OPTICS, LASERS, AND QUANTUM ELECTRONICS

SPECTROSCOPY OF IMPURITY STATES IN Cu–Mn ALLOYS

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The indices of refraction n and absorption χ of disordered Cu–Mn alloys with manganese concentrations of 2, 5, 10, 17.5, 25, 37.5, and 50% are measured in the spectral range 0.23–2.8 μm (0.44–5.39 eV) at room temperature using the ellipsometric technique. Based on these data, the optical conductivity σ related to interband transitions is calculated. The collision frequency γ and the concentration of conduction electrons N are determined in the intraband absorption region. It is established that the addition of manganese results in the formation of a new impurity band in the copper electron spectrum which is located by 2.2 eV lower than the Fermi level and is split into two energy subbands due to the exchange interaction.

1. Introduction

An intensive investigation of the optical properties and the electron structure of alloys of noble metals with transition ones started after the discovery of local magnetic moments in dilute copper-nickel alloys [1] which served as a stimulus for theoretical researches of the magnetic and electron structure of such materials [2].

Data of optical measurements are mainly interpreted with the use of the Anderson theoretical model [1] that describes them only qualitatively. A considerable progress in studying the electron structure was achieved after the construction of theoretical models based on multiple scattering, in particular, the coherent potential approximation [2]. Sometimes, however, this theory cannot adequately describe electron properties of specific metal compounds, particularly, alloys of copper with transition metals [3]. Theoretical calculations of the energy band structure of copper performed in [4,5] allow one to identify the absorption bands observed ex-

perimentally with the corresponding interband electron transitions.

The results of studying the optical properties of binary alloys of copper with ferromagnetic metals (Fe, Co) and antiferromagnetic ones (Cr) in the interband absorption region [3] testify to the fact that their optical conductivity spectra $\sigma(h\nu)$ cannot be obtained as superpositions of spectra of pure components, because these alloys include new bands in addition to the structures typical of pure metals. That is why of special interest is the investigation of the optical properties and, on their basis, the electron structure of alloys of copper with another antiferromagnetic – manganese.

2. Experimental Technique

Optical properties of Cu–Mn alloys were studied at room temperature using samples obtained by the vacuum-arc melting of pure copper and manganese with corresponding weights in the argon atmosphere by means of multiple remelting. To achieve a better homogeneity, the samples were annealed in the same atmosphere at a temperature of 900 °C during 24 h. Mirror surfaces of the samples were prepared by mechanical polishing with the use of diamond pastes with the further recrystallization annealing and the electropolishing. We also performed the X-ray and phase analyses of the samples of Cu–Mn alloys using a DRON-3.0 X-ray diffractometer.

The optical characteristics of the mirror surfaces of Cu–Mn alloys with Mn concentrations of 2, 5, 10, 17.5, 25, 37.5, and 50%, as well as those of pure copper and manganese, were studied in the spectral region 0.23–2.8 μm (0.44–5.39 eV) with the help of the Beattie ellipsometry method [6]. The ellipsometric parameters Δ
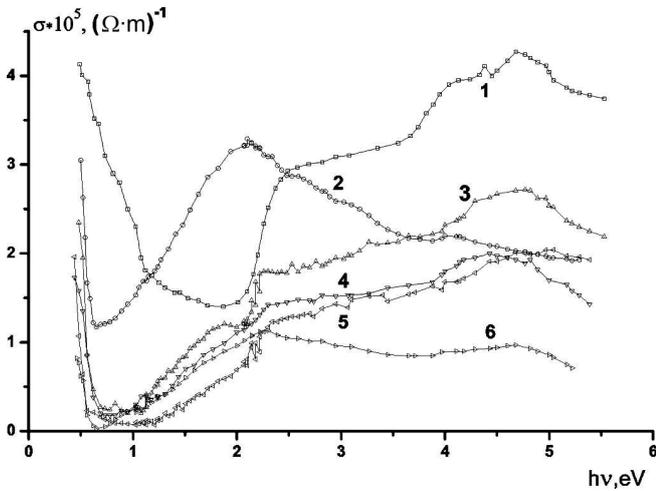
Fig. 1. Dispersion curves of the interband optical conductivities $\sigma(h\nu)$ of pure Cu (*1*), Mn (*2*), and Cu–Mn alloys with Mn concentrations of 2 (*3*), 5 (*4*), 10 (*5*), and 17.5% (*6*). Curves *1, 2* are shifted up by 10^5 (Ohm·m)$^{-1}$

Fig. 2. Dispersion curves of the interband optical conductivities $\sigma(h\nu)$ of pure Cu (*1*), Mn (*2*) and Cu–Mn alloys with Mn concentrations of 25 (*3*), 37.5 (*4*), and 50% (*5*). Curves *1, 2* are shifted up by 10^5 (Ohm·m)$^{-1}$

and ψ in a vicinity of the principal angle of incidence were experimentally measured at various wavelengths and used for the calculation of the optical constants n and χ. The errors of determining the indices of refraction n and absorption χ significantly depended on the spectral region of measurements. Particularly, they did not exceed 1.5% in the ultraviolet, visible, and near infrared spectral regions and increased to 3–4% in the infrared one. The optical constants n and χ served for the calculation of other optical characteristics: dielectric permittivity ε, optical conductivity σ, and coefficient of reflection at normal incidence R.

3. Results and Their Discussion

Analyzing the optical characteristics as functions of the photon energy hν in the studied spectral region $h\nu = 0.44$–5.39 eV, one can obtain information about the variation of the electron structure of copper due to the addition of manganese. Of special interest is the dispersion of the optical conductivity $\sigma(h\nu)$ proportional to the interband density of electron states $G(h\nu)$ [6, 7].

The dependences $\sigma(h\nu)$ obtained experimentally for the investigated alloys and for pure copper and manganese are presented in Figs. 1 and 2. First of all, it is worth to briefly describe the characteristic features of the optical spectra σohν) of pure copper and manganese and then to analyze the optical spectra of Cu–Mn alloys. In the energy range $h\nu < 1.5$ eV, the optical conductivity of copper monotonously grows with decrease in the energy $h\nu$, which testifies to the fact that the dominant
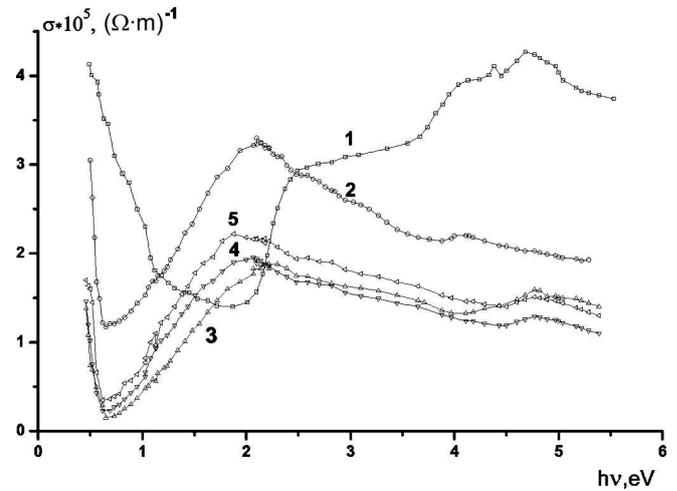
contribution to σ in this region is made by intraband electron transitions within each band in the smearing region of the Fermi level E_{F}. The most characteristic anomalies of copper are the sharp interband absorption edge at $h\nu = 2.1$–2.3 eV with the center at 2.2 eV and the intense absorption band with a maximum close to 4.72 eV, as well as insignificant details of the spectrum in the interval 3.5–4.4 eV [1]. In turn, the interband absorption curve of manganese is characterized by a wide maximum at 2.2 eV.

The principal attention will be paid to the analysis of the dispersion dependences of the optical conductivity $\sigma(h\nu)$ of the investigated Cu–Mn alloys (see Figs. 1 and 2).

Thus, the dispersion dependences of the optical conductivities $\sigma(h\nu)$ of pure copper and manganese are described by comparatively smooth curves with certain anomalies. As one can see from Fig. 1, the addition of small concentrations of manganese to copper does not result in significant changes of the general form of the copper energy spectrum. The characteristic features of the Cu spectrum, particularly, the short-wave maximum at 4.72 eV and the sharp edge at 2.1–2.3 eV manifest themselves, to a certain extent, in all the studied Cu–Mn alloys, as well as in Cu–Co ones [5]. It is found out that the maximum at 4.72 eV is registered in all alloys except for the Cu-50%Mn one, occupying almost the same position on the energy scale. Moreover, the sharp absorption edge at 2.2 eV appears only in the samples with Mn concentrations below 17.5%.

In the infrared spectral region ($h\nu = 0.8$–1.8 eV), the addition of only 2% of manganese results in the abrupt decrease of the contribution of free electrons into the general light absorption; at high Mn concentrations, interband electron transitions prevail. This is due to the abrupt increase of the relaxation frequencies of electrons in alloys as compared to pure components.

It is established that the addition of manganese to copper at Mn concentrations exceeding 10% induces an extremely strong effect – appearance of an intense absorption band with a maximum in the interval $h\nu = 1.9$–2.1 eV in the near infrared spectral region of the $\sigma(h\nu)$ curves. As one can see from Figs. 1 and 2, it is exactly the interval containing the minimum of the $\sigma(h\nu)$ curve in copper, whereas the absorption maximum of manganese is located close to 2.2 eV, according to our experimental data. Thus, the indicated band is not related to pure copper or manganese. It is most probably due to resonance states appearing in the copper electron spectrum after adding manganese.

It is worth noting that the intensity of this impurity band monotonously decreases with increase in the Mn concentration and reaches 205 k(Ohm·m)$^{-1}$ for the Cu-50% Mn sample. In this case, the maximum shifts to the low-energy spectral region – approximately from 2.1 eV for the Cu-17.5% Mn sample to 1.9 eV for the Cu-50% Mn one (see Fig. 2).

It is no doubt that the formation of the additional band in the alloys is caused by changes in the Cu–Mn electron spectra. These changes are induced by the reconfiguration of the Cu energy spectrum and the appearance of the above-mentioned resonance impurity states [7].

As follows from the stated facts, the optical spectra of the studied alloys cannot be obtained by means of the common superposition of the $\sigma(h\nu)$ spectra of pure manganese and copper in accordance with the quantitative relation of these phases. To make sure of it and to establish the nature of the absorption spectra of Cu–Mn alloys, we performed the numerical modeling of their optical properties. For this purpose, we calculated and analyzed the dispersion curves of the residual optical conductivity $\Delta\sigma(h\nu)$ that represents the difference between the experimental $\sigma(h\nu)$ and calculated $\sigma_{Cu}(h\nu)$ values of the optical conductivity of the studied alloys $\Delta\sigma(h\nu) = \sigma(h\nu) - (1-c)\sigma_{Cu}(h\nu) + c\sigma_{Mn}(h\nu)$ (c stands for the Mn concentration). The calculation results for the Cu–Mn alloys with Mn contents of 5, 17.5, and 50% are given in Fig. 3.

One can see that the residual optical conductivity $\Delta\sigma(h\nu)$ for the studied alloys depends on the energy
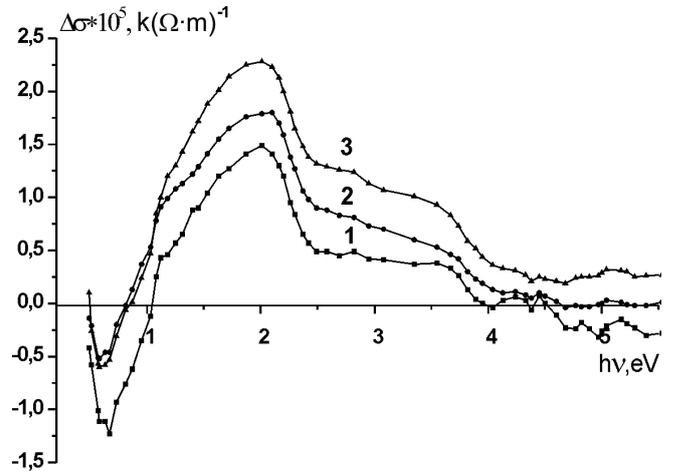

Fig. 3. Dispersion of the residual optical conductivity $\Delta\sigma(h\nu)$ of Cu–Mn alloys with Mn concentrations of 5 (*1*), 17.5 (*2*), and 50% (*3*)

$h\nu$ and abruptly grows with the Mn concentration. For the alloys with Mn contents below 17.5%, it is negative in the ultraviolet spectral region, which is an evidence of the fact that the solubility of manganese in the alloys with a low Mn content is lower than in those with Mn concentrations of 37.5 and 50%. In Fig. 3, one can clearly see a new absorption band with a maximum at 2 eV. The performed calculations of the $\Delta\sigma(h\nu)$ spectra of Cu–Mn alloys imply that, firstly, manganese almost completely dissolves in copper at small Mn concentrations (below 5%). Secondly, the solubility grows with the Mn concentration, and, thirdly, an impurity d-band related to manganese is formed in the electron spectrum of Cu–Mn solid solutions.

In order to create a model describing the energy structure of Cu–Mn alloys, a detailed investigation of their electron characteristics was performed in the IR spectral region ($\lambda > 2$ μm). As was noted, the optical properties of the alloys in this region are mainly determined by intraband transitions of conduction electrons. Applying the method of successive approximations, we determined the collision frequency γ and the electron concentration N for Cu–Mn alloys with the use of the technique described in [1].

In this case, we did not consider the contribution of interband transitions $\tilde{P}$ into the permittivity ε_1, because it does not exceed 0.3% of the value of ε_1 in the investigated spectral region. The collision frequencies γ for Cu–Mn alloys calculated for various wavelengths λ are shown in Fig. 4 in the form of the $\gamma(\omega^2)$ graphs. As one can see from the figure, the collision frequency γ depends on the squared cyclic frequency ω^2. More-
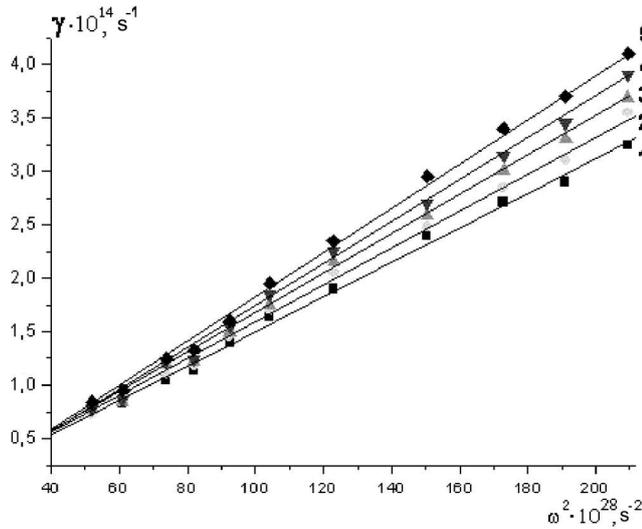
Fig. 4. Collision frequency γ as a function of the squared cyclic frequency ω^2 calculated on the basis of experimental data for Cu (*1*) and samples with Mn concentrations of 5 (*2*), 10 (*3*), 17.5 (*4*), and 25% (*5*)
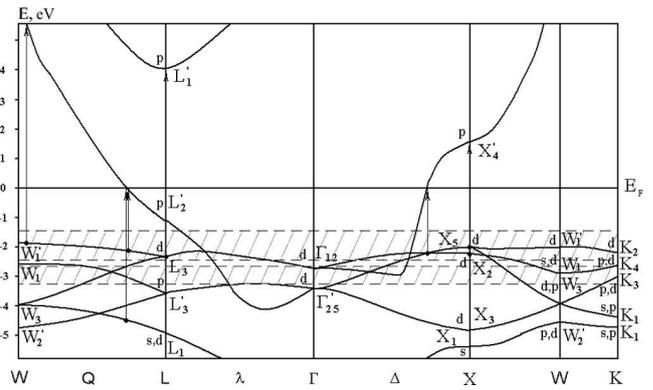

Fig. 5. Copper energy bands. Vertical arrows mark the most intense dipole-allowed transitions. Dotted region corresponds to the impurity band of the Cu-25%Mn alloy split due to the exchange interaction

over, the dependence $\gamma(\omega^2)$ in the interval $\lambda = 1.1$–2.8 μm can be well described by a linear function. For example, $\gamma = 0.18 \times 10^{14} s^{-1} + 0.013 \times 10^{-14}\omega^2$ for pure copper. This fact is an evidence of the strong effect of the electron-electron interaction on the relaxation frequency γ, which agrees with data of theoretical researches [4].

In addition, based on the data obtained for Cu–Mn alloys, we calculated the electron concentration N applying the technique described in [1]. It turned out that, in contrast to the collision frequency, the electron concentration in the region $\lambda = 1.1$–2.8 μm does not depend practically on the wavelength λ (frequency ω). The mean values of N for pure copper and Cu–Mn alloys are listed in Table. It is worth noting that the corrections for the skin effect β_1 and β_2 significantly differ: $\beta_1 \sim 10^{-3}$ and $\beta_2 = 0.07$–0.71. Thus, the skin effect in Cu–Mn alloys is weakly anomalous, and the experimental results in the IR

Mean electron concentrations N for Cu and Cu–Mn alloys

Sample	N, 10^{28}, m^{-3}
Cu	4.24
Cu-5%Mn	4.32
Cu-10%Mn	4.41
Cu-17,5%Mn	4.53
Cu-25%Mn	4.59

region are processed with regard for the correction β_2.

We note that, at room temperature, electron-phonon and electron-impurity collisions also play a certain role even in pure Cu samples and in Cu–Mn alloys with ideal structure. A proper separation of the contributions of electron-electron, electron-phonon, and electron-impurity collisions is possible after temperature measurements of the optical constants of the studied alloys in a wide temperature range.

Based on the obtained data, a model of the electron structure of Cu–Mn solid solutions can be proposed with regard for the results of studying the electron structure of pure copper [8] and its optical spectrum [3]. According to [8], the absorption edge in pure copper at 2.1–2.2 eV is related to the electron transitions from the tops of the d-bands in a vicinity of the point L_3 of the Brillouin zone to free states of the s-p-bands L'_2 in the neighborhood of the Fermi level E_F. Figure 5 presents the energy band structure of copper calculated by the interpolation technique [4]. The vertical arrows mark the dipole-allowed transitions between energy bands that form the most intense absorption bands in the optical conductivity spectrum $\sigma(h\nu)$ of pure copper.

The experimental data on optical properties of Cu–Mn alloys result in the conclusion that the energy gap between the top of the d-bands of copper and the Fermi level remains invariable if manganese is added. In other words, the positions of the d-bands with respect to the Fermi level E_F in the electron spectrum of alloys practically do not change. Above the absorption edge, one observes the intense interband absorption related to

transitions in a large bulk of the Brillouin zone from the second, third, and fourth bands to free states of the sixth band in the L–W and Γ–X directions of the Brillouin zone (corresponding transitions are shown in Fig. 5).

Taking into account that the high-energy maximum on the $\sigma(h\nu)$ curve of copper at 4.7 eV is related to transitions from the sixth to the seventh band, mainly from the d-states L_1 to free levels of the sp-band L_2' [6] (corresponding transitions are marked in Fig. 6 by vertical arrows), one arrives at the conclusion that the structure of the d-bands located by 4.0–4.95 eV lower than the Fermi level is not changed in the alloys and is similar to the d-bands of copper. It is no doubt that the bands in Cu–Mn alloys which are more distant from the Fermi level are also similar to the d-bands of copper. Thus, the energy bands in Cu–Mn alloys conserve the characteristic features of the electron spectrum of pure copper.

Assuming by analogy with Cu–Fe and Cu–Cr alloys [7] that the absorption band with a maximum at 2 eV in the optical spectra $\sigma(h\nu)$ is related to electron transitions from the impurity d-subband to free electron states in a vicinity of the Fermi level E_F and using the obtained data, one can find the distance of the energy center of the impurity band from the Fermi level $E_d - E_\mathrm{F}$, as well as its half-width Δ. According to experimental data, the value of $E_d - E_\mathrm{F}$ in Cu–Mn solid solutions amounts to 2.2 eV and is almost independent of the Mn concentration, whereas the half-width Δ somewhat grows with the Mn density in the solution and is equal to 1.35 (Cu-2%Mn) or 1.4 eV (Cu-50%Mn). The found values of $E_d - E_\mathrm{F}$ and Δ were used for the calculation of the electron state density $g(E)$ of Cu–Mn alloys within the impurity band (Fig. 6).

As an example, Fig. 6 presents the electron state density $g(E)$ of copper, as well as the contribution made to the state density by the impurity band of the Cu-25%Mn alloy. It is found that the new impurity band has a fine structure and is split into two energy subbands due to the exchange interaction. The maximum of the first subband is located at 1.98–2.02 eV, while that of the second one – at 2.8–2.9 eV. The half-widths of the indicated energy bands amount to 1.4 eV and 0.75 eV, respectively. That is why, one can consider that the total state density $g(E)$ of the Cu-25%Mn alloy (for example) represents the sum of the state densities of pure copper with the corresponding weight (0.75) and the impurity d-band of manganese.
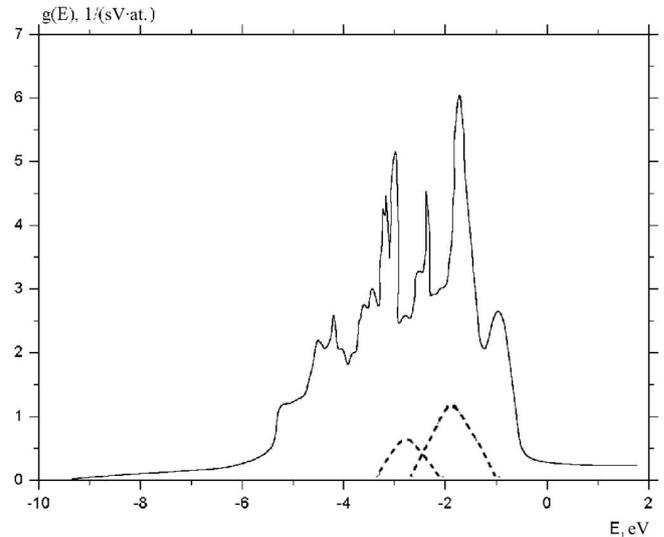

Fig. 6. Electron state density $g(E)$ of copper (solid line) and contribution of the impurity band of Cu-25% Mn alloys (dotted lines)

4. Conclusions

It is established that an impurity of antiferromagnetic manganese added to copper results in the formation of a new impurity energy band in its electron spectrum that is located approximately 2.2 eV below the Fermi level and is split into two energy subbands due to the exchange interaction. It is shown that, roughly speaking, the electron spectra of Cu–Mn alloys represent a superposition of the electron state densities $g(E)$ of pure copper with a certain weight equal to the concentration in the alloy and the state density within the impurity band.

It is shown that the dominant role in the formation of the optical properties of Cu–Mn alloys is played by the d-bands of the solvent (Cu) and the impurity band (Mn). Interband transitions from the d-bands of the solvent to its sp-bands result in the formation of fundamental absorption bands $\sigma(h\nu)$ in Cu–Mn spectra. Additional bands appear due to electron transitions from the impurity band to the Fermi level E_F.

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СПЕКТРОСКОПІЯ ДОМІШКОВИХ СТАНІВ
У СПЛАВАХ Cu–Mn

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Р е з ю м е

Еліпсометричним методом при кімнатній температурі виміряно показники заломлення n та поглинання χ невпорядкованих сплавів Cu–Mn з концентраціями 2; 5; 10; 17,5; 25; 37,5 та 50 % марганцю в широкому спектральному діапазоні 0,23–2,8 мкм (0,44–5,39 еВ). На основі цих даних розраховано оптичну провідність σ, яка пов'язана з міжзонними переходами. В області внутрішньозонного поглинання визначено частоту зіткнень γ та концентрацію електронів провідності N. Встановлено, що в електронному спектрі міді при додаванні марганцю формується нова домішкова зона, розташована на відстані 2,2 еВ нижче від рівня Фермі, і яка розщеплюється внаслідок обмінної взаємодії на дві енергетичні підзони.