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Fine structure of the deep-band probe $K\beta_{2,5}$ in copper

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The x-ray line $K\beta_{2,5}$, formally corresponding to the transitions $4p \rightarrow 1s$ and $4s,3d \rightarrow 1s$, respectively, was studied using electron excitation of polycrystalline copper. The kinetic energy of the electrons ranged from 20 to 40 keV. The spectrum was decomposed by means of successive reflections in two highly perfect Si crystals which were bent elastically in such a manner that optimal intensity and resolving power were achieved. A numerical calculation of the latter quantity yielded an experimental window which was extremely narrow, compared with the theoretical lifetime width of the $1s$ core state (0.03 vs 1.5 eV). The energy position of the Fermi edge was located by means of the observed absorption curve. The profile and apparent strength of the high-energy satellite $K\beta'''$ were found to depend on the high voltage and the take-off angle. The influence of self-absorption is discussed and it is concluded that the main features of the structure earlier known as $K\beta'''$ may be explained as selective absorption of a featureless Fermi-edge tail, which has a substantial intensity and which originates in incomplete relaxation or multiple ionization. The emission band below the edge is shown to exhibit a new feature just at the low-energy side of the main peak, causing a slight local asymmetry. There seems, however, to be no incompatibility between this structure, or the rest of the intensity variations, and density-of-states calculations.

I. INTRODUCTION

The effect of a rapidly varying density of states is believed to be intermingled with various many-body features in x-ray band spectra. Detailed considerations of band structure have so far mostly been limited to x-ray photoemission spectroscopy (XPS) and soft-x-ray spectroscopy (SXS) of light metals. Copper, lying together with the first-row transition metals and at the same time being a noble metal, has also been devoted much study. SXS investigations of polycrystalline samples have been performed.[1-3] Resolved XPS valence-band spectra have also been reported.[4] A discrepancy between SXS and XPS recordings was noted by Hüfner and Wertheim.[5] Copper has formally $10d$ electrons. Although a clear picture of the density of states for the crystalline state has started to emerge[6] some controversy exists as to whether this element should be considered as a transition metal.

The emission band $K\beta_5$ has higher energy than any emissive line in the K series of the $3d$ elements, and corresponds nominally to the quadrupole-allowed transition $4s,3d \rightarrow 1s$. Theoretically, its intensity should be low, and its high, experimentally measured value is usually ascribed to admixtured $4p$ states. The energy difference between β_5 and β_2, corresponding to $4p \rightarrow 1s$, diminishes rapidly as the atomic number Z decreases toward $Z=29$ (Cu). Hence, the K emission band of copper involves formally s, p, and d symmetries for the initial state and should consequently more correctly be designated at $K\beta_{2,5}$. Although core-hole broadening generally must be expected in hard-x-ray spectra, it is of considerable interest to resolve structure due to density of states. Conversely, hard-x-ray spectroscopy (HXS) is an important tool in explicit studies of lifetime effects. We present in this paper evidence for a new low-energy feature in the Cu $K\beta_{2,5}$ profile. Furthermore, an explanation for the variation in the intensity at the high-energy side of the emission band will be proposed. The rest of the spectrum will be interpreted in terms of a one-electron model. The importance of having both high intensity and resolution in x-ray spectroscopy is illustrated by our previous recordings of the emission lines Cu $K\alpha_{1,2}$ (Ref. 7) and Cu $K\beta_{1,3}$ (Ref. 8) which were found to exhibit new features.

II. EXPERIMENTAL METHOD

A detailed description of our two-crystal spectrometer and the principles underlying its use can be found elsewhere.[7,9] The plane view in Fig. 1 shows schematically the applied setting. Radiation from an approximately pointlike source was transmitted through the first crystal, corresponding to the Laue case. Both crystals were elastically bent in specially designed crystal holders to a radius of curvature equal to 400 mm. After bending they very nearly were portions of a cylindrical surface. The radii of the focusing circles were 200 mm. The thickness of the crystals was 0.22 mm with an effectively illuminated area of 30×10 mm^2. Both crystals were, before bending, oriented in such a manner that the $\{111\}$ planes were lying parallel to the surface while the $\{2\bar{1}\bar{1}\}$ planes were normal to it. The actual re-

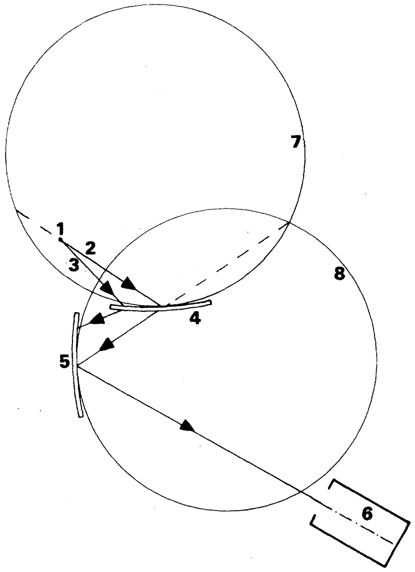

FIG. 1. Schematic plane view of the experimental arrangements. X-rays (2, 3) from a point source (1) (actually a vertical streak-shaped copper anode) are transmitted by means of the Laue mode through the first crystal (4) from the concave side. The various energies of the spectrum are spread out on the concave surface of the second crystal (5). Only the central ray with a relatively well-defined energy is reflected towards the detector (6). (7) and (8) show the position of the focusing circle for the first and second crystal, respectively. (See text and Refs. 7, 9.)

flection order in the first crystal was $4\bar{2}\bar{2}$. The transmitted beam was intercepted by the concave side of the second crystal which deflected it into the opposite direction by means of the $(\bar{3}5\bar{5})$ planes, giving formally an antiparallel setting for the whole spectrometer. The reflection $\bar{3}\bar{5}\bar{5}$ was asymmetrical and the angle of incidence was chosen to be the smaller one. The relatively high Bragg angle at the second crystal (77.62°), made possible because of the antiparallel setting, ensured a narrow instrument function.[9] Before starting to measure the emission band the crystals were adjusted in such a way that the reflection conditions were fulfilled for the wavelength of the central ray. The crystals worked therefore as an effective filter, transmitting one wavelength only for a given setting. Dispersive action was obtained by rotating the second crystal around a vertical axis through the middle of the crystal, while keeping the first crystal stationary. In this way new, well-defined parts of the polished, homogeneous crystal surface were brought into reflection position. The Bragg angle varied accordingly because of the imposed curvature. Although it was, strictly speaking, unnecessary to move the water-cooled scintillator detector, a synchronous rotation around an axis through the center of the focusing circle of the second crystal entailed two advantages: *Firstly*, the range which could be recorded by means of a single setting became substantially extended. *Secondly*, the reflected "monochromatic" beam always hit the same place on the surface of the detector crystal. The detector and the second analyzer crystal were moved by means of a micrometer screw, either manually or with a stepping motor. The width of the detector slit was 5 mm while the spatial width of the beam amounted to roughly 0.08 mm. It is clear that such a width in a detailed fashion will depend on divergence, crystal functions, and focus size. The vertical, streak-shaped copper anode in a sealed, evacuated commercial tube was viewed obliquely, creating an approximate line focus of dimensions 8×0.04 mm^2 when the take-off angle was 6°. This angle was varied within the approximate limits 4°–12°. In spite of having high intensity because of focusing, geometrical broadening of the spectra was found negligible because of the small effective focus size. The applied Siemens generator had a stability of 0.03% and the counting time ranged from 0.5 to 4 min at each measuring point.

III. INTENSITY DISTRIBUTION

The K emission band of copper has been measured by various authors. In addition to older recordings[10] the most reliable studies seem to be those of Nikoforov and Blokhin[11] and Nemoshkalenko *et al.*[12] The more or less accepted shape is as follows, when starting at the low-energy side: After an initial steep rise the peak diminishes and flattens out. Afterwards—near the Fermi edge—the intensity falls abruptly. This has been interpreted as the presence of a more or less hidden two-hump structure, at least after deconvolution. It has even been claimed that the second peak has been observed directly.[12] Therefore, what was expected when starting to measure the emission band with our curved-crystal spectrometer was two peaks with a total halfwidth somewhat narrower than previously reported. The setup used in the beginning did not completely correspond to the favorable arrangement described in Sec. II, with asymmetrical reflections in the second crystal and the source located near the focusing circle. In sum, ten recorded scans did not result in the postulated two-peak structure despite the fact that the intensity and the calculated width compared favorably with other measurements. Instead it was noted that the Auger broadening apparently had a very weak convex appearance.

These introductory recordings were later repeated 12 times with the much better setting described in Sec. II. Furthermore, a new series of measurements consisting of eight scans were later initiated, this time with the help of an automatically operated stepping motor which allowed more measuring points and longer counting times. Figure 2 is representative of all these scans. The intensity at the peak is seen to be 26 000 counts/4 min. Only Nikiforov and Blokhin give the peak value of their counting rate which turns out to be approximately 3% of our value. The energy scale is established with the aid of the treatment given elsewhere[9]; this way of calculating energy separations gives correct values when applied to $K\alpha$ doublets. The spectrometer was set for the emission band itself with $\beta_{1,3}$ as an anchoring point. The nonlinearity across the band is negligible. The uncertainty for the energy scale is estimated to amount to roughly 8%.

Feature 1 is mainly due to Auger broadening. The intensity increases rapidly at 2, which corresponds to the bottom of the band. No evidence for any systematic variation was found here. Feature 3 is interesting in so far as it demonstrates a deviation from a Lorentzian fit for feature 4, the main peak. Detail 4 appeared always as a relatively sharp peak in the recordings, in fact, somewhat sharper than expected from the core-hole width. To the authors' knowledge structure 3 has not been resolved in any previously published K emission band. The shape reproduced by Meisel *et al.*[13] is believed not to be correct. The effect of 3 is to make the main peak asymmetrical, since the upper part of the low-energy side definitely becomes convex. This is even more clearly shown when using a better energy scale, as in Fig. 5(c) which shows an independent scan. After the slightly concave slope 5 the intensity becomes abruptly lower at 6 and reaches plateau 7. The gentle fall 8 stretches out for a considerable distance beyond 7. Details 1–8 were present in all the curves. It can be mentioned that some of the manually recorded spectra, together with three of those

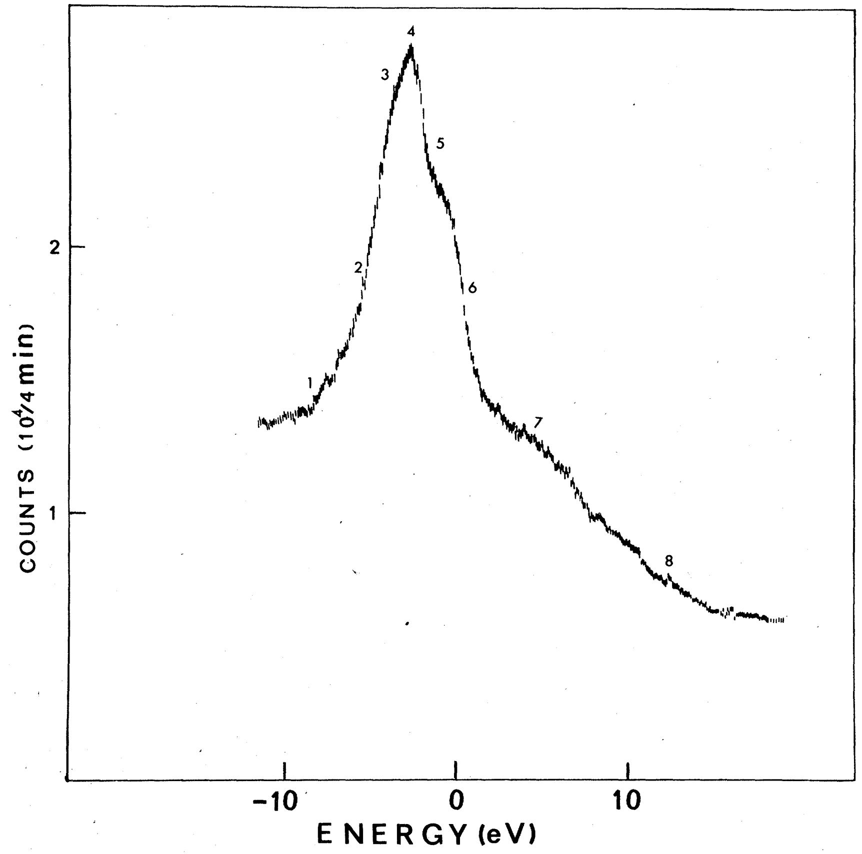

FIG. 2. An overall view of a representative step scan showing the $K\beta_{2,5}$ spectrum of copper as recorded with the curved-crystal spectrometer. Total counting time at each measuring point for this particular scan was 4 min and the current and voltage were 24 mA and 30 kV, respectively. Features 1–8 are discussed in the text. The zero point corresponds to the first inflection point of the absorption curves in Figs. 3 and 4.

scanned by means of the stepping motor, in addition exhibited a very weak satellite at 1. Its width amounted roughly to 5–6 eV, and the high-energy side was located 8–9 eV below the Fermi edge. Some evidence for plasmon formation in the M-band spectrum[3] of copper has been put forward by assuming that the energy and the relative strength is given by the analogous light-metal case. The possibility of plasmons in association with the line spectra $K\beta_{1,3}$ in $3d$ transition metals has also been studied.[14] Although the relative location of our feature is in approximate agreement with the characteristic energy-loss peak (7.6 eV) of copper[15] the reasonable possibility of plasmons will be omitted from consideration because we must take into account that this detail, as distinguished from the rest of the structure, may be a consequence of a slightly fluctuating background intensity. We discuss first 6, 7, and 8 and compare afterwards the band with density-of-states calculations and XPS recordings.

IV. DISCUSSION OF THE HIGH-ENERGY STRUCTURE

Feature 7 can be readily identified with the structure traditionally known as $K\beta'''$. In one case[11] it was thought that this satellite consisted of two separate components called $K\beta'''_{(1)}$ and $K\beta'''_{(2)}$. No satisfactory account of the origin of $K\beta'''$ has, to the authors' knowledge, been put forward. It was discovered during the measurements that its relative intensity clearly depended on the take-off angle and the tube voltage. Hence, the hypothesis that it was simply caused by selective absorption of radiation in the anode was tested. Curve (a) in Fig. 3 shows the Cu K absorption band $\mu = \mu(E)$ as a function of energy E, measured by Yeh and Azároff.[16] This shape is well established. An attempt has been made to put the coefficient on an absolute scale. The values decided upon are taken from the recordings of Sørum[17] and Hubbell *et al.*[18] The scale is usually somewhat uncertain in the edge region of most elements, but this will not affect the final conclusions. Curve (b) shows the absorption factor ($=\exp[-\mu(E)t]$) for radiation in the copper target. It was assumed that an effective depth z_e for the electrons exists and that all radiation originates in this layer. Reliable measurements of penetration depths and/or relevant Monte Carlo calculations of electron paths are in general scarce. The applied value at a voltage of 30–40 kV, $z_e = 0.5\ \mu\text{m}$, was estimated by means of a published study[19] of electron penetration in copper. The x-ray path t in the expression for the absorption factor depends on the take-off angle α via the relationship $t = z_e/\sin\alpha$. The resulting curve in Fig. 3(b) is based on the value of $\alpha = 6°$. It is seen that the absorption factor is practically constant and near unity up to 5 eV to the left of the first inflection point, or the Fermi level. It drops rapidly subsequently and reaches approximately the value of 0.5 at the $4s$-symmetry region.[20] Beyond this region it experiences a further drop because of permitted transitions to empty $4p$ states. Clearly, these steep falls will affect the intensity, as will the hump. In Fig. 4 is shown the result of a scan over the high-energy side of the band when inserting a copper foil with thickness 0.008 mm between the tube and the first crystal. As a matter of fact, the satellite structure thereby becomes more pronounced, while the general background intensity becomes substantially lower. The peak intensity of the band, however, is not seriously affected. Plotting the logarithm of the intensity ratios into Fig. 4 yields a curve (circles) which is in approximate agreement with the corrected and more carefully measured one

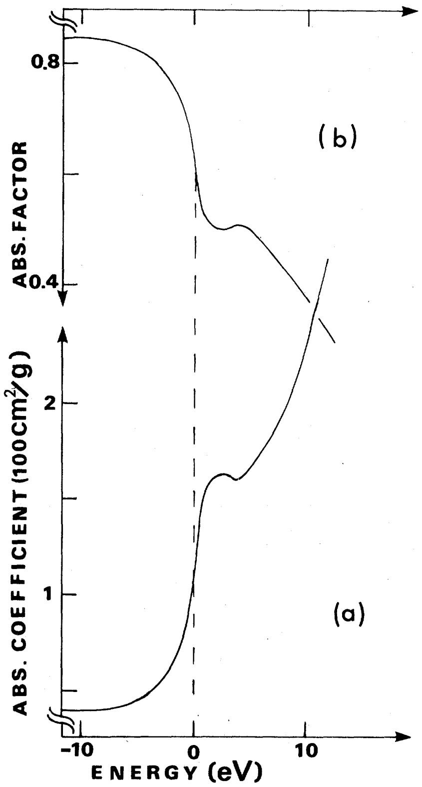

FIG. 3. K absorption band of copper (a), as measured by Yeh and Azároff. (Taken from Ref. 16). The calculated energy dependence of the dimensionless absorption factor corresponding to our experimental conditions is shown in (b). The absolute value of the ordinate scale in (a) is based on data given by Refs. 17 and 18, and the length of the x-ray path in (b) is estimated with the aid of the Monte Carlo simulations of Ref. 19.

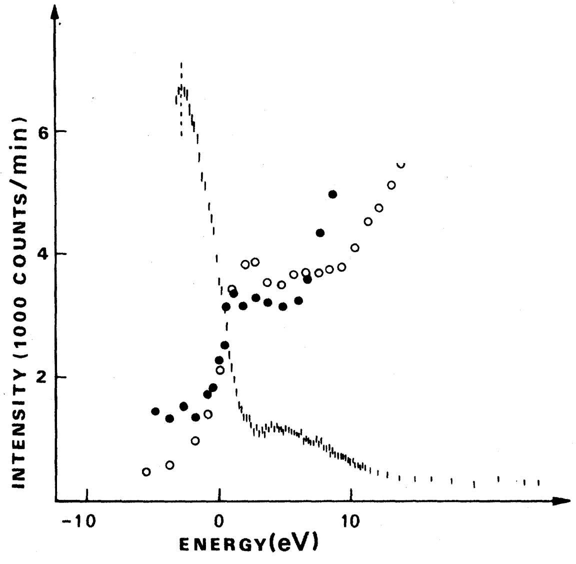

FIG. 4. High-energy side of the K emission band (vertical bars) of copper when inserting a copper foil with a thickness of 0.008 mm into the beam. The uncorrected absorption coefficient (arbitrary units) is assumed to be given by the logarithm to the intensity ratio (circles) when measuring with and without the foil in each point. The third set of points (filled circles) shows the energy dependence of the intensity ratio I_{35}/I_{20} where I_U is the x-ray intensity resulting from the tube voltage U (kV). The zero point corresponds to the first inflection point of the absorption curves.

in Fig. 3(a). The measured voltage dependence of z_e constitutes a final criterion for the correctness of this interpretation of the structure $K\beta'''$. The band was recorded at 40, 35, 30, 25, and 20 kV, and it was noticed that the high-energy structure climbed. The simple proportion $I(E)/I'(E)$ should approximately reproduce the absorption-edge structure, as shown by Liefeld[21] and Hanzeley and Liefeld[2] in studies on self-absorption effects in SXS. $I'(E)$ is here the high-energy profile measured with a voltage not much above the excitation voltage while $I(E)$ is recorded with a much higher voltage. Unfortunately, the lowest possible voltage which could be set with the applied generator was 20 kV,[22] more than twice the energy of the K absorption edge of copper. Nevertheless, the edge structure of such an intensity ratio, also plotted (filled circles) in Fig. 4, is evident. The shape is found to resemble the conventionally measured one.

We finally consider in more detail the contributions to the observed intensity: (i) the bremsstrahlung background, (ii) the high-energy tail of $K\beta_{1,3}$, (iii) the core-hole-broadened high-energy part of the band. (i) can be assumed to be approximately constant. Both the absolute value of the intensity due to (ii) and its change are small so that if it depended upon (i) and (ii) alone the resulting intensity distribution would look something like Fig. 3(b). The fact that our spectra deviate a little from this shape can be ascribed at least partly to (iii). Unfortunately, an exact correction of the measured profile is difficult because of the uncertain absorption coefficient, the unknown effective penetration depth of the electrons, and the difficulties inherent in estimating the relative contribution of fluorescence and scattered background. Despite this, a closer inspection of Fig. 2 shows that the high-energy side of the band must suffer an extra amount of broadening for the results to be reasonable, i.e., the intensity due to (iii) is not sufficient. This can be visualized as a featureless "foot" or tail at the high-energy side of the Fermi level, on the order of a few eV wide, which increases the core-hole-broadened intensity. Additional evidence comes from the fact that feature 8 was found always to be concave, even after correcting for the declining intensity of $\beta_{1,3}$, while the high-energy part of Fig. 3(b) is weakly convex. It appears perhaps more reasonable to ascribe the origin to incomplete relaxation[23] rather than to double-ionization satellites,[24] since the shape probably resembles a tail. The intensity amounts roughly to 20–30% of the peak in the emission band itself. This may also serve to explain why the two curves in Fig. 4 deviate at higher energies: Reducing the voltage does not only reduce the penetration depth of the electrons, but affects the probability for the processes behind the tail as well. We conclude therefore that by permitting the high-energy side of the emission band to suffer extra "broadening" it is unnecessary to ascribe the structure to variations in the emitted intensity itself. Feature 6 in Fig. 2 is due to the first rise of the absorption curve, 7 corresponds to the hump, and 8 to the second rise in the same curve. Similar conclusions may be applied to other elements. An overall survey of K emission and absorption spectra for the neighboring elements of copper is given by Sandström.[10] A study of the edge region of the depicted curves in that work shows that a variation of the absorption coefficient apparently always overlaps with a similar variation in the emitted intensity, so that the above explanation for copper very well may also be qualitatively valid for iron, cobalt, nickel, and zinc. Gallium is an exception, having instead an extremely low intensity at the high-energy side of the band. That fits also into the interpretation scheme since the absorption spectrum has a broad maximum here, predicting no structure. However, it is important to note that a varying absorption coefficient does not exclude the presence of distinct high-energy satellites. In the case of gallium, for instance, there was more recently reported a structure[25] 10 eV above the Fermi level which, if consistent, cannot be explained in this way. In those cases, however, where there are variations in intensity and absorption at the same energy positions, special steps should always be taken in order to ensure that selective absorption is absent. An additional problem here is that true satellites in the K spectrum may be suppressed, as noted long ago by Hanson and Herrera.[26] Photon-excited spectra of high intensity and resolution can be useful since they contain no bremsstrahlung background. Such experimental conditions may therefore be advantageous also when searching for plasmons at the low-energy side of the K bands of the $3d$ elements. On the other hand, the x-ray path t is in general considerably longer, thus perhaps rendering a correct interpretation of high-energy structure more difficult. In addition is the fact that the intensity of the high-energy structure, as measured before absorption, must be expected to be significantly modified when going over to photon excitation, at least when the kinetic energy of the ejected photoelectron is not very high.

If corrected for absorption there is no doubt that our electron-excited K emission band for copper exhibits a more pronounced high-energy tail than the similar spectra of the typical light elements. This is in agreement with the much shorter lifetime of the $1s$ vacancy in copper: The x-ray transition occurs before the shake-up cloud of low-energy electron-hole pairs at the top of the band has time to relax completely. This mechanism may be responsible for the observed fine structure[8] in the x-ray line Cu $K\beta_{1,3}$ as well. Although using a purely atomic model, LaVilla[27] demonstrated by means of Hartree-Fock calculations that the presence of a spectator vacancy in the M shell causes the transition $1s3p^63d^9\ {}^{1,3}D \to 1s^23p^53d^9\ {}^{1,3}PDF$ to display a variety of emission lines. The experimental data for the Cu $K\beta_{1,3}$ line is at least qualitatively in agreement with the calculated energy differences. An experimental absorption correction of the $K\beta_{2,5}$ spectrum can be achieved by increasing the take-off angle substantially. Since the resolving power of our spectrometer depends on the sample size, this can possibly be done by means of a copper micro focus, which preserves the resolution. Another way would be to reduce the kinetic energy of the electrons by using equipment which allows voltages between 9 and 20 kV to be set. A purely numerical correction is also possible, but is hampered by the uncertain effective excitation depths in the sample and the absolute values of the absorption coefficient (including scattering) together with the lack of theoretical expressions for the tail.

V. COMPARISON WITH DENSITY-OF-STATES AND XPS DATA

The question of whether x-ray spectra involving conduction electrons mainly reflect the density of states or the many-body effects have been much discussed. Although various approximate solutions indicate that the many-body influence is most clearly seen near the Fermi edge, it is generally believed to influence the whole emission band. Thus the Mahan[28] enhancement and the Anderson[29] orthogonality catastrophe, as discussed and unified by Nozières and De Dominicis,[30] have been calculated exactly[31] for an independent-electron metal containing a relatively small ($\leqslant 10^6$) number of conduction electrons. However, it is so far not completely clear how these ideas should be applied when analyzing HXS data. The assumption of an infinitely long lifetime for the core hole, with sufficient time for the conduction electrons to respond to the suddenly formed potential before x-ray emission, is not self-evident. Furthermore, the density of states will be strongly influenced by partial states of d and possibly f symmetry, depending on the atomic number. As demonstrated recently by Citrin *et al.*[32] a complete interpretation of SXS data from high-metal spectra require a systematic inclusion of density-of-states effects, transition probabilities, lifetime effects, phonon broadening, spin-exchange effects, and experimental broadening. Indispensable additional factors are the threshold exponents and the various many-body features in the rest of the spectrum below the Fermi edge. Although Grebennikov[33] *et al.* have considered the many-body response in a general narrow-band metal as a function of the band filling and the lifetime of the core state, a necessary starting point for interpreting the copper K emission band must be the density of states.

Assuming that the main part of the emission band is affected by the excitation of the $1s$ orbital only via core-hole broadening, formally given as a convolution, we therefore investigate tentatively whether the recorded profile is in reasonable agreement with other band studies, i.e., whether a one-electron interpretation is adequate. There exist unfortunately no K band calculations for copper, such as those of Goodings and Harris[34] for the M case, which takes transition probabilities into account. In Fig. 5 is the measured K emission band (c) compared with the uncorrected XPS spectrum (b), as measured by Wertheim *et al.*[4] and the density-of-states curve (a) of Janak *et al.*[6] The exact position of the bottom of the recorded emis-

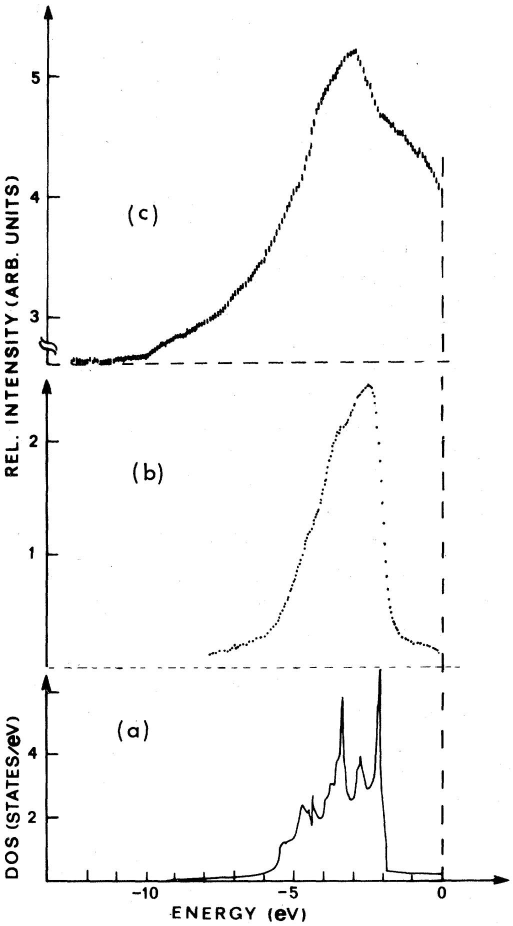

FIG. 5. Comparison between the density of states (DOS) calculations (a) of Ref. 6, the XPS data (b) of Ref. 4, and one of the experimentally recorded K emission bands (c). The curves are brought to the same energy scale, and the position of the Fermi level $E_F = 0$ eV is taken as the first inflection point of the absorption curves in Figs. 3 and 4.

sion band is not easily determined even after correcting for the bremsstrahlung and the Auger broadening. The choice in Fig. 5 has been to subtract only the constant background. The first inflection point of the absorption curve from Fig. 3 is taken as the position of the Fermi energy ($E_F = 0$ eV). It so happens that this corresponds very nearly to the position where the intensity is half of its peak value, but this coincidence has no physical implications. The location of E_F in the spectrum is very similar to the energy value reproduced, for instance, by Burdick,[20] but seems to be different from the choice of Meisel *et al.*[13] Although our energy scale may have a finite uncertainty the relative location of the absorption edge and the high-energy emission edge should be correct. The region within a couple of eV below E_F is suppressed relative to the rest of the curve because of absorption, but its general shape is not seriously affected. The high-energy tail may tend to compensate somewhat for the increased absorption. The depicted uncorrected scan (c) is independent of the one in Fig. 3. It is clear from Fig. 5 that the K emission band is broader than both the density-of-states curve and the XPS recording. This is due to core-hole broadening and the experimental smearing. In order to estimate the contribution from the latter it is assumed that the analogous diffraction curves for two plane crystals could be used as a first approximation for the instrument function. A numerical folding of the two relevant Darwin-Prins curves yields the value 0.03 eV for the experimental window when neglecting geometrical contributions. This value is much less than the core-hole width and the experimental uncertainty of the energy scale. The theoretical width of the 1s vacancy is 1.5 eV.[35] There is no core-hole broadening in curve (b), but the experimental smearing is instead important since it is reported to be equal to 0.55 eV. Despite this the width of (b) is definitely not significantly broader than (a). This may be due to the fact that the XPS technique probes the electronic structure at the surface, and thereby includes contracted bands, which is advantageous when the aim is to study surface effects. Although the penetration depth of the photoelectrons may be controlled to some extent, it is clear that this may be a disadvantage when investigating the bulk electronic structure. A d-band narrowing near the surface of polycrystalline copper has been explicitly observed by Mehta and Fadley.[36] The SXS and especially the HXS technique are generally not bothered by effects of this type, and are, therefore in spite of other shortcomings, well suited for studies of the bulk electronic structure.

A comparison between the experimentally measured M and L emission bands of copper was given elsewhere.[1,3] The L emission band[2] of copper is narrower than the K band as found also for other 3d elements. The M band, however, is broader than the L band. Such differences are caused by unequal experimental resolution, different core-hole widths, and unequal probing of symmetry. The M emission band is definitely broader than the theoretically calculated valence band width. Furthermore, it is well known that correcting for various broadening mechanisms does not bring the measured K emission bandwidth into agreement with the theoretically calculated valence band width.[11] This must be due to the fact that the overall effect of self-absorption has lead to exaggeration of the absolute value and the fall in intensity due to the high-energy tail of $\beta_{1,3}$, with the effect that the intensity at the high-energy side of the emission band erroneously has been included. The overall widths of (a) and (c) in Fig. 5 are seen to be in reasonable agreement when allowing for Auger broadening and lifetime widths in (c). The lifetime widths of holes in the valence band of a copper single crystal have been measured[37] by means of angle-resolved photoemission spectroscopy and polarized synchrotron radiation. The width of a $3d$ hole was found to increase from 0.2 to 0.5 eV when the energy decreased from 2 to 5 eV below E_F. In the energy range 10–7 eV below E_F the Auger broadening for our electron-excited polycrystalline sample is seen to be significantly greater than 0.5 eV when taking the core-hole width of 1.5 eV into account. The fact that there was no systematic behavior in the intensity variations in this range, corresponding to detail 1 of Fig. 2, is probably due to the featureless density of states (a) of predominately s-p symmetry, although it is a small possibility that the absolute level of the net intensity, after all, perhaps was too small. Essentially the same conclusion holds for the region 7–5 eV (feature 2 in Fig. 2). The sharp increase in (a) at 5.5 eV below E_F is not reflected in (b) and (c). In the latter curve this is—apart from the lifetime smearing—a result of the increased d character of the band, and the correspondingly low transition probability. The curve portion around 4 eV (feature 3 in Fig. 2) corresponds within some fraction of eV to similar variations in (a) and (b), and can be interpreted as arising from pronounced density-of-states variations, strongly modified and smeared out because of the transition probabilities and lifetime broadening, respectively. The peak at 3.1 eV, which deviates from a Lorentzian fit, is seen to correspond to a minimum in (a) and to a position to the left of the main peak in (b). The latter is located at 2.5 eV, also in a minimum. Since there are no published calculations for the K emission band of copper it is difficult to predict how transition probabilities and symmetry effects modify the shape of (a) when going to (c). However, peaks in density-of-states curves do not automatically yield intensity maxima at exactly the same energies, as shown, for instance, by the calculations of Szmulowicz and Pease,[38] who arrived at the unconvoluted K emission band of nickel by means of an augmented-plane-wave method. The density-of-states curves of nickel and copper have many common traits. In the nickel case the theoretical K emission band reflects mainly the p partial density of states, except for a few s,d levels causing some of the less pronounced minima. The position and shape of the main peak of (c) can therefore probably be explained as a lifetime convolution of the copper p band, and can consequently still fit into a one-particle picture. For essentially the same reason the relatively sudden decrease in the intensity just at the high-energy side of the main peak—feature 5 in Fig. 2—is not due to the sharp fall in the density of states which occurs at 2.1 eV in (a) and which has a strong d character. The shoulder at a couple of eV below E_F is in agreement with the constant behavior of both (b) and (c). The intensity scale of Fig. 2 is a bit misleading. The shoulder has not a high absolute intensity, but instead feature 4 is substantially suppressed, again because it corresponds to an energy position dominated by d states. Because of the constant behavior of (a) in Fig. 5 it is difficult to imagine a second peak[12] in (c) near E_F; correcting for increased absorption and smearing will only make the plateau longer and the Fermi edge steeper. Broadening due to interference between phonons[39] and the core hole appears to be of minor importance since the decrease in the intensity in the region 2.5–0 eV in Figs. 2 and 5 can be completely explained by the estimated variation of the absorption factor (b) of Fig. 3 when also including the lifetime broadening.

VI. CONCLUDING REMARKS

The experimental setup of the two-curved-crystal spectrometer has thus, due to high intensity and resolution, made it possible to clarify some aspects of the Cu $K\beta_{2,5}$ spectrum. It is suggested that the deviation of the main peak from a Lorentzian fit can be explained as a convolution of the p band, possibly with structure due to s,d levels superimposed. Instead of a distinct high-energy satellite $K\beta'''$ the measured data indicate that selective absorption of a relatively broad and featureless intensity tail, located above the Fermi edge, can explain the change in the shape when varying the high voltage and/or the take-off angle. Given sufficient intensity and resolution it is generally believed that there is considerable information content in the K emission band of elements with medium atomic numbers,[40] despite the fact that selection rules and lifetime effects severely modify the profile and obliterate parts of the structure, respectively. Such measurements can also be done, utilizing polarized x rays as excitation radiation and oriented single crystals as samples.

Although apparently nothing prevents one from interpreting the copper spectrum in terms of symmetry and density of states, a definite conclusion must await the result of calculations of the emitted intensity, as typified by the theoretical K emission band of the neighboring element nickel.

Apart from checking the relationship between a one-electron interpretation and the more controversial many-body features inside the band, such a treatment is interesting also from the point of view of estimating the Auger broadening in the bottom of the band and the incomplete relaxation of created hole-electron pairs near the Fermi[41] edge in the limit of short-lived core states.

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