Comparative Compton scattering studies in Cu$_2$O and Ag$_2$O

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Abstract. Here we report Compton scattering studies in polycrystalline Cu$_2$O and Ag$_2$O with 59.54 keV γ radiation. An interesting comparison has been made between the valence Compton profiles of these two compounds scaled to lattice momentum by normalizing them to equal electron density for outer valence electrons, and this comparison shows some difference between the bonding characters of Cu$_2$O and Ag$_2$O.

1. Introduction

In recent years, Compton scattering has become a popular way of investigating the electronic structure of solids. An interesting comparison between the Compton profiles (CPs) of two materials can be made when the materials are isostructural and isoelectronic. Then the difference CP scaled to lattice momentum provides the difference between the natures of the electronic bondings of the two materials. This type of work has been done for ZnS and ZnSe to see the effect of increased ionic bonding in II–VI semiconductors (Panda and Padhi 1991). We have performed a comparative CP study of Cu$_2$O and Ag$_2$O which are I–VI semiconductors. This is also the first report of an experimental CP study of Cu$_2$O and Ag$_2$O in the literature.

These two compounds are very important and interesting to study because, at present, Cu$_2$O is widely studied in view of the role of copper oxides in high-T_c superconductors. Ag$_2$O is utilized as a modifier oxide in fast-ion conducting glasses of the type AgI–Ag$_2$O–B$_2$O$_3$.

These two compounds Cu$_2$O and Ag$_2$O have a highly symmetrical cubic structure; the metal atoms are linearly coordinated by oxygen atoms, and the oxygen atoms are tetrahedrally coordinated by metal atoms (Czyzyk *et al* 1989). Cu$_2$O and Ag$_2$O are isoelectronic and known to have an unusual low coordination of the metal atoms with the oxygen atoms.

In this paper our objective is to compare the bonding characters of these two isostructural and isoelectronic compounds with the help of a CP study.

2. Experiment

The experimental set-up is similar to the commonly used Compton spectrometer as reported earlier by Sharma *et al* (1988). For convenience here we briefly describe the experimental

set-up. A ^{241}Am radioactive source which emits 59.54 keV γ-radiation was placed in a lead block. The collimated γ-ray was scattered from the sample placed in a brass vacuum chamber kept at 10^{-2} Torr. The geometry was chosen such that the mean scattering angle was around 165°. Ag$_2$O powder was pressed in the form of a pellet of diameter 1.418 cm and thickness 0.06 cm and this pellet was fixed on a Mylar foil attached to a brass ring of diameter 2.76 cm which was held vertically in the brass vacuum chamber. The Cu$_2$O powder could not be pressed to form a pellet; so the powder was tightly packed between two Mylar foils of separation 0.464 cm attached to the previously described brass ring. The Ag$_2$O and Cu$_2$O samples were of the same optical thickness at the 59.54 keV γ-ray photon energy. The scattered radiation was further collimated and detected with an intrinsic Ge detector of thin planar type. The momentum resolution of the detector which depends on the detector properties and beam divergence was about 0.53 au full width at half-maximum. Over 50 000 counts per channel were collected under the Compton peak, with each channel calibrated as 0.1 au. The background was also measured in the same way with no sample at the target position. The measured data were corrected for background, instrumental resolution, multiple scattering, energy dependence cross-section and absorption in the sample. The profiles were normalized for 0–7 au of momentum to the free-atom Hartree–Fock values of 29.36 electrons for Cu$_2$O and 41.82 electrons for Ag$_2$O.

3. Results and discussion

Figures 1 and 2 show the experimental and residual instrumental function (RIF) convoluted free-atom profiles (Biggs *et al* 1975) for Cu$_2$O and Ag$_2$O respectively and the same results are also given in tabulated form in tables 1 and 2 respectively. In both cases, good agreement was found between the experimental and convoluted free-atom values in the high-momentum region. This provides confidence in our measurement and data analysis.

Core atomic profiles of electrons taken from the table of Biggs *et al* are convoluted by the RIF value of the experiment and then subtracted from the experimentally measured CPs to obtain the valence electron CPs. The valence CPs are scaled in terms of lattice momentum. These CPs are then normalized to equal outer valence electron density. The values of Fermi momentum q_F used to scale the momenta are 1.42 au and 1.28 au for Cu$_2$O and Ag$_2$O respectively. In the case of Cu$_2$O, the outer valence electrons are formed by Cu 3d^{10} and O 2p^6 and, in the case of Ag$_2$O, by Ag 4d^{10} and O 2p^6. The areas of these two normalized profiles are equal to the area of the CPs of a free-electron gas containing 26 free electrons. The difference between the scaled valence CPs of Ag$_2$O and Cu$_2$O is plotted in figure 3, where

$$\Delta J(q/q_F) = J_{Ag_2O}(q/q_F) - J_{Cu_2O}(q/q_F).$$

The difference between the scaled valence CPs of two isostructural and isoelectronic compounds arises owing to firstly the core orthogonalization effect and secondly the nature of their electronic bonding.

There is no theory at present to calculate core orthogonalization effects; so it is not possible to estimate the difference between the natures of the electronic bonding of Cu$_2$O and Ag$_2$O from figure 3. That is why we give here only a qualitative idea about this observation.

The effect of core orthogonalization is to reduce the value of $J(0)$ which is a scaled valence CP at $q/q_F = 0$ as the number of core electrons increases. When the number
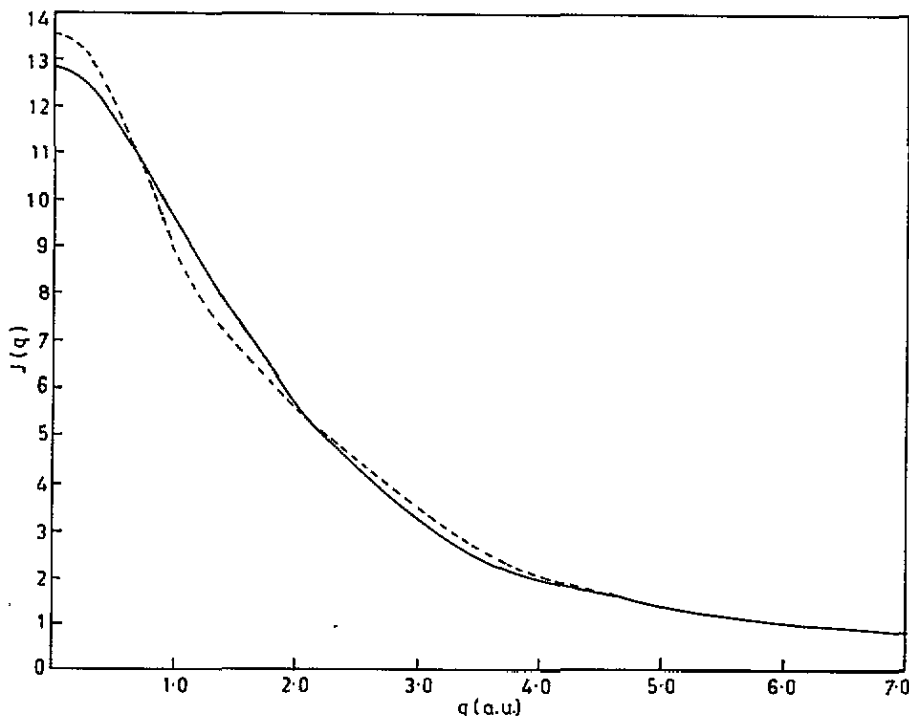
Figure 1. The experimental (———) and the Hartree–Fock free atom (– – –) CPs of Cu_2O.

of core electrons increases, the wavefunctions of the valence electrons must have an increasing number of high-frequency components to remain orthogonal to the core (Reed and Eisenberger 1992). However, figure 3 shows the opposite, i.e. the value of $J(0)$ for Ag_2O is greater than $J(0)$ for Cu_2O. So we think that this difference is not due to a core orthogonalization effect. It might be due to the difference between their bonding characters. The oscillatory nature of the difference valence CP (figure 3) indicates the dissimilarity of the valence CPs of Cu_2O and Ag_2O. Similarity in the nature of profiles is obtained when the electronic bondings of two compounds are identical. So it is inferred here that the natures of the electronic bonding of Cu_2O and Ag_2O are somewhat different.

4. Conclusions

In this paper a comparison of the electronic bondings of Cu_2O and Ag_2O has been discussed from a study of the difference CP. Cu_2O has been widely studied in view of its role in high-T_c superconductors. Marksteiner *et al* (1986) performed a LAPW band structure calculation of Cu_2O with the emphasis on chemical bonding. They have suggested an S–d_z^2 hybridization in Cu which can explain the unusual linear coordination of Cu^+ cations in Cu_2O. The isostructural and isoelectronic Ag_2O is also generally known to have the same electronic structure as Cu_2O, but our difference CP results contradicts this idea. The significant difference between the scaled and normalized valence CP of these two compounds indicates some difference in their bonding natures. In our experiment, samples of the same optical thickness were taken: so this difference does not arise from the multiple-scattering
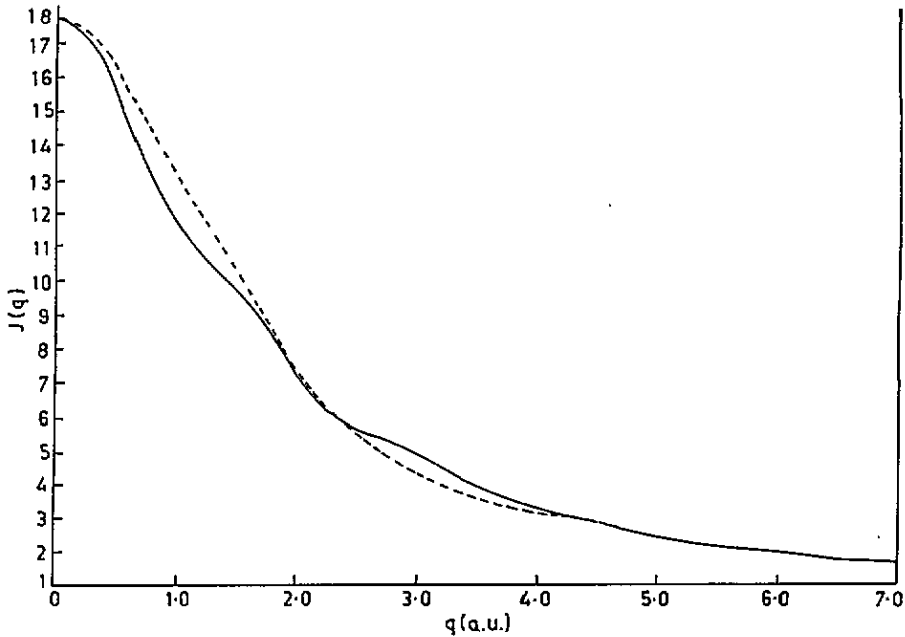
Figure 2. The experimental (——) and the Hartree–Fock free atom (– – –) CPS of Ag_2O.

Table 1. Experimental and RIF convoluted free-atom CPS of Cu_2O.

q (au)	Experimental $J(q)$	Free-atom $J(q)$
0.0	12.87 ± 0.06	13.53
0.1	12.76	13.51
0.2	12.62	13.32
0.3	12.39	13.00
0.4	12.09	12.56
0.5	11.74	12.03
0.6	11.33	11.47
0.7	10.88	10.89
0.8	10.40	10.23
0.9	9.93	9.5
1.0	9.50 ± 0.05	8.70
1.2	8.65	7.7
1.4	7.85	7.12
1.6	7.00	6.6
1.8	6.36	6.30
2.0	5.70 ± 0.04	5.68
2.5	4.33	4.50
3.0	3.30	3.55
3.5	2.44 ± 0.02	2.50
4.0	2.01	2.03
4.5	1.75	1.76
5.0	1.38	1.38
6.0	1.00	1.0
7.0	0.80	0.8

Table 2. Experimental and RIF convoluted free-atom CPs of polycrystalline Ag_2O.

q (au)	Experiment	Free atom
0.0	17.66 ± 0.07	17.65
0.1	17.61	17.65
0.2	17.34	17.47
0.3	16.87	17.12
0.4	16.20	16.63
0.5	15.41 ± 0.07	16.05
0.6	14.56	15.41
0.7	13.69	14.76
0.8	12.88	14.12
0.9	12.17	13.50
1.0	11.58 ± 0.06	12.91
1.2	10.72	11.83
1.4	10.06	10.77
1.6	9.31	9.67
1.8	8.35	8.53
2.0	7.32 ± 0.05	7.45
2.5	5.72	5.43
3.0	5.06	4.29
3.5	3.91	3.52
4.0	3.16 ± 0.03	3.15
5.0	2.51	2.51
6.0	2.01	2.01
7.0	1.60 ± 0.02	1.60
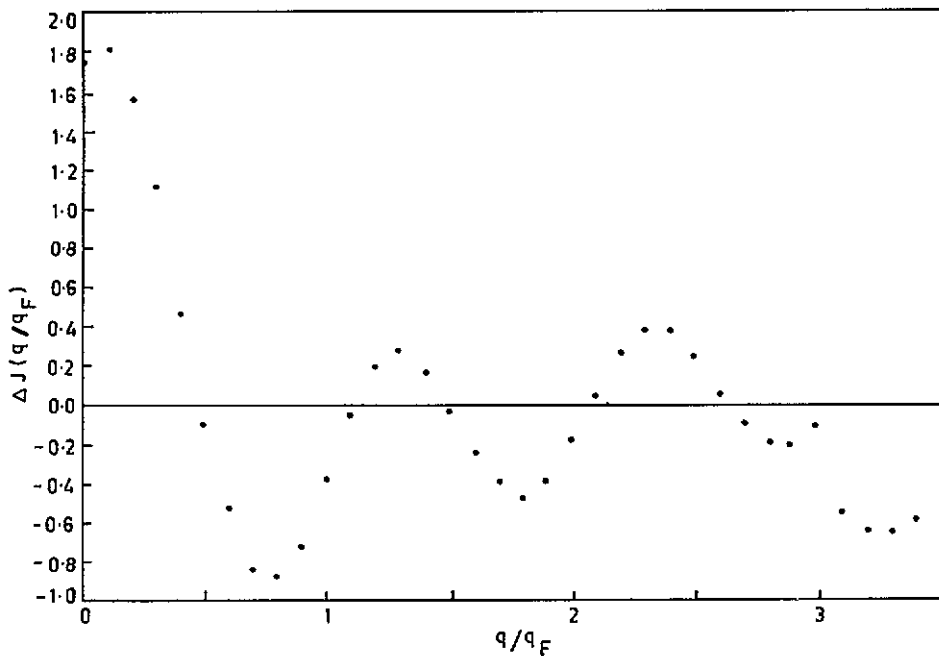
Figure 3. Difference of the scaled valence CPs of Ag_2O and Cu_2O.

effect. The importance of our CP result lies in the fact that it shows that the electronic bondings of Cu_2O and Ag_2O are not exactly identical. We hope that it can shed light on the still incomplete knowledge of the electronic bonding of Ag_2O and also that it will stimulate more theoretical and experimental work on the electronic bondings of these two compounds.

Acknowledgment

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