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 1*s* and 2*s* 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

[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[2] V. H. Sanner, thesis, Uppsala, 1941 (unpublished).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).

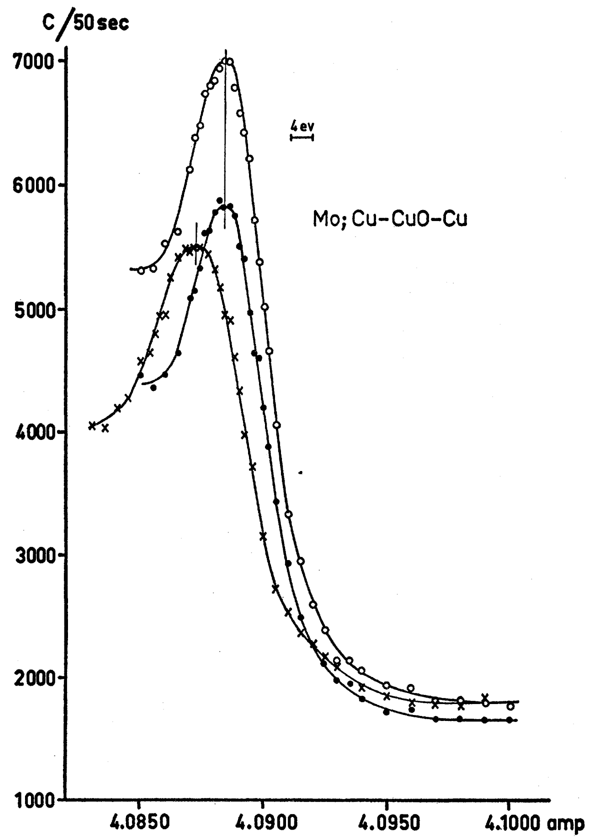

FIG. 1. Cu *K* (Mo $K\alpha_1$) photo-lines. The curves plotted with open and filled circles are the photo-lines of metallic copper. The photo-line of the cupric oxide, which is plotted with crosses, falls at a lower spectrometer current, indicating a higher *K* binding energy in the oxide.

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

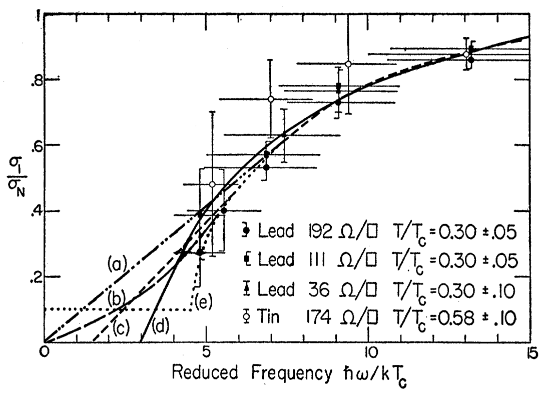

FIG. 1. Various choices of σ_1/σ_N compared with experimental points from GT, reference 1, Fig. 6. They obtain these points directly from transmission data by neglecting the influence of σ_2 whenever $\omega/\omega_c>5$. Their justification on the basis of low-frequency data and their choice of σ_1 [curve (d)] applies equally well to any of the curves shown.

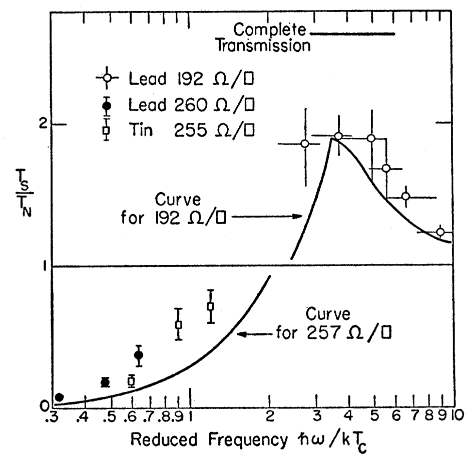

FIG. 3. Comparison between low-temperature transmission data and the theoretical curve calculated from Bardeen and Mattis, reference 5, for $T=0°$K.

represented by curve (d) of Fig. 1 and, allowing for the possibility of slight tailing, concluded that the position of the effective cutoff must lie between 3 and 4 kT_c. In view of specific heat data,[2] most readily interpreted in terms of a gap of 1.5 or 3.0 kT_c, they accepted this as evidence for an energy gap $E_g\approx 3kT_c$.

In their paper, GT failed to consider the possibility that their data were sufficiently insensitive to the choice of σ_1 that equally good fits to the data could be obtained with functions indicating very different gaps or not suggestive of a gap at all. I have examined, using the GT technique, the fit to data resulting from other simple representations of σ_1. The range of functions capable of producing good fits to the GT data is illustrated by those reproduced in Fig. 1. The merits of the various choices may be judged by the relative match to the data of the corresponding transmission curves in Fig. 2.

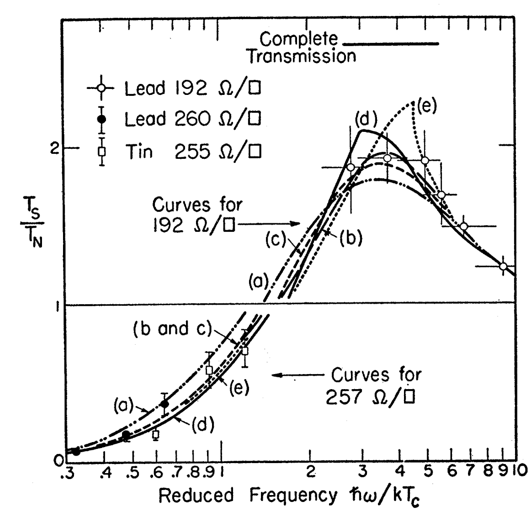

FIG. 2. Transmission ratio curves corresponding to the choices of σ_1 in Fig. 1, and an optimum choice of the coefficient of the conductivity σ_2^L (see reference 1). The horizontal lines through data points represent, not errors, but the half-power widths of the continuous spectrum, so that each measurement is an average over a region of the appropriate curve.

All of these, including (a) and (b),[3] which cannot be associated with an energy gap at all, give transmission curves of the same general shape found experimentally by GT. Even if curves (a) and (e) are rejected as unsatisfactory fits to the transmission data, it appears possible to conclude from their data *only* that *if* there is an energy gap it is not greater than $4.5kT_c$.

In addition to the question of whether the transmission data imply, *per se*, an energy gap, it is interesting to examine the consistency between the GT transmission data and the theory of Bardeen, Cooper, and Schrieffer.[4] This comparison is shown in Fig. 3 where the theoretical curve is calculated from expressions of Bardeen and Mattis.[5] At angular frequencies greater than $4kT_c/\hbar$ the agreement is comparable to that of the empirically fitted curves of Fig. 2, but is much poorer at lower frequencies.[6] Considering the fact that the theoretical curve of Fig. 3 involves no adjustable parameters the agreement is, however, more striking than the discrepancy. It is worth noting that at angular frequencies $<2kT_c/\hbar$, very large corrections for interference effects had to be made by GT to obtain the points shown and a large systematic error in this region would not be surprising. To the extent that the GT data may be judged a confirmation of the Bardeen theory, these can be considered as a secondary evidence for the gap implied by the theory, i.e., $3.5kT_c$. They do not, as shown in Figs. 1 and 2, constitute primary evidence for an energy gap.

I would like to thank M. A. Biondi, M. P. Garfunkel, and T. Holstein for helpful discussions of this paper, and R. C. Bollinger for his computations of the

Kramers-Kronig transforms of the selected σ_1/σ_N functions required for deriving the associated transmission curves shown in Fig. 2.

[1] R. E. Glover, III, and M. Tinkham, Phys. Rev. **108**, 243 (1957).
[2] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956); W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).
[3] These curves cannot be ruled out by the result of E. Fawcett, [Proc. Roy. Soc. (London) **A232**, 519 (1955)]. He finds, for bulk tin, that $R/R_N \to 0$ at $T=0$ for $\omega = 0.5kT_c/\hbar$, but the surface resistance is so limited by the superconducting penetration depth that it is unlikely that a value of $\sigma_1 < 0.04$ would have been noticeable.
[4] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).
[5] J. Bardeen and D. C. Mattis (to be published).
[6] The difference at low frequencies is essentially the same as that pointed out by Bardeen, Cooper, and Schrieffer (reference 4) in their reference 27.

Superconducting Energy Gap Inferences from Thin-Film Transmission Data*

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Since publication[1–3] of results on far-infrared transmission experiments with superconducting films, questions have been raised[4] concerning the justification of the conclusion that there is a gap of width $E_g = \hbar\omega_g \approx 3kT_c$ in the electronic excitation spectrum. This conclusion was based on an extrapolation to zero of data on σ_1/σ_N, the real part of the reduced conductivity. For $\hbar\omega > 5kT_c$ the interpretation of the experimental results is straightforward. It was possible to measure σ_1/σ_N in the range from $36kT_c$ to $5kT_c$ where its value fell from 1.0 to about 0.3 (Fig. 6 of reference 3). In the low-frequency end of this range, σ_1/σ_N was found to be falling very rapidly, and extrapolation indicated an intercept between 3 and 4 kT_c. This behavior suggested a region of very sharply diminished density of states (or a gap) having a width between 3 and 4 kT_c. The data which lead to this conclusion were obtained from films of two different metals with varying thickness, purity, and degree of anneal, indicating that the behavior was inherent in superconductors and was not strongly effected by strains, purity, or surface condition of the samples used. To our knowledge, this was the first indication of a gap of $\approx 3kT_c$ rather than $\approx 1.5kT_c$. Our analysis was based directly on the infrared measurements for $\hbar\omega \gtrsim 5kT_c$ where σ_1 can be determined unambiguously. Unlike the analysis suggested in reference 4, it does not depend critically on our microwave measurements, which are less dependable due to the necessity of introducing large corrections for standing-wave effects.

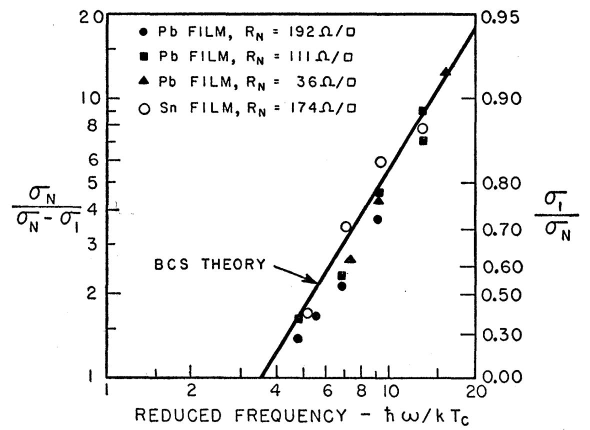

Fig. 1. Logarithmic plot of data (from Fig. 6 of reference 3) showing the onset of absorption expressed in terms of σ_1/σ_N, the real part of the reduced conductivity. This absorption edge is attributed to absorption across an energy gap in the superconducting state. The solid line is the prediction of the theory of Bardeen, Cooper, and Schrieffer (reference 8).

We would like here to reconsider the problem of extrapolating σ_1/σ_N to zero. In making such an extrapolation one could proceed purely empirically to find a way of plotting which would make the data fall on a straight line. This could then be extrapolated to an intercept. However, theoretical considerations help in choosing a suitable form. An elementary argument for a simple gap[2] in the density of states function would suggest $\sigma_1/\sigma_N = 1 - \omega_g/\omega$. The observed rise was found to be faster than this, more like $1 - \omega_g^2/\omega^2$. This was attributed to a humping up of states displaced from the gap to either side. Such humping is also required to explain the observed specific heat[5,6] and the nuclear relaxation data.[7] Subsequently, Bardeen, Cooper, and Schrieffer[8] have proposed a detailed theory which has enjoyed remarkable success in explaining most of the phenomena of superconductivity. This theory predicts the humping of states, and it makes a definite prediction for the shape of the absorption edge, namely

$$\frac{\sigma_1}{\sigma_N} = \left(1 + \frac{\omega_g}{\omega}\right) E(k) - 2\frac{\omega_g}{\omega} K(k),$$

where $\hbar\omega_g = 3.5kT_c$, $k = (\omega - \omega_g)/(\omega + \omega_g)$, and $E(k)$ and $K(k)$ are complete elliptic integrals. This function is fitted within a few percent by the simple approximation

$$\frac{\sigma_1}{\sigma_N} = 1 - \left(\frac{\omega_g}{\omega}\right)^{1.65}.$$

These considerations suggest that the data be plotted in the form $\log[(1 - \sigma_1/\sigma_N)^{-1}]$ *vs* $\log(\hbar\omega/kT_c)$. In such a plot, any function of the form $1 - (\omega_g/\omega)^n$ will result in a straight line, from which ω_g and n may be read off. Data from Fig. 6 of reference 3 are plotted in this way in Fig. 1, and the straight line is the prediction of the BCS theory. Within the scatter (which is of about the same magnitude as the statistical error of the points)