable amorphous state can exist at room temperature for a long time. The transition of films in the crystalline stable state occurred at a temperature of 450 °C. The measurement of optical characteristics was carried out on specimens in the amorphous state and then after their transition in the crystalline state. This allowed us to decrease the influence of the technology of fabrication of specimens on the solution of the problem of the interconnection of a structural order and optical properties of cobalt. The transition of cobalt in the crystalline state was realized by thermal annealing of amorphous strips in vacuum of 0.1 mPa at 500 °C for 3 h. The structural state of films was controlled with an x-ray diffractometer and by studying the temperature dependence of the specific conductivity. Optical characteristics of the specular surface of cobalt in the amorphous and crystalline states were studied in the spectral interval 0.25–17.0 μm (0.07–4.96 eV) with the help of spectral ellipsometry by the Beattie method [1]. In experiments, we measured the ellipsometric parameters Δ and ψ near the principal incidence angle. On their basis, we calculated the optical constants n and $\varkappa$. Errors of the determination of the refractive n and absorption $\varkappa$ indices depend significantly on a spectral region, in which the measurements were carried out: for example, they were at most 1.5% in the ultraviolet, visible, and near-IR regions of the spectrum, increased to 3–4% in IR, and became about 6% at the wavelengths $\lambda = 16$–17 μm. On the basis of the optical constants n and $\varkappa$, we calculated the other optical characteristics such as the dielectric permittivity ε, optical conductivity σ, and the reflection coefficient R at the normal incidence of light on a specimen. The analysis of a dependence of the optical characteristics on the photon energy $h\nu$ in the studied spectral interval $h\nu = 0.07$–4.96 eV allowed us to get information about the electronic structure of the systems under study. Of special interest is the dispersion of optical conductivity $\sigma = (h\nu)$ proportional to the interband density of electron states $G(h\nu)$ [7].

3. Results and Their Discussion

The dispersion dependences of the reflection coefficient $R(h\nu)$ of studied specimens in the amorphous and crystalline states are described by smooth curves without

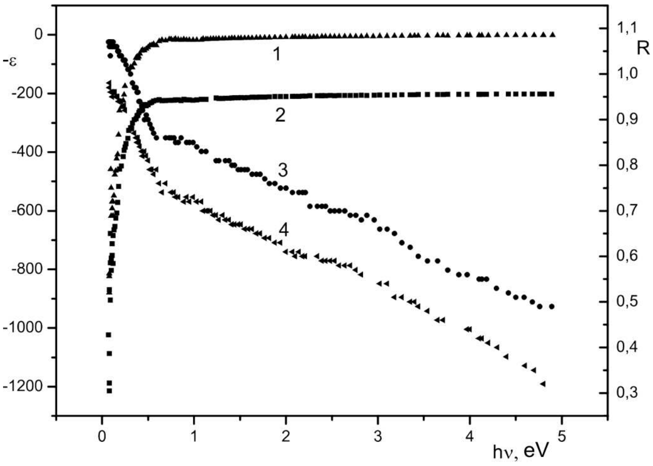

Fig. 1. Dispersion dependences of the dielectric permittivity ε $(h\nu)$ (*1, 2*) and the coefficient of reflection $R(h\nu)$ (*3, 4*) of amorphous (*1, 3*) and crystalline (*2, 4*) cobalt. Curves (*2,4*) are shifted below by 200 and 0.1, respectively

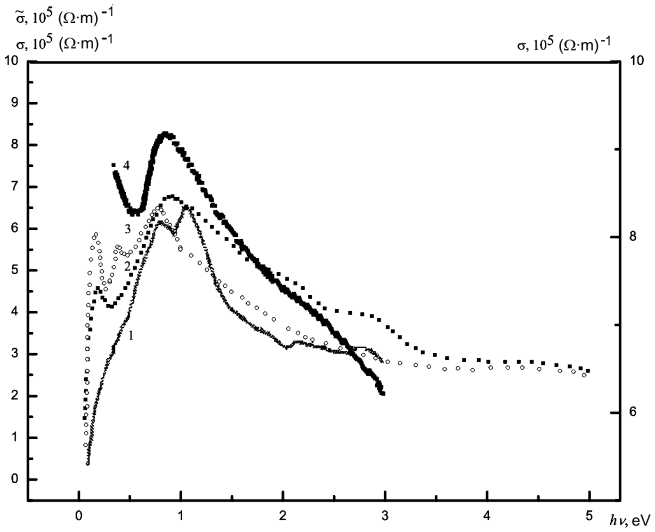

Fig. 2. Dispersion dependences of the interband optical conductivity of cobalt films in the amorphous (*3*) and crystalline (*2*) states, as well as those of massive (*1*) and liquid (*4*) cobalt according to the data of works [3, 8]. The right and left scales are referred, respectively, to liquid cobalt and to the rest of specimens

explicit anomalies; the same is true for the curves $\varepsilon(h\nu)$ (see Fig. 1).

In what follows, the main attention will be paid to the analysis of the dispersion dependence of the optical conductivity σ $(h\nu)$ of film specimens in various structural states, as well as that of massive specimens.

In Fig. 2, we present the spectra of the optical conductivity σ $(h\nu)$ of cobalt films in the amorphous and crystalline states. It is seen that the light absorption in the whole studied spectral region is only due to the interband transitions of electrons. In other words, as distinct from the case of massive cobalt, the specimens under study in the long-wave region of the spectrum have no contribution from the intraband transitions of electrons which is revealed for massive specimens as a monotonous increase of the optical conductivity σ with the wavelength λ (at a decrease in the light quantum energy $h\nu$).

On the curve $\sigma(h\nu)$ for amorphous cobalt, we observe at least three characteristic peculiarities: a wide maximum at 0.77 eV and two less intense narrow maxima at 0.38 and 0.16 eV. At the same time, only two maxima in this spectral region for crystalline Co are registered: the main maximum at 0.88 eV and the additional one at 0.18 eV. The third maximum at 0.38 eV in the amorphous state disappears at the transition into the crystalline state, and the less intense bands arise in the short-wave region of the spectrum at 2.1–2.2, 2.6–2.7, and possibly at 4.4–4.5 eV. In addition, at the transition into the crystalline state, the peak of the basic band shifts by 0.11 eV to the short-wave region and almost coincides with the maximum for cobalt in the liquid state (curve *4*), and the long-wave band (at 0.16 eV) becomes less intense. We note that the absorption starts to monotonously increase in the liquid state at energies $h\nu < 0.6$ eV, which allows the authors of work [8] to assign it to intraband transitions. In our opinion, it would be necessary to execute the additional measurements in the long-wave region of the spectrum ($\lambda < 3\,\mu$m), because it is most probable that this absorption is caused by interband transitions, like that in our specimens under study.

By comparing the results obtained for film systems with the spectrum $\sigma(h\nu)$ of massive cobalt (Fig. 2), we see that the most intense band of absorption which corresponds to intraband transitions is practically invariable on the energy scale. This concerns also the intensity of the indicated absorption band, which testifies to the dominant role of the nearest neighborhood in the formation of energy states responsible for the intraband absorption.

The influence of a topological order on the optical conductivity is revealed only in the long-wave region of the spectrum (see Fig. 2). For example, σ decreases to zero in the short-wave region by almost identical laws for crystalline and amorphous specimens. As the energy of photons increases and, respectively, the wavelength decreases and becomes significantly less than the size of inhomogeneities of the structure, the local difference between groups of atoms in different states is not considerable. In this case, the character of the interaction with

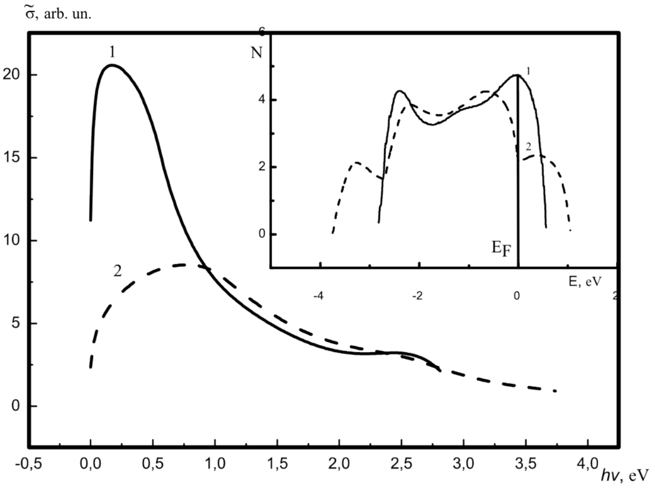

Fig. 3. Calculated dispersion curves for the interband optical conductivity of liquid (*1*) and amorphous cobalt (*2*). The insert presents the densities of electron states $N(E)$ of liquid (*1*) and amorphous cobalt (*2*) [9]. Along the abscissa axis, the origin corresponds to the Fermi level position

radiation is affected only by the nearest neighborhood, which is testified by the behavior of both curves $\sigma(h\nu)$ in the short-wave region.

The band at 0.35 eV is related to interband transitions. For massive specimens, it is possibly masked by intense intraband transitions in this region of the spectrum, though we observe an inflection on the curve of interband conductivity $\tilde{\sigma}(h\nu)$ in the region 0.35–0.45 eV testifying to the additional absorption.

Let us compare the curves for cobalt films in the crystalline state (Fig. 2) with results [3] for a massive specimen given in Fig. 2 (curve *1*), where we present the interband component of optical conductivity $\tilde{\sigma}(h\nu) = \sigma_{\exp}(h\nu) - \sigma_e(h\nu)$, ($\sigma_{\exp}$ – experimental values, and σ_e – contribution of intraband transitions). In a massive cobalt specimen, we observe a double structure of the basic band of absorption which is positioned near 1 eV and the absence of the long-wave maximum at 0.18 eV. Instead of the latter, we see an inflection on the curve $\tilde{\sigma}(h\nu)$ in massive cobalt, which is caused, in our opinion, by the superposition of the long-wave band of absorption with the basic one whose intensity is higher. In addition, intraband transitions in this region of the spectrum become more intense than interband ones.

The splitting of the basic band of absorption of massive cobalt near 1 eV [3] which is due to the exchange interaction is not manifested in film systems. This is explained by its small value (~ 0.4 eV) and the additional widening caused by a decrease in the lifetime of charge carriers. In the short-wave region for massive cobalt, $\sigma(h\nu)$ falls not so sharply, since this region contains the absorption band less intense than the basic one.

The obtained data indicate the significant changes in the electron spectrum of cobalt near the Fermi level at the loss of translation symmetry. These changes are related to the defect structure of specimens under study not only in the amorphous state, but also in the crystalline one.

A shift of the main maximum for the crystalline state relative to that for an amorphous one (approximately by 0.11 eV) into the high-energy region of the spectrum (see Fig. 2) and an increase in its half-width is related to the widening of bands as a result of structural transformations. It is obvious that the increase in $\sigma(h\nu)$ in the high-energy region of the spectrum testifies to an increase in the probability of interband transitions. Indeed, it is known [6] that if atoms become closer, then their energy levels become broader due to the overlapping of wave functions, whereas the energy gaps become, on the contrary, narrower. But the broadening of energy bands cannot explain a significant decrease in σ in the low-energy region of the spectrum $h\nu < 0.5$ eV.

It is clear that the maxima on the curve of optical conductivity $\sigma(h\nu)$ and its interband component determine the energy gaps в the electron spectrum of cobalt (see [5, 6]). As was mentioned above, the interband optical conductivity is proportional to the interband density of electron states. The last is calculated on the basis of data on the density of electron states [9] in free and filled bands by the well-known Spicer formula [7]

$$\sigma(h\nu) = \frac{A}{h\nu} \int\limits_{E_{\mathrm{F}}}^{E_{\mathrm{F}}-h\nu} N_j(E) N_i(E - h\nu)\, dE, \qquad (1)$$

where is the mean value of matrix elements, and the indices j and i of the densities of states N stand for free and filled bands, respectively.

The results of calculations are given in Figs. 3 and 4. There, we show the curves of absorption calculated by us for liquid and amorphous (Fig. 3) and crystalline cobalt with face-centered cubic (fcc) and hexagonal close-packed (hcp) lattices (Fig. 4) on the basis of theoretical data on the densities of electron states [9] (they are shown in the inserts in these figures). On the whole, the experimental data (see Fig. 2) agree with the results of calculations by the model of indirect transitions only qualitatively. That is, no details of experimental spectra are manifested, and the main maxima are positioned at different energies. The results of theoretical calculations [6] agree with our experimental data

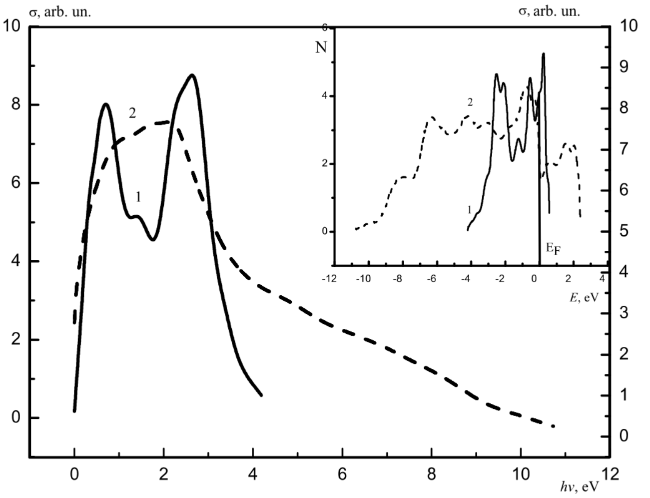

Fig. 4. Calculated dispersion curves for the interband optical conductivity of crystalline cobalt with the fcc (*1*) and hcp (*2*) lattices. The left and right scales on the ordinate axis are related to the fcc and hcp lattices of crystalline cobalt. The insert presents the densities of electron states of crystalline cobalt with the fcc (*1*) and hcp (*2*) lattices [9]. Along the abscissa axis, the origin corresponds to the Fermi level position

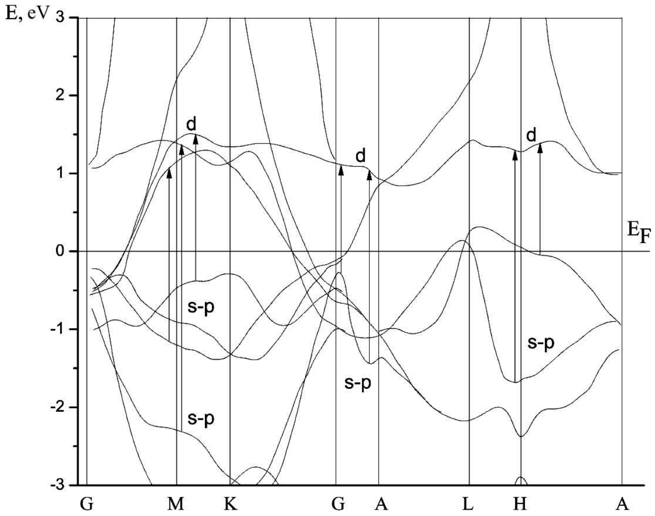

Fig. 5. Energy band structure of cobalt with a hexagonal close-packed lattice for electrons with spin directed against the spontaneous magnetization [6]. The vertical lines with arrows show possible interband transitions of electrons

much better within the model of direct transitions. In this case, we observe a fine structure of the basic band of absorption with the splitting $\sim$0.55 eV, which satisfactorily agrees with experiments ($\sim$0.42 eV). However, both maxima on the calculated curve are shifted approximately by 0.45 eV in the short-wave region of the spectrum, which exceeds significantly the experimental error. Thus, we failed to attain the full correspondence of experimental and theoretical data even in the case of massive cobalt.

As for the films under study, the situation becomes more complicated, which is related to the conditions of their fabrication. Aside from the other things, such films are characterized by a strong defectiveness of the structure, especially in the amorphous state. This factor can be considered as a means to modify the structure and hence the optical and electronic properties of the systems under study.

We now consider changes in the electron spectra of cobalt at the loss of translation symmetry in more details. We note that even small variations in the structure of the nearest neighborhood lead to essential changes in the electron subsystem [7, 10].

So, a shift of the main maximum of absorption in the observed region of the spectrum (approximately by 0.11 eV) and an increase in the half-width of this absorption band in cobalt crystals, as compared with amorphous cobalt, testify to the broadening of energy bands due to a decrease in interatomic distances and an increase in the probabilities (matrix elements) of the corresponding transitions (see Fig. 5). However, the decrease in the absorption in the low-energy region of the spectrum ($h\nu < 0.5$ eV) cannot be explained by the broadening of energy bands of cobalt.

The appearance of a new absorption band at 0.38 eV in the spectrum $\sigma(h\nu)$ of amorphous cobalt testifies to the formation of a new energy band. Most probably, it is related to vacancies which relax partially at the transition to the crystalline state, which which leads to the disappearance of the corresponding band. Another possible reason for the additional band to arise is a modification of the electron energy spectrum in a vicinity of the Fermi level [6, 9]. If electron traps, e.g. surface states, appear in the near-surface region (skin-layer), then they deplete the filled bands and, therefore, decrease the Fermi level. In addition, the paramagnetic phase of cobalt can exist on the surface due to a strong inhomogeneity of an amorphous specimen. As a result, the bands corresponding to different spin orientations become closer to one another. Therefore, new interband transitions of electrons can be realized in the infra-red region. However, the intensity of a new band will be low in this case. Therefore, we consider that it is caused by the transitions of electrons from the new band related to vacancies on the Fermi level E_{F}. Then we can evaluate the position of this band in the electron spectrum and its half-width on the basis of experimental data. The experiments indicate that this band is positioned approximately by 0.38 eV lower than the Fermi level E_{F}, and its half-width is equal approximately to 0.15 eV. The exact estimate would be possible, if we would succeed to separate the contributions of the basic and additional bands to the absorption of amorphous cobalt. Eventually, a significant decrease in the intensity of intraband transitions in both amorphous and crystalline specimens, as compared with massive cobalt, is related, in our opinion, to two factors: first, to a considerable increase in the frequency of collisions of electrons with defects of the structure; and, second, to a significant decrease in the size of grains in film specimens.

4. Conclusions

Thus, we believe that a new energy band is formed in the electron spectrum of amorphous cobalt, and it is positioned by 0.38 eV lower than the Fermi level E_{F}, which is related to defects of the structure. We have established that the character of the nearest neighborhood is not significantly changed at structural transformations from the amorphous state in the crystalline one, though the appearance of a structure order causes the broadening and shift of energy bands of the metal to the high-energy region. The structural transformations induce a reconstruction of the electron spectrum of cobalt. Moreover, the appearance of an additional band of absorption in the long-wave region of the spectrum indicates that the significant changes in the electron spectrum occur near the Fermi level.

1. V.S. Stashchuk, A.P. Shpak, and Yu.A. Kunitskii, Uspekhi Fiz. Met. **5**, 1 (2004).
2. M.M. Kirillova, G.A. Bolotin, and L.V. Nomerovannaya, Opt. Spektr. **49**, 4 (1986).
3. V.S. Stashchuk and L.R. Movsesyan, Ukr. Fiz. Zh. **31**, 11 (1986).
4. Yu.V. Kudryavtsev and I.V. Lezhnenko, Fiz. Tverd. tela **23**, 2 (1981).
5. S. Wakoh and J. Yamashita, J. Phys. Soc. Japan **28**, 5 (1970).
6. N.I. Kulikov and E.T. Kulatov, J. Phys. F2 **10**, 2267 (1982).
7. L.V. Poperenko, V.S. Stashchuk, I.A. Shaikevych, and V.A. Odarych, *Diagnostics of Surfaces with Polarized Light* (Kyiv Univ., Kyiv, 2006) (in Ukrainian).
8. V.S. Gushchin, K.M. Shmarev, and B.A. Baum, Izv. AN SSSR. Met. **6**, 58 (1982).
9. S.N. Khanna, F. Cyrot-Lackmann, and M.C. Desjonqueres, J. Phys. F: Met. Phys. **9**, 1 (1979).
10. L.V. Poperenko, V.S. Staschuk, and V.V. Vovchenko, Funct. Matter **7**, 3 (2000).
11. V.P. Shirokovskii, M.M. Kirillova, and N.A. Shilkova, Zh. Eksp. Teor. Fiz. **82**, 3 (1982).

Received 25.09.09.
Translated from Ukrainian by V.V. Kukhtin

ОПТИЧНІ ТА ЕЛЕКТРОННІ ВЛАСТИВОСТІ МЕТАЛІЧНОГО КОБАЛЬТУ В РІЗНИХ СТРУКТУРНИХ СТАНАХ

В.С. Стащук, О.П. Полянська, С.І. Сташенко

Резюме

При кімнатній температурі виміряно показники заломлення і поглинання тонких плівок аморфного і кристалічного кобальту у спектральній області 0,25–17,0 мкм (0,07–4,96 еВ). На основі цих даних розраховано оптичну провідність, яка пов'язана з міжзонними переходами. Показано, що при структурних перетвореннях "аморфний–кристалічний стан" оптичні властивості металічного кобальту визначаються насамперед найближчим оточенням і електронна структура не зазнає суттєвих змін.