STUDIES OF THE PHOTOCHROMIC PROPERTIES OF THE SYSTEM CuCl(s)–H$_2$O(l) USING AUGER ELECTRON SPECTROSCOPY

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Summary

The photochromic disproportionation of Cu$^+$ into Cu^{2+} and Cu^0 has been studied in the system CuCl(s)–H$_2$O(l) by obtaining Auger electron spectroscopy measurements of copper in CuCl. The MMM Auger spectrum of CuCl consists mainly of one broad peak with a maximum at an energy 4 eV lower than the two main peaks in the spectrum of metallic copper. In photochromic coloured CuCl only one additional peak appears within the energy range of the peaks of metallic copper, but in the spectrum of CuCl exposed to a concentrated electron beam both metallic copper peaks are visible. This provides experimental evidence that photochemically produced metallic copper clusters in CuCl are extremely small compared with the metallic copper particles formed during electron exposure.

1. Introduction

An aqueous suspension of CuCl exhibits photochromism involving a colour change from white to dark green. The phenomenon has been explained by the following reaction [1]:

$$2CuCl(s) \underset{\rightleftarrows}{\overset{h\nu}{}} Cu^0_{CuCl} + Cu^{2+}_{aq} + 2Cl^-_{aq} \tag{1}$$
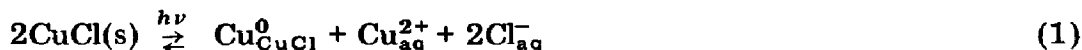
The photochemically produced metallic copper gives rise to the dark green colour. The absorption spectrum in the visible wavelength region agrees with calculated spectra of metallic copper particles with a diameter of about 3 nm [2]. The calculations of these spectra were derived assuming an extended Mie theory.

In attempts to verify that the dark green colour arises from small metallic copper particles, the system CuCl(s)–H$_2$O(l) has previously been studied by means of electron spin resonance (ESR), electron microscopy [3] and powder X-ray diffraction [4]. However, in none of these studies could the formation of metallic copper be observed upon exposure of the photo-

chromic system to light. The results from the studies by electron microscopy and powder X-ray diffraction suggest that metallic copper, if formed at all, must exist in a small concentration or as particles of small size within the CuCl crystals. The ESR measurements indicated that the Cu^{2+} impurity concentration decreases in the CuCl crystal upon exposure to light.

This paper presents a study of the same photochromic system using Auger electron spectroscopy. MMM Auger transitions which reflect conditions in the valence band of copper have been studied in films of CuCl before and after illumination in an aqueous solution.

1.1. Auger electron spectroscopy

Auger electron spectroscopy (AES) is one of the most widely used methods for elemental analysis in the 5 - 20 Å region near the surface of a condensed phase. In the Auger process an incident electron with sufficient energy ionizes a core level. The vacancy is immediately filled by an electron from a higher level. The energy from this transition can either be released as characteristic X-rays or be transferred to another electron. If the transition energy exceeds the binding energy of the third electron, this electron may be ejected from the atom as an Auger electron.

Several Auger transitions involve valence electrons. If the valence band is affected by changes in chemical environment, corresponding changes are observed in the shape and position of Auger peaks involving valence electrons.

For a more detailed description the reader is referred to review articles on Auger electron spectroscopy given elsewhere [5, 6].

2. Experimental

2.1. Sample preparation

Metallic copper foils (99.9% Cu, Baker Chemical Co.) 0.005 in thick were used. The foils were treated with HNO_3 to eliminate oxide films and were then placed in a cuvette filled with 0.1 M HCl and 0.1 M $CuCl_2$ to produce a film of CuCl. One part of the foil was then illuminated in the cuvette by using a 500 W Xe lamp. After the illumination the foils were washed with absolute ethanol and cut into exposed and non-exposed samples (0.5 cm^2).

2.2. Analysing system

The Auger electron spectrometer used in these studies consists of a high resolution semicylindrical mirror analyser 850 CMA (Vacuum Generators), fitted with a microfocus electron gun LEG 32. The elctron gun is directly coupled to a quadrupole reflection system which enables the electron beam to be scanned over a specimen area of up to 2 × 2 mm. Without baking the vacuum chamber, a base pressure of 10^{-7} Pa was reached after 2 h sorption and ion pumping.

All Auger spectra shown were recorded after electronic differentiation of the total backscattered energy distribution function $N(E)$, using a modulation voltage of 1 V peak-to-peak (p–p).

3. Results

A differentiated Auger spectrum between 40 and 70 eV of CuCl which was not exposed to light is shown in Fig. 1. The curve shows a strong maximum around 51 eV and a minimum around 57.5 eV. The Auger curve was obtained by a non-focussed incoming electron beam, which was scanned over a sample area of 2 × 2 mm.
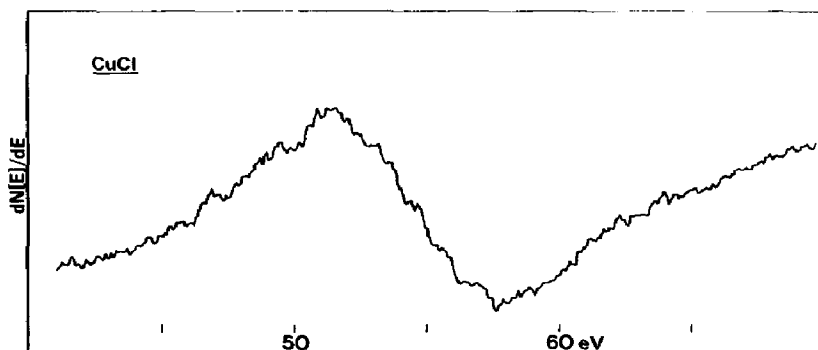

Fig. 1. The low energy Auger spectrum of CuCl obtained with a defocussed electron beam at 1 V p–p modulation amplitude.

The effect of the concentrated electron beam, 0.1 μA in a 5 μm spot, is clearly shown in the upper part of Fig. 2. In this curve two minima are observed around 57.5 eV and 60.5 eV. The lower Auger curve is that of pure single crystalline Cu (110) and is presented here for comparison. In addition the upper curve exhibits a broad hump around 52 eV which is not visible in the lower curve. This hump is probably the same as that seen in Fig. 1 and therefore is probably representative of CuCl. Thus Fig. 2 shows that, on exposure to a concentrated electron beam, there is a partial transformation of CuCl into metallic Cu domains. This tendency was also observed when thin CuCl films were examined in a 100 keV transmission electron microscope; as a result of concentrated electron exposure, small (approximately 1 μm) regions of metallic Cu were formed.

In Fig. 3, the upper and lower curves represent Auger spectra of CuCl after light exposure of 3 min and 30 min, respectively. The result is similar to that which was observed previously for Auger spectra; the maximum of around 51 eV is associated with the presence of CuCl. With increasing light exposure this maximum decreases whereas the single minimum around 60 eV increases in amplitude. However, when the above samples were exposed to a concentrated electron beam, both peaks characteristic of metallic copper appeared.
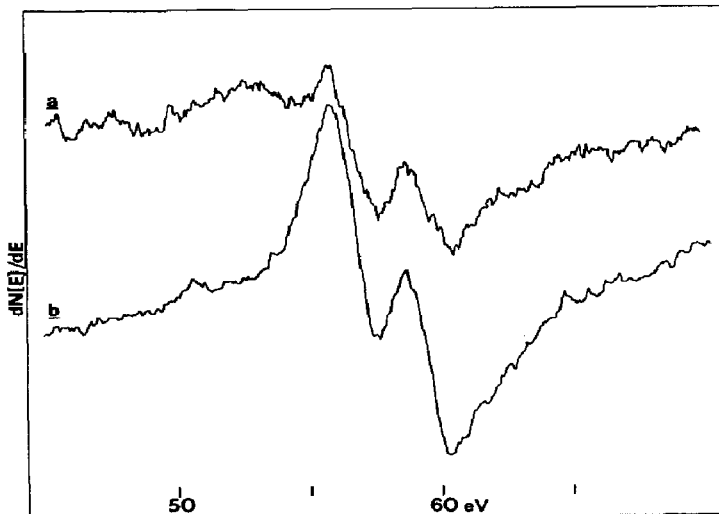
Fig. 2. The low energy Auger spectrum of (a) CuCl after 15 min exposure to a focussed electron beam and (b) pure Cu (110), both at 1 V p–p modulation amplitude.
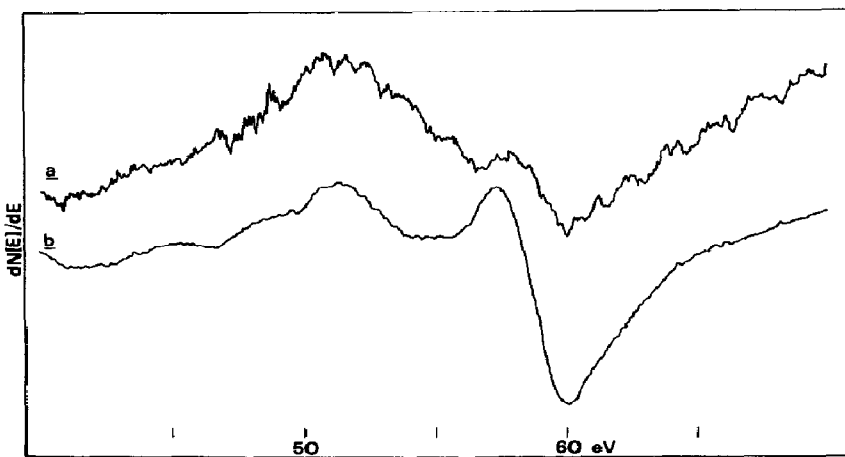

Fig. 3. The low energy Auger spectra of CuCl after exposure to light for (a) 3 min and (b) 30 min at 1 V p–p modulation amplitude.

To summarize, large Cu domains formed during electron exposure give rise to both metallic Cu Auger peaks whereas photochemically formed metallic copper in CuCl gives rise to only one additional peak.

4. Discussion

In estimating values for possible Auger transitions of Cu or CuCl the equation

$$E_{vxy(Z)} = E_{v(Z)} - \frac{1}{2} \{E_{x(Z+1)} + E_{x(Z)}\} - \frac{1}{2} \{E_{y(Z+1)} + E_{y(Z)}\} - \phi_A \qquad (2)$$

will be used. Here the subscripts v, x and y denote different subshells involved in a specific Auger transition. The corresponding energy levels are E_x, E_y and E_v. ϕ_A represents the work function of the analyser material (5.0 eV in these studies) and Z is the atomic number of the atom.

For convenience, the peaks characteristic of CuCl for metallic pure Cu and for photochemically coloured CuCl have been integrated after subtraction of a linear background in the $dN(E)/dE$ spectra. These integrated peaks are given in Fig. 4 and the locations of their Auger peak energies are associated with the maximum of each peak.

The two peak maxima at around 57.5 and 59 eV, characteristic of pure metallic Cu (Fig. 4), have previously been labelled $M_3M_{4,5}M_{4,5}$ and $M_2M_{4,5}M_{4,5}$, respectively [8, 9]. Using conventional nomenclature, an $M_3M_{4,5}M_{4,5}$ transition implies that the initially ionized core level is $M_3(3p_{3/2})$. The level from which the electron that fills the vacancy originates is $M_{4,5}(3d_{3/2}, 3d_{5/2})$ and the level from which the ejected Auger electron escapes is $M_{4,5}$. According to eqn. (2) the electron binding energies of metallic Cu and of metallic Zn are needed in order to calculate the Auger transitions mentioned above. These binding energies, taken from photoelectron spectroscopic measurements, are listed in Table 1. The calculated values of the peak positions of $M_3M_{4,5}M_{4,5}$ and $M_2M_{4,5}M_{4,5}$ at 57.4 eV and 59.3 eV are in good agreement with the observed peak positions at 57.5 eV and 59 eV.

In the spectrum of CuCl only one broad peak with a maximum at 54.5 eV is visible (Fig. 4). The valence band of CuCl is a mixture of Cu 3d and Cl 3p which gives rise to two bands with binding energies at around 1.5 eV and 5.3 eV [12]. The band at 1.5 eV is mainly composed of Cu 3d
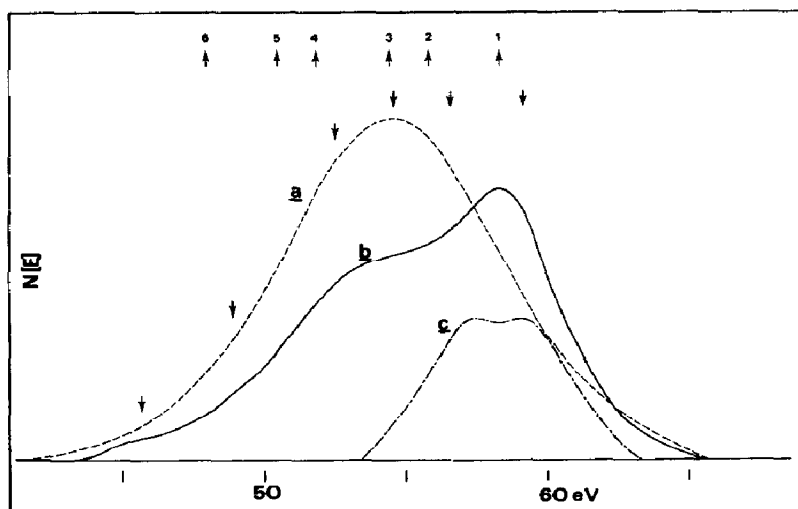

Fig. 4. Integrated Auger peaks of (a) CuCl, (b) CuCl after exposure to light and (c) metallic pure Cu. Arrows with numbers refer to calculations and assignments in Table 3. Arrows without numbers indicate possible Auger peak locations as observed in the fine structure of the curves in Figs. 1 and 3.

TABLE 1

The electron binding energies in Cu and Zn which have been used for calculating Auger peak positions in metallic Cu (all energy values have been corrected to give the carbon 1s signal at 284.8 eV)

Electron level	Binding energy (eV)	Method
Cu $3p_{1/2}(M_2)$	77.1 ± 0.1	XPS [10]
Cu $3p_{3/2}(M_3)$	75.2 ± 0.1	XPS [10]
Cu $3d_{3/2,5/2}(M_{4,5})$	3.0 ± 0.1	XPS [10]
Zn $3d_{3/2,5/2}(M_{4,5})$	9.8 ± 0.2	XPS [11]

and the band at 5.3 eV mainly of Cl 3p. In order to get an estimate of possible Auger transitions, eqn. (2) has been applied using the binding energies of the M_2, M_3 and $M_{4,5}$ subshells in CuCl, the $M_{4,5}$ subshell in $ZnCl_2$ and also the $M_{2,3}$ subshell of Ar. Data for electron binding energies have been taken from photoelectron spectroscopy (XPS and UPS) measurements and are shown in Table 2.

Calculations of possible Auger transitions in CuCl are summarized in Table 3 and also indicated by arrows in Fig. 4. From a comparison of observed and calculated Auger peak energies it seems that those Auger transitions involving a final state of one hole in each of the two valence bands tend to dominate, namely those with peaks numbered 3 and 4.

The additional peak in the spectrum of light-exposed CuCl in Fig. 4 (curve b), characteristic of the photochromic change, is within the energy range of the spectrum of pure metallic copper. However, the observed Auger peak does not exhibit the well-resolved doublet structure characteristic of bulk Cu but a weakly resolved fine structure like that observed in CuCl. The most plausible explanation for this is a strong coupling between the valence band (i.e. Cu^+V) of CuCl and the valence or conduction band of metallic copper (i.e. Cu $M_{4,5}$). In such a strongly coupled system it is not relevant to consider the Auger transitions characteristic of pure CuCl or pure Cu. Instead, altered Auger peaks will appear as a result of the perturbed density of states in CuCl.

Thus, whereas large Cu domains as in pure metallic copper or in electron-exposed CuCl exhibit a doublet structure (curves a and b in Fig. 2) it now follows that the Auger peak formed after light exposure originates from very small copper particles which can interact with the surrounding CuCl matrix. This supports earlier assumptions that photochemically formed metallic copper in CuCl exists as extremely small particles (about 3 nm) [2]. Furthermore, the experimentally observed interaction between the small metallic copper clusters and the surrounding CuCl matrix can also explain how photochemically formed metallic copper acts as an optical sensitizer for the photochromic reaction when activated by visible light [1].

TABLE 2

The electron binding energies in CuCl, $ZnCl_2$ and Ar which have been used for calculating Auger peak positions in CuCl

		Electron level	Binding energy (eV)	Method
CuCl	core levels	Cu^+ $3p_{1/2}(M_2)$	76.5 ± 0.1	XPS [12]
		Cu^+ $3p_{3/2}(M_3)$	74.0 ± 0.1	XPS [12]
	valence band (main peaks)	I (mainly Cu^+, 3d)	0.8 ± 0.1 $\Big\}$ 1.5 eV^a (Cu^+V)	UPS [12]
		II (mainly Cu^+, 3d)	1.9 ± 0.1	
		III (mainly Cl^-, 3p)	4.9 ± 0.1 $\Big\}$ 5.3 eV^a (Cl^-V)	
		IV (mainly Cl^-, 3p)	6.1 ± 0.1	
$ZnCl_2$		Zn^{2+} 3d	11.8 ± 0.2 C 1s 284.8 eV)	XPS [13]
Ar		Ar $3p_{1/2}$, $3p_{3/2}$	15.8^a	XPS [14]

^{a}Weighted mean value.

TABLE 3

Possible Auger transitions in CuCl: assignments and calculated peak energies

Peak number	Assignment			Calculated peak energy (eV)	Observed peak energy (eV)
1	Cu^+M_2	Cu^+V	Cu^+V	58.2	59.1^b
2	Cu^+M_3	Cu^+V	Cu^+V	55.7	57.4^b
3	Cu^+M_2	Cl^-V	Cu^+V	54.3	54.5^a
4	Cu^+M_3	Cl^-V	Cu^+V	51.8	52.5^b
5	Cu^+M_2	Cl^-V	Cl^-V	50.4	48.9^b
6	Cu^+M_3	Cl^-V	Cl^-V	47.9	45.8^b

^{a}Peak maximum.
^{b}Weakly resolved shoulder.

Acknowledgments

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