Chemical Shift Effect in Inner Electronic Levels of Cu Due to Oxidation

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THE energies of some inner electronic levels of Cu with respect to the Fermi level have been studied in metallic copper and in the cuprous and cupric oxides. The basis for these studies was the magnetic analysis of photoelectrons produced by x-radiation.[1] In all cases a shift has been observed towards greater binding energy on going from the metal to the oxide, this shift being greatest for the $1s$ and $2s$ levels in the cupric oxide (Fig. 1). The observed K level shift of CuO, taken together with the shift, reported in an earlier investigation,[2] of the x-ray K absorption edge, gives a gap between the valence and conduction bands in CuO of 0.6 ev. This is in agreement with the value 0.3 ev deduced from conductivity data.

Further, a line in the KLL Auger spectrum ($KL_{II}L_{III}$, assuming pure $j-j$ coupling) from metallic copper has been compared with the corresponding line from CuO. The line from the oxide has been found to be somewhat lower in energy, in agreement with the shifts observed for the K and L levels. A change in the width and relative intensity of the Auger line on going from the metal to cupric oxide indicates that the Auger yield depends on the chemical composition of the source.

The results of the investigation on CuO are summarized in Table I. A detailed report will be published.[3]

TABLE I. Energy shifts, Cu→CuO.

Level	Energy shift (ev)
K	$+4.4\pm0.5$
L_I	$+4.4\pm1.0$
L_{II}	$+3.3\pm1.5$
L_{III}	$+2.5\pm0.8$
Auger line	-1.0 ± 0.3

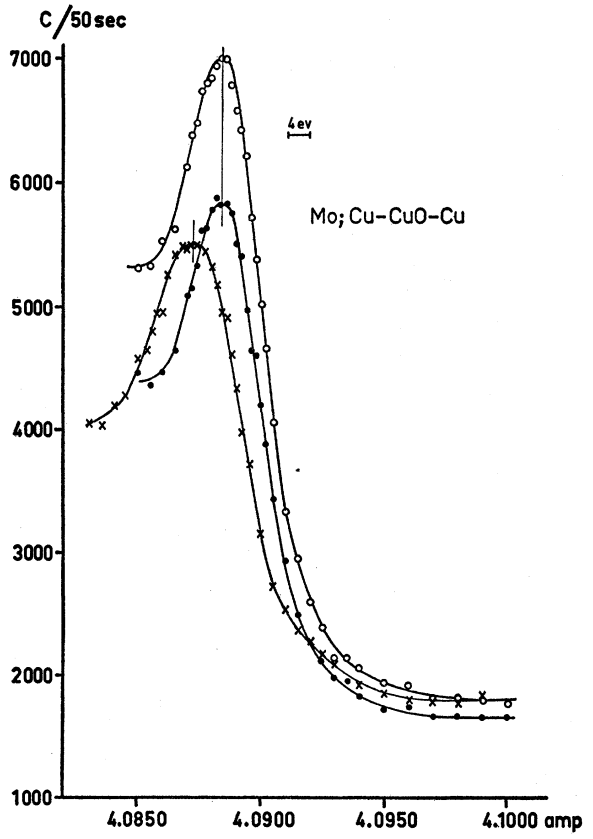

FIG. 1. Cu K (Mo $K\alpha_1$) photo-lines. The curves plotted with open and filled circles are the photo-lines of metallic copper. The photo-line of the cupric oxide, which is plotted with crosses, falls at a lower spectrometer current, indicating a higher K binding energy in the oxide.

[1] Sokolowski, Nordling, and Siegbahn, Arkiv. Fysik. **12**, 301 (1957).
[2] V. H. Sanner, thesis, Uppsala, 1941 (unpublished).
[3] Nordling, Sokolowski, and Siegbahn, Arkiv. Fysik. (to be published).

Superconducting Energy Gap Inferences from Thin-Film Transmission Data

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GLOVER and Tinkham[1] (GT) have recently reported measurements on the transmission by superconducting thin films of radiation with photon energies from 0.3 to 40 kT_c. Their data showed a rise to maximum transmission in the region of 3–5 kT_c and a decrease to normal state transmission at high frequency. The existence of a prominent maximum is not *ipso facto* evidence for an energy gap. The London theory and its modification by Pippard predict an approach to transparency at high frequency. The maximum may, therefore, be the result of the processes which produce superconductivity and those which cause an approach to normalcy at high frequency. Whether this approach to normalcy is due to the excitation of electrons across an energy gap requires a quantitative examination of the data.

The GT analysis was through a complex conductivity $\sigma=\sigma_1-i\sigma_2$ which, when normalized by the normal-state conductivity σ_N, appeared to be a universal function of $\hbar\omega/kT_c$. It is the σ_1 which is reponsible for absorption and GT sought, as evidence of a gap, a σ_1 rising sharply with photon energy at a specific frequency. They found a satisfactory fit to their transmission data for a σ_1