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THE VALENCE OF Au IN $AuTe_2$ AND AuSe STUDIED BY X-RAY ABSORPTION SPECTROSCOPY

A.R.H.F. Ettema, T.A. Stegink and C. Haas

Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The gold compounds $AuTe_2$ and AuSe contain Au atoms in two different chemical surroundings. In the literature these different coordinations have been associated with a difference in valency of the Au atoms. In this paper the occupation of the $5d$ shell in AuSe and $AuTe_2$ is deduced from a study of the $4f \rightarrow 5d$ X-ray absorption edge. A comparison is made with the absorption edges of Au, AuCl and $AuCl_3$. The results show that only $AuCl_3$ has Au atoms in a valence state of III, and that the Au atoms in $AuTe_2$ and AuSe are all in the same monovalent state I, independent of their chemical environment.

1. INTRODUCTION

GOLD COMPOUNDS like AuSe, $AuTe_2$ and $CsAuCl_3$ have a remarkable chemical composition, because the stoichiometry suggests that the Au atoms have a formal valency of II. In comparison with many other gold compounds this is an exceptional valency for Au, since in most gold compounds valencies of I and III are observed. This is the case for AuCl and $AuCl_3$ with valencies of I and III, respectively. Crystallographic studies showed that the coordination of Au(I) is linear and Au(III) is square planar [1, 2]. In the compounds with an assumed average valency of II, two types of gold atoms are present, one with a linear and the other with a square planar coordination. This suggests that gold appears with two different valencies in these compounds (mixed valent). An example is the compound $AuCl_2$. The crystal structure consists of a stacking of Au_4Cl_8 molecules [3]. Each molecule has two Au atoms in a linear coordination and two in square planar coordination. For $CsAuCl_3$ it has been shown that Au appears in both coordinations (linear and square planar) and with valencies I and III [4-6]. For the compound AuSe two modifications α-AuSe and β-AuSe have been reported [7]. In both modifications two types of the Au atoms are present, one with linear and one with square planar coordination. On the basis of the analogy with other Au compounds, i.e. the chlorides AuCl and $AuCl_3$, it was concluded that AuSe is a mixed valence compounds with Au(I) and Au(III) atoms in linear and square planar coordination, respectively [7, 8]. X-ray photoelectron spectroscopy (XPS) measurements on AuSe [9] show a splitting of the Au $4f$ peaks. This could be due to the presence of Au atoms with different valencies. However, the sample on which the measurements were carried out, consisted of a mixture of α-AuSe and β-AuSe, and the splitting could be due also to the Au atoms in the two modifications or to surface effects.

A more complicated case is provided by $AuTe_2$. This compound has an incommensurately modulated crystal structure [10] in which the coordination of the Au atoms is changing continuously between square planar and linear in the incommensurate direction. The changes in the coordination are directly associated with the incommensurate modulation of the structure. It was stated by the authors, who presented the crystal structure of $AuTe_2$, that Au showed valence fluctuations in this compound. However XPS data [11] and band structure calculations [12] showed that the modulation hardly effects the valency of the Au atoms. All the Au atoms in this compound are in the same Au(I) d^{10} state, according to these data.

In this paper X-ray absorption (XAS) data are presented of the Au $4f \rightarrow 5d$ absorption edge. These transitions are not expected to have a high dipole transition probability, but the small line width of the Au $4f$ core level allow a spectrum with high resolution and a high selectivity. The $4f \rightarrow 5g$ transition is expected at much higher energies. XAS is a suitable technique to study the presence of holes in a nearly filled shell. It provides direct evidence for empty states above the Fermi level with a selected symmetry. Moreover XAS data are less sensitive to surface contaminations than XPS or ultraviolet photoemission spectroscopy (UPS).

2. EXPERIMENTAL

2.1. *Syntheses*

The samples were obtained by syntheses from the elements. $AuCl_3$ was prepared by dissolving an Au wire in a mixture of concentrated HCl and HNO_3 acids (aqua regia) by mild heating (60°C) and stirring under a dry N_2 atmosphere. After dissolution of the Au wire (1 h), the excess of H_2O, HNO_3 and HCl was removed by heating the mixture for several hours at 140°C. The $AuCl_3$ obtained with this process had a red colour and was highly hygroscopic. AuCl was synthesized from $AuCl_3$ by heating under a dry N_2 atmosphere at 195°C. After 15 h all the $AuCl_3$ had been decomposed into AuCl [13].

The first step in the synthesis of AuSe is the preparation of reactive Au powder. This was made by dissolving an Au wire again in a mixture of concentrated HCl and HNO_3 acids (aqua regia). Excess of oxidizing agents was removed by evaporation. After adding an aqueous solution of hydrazine, the reduced Au precipitated from the solution as a very fine powder. This powder was washed with water and dried in a furnace at 120°C. Stoichiometric amounts of Au and Se powder were heated in an evacuated pyrex tube at 280°C for a period of two weeks. After this period a mixture of α-AuSe and β-AuSe was formed [7].

The $AuTe_2$ was synthesized by using the Bridgman technique. Solid pieces of Au and Te were molten in an evacuated quartz tube, which had a vertical position in a two zone furnace. The temperature of the lower zone was controlled at 470°C and the higher zone at 600°C. Single crystals, with lengths of up to 50 mm, were obtained by cooling very slowly at a rate of $5°C\,h^{-1}$ [14].

2.2. *Measurements*

The absorption spectra were obtained from the undulator beamline at the synchrotron radiation facility at Daresbury (UK). The monochromator of this beamline is a double plane grating with a Pt coating. The samples were glued with a two-component silver glue on stainless steel sample holders. At the manipulator 10 samples could be mounted. Due to a thin window between the chamber and the monochromator only high (not ultra high) vacuum conditions were required. The base pressure in the chamber was 10^{-7} Torr during the measurements. The spectra were measured both in total yield mode and drain current mode. Throughout the measurements rutile was used as a calibration sample, which was measured frequently.

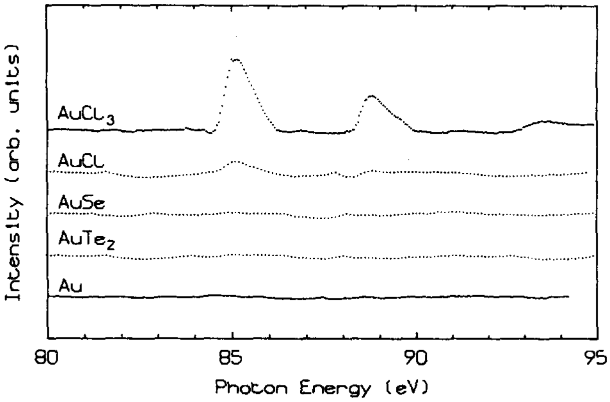

Fig. 1.

3. RESULTS AND DISCUSSION

The spectra in Fig. 1 show the 4*f* absorption of $AuCl_3$, AuCl, AuSe, $AuTe_2$ and Au after background subtraction. The spectrum of $AuCl_3$ shows two absorption edges at 84.6 eV and 88.3 eV, which correspond to $4f_{7/2} \rightarrow 5d$ and $4f_{5/2} \rightarrow 5d$ transitions, respectively. This observation clearly proves the presence of holes in the Au 5*d* band in $AuCl_3$, which was expected for Au atoms in a valence state Au(III), i.e. with electronic configuration $5d^8$. The total width of the absorption feature is only 1.5 eV, which is very narrow. XPS data of the Au 4*f* core level show widths of 1.1 eV (full width at half maximum) or more. This could indicate that the 5*d* states above the Fermi level in $AuCl_3$ form a narrow band. However, it is also possible that the sharp absorption peak is the result of the Coulomb interaction between the core 4*f* hole left behind after the excitation process, and the excited electron in the 5*d* state. (The Coulomb interaction can lead to a localized 5*d* state split off from the 5*d* band above the Fermi level). The spectrum of AuCl shows only a very weak absorption edge in this region. This is likely due to a partial decomposition of the metastable AuCl which decays at room temperature into Au and $AuCl_3$ ($3AuCl \rightarrow 2Au + AuCl_3$). Therefore the spectrum of AuCl represents the absorption of Au in a valence state of I. In this case the Au 5*d* band is completely filled ($5d^{10}$) which inhibits the promotion of an Au $4f$ electron to the Au $5d$ band. The absorption spectra of $AuTe_2$, AuSe and Au metal show no sign of $4f \rightarrow 5d$ excitation, and therefore allow only one interpretation. In AuSe and $AuTe_2$ the Au $5d$ band is completely filled, as is the case for AuCl and Au metal.

5. CONCLUSION

We conclude that the square planar coordination of Au in $AuCl_3$ can be associated with a $5d^8$ configuration for the Au atoms, and the linear coordination of Au in AuCl with a Au $5d^{10}$ configuration. For the compounds $AuTe_2$ and AuSe, both Au coordinations are present but all Au atoms are in the same valence state with a full $5d$ band and a valency of I.

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