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## Optical and electronic properties of Cu-Mn solid solutions

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**Abstract.** The optical properties of Cu-Mn alloys with Mn concentrations of 2, 5, 10 and 17.5% (which corresponds to the  $\gamma$ -solid solutions) were studied within a wide spectral range of 0.23 to 2.8  $\mu\text{m}$  (0.44...5.39 eV). Real and imaginary parts of the refractive index were measured, other optical properties such as dielectric constant, optical conductivity and the coefficient of specular reflectance at normal incidence were calculated being based on them. The analysis of the dispersion dependences  $\varepsilon(h\nu)$ ,  $R(h\nu)$  and  $\sigma(h\nu)$  enabled us to offer the electronic structure model for these alloys. According to this model, the electronic spectra (dependence of the density of electronic states on energy  $N(E)$ ) of alloys with the indicated concentrations of components are the superposition of electronic spectra of Cu host, with weights equal to Cu concentrations, and the density of states within the impurity band, calculated using the experimental data.

**Keywords:** Cu-Mn alloy, electronic structure, impurity band, collision rate, density of electronic states, optical conductivity spectrum.

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### 1. Introduction

Cu-Mn alloys, unlike Cu-Ni alloys, which are single-phase [1] in a wide range of concentrations, form two-phase solid solutions with  $\gamma$ -phase Cu and  $\varepsilon$ -phase Mn. At the same time, other transition metals such as Fe, Co or Cr are almost insoluble in Cu [2]. On the other hand, it is well known that the impurities of 3d-transition metals form localized magnetic moments [3], which gave impetus to theoretical studies of electronic properties of the compounds with 3d-transition metals [4]. It was found that with the addition of 3d-transition metals to copper, new impurity bands are formed in the electronic spectrum of the solvent. They are located below the Fermi level  $E_F$  [5]. This enabled to determine the parameters that characterize the impurity band, as in the case of alloys Cu-Fe [6], Cu-Co [7] and Cu-Cr [8]. However, so far, to our knowledge, the optical properties of alloys of copper with another 3d-transition metal – antiferromagnetic Mn – were not studied. Therefore, in this work we study the optical properties and, being based on them, the electronic structure of Cu-Mn compounds rich in Cu.

### 2. Experimental procedure

Optical properties of solid solutions of Cu-Mn with Mn concentrations of 2, 5, 10 and 17.5%, and pure Cu and Mn were investigated within the spectral range  $\lambda = 0.23...2.8 \mu\text{m}$  ( $h\nu = 0.44...5.39 \text{ eV}$ ) by Beattie ellipsometric method using an original spectral ellipsometer [9]. The ellipsometer included the following functional units: block of light sources, consisting of deuterium-mercury lamp ART-250, hydrogen lamp ICE-25 and halogen lamp KGM-150; block of radiation detectors, which included photoelectron multipliers PEM-39A and PEM-62; G-5 goniometer, which housed the Glan prism polarizer and analyzer. The studied samples were located on the goniometer sample stage. The setup also included the electrical components for amplifying electrical signals and their registration by standard digital voltmeters and PC. Ellipsometric parameters  $\Delta$  (phase shift between p- and s-polarization components) and  $\psi$  (azimuth of the restored linear polarization) were measured within this setup in the specified spectral range at a fixed angle of incidence close to the principal one. Based on  $\Delta$  and  $\psi$

the refraction and absorption indices  $n$  and  $\chi$  were calculated, and then the dielectric constant  $\varepsilon = n^2 - \chi^2$ , optical conductivity  $\sigma = 4\pi\varepsilon_0 n \chi \nu$  ( $\nu$  – light frequency) and the reflection coefficient at normal incidence

$$R = \frac{(n-1)^2 + \chi^2}{(n+1)^2 + \chi^2}$$
 were obtained.

Cu-Mn alloy samples were obtained by vacuum-arc melting of pure Cu and Mn with corresponding weights in argon atmosphere by repeated melting. To achieve greater uniformity samples were annealed in the same atmosphere at 900 °C for 24 h. Sample mirror surfaces were prepared by mechanical grinding and polishing with diamond paste with subsequent recrystallization annealing and electropolishing. X-ray structure and phase analysis of alloy samples was also performed with ДРОН-3.0 X-ray diffractometer.

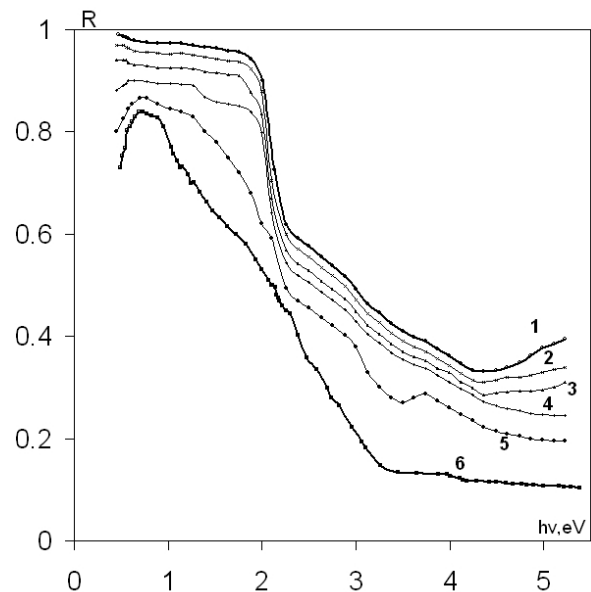
### 3. Results and discussion

Analysis of optical properties' dependence on the photon energy  $h\nu$  in the investigated spectral range  $h\nu = 0.44 \dots 5.39$  eV provides information about changes in the electronic structure of Cu with the addition of Mn. First, we consider the dispersion curves of reflection coefficient  $R(h\nu)$  of studied Cu-Mn alloys and pure Cu and Mn, shown in Fig. 1. The figure shows that the reflection curve  $R(h\nu)$  for pure Cu is a smooth curve without any anomalies, although the value of  $R$  varies within wide limits (35...99%), except for the shallow minimum located at about 4.2 eV, caused by electron interband transitions. At the same time, the value of  $R$  of Mn is much lower than that for Cu, especially in the ultraviolet region, where the values of  $R$  differ by almost 3.5 times. A broad maximum is observed in the infrared region ( $h\nu < 1.1$  eV) for Mn, located at about 0.95 eV. It is seen that in this area  $R$  value for Cu depends weakly on energy, indicating the dominance of interband electron transitions. With addition of Mn, the  $R$  value in the ultraviolet spectral region ( $h\nu > 3.0$  eV) decreases with increasing the Mn concentration, and the minimum at 4.2 eV characteristic for pure Cu does not appear in  $R(h\nu)$  curves of alloys with Mn concentrations higher than 10%. The behavior of the curve  $R(h\nu)$  for Cu-17.5% Mn alloy is quite peculiar, as a maximum at 3.85 eV clearly appears in the curve, which is virtually absent in other alloys. It is speculated that with further increase in the manganese concentration this maximum intensity will increase, as it is observed in the  $R(h\nu)$  curve of pure manganese. Therefore, the most significant changes in the  $R(h\nu)$  spectra of alloys are observed in the infrared region (with  $h\nu < 1.5$  eV), which indicates the increasing role of interband transitions with the increase of manganese concentrations.

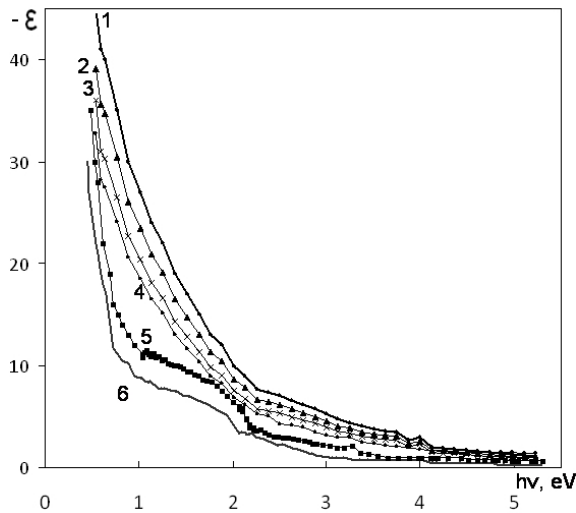
In what follows, we proceed to analyze the dispersion of the dielectric constant  $\varepsilon(h\nu)$ , shown in Fig. 2. The figure shows that the  $\varepsilon(h\nu)$  curves for alloys

with a low Mn content are similar to the pure copper  $\varepsilon(h\nu)$  curve, which decreases monotonically with the decrease in energy, which is typical for normal dispersion. In the samples with high Mn concentrations, as well as for pure Mn, the anomalous dispersion is observed in  $\varepsilon(h\nu)$  curves at 1.0...3.0 eV, which indicates the dominance of interband electron transitions within this spectral range. Additional information can be obtained by analyzing the  $\varepsilon(h\nu)$  curves at  $(h\nu) = 3.3 \dots 4.5$  eV, where the value of  $\varepsilon$  for all studied alloys is close to zero, which is a necessary condition for the excitation of plasma oscillations.

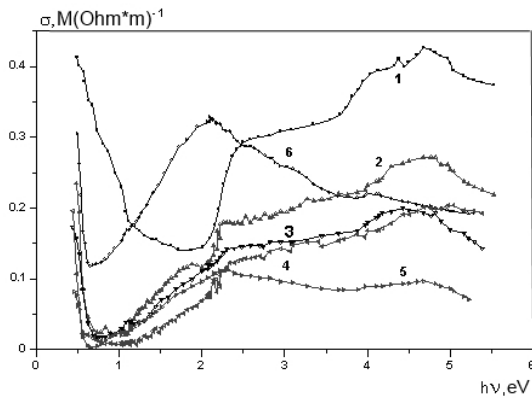
Let us make a more detailed look at the dispersion of optical conductivity  $\sigma(h\nu)$ , which is proportional to the interband density of electronic states  $G(h\nu)$  [10]. Experimental  $\varepsilon(h\nu)$  curves of the investigated alloys and pure Cu and Mn are shown in Fig. 3. The features of  $\sigma(h\nu)$  spectra of pure Cu and Mn are significantly different. At the energies  $(h\nu) < 1.5$  eV, the optical conductivity value for Cu increases monotonically with the decrease in the energy  $h\nu$ , which indicates the dominance of intraband transitions that occur within each of the bands that cross the Fermi level  $E_F$ . Characteristic features of  $\varepsilon(h\nu)$  spectrum of Cu are the sharp interband absorption edge at  $h\nu = 2.1 \dots 2.3$  eV, centered at 2.2 eV, and an intense absorption band with a maximum near 4.72 eV, as well as minor spectrum features at 3.5...4.4 eV.  $\sigma(h\nu)$  curve of Mn is in turn characterized by a wide maximum at 2.2 eV and a slight increase in  $\sigma$  value in the IR range ( $h\nu < 0.5$  eV) caused by intraband electron transitions. We analyze further the dispersion of optical conductivity  $\sigma(h\nu)$  of Cu-Mn alloys with the increase in the Mn concentration (Fig. 3).



**Fig. 1.** Dispersion curves of reflectance  $R(h\nu)$  for Cu (1), Mn (6) and their alloys containing 2 (2), 5 (3), 10 (4) and 17.5% Mn (5).



**Fig. 2.** Dispersion curves of the dielectric permittivity  $\epsilon(h\nu)$  for pure Cu (1) and Mn (6), and Cu-Mn alloys containing 2 (2), 5 (3), 10 (4) and 17.5% Mn (5).



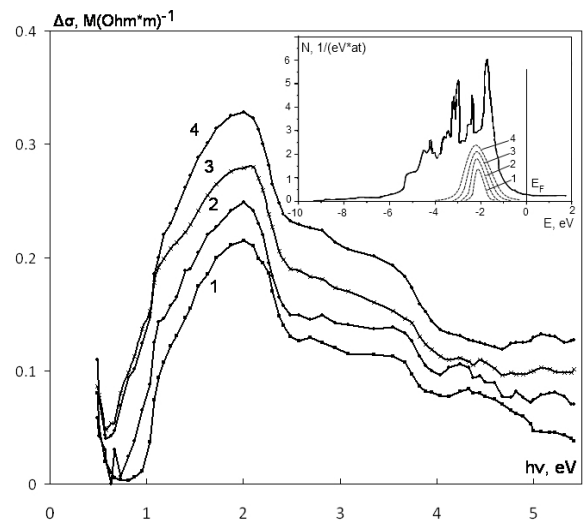
**Fig. 3.** Dispersion curves of interband optical conductivity  $\sigma(h\nu)$  for pure Cu (1) and Mn (2) and Cu-Mn alloys containing 2 (3), 5 (4), 10 (5) and 17.5% Mn (6). Curves (1) and (2) for the pure component raised by  $0.1 \text{ M} (\text{Ohm}\cdot\text{m})^{-1}$ .

Fig. 3 shows that the addition of low quantities of manganese to copper does not introduce significant changes in the overall shape of the absorption spectrum of copper. Characteristic features of the  $\sigma(h\nu)$  spectrum of pure copper, in particular a short peak at 4.72 eV and a sharp edge at 2.1...2.3 eV, to some extent, appear in all the investigated Cu-Mn alloys, as in Cu-Co alloys [7]. It is found that the peak at 4.72 eV is observed in all the alloys, hardly shifting along the energy scale. The sharp absorption edge at 2.2 eV appears only in samples with the concentration of manganese below 10%. At the same time, in the infrared spectral range  $h\nu = 0.8...1.8 \text{ eV}$  it is found that with addition of only 2% Mn to Cu the contribution of “free” electrons in the overall absorption decreases sharply. At high concentrations of Mn, this spectral area completely dominates due to interband electron transitions. This is due to the sharp increase of relaxation frequency of electrons in alloys as

compared to pure components. It is found that addition of Mn to Cu at Mn concentrations higher than 5% gives a very strong effect – the appearance of an intense absorption band in the  $\sigma(h\nu)$  curves in the near-IR range with a peak at  $h\nu = 1.9...2.0 \text{ eV}$ . Fig. 3 shows that a minimum is observed in the Cu  $\sigma(h\nu)$  curve in this region, while the maximum of absorption of pure Mn, according to our experimental data, is located at 2.2 eV. Consequently, this band is not associated with pure Cu and Mn, and is most likely associated with the resonant states arising in the electronic spectrum of Cu by addition of Mn. The maximum, which is located at 2.5 eV for the Cu-2% Mn alloy, shifts in high-energy region of the spectrum, for example, for the Cu-17.5% Mn alloy it is located at 2.15 eV (see Fig. 3). Clearly, the formation of an additional band in alloys is due to changes in the electronic spectra of Cu-Mn alloys. These changes are associated with the restructuring of the energy spectrum of Cu and the appearance, as noted above, of resonant impurity states [10].

Further, we analyze the dispersion curves of the residual optical conductivity  $\Delta\sigma(h\nu)$ , which represents the difference between the experimental values  $\sigma(h\nu)$  for alloys and the values of the optical conductivity of pure copper  $\sigma_{\text{Cu}}(h\nu)$  and pure manganese  $\sigma_{\text{Mn}}(h\nu)$  with respective weights  $\Delta\sigma(h\nu) = \sigma(h\nu) - (1-c)\sigma_{\text{Cu}}(h\nu) + c\sigma_{\text{Mn}}(h\nu)$  ( $c$  is the Mn concentration), which for Cu-Mn alloys containing 2, 5, 10, and 17.5% are shown in Fig. 4.

It is seen that for all the investigated alloys a new absorption band with a maximum at 2.05...2.15 eV appears. From the obtained data presented in Figs 3 and 4, the following conclusions can be made: first, at low concentrations of Mn (5%) it solves almost completely



**Fig. 4.** Dispersion of residual optical conductivity  $\Delta\sigma(h\nu)$  for Cu-Mn alloys containing 2 (1), 5 (2), 10 (3) and 17.5% Mn (4). All the curves are shifted upwards by  $0.1 \text{ M} (\text{Ohm}\cdot\text{m})^{-1}$ . Inset shows the density of states  $N(E)$  curves for Cu [11] and Cu-Mn alloys within the impurity band (dashed lines).

in Cu, second, the solubility increases with increasing the Mn concentration, and third, the impurity d-band forms in the electronic spectrum of the Cu-Mn solid solution, associated with Mn, which is located at 2.05...2.15 eV below the Fermi level  $E_F$ .

Using the results of studies of the electronic structure of pure copper and its optical spectrum [12], we can propose a model of the electronic structure of Cu-Mn solid solutions. According to [12], the absorption edge in pure copper at 2.1...2.2 eV is associated with transitions of electrons from the peaks of d-band near the  $L_3$  Brillouin zone (BZ) to free states of s-p-bands  $L'_2$  in the vicinity of the Fermi level (FL)  $E_F$ . Based on the data of experimental studying the optical properties of Cu-Mn alloys, it follows that the energy gap between the top of d-Cu bands and Fermi level with addition of Mn remains unchanged. That is, the position of d-band relative to Fermi level is virtually unchanged in the electronic spectrum of alloys. Intense interband absorption is observed above the absorption edge, which is associated with transitions in the large volume of BZ from 2-nd, 3-rd and 4-th bands into the free states of the sixth band in  $L-W$  and  $D-X$  directions of the Brillouin zone [10]. Taking into account that the high-energy peak in the  $\sigma(h\nu)$  curve of copper at 4.7 eV is related to transitions from the sixth to the seventh band, mainly from d-states of  $L_1$  to free sp-band levels of  $L'_2$  [11], one arrives to conclusion that the structure of d-bands located at 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. Thus, the energy bands in the investigated Cu-Mn alloys retain the characteristics of the electron spectrum inherent to pure copper.

Assuming by analogy between Cu-Fe and Cu-Cr alloys [6, 8] that the absorption band with a peak at 2 eV in the  $\sigma(h\nu)$  optical spectra is related to electron transitions from the impurity d-subband to free electron states in the 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  $E_d - E_F$  as well as its half-width  $\Delta$ . According to the experimental data in Cu-Mn solid solution the value of  $E_d - E_F$  is about 2.1 eV and almost independent of the Mn concentration, and  $\Delta$  increases slightly with increasing the Mn content in the solution and equals 1.35 eV (Cu-2% Mn), 1.4 eV (Cu-17.5% Mn). Based on the obtained  $E_d - E_F$  density of electronic states,  $N(E)$  was calculated for Cu-Mn alloys within the impurity band shown in the inset to Fig. 4. Consequently, the resulting electron spectrum of any alloy is a superposition of the spectrum of pure copper with a weight equal to the concentration of Cu in the alloy, and the density of states of the alloy within the impurity band.

#### 4. Conclusions

It is found that a new impurity energy band forms in the electronic spectrum of Cu with the addition of antiferromagnetic Mn impurities, located approximately

2.1 eV below the Fermi level  $E_F$ , which may split into two energy subbands due to exchange interaction. It is shown that the electron spectrum  $N(E)$  of Cu-Mn alloys is, in a rough approximation, the superposition of densities of electronic states  $N(E)$  of pure copper with a weight equal to its concentration in the alloy, and the density of states within the impurity band.

It has been shown that the optical properties of Cu-Mn alloys are determined by solvent (Cu) d-bands and impurity bands (Mn). Due to interband transitions from the solvent d-band to its sp-band, the main absorption band in the  $\sigma(h\nu)$  spectra of Cu-Mn alloys is formed. Additional bands appear due to transitions of electrons from the impurity band to the Fermi level  $E_F$ .

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