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Compton scattering study of the electronic structure of CuO

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Abstract. The Compton profile (CP) of polycrystalline CuO has been measured using 60 keV γ -rays. In the absence of rigorous theoretical results the obtained data have been analysed in terms of CPs calculated within the framework of the renormalized-free-atom model, employing several wavefunctions for the O 2p state. Compared with $3d^{10}2p^5$, the CP for the $3d^9 2p^6$ configuration was found to be in better agreement with the experimental data. As in MgO, here also Watson's +1 well solution for the O 2p state was found to provide better results than the rest. However, the best results were obtained with a configuration given by $3d^9.42p^{5.6}$. The implications of this are discussed.

1. Introduction

The discovery of high-temperature superconductivity (Bednorz and Mueller 1986) in Cu-based ceramic oxides has revived interest in the study of copper oxides with a view to the fact that an understanding of the properties of these (Cu) oxides may provide a clue to the understanding of the mechanism for high-temperature superconductivity. It has been recognized that the CuO_2 layers in the high- T_c superconductors are responsible for superconductivity. CuO has Cu–O planes which are structurally similar to the CuO_2 layers in high- T_c superconductors. Moreover, the suggestion by some workers (De Jongh 1988, Guo *et al* 1988, Xiang 1988) that a homogeneous mixed-valence state could exist in the CuO_2 layers in the high- T_c ceramic oxides and recent x-ray photoelectron spectroscopy (XPS) observation (Shen *et al* 1987, Ghijsen *et al* 1988, Parmigiani and Samoggia 1988) of a fluctuating charge state in cupric oxide emphasizes the close relationship between these ceramic oxides and CuO. This calls for a thorough understanding of the properties of copper oxides.

Of the two stable oxides of copper, namely cuprous oxide Cu_2O and cupric oxide CuO, the former is relatively better understood. The electronic structure of Cu_2O , determined by XPS, AES and BIS agrees well with the one-electron band-structure calculations whereas those for CuO show strong deviations (Ghijsen *et al* 1988), which have been attributed to electron correlation effects in the open-shell d band of Cu. As mentioned in the previous paragraph, CuO also shows valence fluctuations, which are manifested in the split observed in the O 1s line in the XPS spectrum (Ghijsen *et al* 1988, Parmigiani and Samoggia 1988). In conjunction with the analysis of the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spectra it has been shown that the ground state of the system is an admixture of $3d^9$ and $3d^{10}\text{L}$ (L denoting an oxygen ligand hole), leading to an occupancy of the 3d

levels given by $n_d \approx 9.5$. Since the Compton profile (CP) of such a system is expected to be very sensitively dependent on the average d-electron population, it is tempting to carry out such a measurement in this material.

There are also other reasons behind the present study of CuO. One expects the oxygen ion in CuO to be in the O^{2-} state. As such, a free O^{2-} ion is unstable and is stable only in a crystalline environment. Thus its state is very sensitively dependent on the way that one simulates its surroundings. That is why CuO forms an ideal system to study through a CP analysis. The study of the O^{2-} ion in MgO using CP data (Aikala 1982, Podloucky and Redinger 1984, Fuji *et al* 1986, 1988) is a classic example. When there is valence fluctuation, part of the time the oxygen ion remains in the O^{2-} state. Therefore it is tempting to carry out a CP measurement and to derive some information regarding its charge state using an analysis based on variable occupancy in valence states as done in the renormalized-free-atom (RFA) model (Berggren 1972, Panda *et al* 1987).

In the next section we give a brief description of the experiment which is then followed by a section on the RFA model. The results are discussed in the final section.

2. Experiment

The CuO sample for the present study was a pellet 2.1 mm thick and 25 mm in diameter prepared from high-purity CuO powder. The isotropic CP was measured using 59.54 keV γ -rays from a 3 Ci annular ^{241}Am source. Measurements were carried out at a scattering angle of $176 \pm 1.5^\circ$. The details of the spectrometer and the method of data analysis have been given elsewhere (Mahapatra and Padhi 1982, Pal *et al* 1987). About 50 000 counts/channel were collected at the Compton peak at a gain of about 30 eV/channel. In this sample, multiple-scattering corrections were restricted to double scattering only. Such events were estimated to contribute about 6% of the total intensity under the Compton peak and the corresponding correction led to a 1.3% increase in $J(0)$. The final CP was normalized to the Hartree-Fock (HF) free-atom value of 16.3699 electrons between 0.0 and 7.0 au. This takes care of the fact that there is no contribution due to the 1s orbital of Cu beyond 4.0 au. The experimental CP (table 1) and the HF free-atom CP obtained from the data of Biggs *et al* (1975), of CuO are shown in figure 1. One can see that, beyond 4.0 au, there is excellent agreement between the two.

3. Theory

The RFA model has been described in detail elsewhere (Berggren 1972). In the present case we employ the formalism as applied for LiH (Mahapatra 1986) and TiC (Panda *et al* 1987). However, unlike those calculations, for the valence electrons here we take an ionic wavefunction and renormalize it to the ionic charge in a volume Ω_0 as occupied by the ion in the crystal. The contributions from the positive and negative ions can be calculated separately. For copper and oxygen ions we take 3d and 2p as the valence states respectively. Isotropic CPs for these states were calculated within the framework of the RFA model in the extreme tight-binding limit.

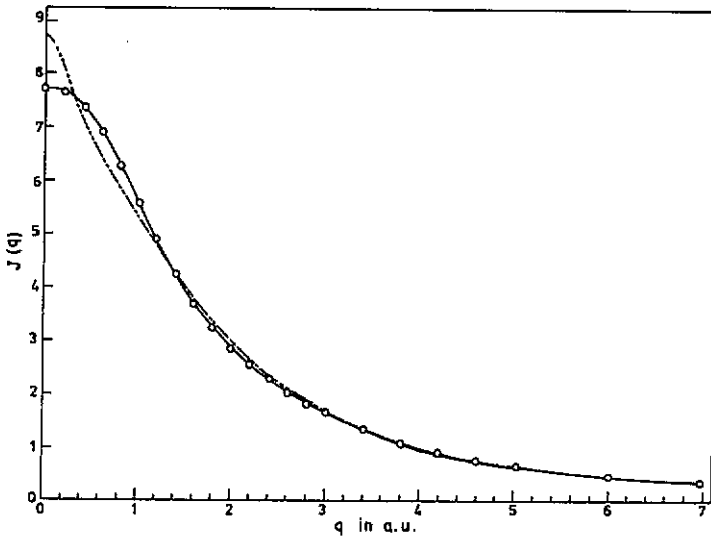


Figure 1. The experimental (—○—) and the HF free-atom (-----) cps of CuO.

In this formalism the Bloch function for a k -value is given by

$$\Psi_k(\mathbf{r}) = N^{-1/2} \sum_g \exp(i\mathbf{k} \cdot \mathbf{R}_g) \chi_l(\mathbf{r} - \mathbf{R}_g) \quad (1)$$

where χ_l represents an atomic orbital centred at site \mathbf{R}_g , the sum extending over all lattice sites g .

The momentum density is given as

$$\rho(\mathbf{p}) = 2 \frac{2l+1}{4\pi} \sum_{k, \mathbf{G}} |R_l(\mathbf{p})|^2 \delta_{\mathbf{p}, \mathbf{k}+\mathbf{G}} \quad (2)$$

where \mathbf{G} is a reciprocal lattice vector and $R_l(\mathbf{p})$ is the Fourier transform of the normalized radial wavefunction $R_l(r)$:

$$R_l(\mathbf{p}) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^{r_0} dr r^2 R_l(r) j_l(pr). \quad (3)$$

Here r_0 measures the region over which the orbital is renormalized and is determined from $\Omega_0 = 4\pi r_0^3$. For the d state, replacing r_0 by ∞ does not seem to change anything; however, for a p state there is a small difference.

Following Berggren (1972), one can evaluate the spherical average of $\rho(\mathbf{p})$ as

$$\langle \rho_l(\mathbf{p}) \rangle = 2 \frac{2l+1}{4\pi} |R_l(\mathbf{p})|^2 \sum_n F_n(\mathbf{p}) \quad (4)$$

where

$$F_0(\mathbf{p}) = \begin{cases} 1 & p \leq p_F \\ 0 & p > p_F \end{cases} \quad (5)$$

and for $n \neq 0$

$$F_n(\mathbf{p}) = N_n [p_F^2 - (G - p)^2] / 4Gp \quad (6)$$

where N_n is the number of reciprocal lattice vectors in the n th shell and p_F denotes the

Table 1. Experimental CP of CuO normalized to 16.3699 electrons between 0.0 and 7.0 au.

q (au)	$J(q)$ (au)	q (au)	$J(q)$ (au)	q (au)	$J(q)$ (au)
0.0	7.716 ± 0.055	0.8	6.327	2.5	2.172
0.1	7.700	0.9	5.971	3.0	1.675 ± 0.035
0.2	7.643	1.0	5.604 ± 0.045	3.5	1.280
0.3	7.543	1.2	4.876	4.0	0.998
0.4	7.394	1.4	4.232	4.5	0.806
0.5	7.196	1.6	3.699	5.0	0.666
0.6	6.948	1.8	3.259	6.0	0.480
0.7	6.655	2.0	2.890	7.0	0.357

Fermi momentum corresponding to the particular orbital in question which is decided by the occupation number.

Now the CP is evaluated using

$$J_l(q) = 2\pi \int_q^\infty \langle \rho_l(p) \rangle p dp \quad (7)$$

which can be written as

$$J_l(q) = 2 \frac{2l+1}{4\pi} \sum_{n=0}^{\infty} \int_{p_1}^{p_2} |R_l(p)|^2 F_n(p) p dp \quad (8)$$

where

$$p_2 = G + p_F \quad (9)$$

and

$$p_1 = \begin{cases} q & G - p_F \leq q \leq G + p_F \\ G - p_F & q < G - p_F. \end{cases} \quad (10)$$

When there is more than one atom per unit cell, one has to include an extra factor in the sum over the shell which corresponds to an average value of the structure factor for all G -values in the shell.

The crystal structure of CuO is shown in figure 2. Although the full unit cell contains four formula units, we take a unit cell which has half the volume as shown in the centre. Its volume is 40.58 \AA^3 . Since each type of ion is treated independently of the other, one has essentially two ions in this volume. This yields an r_0 -value of 3.197 au in which each ionic charge is to be renormalized. Taking Watson's (1958) +1 well 2p solution for the oxygen ion, one can see that it is about 85% confined within this radius. The wavefunction corresponding to the 3d state of free copper atom is more than 90% confined in this volume.

In the present case we have employed a line of analysis very similar to that used by Aikala (1982) in the case of MgO. We have taken several wavefunctions for the 2p of O and the corresponding CPs were calculated for different valence populations. The only difference between Aikala's method and the present method of analysis is that he employed the LCAO method while we have employed the RFA model. In all, we have

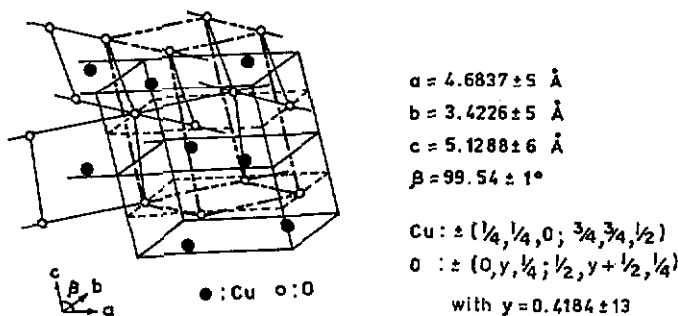


Figure 2. The full unit cell of CuO. The smaller cell indicated by thick broken lines is the one which contains two formula units and represents our unit cell.

Table 2. Core-subtracted $J(0)$ -values for various configurations with different O 2p wave functions.

Experiment	3.903 ± 0.055
$\text{Cu}^{2+}\text{O}^{2-}$, Watson's solution	3.903
$\text{Cu}^{2+}\text{O}^{2-}$, Yamashita and Asano's solution	3.812
$\text{Cu}^{2+}\text{O}^{2-}$, Free-atom solution	3.781
Cu^+O^- , Watson's solution	3.724
Cu^+O^- , Yamashita and Asano's solution	3.648
Cu^+O^- , Free-atom solution	3.612

tried three different wavefunctions for the 2p state of the oxygen ion, namely Watson's +1 well solution, an analytic solution due to Yamashita and Asano (1970) and the HF free-atom solution (Clementi and Roetti 1974). For the 3d state of Cu we have taken the HF free-atom solution which has been shown to yield the best results in MgO (Fuji *et al* 1986).

4. Results and discussion

In the present analysis we have employed two possible configurations: one with Cu^+ and the other with Cu^{2+} states. The lattice sum was evaluated up to 630 orders which ensures convergence to less than 1.0% in $J(0)$. In order to compare the theoretical results with the experimental data the calculated CPS were finally convoluted with the residual instrumental function of the experiment. The core-subtracted $J(0)$ -values are compared with the corresponding experimental data in table 2. One can see that the results obtained with HF free-atom orbitals are much smaller than the experimental value. This is not surprising since free-atom wavefunctions are expected to underestimate the screening effect which becomes important in an ionic system. The 2p states for O^{2-} and O^- states are very different from the 2p state of a free O atom owing to additional screening effects. An increase in screening is expected to result in an increase in $J(0)$. A change in configuration from Cu^+O^- to $\text{Cu}^{2+}\text{O}^{2-}$ with free-atom wavefunctions approximates this

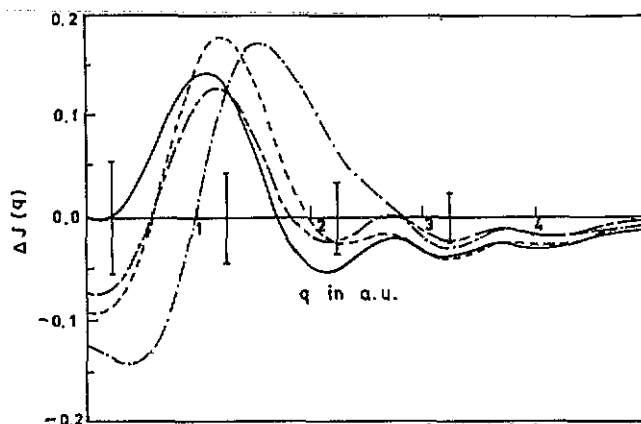


Figure 3. The difference cps $\Delta J(q)$ ($=J_{th}(q) - J_{exp}(q)$), for the three different wavefunctions for the oxygen ion: —, best-fit result with the $3d^{9.4}2p^{5.6}$ configuration obtained with Watson's 2p solution; —, $3d^92p^6$ result obtained with Watson's 2p solution; ---, $3d^92p^6$ result obtained with the 2p solution of Yamashita and Asano; - · -, $3d^92p^6$ result obtained with the HF free-atom 2p solution.

effect through an increase in the number of 2p electrons and there is a slight improvement in $J(0)$, but use of ionic 2p wavefunctions is seen to result in a much improved peak value. One can also observe that the $J(0)$ for the $Cu^{2+}O^{2-}$ ($3d^92p^6$) configuration is closer to the experimental value than is $J(0)$ for the Cu^+O^- ($3d^{10}2p^5$) configuration. One gets the best $J(0)$ -value with Watson's 2p solution for the $Cu^{2+}O^{2-}$ state which is higher by about 0.1 than the value obtained with the 2p solution of Yamashita and Asano for the same configuration. It is very interesting to note that the LCAO calculation in the case of MgO by Aikala also resulted in a similar difference at $J(0)$ for the same two wavefunctions. The reduction in the peak value as one goes from the Cu^{2+} to the Cu^+ state can again be understood as primarily due to a reduction in screening effect particularly for the 2p state of the oxygen ion. However, if one takes the entire valence CP, one finds that none of the theoretical CPS mentioned earlier is in very good agreement with experiment. Defining a root-mean-square (RMS) deviation as

$$\Delta_{RMS} = \sqrt{\frac{1}{N} \sum_i [J_{th}(q_i) - J_{exp}(q_i)]^2} \quad (11)$$

one finds that, for q lying between 0.0 and 5.0 au, Δ_{RMS} for the CP with the solution of Yamashita and Asano is 0.07 while that for the CP with Watson's solution is 0.054. The best result was obtained with Watson's 2p solution with a configuration of $3d^{9.4}2p^{5.6}$ with an RMS deviation of 0.049. The corresponding difference curves are shown in figure 3. Before drawing any more conclusions we must mention that a spherically averaged CP is very sensitively dependent on the radial extension of the underlying wavefunctions. Compared with this, other finer details such as hybridization and overlap effects are probably not so important in a spherically averaged CP calculation as in the directional calculation. That is why one gets very similar results from simple RFA-type calculations as one obtains from a more exact LCAO formulation. If one calculates r_0 for MgO, one would get a value of 3.11 au which is very close to the present value of 3.197 au. This suggests that the same O 2p wavefunction (Watson's solution) which gives the best spherically averaged CP in the case of MgO would also yield similar results for CuO if the oxygen ion is in the O^{2-} state as in MgO. However, the improvement in agreement between experiment and theory obtained with the $3d^{9.4}2p^{5.6}$ configuration can be considered to be in line with a fluctuating charge state as observed in the XPS experiments.

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