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Abstract

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PHYSICS

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X-RAY EMISSION L_{II} - AND L_{III} -BANDS AND THE STRUCTURE OF THE $3d$ -BAND OF COPPER

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Transitions of electrons from the conduction band of a metal to vacancies of inner levels, formed upon x-ray excitation of an atom, are accompanied by the emission of photons of the emission bands. If one restricts oneself to the dipole selection rules, then the symmetry of the inner level will determine the symmetry of the conduction electrons participating in the transitions. In works ^(1,2) it was shown that the emission K_{β_5} -band of copper arises in transitions to the K -level of conduction-band electrons predominantly of p -symmetry. The shape of the K_{β_5} -band could be calculated in good agreement with experiment only when both the density of states and the transition probability were taken into account jointly.

For the emission L_{II} - and L_{III} -bands of copper there are no analogous calculations, and it is assumed *a priori* ⁽³⁾ that their shape reproduces the curve $N(E)$ of the density of states of d -electrons in the conduction band. The validity of this assumption can be checked by comparing the results of theoretical calculation and experiment. In addition, this will make it possible to clarify the limits of applicability of one or another quantum-mechanical method for calculating the band structure of a metal, provided that such a calculation is carried out consistently within the framework of the chosen method.

In the present work the shape of the emission L_{III} -band of copper was calculated by the cellular method according to the formula:

$$I(E) \approx \sum_{i=1}^6 \int_{(S)} \frac{|M_i(E, \mathbf{k})|^2}{|\text{grad}_{ik} E(\mathbf{k})|} ds. \quad (1)$$

Here $I(E)$ is the intensity distribution in the emission band over energies; $M_i(E, \mathbf{k})$ is the matrix element of the transition probability from the initial $2p$ -state; integration is performed over the isoenergetic surface of k -space, and summation is over all subbands. The dependence of the transition-probability matrix element on energy is determined ⁽⁴⁾ by the expression

Fig. 1. Shape of the copper emission L_{III} band: 1 —calculated by the cell method; 2 —experimental at a voltage of 3 kV; 3 —at a voltage of 1 kV; 4 — L_{III} absorption edge

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$$M_i(E, \mathbf{k}) = v \sum_l a_{il}(E, \mathbf{k}) \int_0^\infty R_{2p}(r) R_l(r, E) r^3 dr, \quad (2)$$

where $a_{il}(E, \mathbf{k})$ are the expansion coefficients of the wave function of the valence electron in cubic harmonics; $R_{2p}(r)$ is the wave function of the initial $2p$ -state, and $R_l(r, E)$ is the wave function of electrons in the conduction band. The calculation results are shown in Fig. 1 (curve 1).

In the course of the calculation it was found that the probability of the dipole transition $p \rightarrow s$ is two orders of magnitude smaller than that of $p \rightarrow d$. The squares $|a_{il}(E, \mathbf{k})|^2$ determine the fractions of participation of electrons of different symmetries in the formation of the conduction band. It turned out that the fraction of d -electrons in the first four subbands is close to 1 and does not depend on the energy or the direction $\mathbf{k}$. In the fifth subband there are electrons mainly of p -, d -, and s -symmetry. The sixth subband, of width ~ 0.7 eV, consists of d - and s -electrons, and the contribution of this subband to the total density-of-states curve is small. Taking into account the dependence of the fraction of d -electrons on $\mathbf{k}$ in the fifth subband leads to small corrections to the total curve of the intensity distribution of the L -band over energies.

Thus, it was established that the shape of the emission band calculated theoretically is determined mainly by the d -electrons of the first four subbands, in which the fraction of these electrons does not depend on $\mathbf{k}$. The contributions of the s -electrons to the intensity of the emission band are negligibly small because of the smallness of their shares in the individual subbands, as well as the small transition probability.

For comparison with experiment, the intensity distribution calculated by formula (1) was “smeared” over the width of the inner L_{III} level. Its width (~ 1.0 eV) and shape were taken from Ref. (5). The theoretical width of the copper emission L_{III} band was found to be 8.5 eV.

Fig. 1. Shape of the copper emission L_{III} band: **1** —calculated by the cell method; **2** —experimental at a voltage of 3 kV; **3** —at a voltage of 1 kV; **4** — L_{III} absorption edge.

A calculation of the shape of the copper L_{III} band was also carried out using the simplified formula

$$I(E) \simeq |M_d(E)|^2 \sum_{i=1}^6 \int_{(S)} \frac{ds}{|\text{grad}_{i\mathbf{k}} E(\mathbf{k})|}, \quad (3)$$

where it was assumed that $|a_{id}(E, \mathbf{k})|^2 = 1$ for all subbands, energies, and directions $\mathbf{k}$. In this case $M_d(E)$ is determined by the integral in the right-hand part of expression (2).

The resulting shape of the copper emission L_{III} band practically coincided with that calculated by the exact formula (1). This can be explained only by the fact that, in this particular case, the predominant contribution to the intensity of the emission band is made by electrons of d -symmetry, and their distribution depends only weakly on $\mathbf{k}$.

In order to make a comparison with experiment, it is necessary to obtain the true shape of the copper emission L_{III} band. Usually the L levels of atoms of $3d$ -metals are excited by electrons with energies of several kiloelectronvolts. In this case vacancies are formed not only in the L_{II} and L_{III} levels, but also in L_{I} . It is known (6) that vacancies in the L_{I} and L_{II} levels of atoms with $Z \leq 32$ can be filled by nonradiative Coster-Kronig transitions of the following types:

1. $L_{\text{I}} \rightarrow L_{\text{II}} M_{\text{I}}$.
2. $L_{\text{I}} \rightarrow L_{\text{II}} M_{\text{II,III}}$.
3. $L_{\text{I}} \rightarrow L_{\text{II}} M_{\text{IV,V}}$.
4. $L_{\text{I}} \rightarrow L_{\text{III}} M_{\text{I}}$.
5. $L_{\text{I}} \rightarrow L_{\text{III}} M_{\text{II,III}}$.
6. $L_{\text{I}} \rightarrow L_{\text{III}} M_{\text{IV,V}}$.
7. $L_{\text{II}} \rightarrow L_{\text{III}} M_{\text{IV,V}}$.

The probability of these transitions is very large. As a result of such processes, doubly ionized states of atoms arise, and radiative transitions between them give satellites of the main band. For the L_{III} band, four groups of satellites are formed, caused by Coster-Kronig transitions of types 4-7. Transitions of types 1-3 lead to the appearance of satellites of the L_{II} band. These satellites are superposed on the short-wavelength part of the main emission band and substantially distort its shape. If the voltage on the x-ray tube is chosen between the excitation potentials

excitation of the L_{I} - and L_{II} -levels, i.e., as it were, to "switch off" the L_{I} -level, the intensity of the satellites of the L_{III} -band will sharply decrease (only the satellites due to a transition of the $K-K$ type 7 will remain), while the satellites of the L_{II} -band should disappear.

Figure 2

Figure 2: Figure 2

Fig. 2. Shape of the emission L_{II} -band of copper: **1**—experimental at a voltage of 3 kV; **2**—at a voltage of 1 kV; **3**— L_{II} absorption edge

The ionization potentials are: for the L_I -level, 1102 V; for the L_{II} -level, 953 V; and for the L_{III} -level, 933 V (7).

The emission L_{II} - and L_{III} -bands of copper were recorded on a DRS-2 spectrograph with a mica crystal bent to a radius of 500 mm. A three-phase six-valve high-voltage rectifier, assembled with D1010-type diodes and having a choke-capacitor smoothing filter, gave a rectified voltage with ripples of about 20 V at a voltage of 1 kV and a current of 50 mA. The emission L_{III} -bands obtained at voltages of 3 and 1 kV and a current of 50 mA are shown in Fig. 1. A voltage of 1 kV is insufficient for ionization of the L_I -level; therefore transitions of types 1–6 are impossible. The remaining satellites of the L_{III} -band are due not only to transitions of the $K - K$ type 7, but also to the formation of multiply ionized states upon simultaneous ionization of the $L_{II,III}$ - and $M_{IV,V}$ -levels (8). Such satellites are observed for the L_{II} -band recorded at a voltage of 1 kV, when $K - K$ transitions involving the L_I - and L_{II} -levels are completely excluded (Fig. 2, curve 2).

Excluding a considerable part of the short-wavelength satellites makes it possible to reveal the true shape of the emission L_{II} - and L_{III} -bands and to estimate certain parameters of the conduction band of copper from the experimental curves. The width of the filled part of this band is 5.5–6.0 eV. This width was measured along the bases of the emission bands from their onset (obtained after cutting off the long-wavelength “tails” by linear extrapolation) to the point of inflection of the main absorption edge. The maximum density of states lies at a distance of 3.5 ± 0.1 eV from the Fermi boundary. The fact that calculation of the shape of the emission L_{III} -band of copper by the cellular method did not give satisfactory agreement with experiment indicates that this method is apparently not applicable to comparatively strongly bound electrons such as the 3d-electrons of copper.

A self-consistent calculation of the density-of-states curve of the conduction band of copper by the APW method, carried out in (9), agrees well with the experimental results obtained in the present work and gives the same values both for the width of the d -subband of the occupied part of the conduction band and for the distance from the Fermi boundary to the maximum of the density of states.

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