Electron-bombardment-induced photon emission from copper

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(Submitted 26 July 1983)
Zh. Eksp. Teor. Fiz. **86**, 1117–1123 (March 1984)

Spectra of light emission from copper films and polycrystalline samples, induced by bombardment with low energy electrons, are measured. The light emission spectra expected under a variety of assumptions concerning the mechanism of the effect are calculated and it is shown that interband recombination of nonequilibrium holes with electrons from the occupied bands makes the principal contribution to the spectrum. A previously developed model for recombination radiation from metals is extended to the case where the lifetime of the nonequilibrium carriers depends on their energy.

1. INTRODUCTION

The emission of photons from metals bombarded by low energy electrons—electron-photon emission—is the subject of increasing attention at the present time because in a number of cases the phenomenon makes it possible to obtain exclusive information about the electronic structure and the relaxation of nonequilibrium excitations in metals and about the state of the metal surfaces.[1–4] Experiments in this field have become possible only in the last decade because of the development of methods of detecting weak light fluxes and of means of producing atomically clean metal surfaces in ultrahigh vacuum.

Definite progress has been made in the understanding of the mechanism of electron-photon emission. This progress is primarily associated with the ascertainment that for frequencies $\omega < \omega_p$, where ω_p is the plasma frequency, the main contribution to the spectrum is due to interband radiative recombination of nonequilibrium carriers.[1,3] However, the problem of transition probabilities and of the lifetimes of the nonequilibrium carriers has as yet not been adequately treated. Therefore in this investigation we pay particular attention to information bearing upon this problem and obtainable from electron-photon emission spectra.

Copper was chosen as the material for investigation. This choice was based on a number of circumstances, and the following are the most important of them. First there exist for copper[5] electronic structure calculations verified by experiment. Second, copper is one of a number of materials of which sufficiently clean samples can be made by comparatively simple techniques. Third, there are inconsistencies and contradictions in the published data for electron-photon emission of copper[6–10] and it is of interest to determine the reason for this situation, because for the problems of interest to us the reliability of experimental data is particularly important.

2. EXPERIMENTAL METHOD

Films and polycrystalline samples of copper were used as targets. The films were 300–500 Å thick, as calculated from the mass determined with a quartz crystal oscillator microbalance, and they were deposited on glass substrates at a residual gas pressure of 10^{-8} Pa. The structure of the films was examined in a JSM-35 scanning electron microscope. The surface of the polycrystalline samples was cleaned by heating with an electron beam from an electron gun having a directly heated cathode.

The monoenergetic electron beam of energy from 10 to 1000 eV, used for the excitation of the electron-photon emission, was produced in a 90°-sector cylindrical electrostatic analyzer, which also prevented the light from the cathode from falling on the target. The construction of the apparatus and the methods of making the optical measurements and calibrating the system did not differ in principle from those described previously.[6,11]

Figure 1 (curve 1) shows the spectral distribution of the radiation intensity $I_\lambda = dN/d\lambda$, where dN is the number of photons detected in a wavelength interval $d\lambda$ for a 300 Å (by mass) thick copper film excited by 320 eV electrons incident on the surface of an angle $\alpha = 45°$, at an observation angle of 15°. These measurements were made at the lowest residual gas pressure attainable in these experiments, which was $7\cdot10^{-9}$ Pa. When the residual gas pressure is increased to 10^{-6} Pa, some other features appear and are most pronounced in the vicinity of the wavelengths $\lambda_1 \approx 4000$ Å and $\lambda_2 \approx 6000$ Å (Fig. 1, curve 2).

The electron-photon emission of the copper films and polycrystalline samples is practically independent of elec-

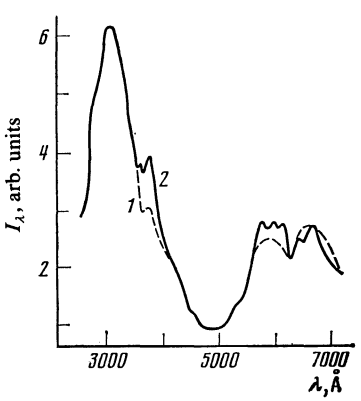

FIG. 1. Spectral distribution of emission intensity for copper film of 300 Å thickness by mass ($E = 300$ eV, $\alpha = 45°$, $\beta = 15°$) at residual gas pressure $7\cdot10^{-9}$ Pa (1) and 10^{-6} Pa (2).

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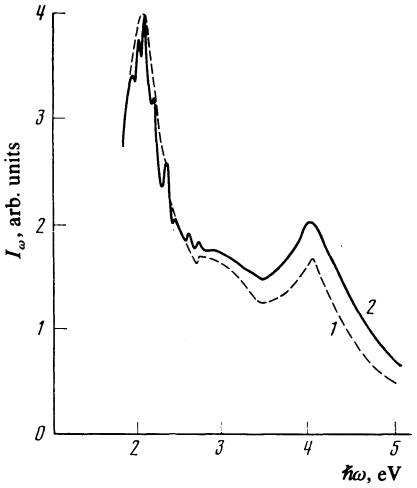

FIG. 2. Frequency dependence of electron-photon emission intensity for polycrystalline copper ($E = 500$ eV, $\alpha = 40°$) for different observation angles: 1) $\beta = 0°$, 2) $\beta = 40°$.

tron energy in the range 100–1000 eV and of α the angle of incidence of the electron beam but changes were observed as a function of β the angle of observation. The nature of these changes is illustrated in Fig. 2, which shows the frequency dependence of the electron-photon emission intensity $I_\omega = dN/d\omega$ ($d\omega$ is the frequency interval in which the number of photons dN is detected) for polycrystalline copper bombarded by electrons of energy 500 eV at $\alpha = 40°$ and $\beta = 0°$ (curve 1) and $\beta = 40°$ (curve 2). It can be seen that with increasing β the peak around $\hbar\omega \approx 4$ eV shifts towards lower energy and the structure in the low-energy part of the spectrum becomes considerably more pronounced.

Because the electron-photon emission spectra depend on β, the spectra for films and polycrystalline samples were compared for the same angle of observation $\beta = 0°$. As can be seen from Fig. 3, both in the spectrum of the film (curve 1) and in that of the polycrystalline sample (curve 2) there are two main peaks: at $\hbar\omega_1 \approx 2$ eV and $\hbar\omega_2 \approx 4$ eV. The positions of the other weaker peaks are also duplicated in the electron-photon emission spectra; however there are discrepancies in the region 2.3 to 3.2 eV.

Measurements of the absolute radiation yield B at the wavelength $\lambda = 3580$ Å for $E = 500$ eV, $\alpha = 45°$ and $\beta = 0°$ showed that $B = 2 \cdot 10^{-11}$ photons/electron·nm·sr·eV (measurement error $\pm$ 20%). The radiation yield integrated over the wavelength interval 2400 to 7000 Å is 10^{-8} photons/electrons·sr·eV.

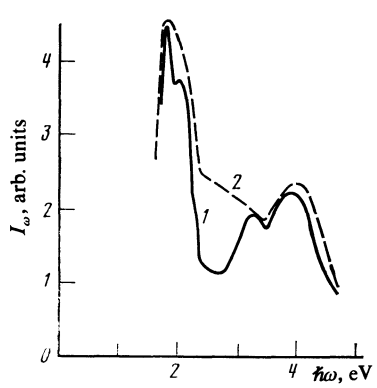

FIG. 3. Electron-photon emission spectra of film (1) and polycrystalline (2) copper for $\beta = 0°$.

3. DISCUSSION OF THE RESULTS

3.1. Comparison with other experimental results

Electron-photon emission spectra of copper have been studied in a number of investigations[6,9,10] and have been compared with light emission spectra obtained by irradiating the target with a laser[7] and by bombardment with high-energy electrons.[8] This comparison was only qualitative, since in Refs. 7 and 8 the authors did not correct their spectra for the sensitivity of the measuring apparatus because calibration of their system over a wide spectral range is a very complicated problem.

A quantitative comparison of the results obtained in the present investigation with the data of Refs. 4, 6, and 10 indicates that the general shape of the spectra is quite reproducible (it must be kept in mind that the factor $1/\omega^3$ is omitted in the calculation of the spectrum $I_\omega(\omega)$ in Ref. 10). The electron-photon emission spectra of copper in Ref. 9 were studied over a narrower interval, so that the peak at $\hbar\omega \approx 2$ eV was not observed. It is interesting to note that in Ref. 9 an extra band having a maximum at $\hbar\omega = 2.3$ eV appeared when oxygen was adsorbed. We did not see this feature in our spectra, meaning that our sample surfaces were quite free of oxygen.

The effect of the residual gas pressure on the electron-photon spectrum and its dependence on the observation angle β, which are manifest in the formation of an additional fine structure on a background of a practically constant very smooth spectrum, indicate that residual gas molecules adsorbed on the copper surface make a contribution to the electron-photon emission spectrum. This fact may be of independent interest in connection with the study of surface cleanliness and adsorption processes, but for the purposes of comparing experimental results with theoretical calculations that pertain to clean copper it is necessary to select the smoothest curves obtained in ultrahigh vacuum at zero angle of observation.

3.2. Theoretical approach to describing electron-photon emission spectra of copper

From the very first investigations of electron-photon emission of metals the point of view has been taken that the emission of light from metals bombarded by low-energy electrons can be considered as transition radiation. Estimates of the yield of radiated light[9,12] have been very conflicting, but our calculations support the conclusion of Ref. 9 that the observed radiated intensity exceeds that expected on the basis the theoretical calculations by several orders of magnitude. Furthermore, it is not difficult to calculate the transition radiation spectrum for copper (Fig. 4, curve 1) and, as can be seen from a comparison with Fig. 3, this calculation does not describe the main features in the spectrum. This is to be expected since, as noted in Ref. 3, the low energy

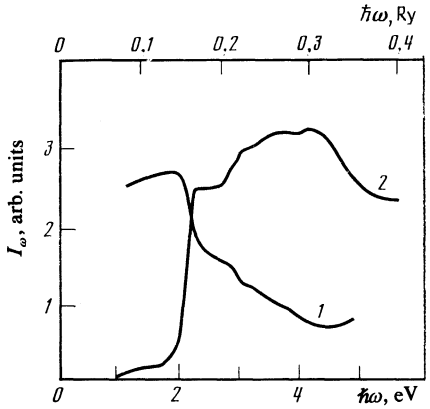

FIG. 4. Calculated spectra of transition radiation (1) and Hot luminescence (2).

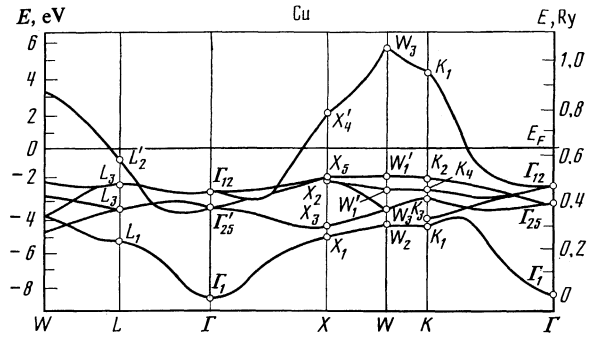

FIG. 5. Calculated dependence $E(\mathbf{k})$ of copper along some symmetry directions of the Brillouin zone.

electrons cannot be regarded as crossing the vacuum-metal interface without change of velocity, yet this assumption is at the basis of the model of transition radiation.[13]

Recently another approach to the description of electron-photon emission spectra has been proposed in which the emission is represented as hot luminescence.[14] However, this model does not stand up under comparison with experiment, as is shown by a comparison of the hot luminescence spectrum of copper, calculated on the basis of Ref. 14 (Fig. 4, curve 2), with the experimentally measured spectrum.

In our opinion, the real situation is most closely described by the recombination radiation model, according to which the observed electron-photon emission is due to radiative relaxation to the ground state by nonequilibrium carriers produced by the electron bombardment of the metal. From this point of view it is understandable why the hot luminescence model is untenable, since, in this model, according to Ref. 14, the shape of the spectrum is determined mainly by the imaginary part of the dielectric constant $\varepsilon_2(\omega)$, which in turn is determined by transitions between initially filled and empty states, and these transitions make only an insignificant contribution to the electron-photon emission spectrum.[1] Accordingly, we have calculated the recombination-radiation spectra of copper under various assumptions concerning the transition probabilities and lifetimes of the nonequilibrium carriers. The results are presented in the next section.

3.3. Calculations of electron-photon emission spectra of copper

Calculation of the electron-photon emission spectrum of copper was carried out on the basis of the one-electron band model, using the ideas developed in Ref. 1. The energy band structure of copper was calculated with the use of the Hodges-Ehrenreich interpolation scheme,[15] in which the parameters that are used are the energy eigenvalues at five points of high symmetry, Γ, X, L, W, and K, determined in Ref. 5. In the case of copper (fcc lattice) the calculations reduce to diagonalization of a 9×9 Hamiltonian matrix at each point $\mathbf{k}$ of the Brillouin zone. The calculated $E(\mathbf{k})$ dependence along some symmetry directions is shown in Fig. 5.

The calculations showed that the indirect-transition model cannot account even qualitatively for the experimental results. Therefore, the approximations that are common to all the models considered below consist in the following: 1) the spectra are formed as a result of direct interband dipole transitions; 2) with similar but not necessarily identical probability, empty states above the Fermi energy can be filled and any states below the Fermi energy can be emptied under the action of the electron bombardment. To make the models more specific, additional assumptions about the transitions probabilities are required.

In the first model it is assumed that the probability of transitions between filled and empty states beneath the Fermi level is large and the hole that exists can with equal probability be filled by an electron fron any state with a higher energy. In this way the holes "float upward" until they reach the Fermi level. The totality of all possible transitions gives the spectrum depicted by curve 1 of Fig. 6. It should be noted that according to this model the emission intensity begins to increase at low energies because of the contribution of elec-

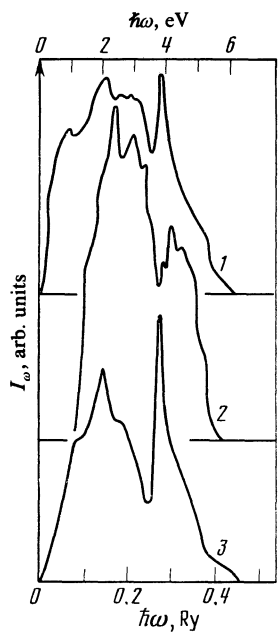

FIG. 6. Theoretically calculated electron-photon emission spectra with various assumptions about interband transition probabilities.

tronic transitions between p and d states in the region of energy localization of the d bands.

The second model is based on the assumption that a hole in the valence band is filled with the greatest probability by an electron with energy close to the Fermi energy. In the calculations it was assumed that the width of the band containing the initial states is 0.08 Ry, and that the Fermi level lies at the middle of this band. Since the energy of the initial states is fixed, it is possible to associate the individual peaks in the spectrum with definite points in the Brillouin zone. In this case (curve 2, Fig. 6) the minimum energy in the spectrum is about 0.1 Ry and the width of the spectrum is close to the width of the d band.

In the third model it is assumed that a transition can occur at any point $\mathbf{k}$ of the Brillouin zone, and transitions from the highest occupied bands have the highest probability (Fig. 6, curve 3). A comparison of the theoretically calculated electron-photon emission spectra for copper shows that the shape of the spectra is very sensitive to the model assumptions concerning the interband transition probabilities, which justifies the approach used in this investigation.

A comparison of the measured spectrum with those calculated shows that the third model is the preferred one. This model is also at the basis of the subsequent discussion.

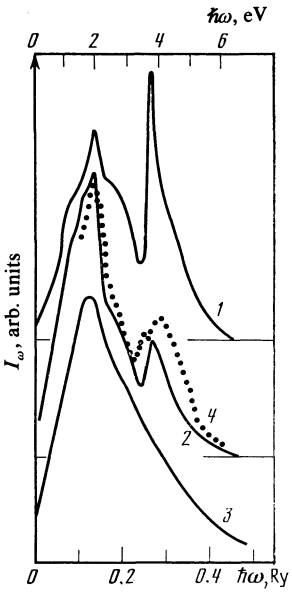

FIG. 7. Comparison of calculated electron-photon emission spectra of copper for various values of k: 1) $k = \infty$; 2) $k = 0.1$; 3) $k = 0.01$; with the experimentally measured spectrum of polycrystalline copper (4).

3.4. The effect of hole lifetime. Comparison with experiment

Subsequent development of the third model consisted of taking into account the effect of hole lifetime on the shape of the electron-photon emission spectrum. Without going into a detailed investigation of the physics of many-particle processes, we approximated the lifetime $\tau(\mathscr{E})$ of a hole of energy $\mathscr{E}$ by the function

$$\tau(\mathscr{E}) = 1/\Gamma(\mathscr{E}) = k(\mathscr{E}_F^{1/2} - \mathscr{E}^{1/2})^{-2}, \quad k = \text{const} \qquad (1)$$

in accordance with the result of Ref. 16 obtained for metals whose valence-electron wave functions are approximately plane waves. Of course, in the case of d metals, because of the complicated structure of the valence band the energy dependence of the lifetime will not be so simple, but we believe that this approximation is entirely admissible for a qualitative analysis.

In the calculation of the electron-photon emission spectrum the contribution of an optical quantum emitted in the transition of an electron into a state of energy $\mathscr{E}$ is blurred out by a dispersion curve of halfwidth $\Gamma(\mathscr{E})$. Figure 7 shows the electron-photon emission spectrum corresponding to an infinite hole lifetime (curve 1) as well as broadened spectra for which in the calculations the value of k in formula (1) was taken to be $k = 0.1$ (curve 2) and $k = 0.01$ (curve 1). As can be seen from the figure, allowance for a finite hole lifetime markedly suppresses the intensity of the high-energy part of the spectrum. For $k = \infty$ the ratio of intensities at the main peaks at $\hbar\omega_1 = 1.9$ eV and $\hbar\omega_2 = 4$ eV is 0.8; for $k = 0.1$ the ratio is 2.4, and for $k = 0.01$ the peak at 4 eV is generally hard to distinguish. In the measured experimental spectrum this ratio is 1.8. Of course, it is possible to pick a value of k so as to make the intensity ratio of the two peaks agree with the measured value; however, in view of the approximate nature of the calculations, we did not consider this to be appropriate. Using $k = 0.1$ we can assess the energy-dependent nonequilibrium-carrier lifetime, which falls off rapidly with distance from the Fermi level, reaching a value $4 \cdot 10^{-14}$ sec for $\mathscr{E} - \mathscr{E}_F \approx 0.5$ eV.

These results show that, in the determination of the shape of the spectra the energy dependence of the lifetime of the holes is no less an important characteristic than the transition probabilities. It is important to note that under the influence of these factors the positions of the peaks change little, but their relative intensities change substantially. From this it can be concluded that the main peaks in the spectrum are a result of transitions near the X and K points in the Brillouin zone. However, since the d band is flat, the entire neighborhood of these points contributes to the spectrum; this in all probability is responsible for the additional structure experimentally observed in the spectra.

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Translated by J. R. Anderson