ELECTRONIC STRUCTURE AND PHOTOCONDUCTIVITY OF A $Fe_{0.5}Co_{0.5}$ ALLOY

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Frequency dependences of the photoconductance of $Fe_{0.5}Co_{0.5}$ alloy in the spectral range of 1.0 – 4.9 eV have been studied by the method of optical ellipsometry. The absorption in the main band region has been established to be due to interband transitions of electrons with spins directed oppositely to magnetizations. The electron density of states and the photoconductance of $Fe_{0.5}Co_{0.5}$ alloy have been calculated taking into account the electron-phonon interaction. The experimental and theoretical results have been compared. The variations in the electronic structure of the alloy at the order-disorder phase transition have been identified.

1. Introduction

The improvement of experimental facilities and the development of photoelectronic methods, along with x-ray ones, for studying and direct measuring the Fermi surface have essentially enriched our body of knowledge concerning the electronic structure of specific materials. In turn, this changed the trend of theoretical studies of their electronic properties: from general topics to the properties of specific materials, which possess required technological parameters for industry. The class of such materials includes ordered alloys and the compounds of transition metals such as NiTi, TiFe, FeCo, NiMn, CuZn, and others, which, along with simple structures of the CsCl-type, have various technically important properties, namely, the "shape memory" in NiTi, NiMn, and CuZn, high stability of TiFe and its enhanced capability to absorb hydrogen, ferromagnetism of FeCo, and so on.

Researches in the optical range give the detailed information concerning the fine structure of the electron energy spectrum of alloys. It has been shown in a number of works (see, e.g., [1, 2]) that if an alloy is characterized by a short-range ordering, the distinctive dips appear on the curve of the electron density of states, resulting in emerging a quasigap in the electron energy spectrum, when the alloy becomes long-range ordered, which is connected to the splitting of bands. Therefore, the optical methods for researching the electronic structure and electronic properties of alloys are sensitive to the structural "order—disorder" phase transitions.

To study the influence of phase transformations at the order—disorder transition in the alloy on the energy band structure, the ellipsometric method [3] was applied. It allows the electronic structure of objects to be investigated in a rather wide spectral interval: from almost zero to tens of electron-volts near the Fermi level. If the experimentally obtained bands of interband absorption are compared with electron transitions between the corresponding energy states and if the variations of those bands are observed at phase transformations, it becomes possible to study the influence of these transformations on the electron energy spectrum in alloys.

In the majority of works (see, e.g., [4, 5]), the influence of atomic ordering on the photoconductance of alloys was investigated only qualitatively, any quantitative estimations of atomic ordering parameters being absent.

This work aimed at studying, experimentally and theoretically, the photoconductance of $Fe_{0.5}Co_{0.5}$ alloy and elucidating the changes of its electronic structure at the order—disorder phase transition.

2. Temperature Dependence of the Photoconductance of $Fe_{0.5}Co_{0.5}$ Alloy

Specimens for researches were obtained by smelting in a vacuum furnace at a temperature of 1100 °C during 30 h. Their unruffled surfaces were obtained by polishing with diamond brightener. Then, they were hardened: the specimens were heated up in the environment of inert Ar to the necessary temperature (300 or 500 °C) and subsequently quenched with water. Afterward, a thin film of oxide, which arose owing to the quenching in water, was removed from the specimen surface through chemical or electrochemical polishing. The phase difference Δ between the p- and s-components of a light wave reflected from the metal surface and the azimuth ψ of the restored linear

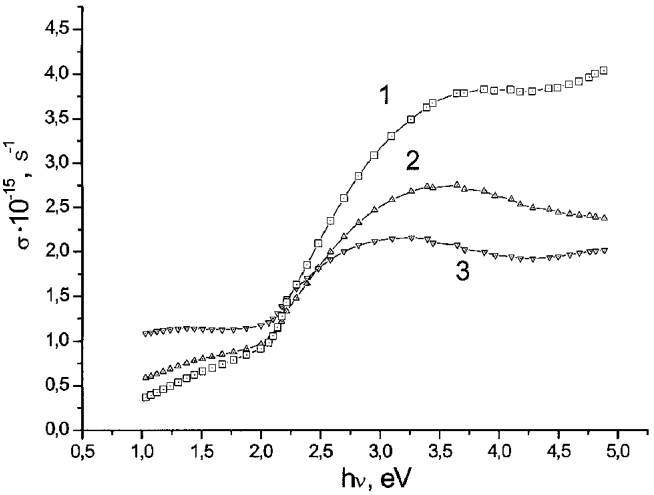

Fig. 1. Dispersion curves of the photoconductance of $Fe_{0.5}Co_{0.5}$ alloy for various hardening temperatures of a specimen: a non-hardened specimen (*1*), 300 (*2*), and 500°C (*3*)

polarization were measured by the Beathie method [3] at ambient temperature.

According to the measured values of Δ and ψ, the indices of refraction, n, and extinction, χ, and thus the photoconductance $\sigma = n\chi\nu$, where ν is the frequency, were calculated [3]. The dependences $\sigma(h\nu)$, where h is Planck's constant, in the spectral range of 1.0–4.9 eV are shown in Fig. 1 for various hardening temperatures.

The most comprehensive information on the contributions of various bands to the light absorption is obtained from the analysis of photoconductance spectra. The main maximum in the absorption spectra of $Fe_{0.5}Co_{0.5}$ alloy is related to the transitions of electrons, the spins of which are directed oppositely to the specimen magnetization, from the states, which have the maximal density below the Fermi level and hence the energies smaller than the Fermi level, into the empty states which are located above the Fermi level. In the spectrum of ordered $Fe_{0.5}Co_{0.5}$ alloy, one more band connected to the phase ordering appears [6] with a maximum which corresponds to the maximum of the additional band. In [1], the stabilization of a superstructure is explained by the emergence of a gap in the electronic spectrum, when the long-range order is established, with the gap manifesting itself as a dip on the density-of-states curve near the Fermi level.

The reduction of the intensity of the maximum occurs because of the reduction of the density of states above the Fermi level. Absorption in the range of the main band is caused by interband transitions of electrons with spins directed oppositely to magnetizations. It is related to the features of the electron energy spectra of alloys which are ferromagnets. The Fermi level rises owing to an increase of the electron concentration of the components, which results in a shift of the maximum and in a reduction of its intensity as the alloy becomes disordered.

The analysis of experimental and theoretical dispersion curves of the photoconductance σ showed that the additional band is related to the ordered phase of $Fe_{0.5}Co_{0.5}$ alloy rather than to the impurity band [7]. The curves $\sigma(h\nu)$ result from imposing the absorption in the ordered and disordered phases in this alloy, and the difference of the spectra of those phases stems from the difference of their electronic structures.

3. Comparison of Experimental and Theoretical Results

In [8], an approach to study the charge transfer processes is suggested, which is based on a direct calculation of the energy-dependent conductance σ_E according to the well-known Kubo-Greenwood relation.

To calculate the conductivity tensor $\sigma_{\alpha\beta}(\omega)$, we used the well-known methods of the theory of disordered systems [9,10]. We obtain

$$\mathrm{Re}\sigma_{\alpha\beta}(\omega) = \frac{e^2\hbar}{4\pi N\nu\Omega_0\varepsilon}\left[\int\limits_{-\infty}^{\infty} d\varepsilon_1[f(\varepsilon_1+\varepsilon) - f(\varepsilon_1)]\times\right.$$

$$\left.\times \mathrm{Sp}\sum_{s,s'=+,-}(2\delta_{ss'}-1)\,v_\beta \tilde{K}\left(\varepsilon_1^s, v_\alpha, \varepsilon_1^{s'}+\varepsilon\right)\right], \qquad (1)$$

where Ω_0 is the volume, N is the number of elementary cells in the crystal,

$$\tilde{K}\left(\varepsilon_1^s, v_\alpha, \varepsilon_1^{s'}+\varepsilon\right) = \tilde{G}^{aa^+}(\varepsilon_1^s)\, v_\alpha \tilde{G}^{aa^+}\left(\varepsilon_1^{s'}+\varepsilon\right),$$

$\tilde{G}^{aa^+}(\varepsilon_1^s)$ is the one-particle Green's function of the electrons in the alloy calculated in the coherent-potential approximation,

$$\tilde{G}^{aa^+}(\varepsilon) = \left[[G_0^{aa^+}(\varepsilon)]^{-1} - \left(\Sigma_{\text{e-ph}}(\varepsilon) + \sigma_e(\varepsilon)\right)\right]^{-1}. \qquad (2)$$

The mass operator of the electron-phonon interaction of the pure crystal looks as

$$\Sigma_{\text{e-ph}} ni\gamma, n'i'\gamma'(\varepsilon) = -\frac{1}{4\pi i}\int\limits_{-\infty}^{\infty} d\varepsilon' \nu'^{n_1 i_1 \alpha_1}_{ni\gamma, n_3 i_3 \gamma_3}\times$$

$$\times\left\{\mathrm{ctgh}\left(\frac{\varepsilon'}{2\Theta}\right)\left[G^{uu}_{n_1 i_1 \alpha_1, n_2 i_2 \alpha_2}(\varepsilon') - G^{uu^*}_{n_2 i_2 \alpha_2, n_1 i_1 \alpha_1}(\varepsilon')\right]\times\right.$$

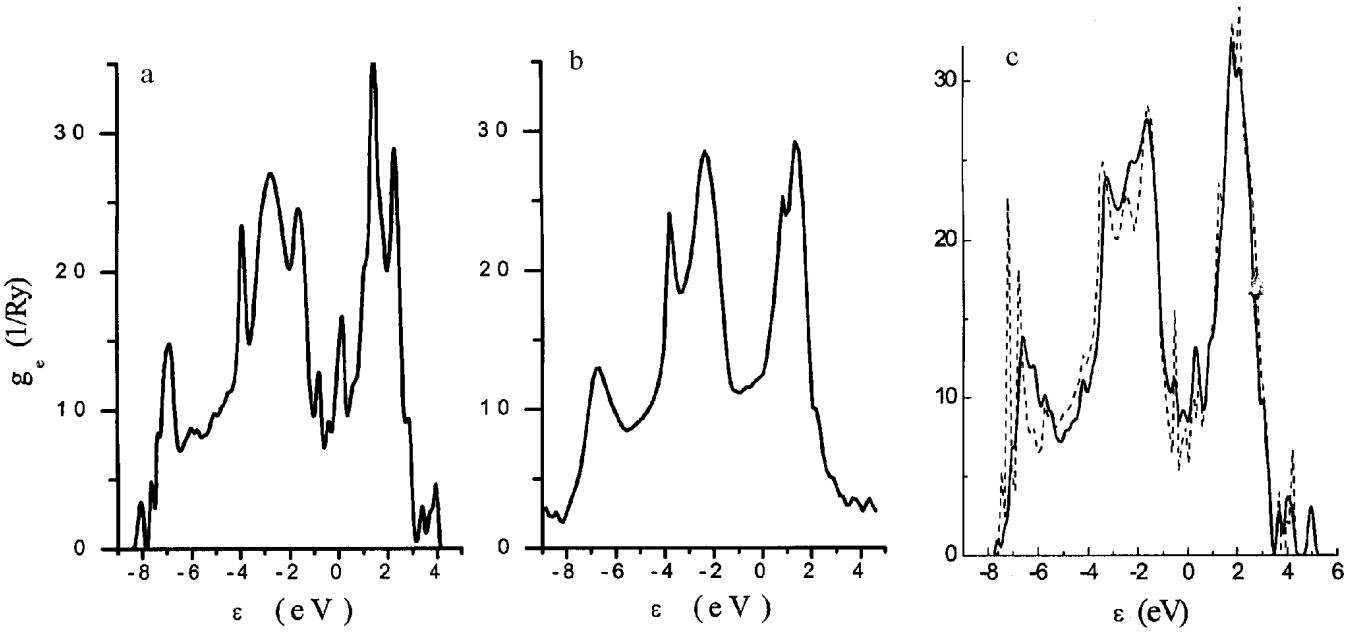

Fig. 2. Electron densities of states in $Fe_{0.5}Co_{0.5}$ alloy, calculated according to formula (6), at the temperatures $T = 0$ (a), 1100 (b), and 500 K (c), with the electron-phonon interaction being taken (solid curves) and not being taken (dashed curve) into account

$$\times G^{aa^+}_{n_3 i_3 \gamma_3, n_4 i_4 \gamma_4}(\varepsilon - \varepsilon') + \mathrm{ctgh}\left(\frac{\varepsilon' - \varepsilon - \mu}{2\Theta}\right) \times$$

$$\times G^{uu}_{n_1 i_1 \alpha_1, n_2 i_2 \alpha_2}(\varepsilon - \varepsilon') \Big[G^{aa^+}_{n_3 i_3 \gamma_3, n_4 i_4 \gamma_4}(\varepsilon') -$$

$$- G^{aa^+ *}_{n_4 i_4 \gamma_4, n_3 i_3 \gamma_3}(\varepsilon') \Big] \Big\} \nu'^{n_2 i_2 \alpha_2}_{n_4 i_4 \gamma_4, n' i' \gamma'}. \qquad (3)$$

The coherent potential is obtained from the equation [11]

$$\sigma_e^{0 i_1}(\varepsilon) = \langle [1 - (\Sigma_e^{0 i_1}(\varepsilon) - \sigma_e^{0 i_1}(\varepsilon)) \tilde{G}^{aa^+}]^{-1} \rangle^{-1} \times$$

$$\times \Big\langle [1 - (\Sigma_e^{0 i_1}(\varepsilon) - \sigma_e^{0 i_1}(\varepsilon)) \tilde{G}^{aa^+}]^{-1} \Sigma_e^{0 i_1}(\varepsilon) \Big\rangle, \qquad (4)$$

where $\Sigma_e^{0 i_1}(\varepsilon)$ is the single-node mass operator of the Green's function of electrons in the alloy and $\langle f_i \rangle$ denotes the configuration-averaged value of the quantity f_i which is defined for a binary alloy by the expression

$$\langle f_i \rangle = c_i^A f_i^A + c_i^B f_i^B,$$

where c_i^λ is the probability of occupying a site of the i-th sublattice by an atom of the sort λ ($\lambda = A, B$).

In the case of crystals of a binary alloy with cubic symmetry, we have $c_i^A = x_i = c^A - \frac{\nu_2}{\nu}\eta$ and $c_i^B = y_i = 1 - x_i$ for ν_1 sublattices of the first type and $x_i = c^A + \frac{\nu_1}{\nu}\eta$ for ν_2 sublattices of the second type, $\nu = \nu_1 + \nu_2$ is the number of sublattices, η is the long-range order parameter, and c^A and $c^B = 1 - c^A$ are, respectively, the concentrations of components A and B of the crystal.

The Fermi level μ_e in expression (1) for the conductivity tensor is determined by the equation

$$\langle Z \rangle = \int_{-\infty}^{\infty} f(\varepsilon, \mu_e) g_e(\varepsilon) d\varepsilon, \qquad (5)$$

where $\langle Z \rangle = \langle N \rangle / \nu N = c^A Z_A + c^B Z_B$ is the average number of electrons per atom.

The electron density of states is determined by the expression

$$g_e(\varepsilon) = -\frac{1}{\pi \nu N} \mathrm{Im Sp} \tilde{G}^{aa^+}(\varepsilon). \qquad (6)$$

The electron-phonon interaction, which is described by the mass operator of electron-phonon interaction (3), was taken into account as an additive to the coherent potential (4). When calculating the mass operator of the electron-phonon interaction, the Green's function of phonons was considered, for simplification, to be equal to the phonon Green's function of a perfect crystal.

In Fig. 1, the experimental values of the photoconductance of $Fe_{0.5}Co_{0.5}$ alloy are presented for various hardening temperatures of a specimen and,

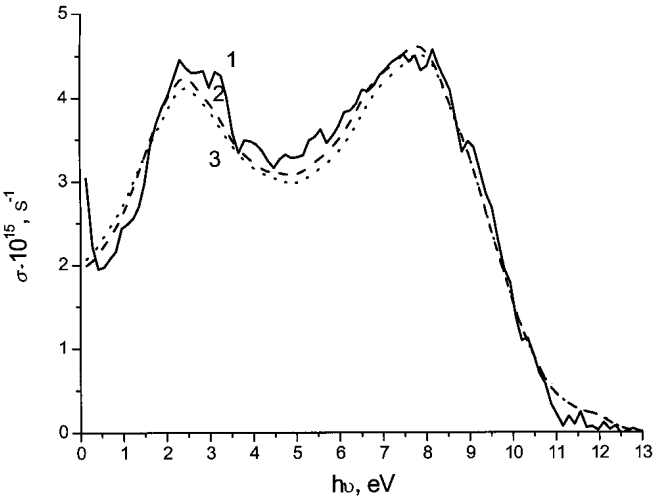

Fig. 3. Calculated photoconductance of ordered ($\eta = 1$, curve *1*) and entirely disordered ($\eta = 0$, curve *2*) $Fe_{0.5}Co_{0.5}$ alloys. Curve *3* corresponds to the photoconductance of the entirely disordered ($\eta = 0$) alloy without taking into account the electron-phonon interaction

accordingly, for various values of the long-range order parameter.

In Fig. 2, the electron densities of states calculated according to formula (6) for $Fe_{0.5}Co_{0.5}$ alloy (the bcc lattice) at the temperatures $T = 0$ (a), 1100 (b), and 500 K (c) are depicted. Here, the energy is reckoned from the Fermi level. In the course of calculations, we used the values of the localized magnetic moments and the correlation parameters of the atomic arrangement and the magnetic moment orientation at the lattice sites which had been found in [11] by minimizing the free energy of $Fe_{0.5}Co_{0.5}$ alloy. The alloy is in the ferromagnetic phase in a specified range of temperatures. The localized magnetic moment is $\mu_{Fe} = 2.8\mu_B$ at a Fe atom and $\mu_{Co} = 1.4\mu_B$ at a Co one, μ_B being the Bohr magneton. The alloy is entirely ordered (the long-range order parameter $\eta = 1$) at $T = 0$ K and is disordered ($\eta = 0$) at $T = 1100$ K.

Fig. 2,*c* demonstrates the influence of the electron-phonon interaction on the formation of the electron density of states in a specimen of $Fe_{0.5}Co_{0.5}$ alloy at $T =$ 500 K. The Fermi level μ_e of the alloy lies in the region of a quasigap that arises owing to the splitting of the *p*- and *d*-bands, when a long-range order is established.

It is seen from Fig. 2 that the electron density of states in the vicinity of the Fermi level diminishes as the alloy becomes atomically ordered (solid lines). As was noted above, it is connected to the energy band splitting if a long-range order is established. The electron-phonon interaction results in an imaginary additive to the mass operator of the electron Green's function and in a smearing of the quasigap [6,10].

The photoconductance of $Fe_{0.5}Co_{0.5}$ alloy, calculated according to formula (1), is shown in Fig. 3. Figs. 1 and 3 yield that the theoretical curves of the photoconductance describe experimental data rather well. A comparison of the experimental and theoretical results makes it possible to understand the microscopic mechanism of the influence of atomic ordering on the photoconductance of the alloy, which is connected to the emergence of a quasigap in the electron energy spectrum. For lower hardening temperatures, a more pronounced peak can be observed on the dispersion curve of the photoconductance, the position of the left side of which corresponds to the position of the right edge of the energy gap reckoned from the Fermi level (Fig. 2).

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ЕЛЕКТРОННА СТРУКТУРА ТА ОПТИЧНА ПРОВІДНІСТЬ СПЛАВУ $Fe_{0,5}Co_{0,5}$

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Р е з ю м е

Методом оптичної еліпсометрії досліджено частотну залежність оптичної провідності сплавів $Fe_{0,5}Co_{0,5}$. Встановлено, що поглинання в області основної смуги зумовлене міжзонними

переходами електронів зі спіном, напрямленим протилежно намагніченості. З урахуванням електрон-фононної взаємодії розраховано щільності електронних станів та оптичну провідність для сплаву $Fe_{0,5}Co_{0,5}$. Проведено порівняння експериментальних та теоретичних результатів. З'ясовано зміни в електронній структурі сплаву при фазовому переході порядок—непорядок.