Anionic Gold in Cs_3AuO and Rb_3AuO Established by X-ray Absorption Spectroscopy

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Abstract: The novel ternary oxides Cs_3AuO and Rb_3AuO contain auride anions according to the ionic description $(M^+)_3Au^-O^{2-}$ (M = Cs, Rb). They exhibit various properties that signal the non-metallic features of gold, e.g. in the case of Cs_3AuO the color and the transparency of the crystals and the semiconducting properties and for both compounds the decreased molar volumes. The anionic character of gold in these two compounds is confirmed by the X-ray absorption near edge structure (XANES) of the Au L_I and L_{III} spectra, using Au_2O_3, $AuCl_3$, AuCN, AuCl, Au, and CsAu as reference compounds representing gold in various definite oxidation states. Comparison of the L_I XANES spectra proves the anionic character of gold in the ternary oxides Cs_3AuO and Rb_3AuO because of the energy position of their absorption edges. In agreement to the empirically established law, the absorption edge shifts to higher energy with increasing valency of the absorbing atom.[1] This shift is not directly observable in the Au L_{III} XANES spectra since a prominent peak is superposed onto the actual absorption edge for the Au(0), Au(1), and Au(3) compounds. Nevertheless, the expected shift to higher energy becomes apparent if the Au L_{III} XANES spectra are deconvoluted. Thus the L_{III} spectra, as well as the L_I XANES spectra, are suitable for determining the valency if a deconvolution is carried out. The L_{III} XANES spectra also confirm the presence of anionic gold in Cs_3AuO and Rb_3AuO. Finally, the areas of the pre−edge peaks in the L_{III} XANES spectra give qualitative support to the interpretation given.

Introduction

CsAu was the first compound thought to contain anionic gold.[2] The chemical nature of CsAu is completely contrary to that expected for an intermetallic phase. The contraction of the bond length and molar volumes,[3,4] the semiconducting properties,[5,6] and the optical features[3,7−9] were attributed to a high degree of ionic bonding. Considering the vast difference between the electronegativities of the constituent metals (Cs 0.79, Au 2.54)[10] and the electron affinity of gold (222.7 kJ mol^{-1}), which corresponds in value to iodine (295.3 kJ mol^{-1}),[11] this situation is not surprising. Thus, a compound consisting of the least and the most electronegative metal behaves more like a Zintl phase (intermetallic phase) than like a real alloy.[12]

Because of these irregularities the character of the chemical bonding in CsAu has been the subject of many theoretical studies.[13−15] If the bond character is assumed to be mainly ionic, calculations of the optical features and the band gap are in good agreement with the experimental data. An ionicity of about 50% is discussed, a value which corresponds to typical salts such as CsCl (56%).[16,17] Furthermore, the anionic character of gold has been established by ESCA (Electron Spectroscopy for Chemical Analysis)[16] and Mössbauer spectroscopy.[18,19] A comparison of the respective spectra for CsAu and compounds with gold in other definite oxidation states confirms the existence of auride anions in CsAu.[16,18]

Various other compounds have been reported to contain negatively charged gold: some binaries M_xAu_y (M = alkali metal, Mg, Zn; x, y < 10)[19−21] and the ternary compound Ca_3AuN.[22] However, in contrast to CsAu these are metallic in character.

In order to gain further insight into the chemistry of aurides and their bonding features, we have investigated the existence of auride anions in ternary oxides. In the hope of establishing an ionic bonding in these oxides, we have studied the systems Cs−Au−O and Rb−Au−O. During this investigation, we have found the novel compounds Cs_3AuO and Rb_3AuO. We have recently reported details of their preparation and their crystal

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structure determination.[23,24] Both of these compounds crystallize in ideal anti-perovskite-types of structure, with the difference that Rb_3AuO is cubic (anti-$CaTiO_3$) while Cs_3AuO is hexagonal (anti-$CsNiCl_3$).

Using the ionic formulation $(M^+)_3Au^-O^{2-}$ (M = Cs, Rb), the oxidation state of gold is obviously negative, and in fact various evidence confirms this view. The transparency of the crystals, and the decreased M−Au and M−M distances in contrast to the sum of the metallic radii, which is also accompanied by a contraction of the molar volume, are strong indicators for a high degree of ionic bonding. Especially Cs_3AuO is marked by its non-metallic features, and its semiconducting properties have been established by conduction measurements.[25]

The focus of the present work is to confirm the presence of auride anions and to verify the degree of ionicity in Cs_3AuO and Rb_3AuO. A suitable method for this purpose is X-ray absorption spectroscopy (XAS). In particular the X-ray Absorption Near Edge Structure (XANES) indicates efficiently the valency of the absorbing atom.[26,27] We report here the results of the Au L_I and Au L_{III} XANES spectra.

Experimental Method and Data Analysis

The XANES spectra were obtained at the beamline BN3 using the synchrotron radiation of the Electron Stretcher Accelerator (ELSA) in Bonn, operating in storage mode at 2.3 or 2.7 GeV and with an average current of about 40 mA.[28] The synchrotron light is monochromatized by a double-crystal X-ray monochromator of the Lemmonier type[29] equipped with two Si(400) crystals. They have a 2*d* of 2.715 Å. The monochromatized beam first passes through a reference ionization chamber, then through a sample chamber, and finally through the detector ionization chamber. In accordance to Lambert-Beer's law the absorption cross section can be obtained by recording the logarithmic ratio of the current of the reference and detector chambers, as a function of the incoming photon energy. The photon energy was scanned from 14310 to 14400 eV at the Au L_I edge and from 11890 to 11970 eV at the Au L_{III} edge, in steps of 0.6 eV and with an integration time of 1 s per step. The experimental setup was calibrated to the maximum absorption of a thin gold foil (50 μm) at the Au L_{III} edge (11919 eV) and to the turning point of the absorption edge at the Au L_I edge (14353 eV). The calibration could be reproduced with an accuracy of 0.3 eV. Since the samples immediately decompose upon exposure to air or moisture, the whole procedure of preparation, sealing in kapton foil (25 μm), as well as storage and transportation, was performed under inert atmosphere (Ar) conditions. The sealed samples could then be placed directly into the apparatus for the measurements. Thus, oxidation of the samples was avoided.

In order to analyze the near-edge region, a linear background was subtracted from the raw data, followed by a normalization of the spectra at a point about 60 eV above the edge. This enables us to directly compare the relative oscillator strengths of the various electron transitions. In order to extract information about resonances within the near-edge region, i.e. transitions into empty molecular orbitals, a least-squares fit of the XANES spectra at the Au L_{III} edge was necessary. The line shape of the resonances has been assumed to be a Voigt profile, which is a convolution of a Gauss function and a Lorentz profile. Since the Gaussian line width represents the resolution of the monochromator, this parameter was set to a constant value of 5.0 eV. The Lorentz profile represents the natural line width, which is 5.3 eV.[30]

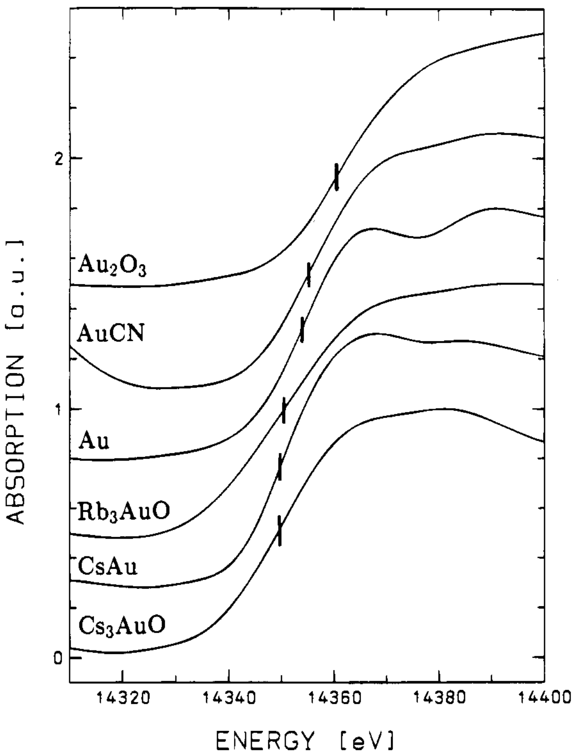

Figure 1. Au L_I XANES spectra, normalized to their maximum intensity.

Table 1. Electron Configuration of Gold

Au(−1)	[Xe] $4f^{14}5d^{10}6s^2$
Au(±0)	[Xe] $4f^{14}5d^{10}6s^1$
Au(+1)	[Xe] $4f^{14}5d^{10}6s^0$
Au(+3)	[Xe] $4f^{14}5d^8 6s^0$

Discussion

Figure 1 represents the Au L_I XANES spectra of Cs_3AuO, CsAu, Rb_3AuO, Au, AuCN, and Au_2O_3. The compounds CsAu, Au, AuCN, and Au_2O_3 were chosen as reference compounds representing the most stable oxidation states of gold (−1, 0, +1, +3). CsAu and Au_2O_3 (as well as AuCl and $AuCl_3$ investigated at the Au L_{III} edge) were prepared according to the procedure given by Brauer.[31] X-ray diffraction measurements and chemical analysis established a purity of 99.9%. Cs_3AuO and Rb_3AuO were prepared in accordance with the procedure given by Feldmann,[23,24] whereas AuCN, with a purity of 99.9%, was commercially acquired (Aldrich/Steinheim). In accordance to the dipole selection rule, $\delta l = \pm 1$, only transitions to unoccupied orbitals with p-character are allowed when a 2s electron is excited. However, according to the valence electron configurations of the investigated samples (Table 1), the 5p-valence states are fully occupied. Thus, no strong electron transitions below the ionization limit are available. Hence, apart

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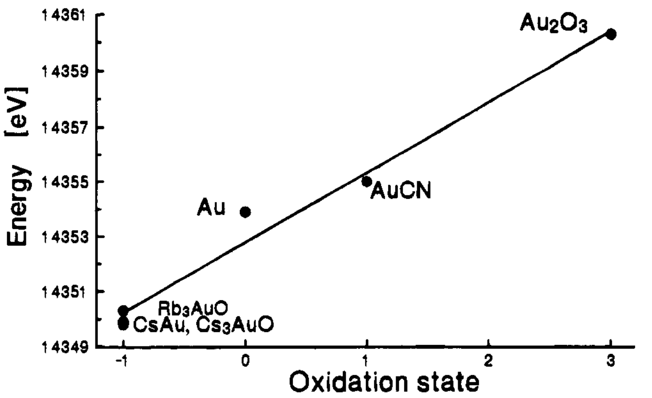

Figure 2. Dependence between the energy position of the Au L_I absorption edges and the oxidation state of gold.

from weak Rydberg resonances, no strong resonance below the Au L_I absorption edge is expected. For this reason, the unadulterated absorption edges can be examined, and their turning points can be regarded as representing the 2s ionization limit. The turning points were determined by numerical differentiation of the data, since the energy position of the maximum value of the absorption derivative represents the energy position of the turning point. The determination of these values could be reproduced with an accuracy of 0.6 eV, also at different beam times. By comparing the energy positions of the turning points of these absorption edges an increase of the ionization potential with increasing oxidation state of gold can be observed. The absorption edge of the CsAu (Au(−1)) spectrum appears at 14349.8 eV, whereas the turning point of the absorption edge of Au_2O_3 (Au(+3)) is found at 14360.3 eV. This effect is in agreement with the empirically established law, that the absorption edge shifts to higher energies with increasing valency of the absorbing atom.[1] Figure 2 demonstrates the good linear dependence between the energy position of the edges and the corresponding oxidation state of gold. This behavior is not surprising, since it has often been observed in the investigation of other systems, for example, in the absorption spectra of V- or Cr-containing compounds.[1,32,33] Usually, a spread in values can be observed for compounds of the same formal oxidation state, as the energy position of the absorption features also mirrors the electronegativity of the neighboring atoms. However, this effect has never been found to be bigger than the energy shift caused by an increase in oxidation state. Possibly, the coordination geometry of the excited element also has an additional influence on the energy position, but generally this has been found to be minor.[1,33] Hence we are able to determine the valence state of gold in the unknown compounds from the energy position of the turning point of Cs_3AuO (14349.8 eV) and Rb_3AuO (14350.3 eV) as being −1.

The turning point of the absorption edge of Cs_3AuO is nearly the same as that of CsAu (14349.9 eV), whereas the absorption edge of Rb_3AuO is shifted 0.5 eV to higher energies. This means that the anionic character of gold in Cs_3AuO is very similar to that in CsAu, whereas in the case of Rb_3AuO the anionic character is less pronounced than in the cesium compounds. This can be interpreted as being due to the higher electronegativity of rubidium. This increase in metallic character and hence a decrease in the ionic contribution to the chemical bonding corresponds to the properties as calculated for the binary alkali metal gold compounds MAu (M = Cs, Rb, K, Na, Li).[15,34,35]

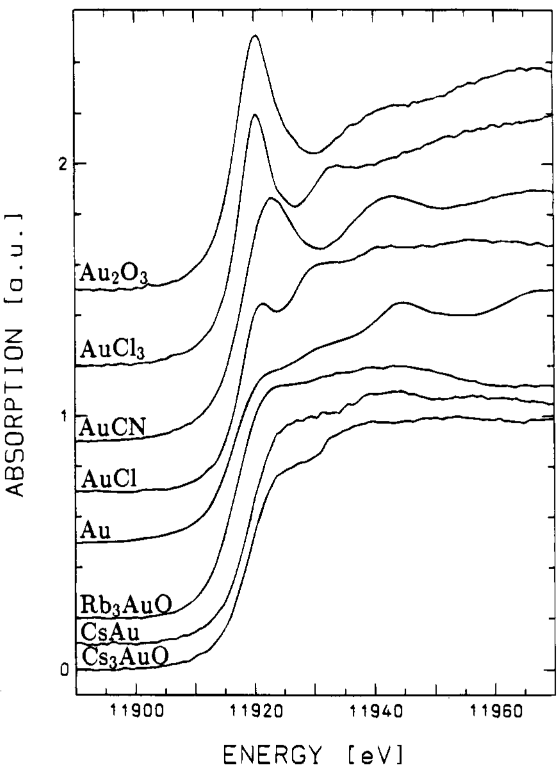

Figure 3. Au L_{III} XANES spectra, normalized to their maximum intensity.

Additional information can be obtained from the Au L_{III} absorption spectra. Here, the Au $2p_{3/2}$ electrons are excited. In this case, however, a dipole allowed transition to the Au 5d and 6s valence states is possible, depending on the oxidation state of Au (Table 1), close in energy to the absorption edge corresponding to the $2p_{3/2}$ ionization limit. In Figure 3 the Au L_{III} XANES spectra of Cs_3AuO and Rb_3AuO are again compared to various reference spectra (Au_2O_3, $AuCl_3$, AuCN, AuCl, Au, CsAu). The resonance due to the $2p_{3/2} \rightarrow 6s$ transition is not observed, because of the small spatial overlap between the 2p and the 6s wave functions and hence correspondingly small transition dipole moment.[36] Thus, in the Au L_{III} near-edge region, only the $2p_{3/2} \rightarrow 5d$ transition can be observed. Because of the resulting pre-edge feature in the Au L_{III} XANES spectra the expected energy shift of the absorption edge cannot be observed in all cases, since the actual edge is superposed to a varying extent by a prominent peak, which depends on the oxidation state of gold. Notably, the intensity of this peak increases with increasing oxidation state.

In spite of this, we can obtain information about the oxidation state of gold in Cs_3AuO and Rb_3AuO, not by direct comparison of the energy position of the absorption edges (as was done with the Au L_I XANES spectra), but by simply using XANES as a fingerprint method. Both spectra (Cs_3AuO and Rb_3AuO) are similar to that of CsAu in shape and energy position of the rising edge, and both are completely different from the XANES spectra of the compounds containing positively charged gold. A comparison of the spectra shows that the spectrum of Rb_3AuO lies between those of CsAu and Au in similarity, whereas the Cs_3AuO spectrum is almost identical to the CsAu spectrum. This indicates that the negative charge in Cs_3AuO is the same as in CsAu, and that the anionic character of gold in Rb_3AuO is diminished. These results confirm the conclusions that were deduced from the Au L_I spectra.

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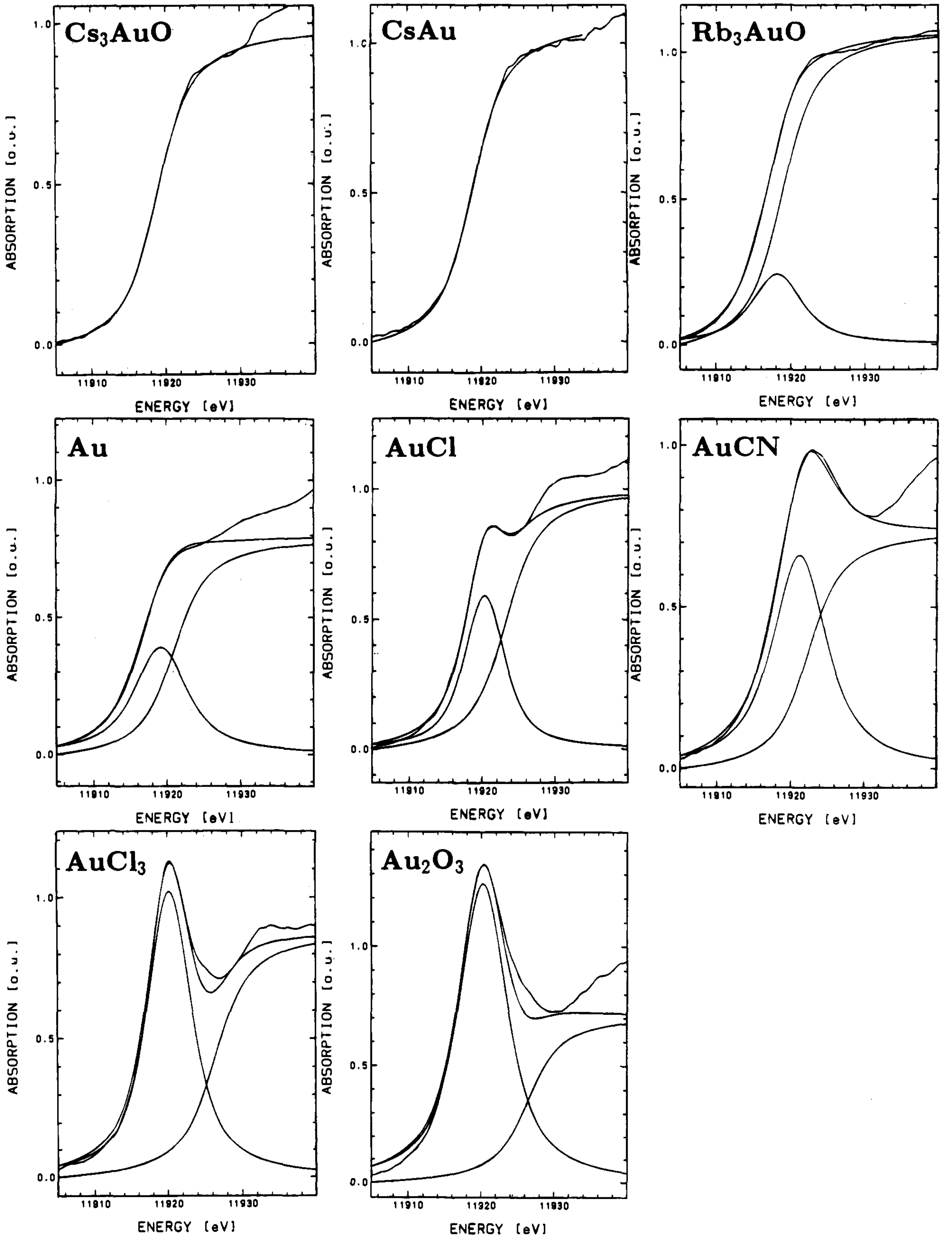

Figure 4. Least-squares fit of the Au L_{III} near-edge region for the investigated samples, showing the measured data with the fitted edge, the fitted prominent peak, and their sum.

To get further quantitative information about the single resonance within the near-edge region and about the position of the Au L_{III} absorption edges, a least-squares fit of the energy range between 11905 and 11940 eV was made by using a Voigt-profile as the line shape of the resonance and an arctangent function as representing the absorption edge (Figure 4). The fit parameters are listed in Table 2. When going from Cs_3AuO (Au(−1)) to Au_2O_3 (Au(+3)), the energy position of the turning point of the arctangent function, which represents the $2p_{3/2}$ ionization limit, shifts substantially (on average 1.9 eV per unit change in valence) to higher energy. This is in agreement with the results of the Au L_I spectra, where the absorption edge was found to shift to higher energies with increasing valency of the absorbing atom, even if the chemical shift for the Au L_I spectra

Table 2. Energy Positions (eV) of the Au L_I Absorption Edges (Turning Point)

Cs_3AuO	14349.8	Au	14353.9
CsAu	14349.9	AuCN	14355.0
Rb_3AuO	14350.3	Au_2O_3	14360.3

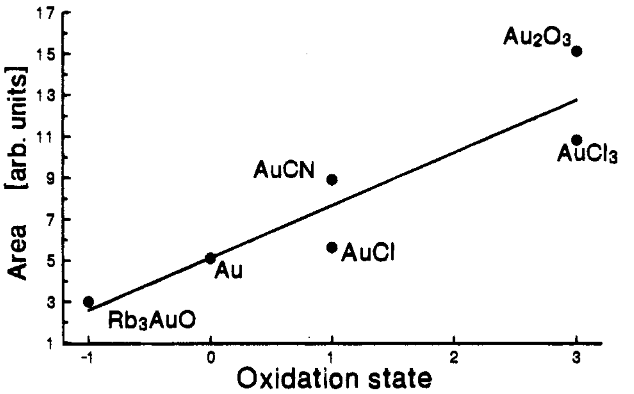

Figure 5. Dependence between the area of the Au L_{III} peak and the oxidation state of gold.

Table 3. Fit Parameters of the Au L_{III} XANES Spectra

		energy, eV	absorption, au	area, au	color
Cs_3AuO	IP	11918.9	1.0		brown/yellow
CsAu	IP	11918.9	1.0		pale yellow
Rb_3AuO	peak	11918.1	0.25	3.0	grey/black
	IP	11919.1	1.0		
Au	peak	11919.2	0.4	5.1	golden
	IP	11921.1	0.8		
AuCl	peak	11920.3	0.6	5.6	yellow
	IP	11923.2	1.0		
AuCN	peak	11920.7	0.7	8.9	orange
	IP	11922.5	0.7		
$AuCl_3$	peak	11920.3	1.0	10.8	red
	IP	11926.4	0.85		
Au_2O_3	peak	11920.3	1.3	15.1	brown
	IP	11926.4	0.7		

is larger (on average 2.6 eV per unit change in valence). Again, a good linear relationship between the $2p_{3/2}$ ionization limit and the corresponding oxidation state of gold is found, and hence the interpretation of the Au L_I spectra is confirmed.

Considering the dipole selection rule, the peak below the ionization limit results from the Au $2p_{3/2} \rightarrow 5d$ electron transition. Its intensity should be proportional to the density of unoccupied 5d states. Therefore, the peak should only appear in the spectra of Au_2O_3 and $AuCl_3$, with their partially occupied 5d shell (Au^{3+}: $6s^05d^8$). No such transition is expected to occur for Au(0)- and Au(+1)-containing compounds that possess a closed d^{10} shell. Formally, their valence electron configurations are described by $5d^{10}6s^1$ or $5d^{10}6s^0$, respectively. However, the possible incorporation of d electrons from the closed d^{10} subshell for chemical bonding[37−40] means that the electron configuration of Au(0)- and Au(+1)-containing compounds has to be formulated as $5d^{10-\delta}6s^{1+\delta}$ or $5d^{10-\delta}6s^{\delta}$. For the Au^+ ion in a linear 2-fold coordination as in AuCN, it has been proposed that hybridization between the $5d_{z^2}$ and the 6s orbitals leads to a valence electron distribution that can be described as $5d^{10-\delta}6s^{\delta}$. This implies the presence of unoccupied d states above the Fermi level, similar to the electron configuration in Au(+3) compounds. In fact, the occurrence of a peak confirms the presence of these vacancies in the Au 5d valence level. Consequently, the area of the resonance below the ionization limit that has been determined by the least-squares-fit increases with increasing oxidation state of gold (Figure 5). As the Au $2p_{3/2} \rightarrow 5d$ electron transition is a dipole-allowed transition, the influence of the coordination geometry on the change in peak area can be assumed to be negligible. Such an effect was found, e.g., in the investigation of the Cr K-edge XANES spectra of various chromium compounds.[33] Here, a dependence of the peak area on structure was observed only for dipole-forbidden but not for dipole-allowed electron transitions. Hence, the differing intensities in the case of identical oxidation state as in Au_2O_3 and $AuCl_3$, as well as in AuCN and AuCl, can be associated with the proportion of covalent bonding in these compounds (Table 3). This is also indicated by the color of the compounds, which is associated with the strength of covalent bonding.[39] The degree of covalency directly mirrors the number of vacancies in the Au 5d level. This relation can be rationalized by assuming that an increase in covalent bonding is related to an increased hybridization of Au 5d states. Similar results have been obtained for Ag L_{III} XANES spectra by Behrens.[39] He investigated various silver−oxygen compounds and also found a prominent peak at the rising edge. Due to band structure calculations computed for Ag_2O,[40] this peak could be assigned to the $2p_{3/2} \rightarrow 4d$ transition and the intensity correlated to the degree of covalent bonding in a compound. The similarity to the Ag L_{III} spectra is further evidence for our interpretation of the Au L_{III} spectra.

Conclusion

XANES spectroscopy is used as a fingerprint method in order to determine the valence state of gold in the new ternary oxides, Cs_3AuO and Rb_3AuO. It was found to be −1 by comparing the absorption edges of the Au XANES spectra of the investigated compounds with those of various suitable model compounds. The investigations were carried out at the Au L_I and Au L_{III} edges. For both of these edges a linear dependence of the position of the absorption edge to the corresponding valency of the absorbing atom (Au) was found. Hence, the oxidation state of the novel compounds could be determined. A peak that is superposed on the Au L_{III} absorption edges is attributed to the electron transition Au $2p_{3/2} \rightarrow 5d$. It indicates the presence of empty Au 5d states even in Au(0)- and Au(+1)-containing compounds, where formally a filled d^{10} subshell is assumed. No pre-edge absorption line was found in the spectra of CsAu and Cs_3AuO. Thus, the intensity of the peak is connected to the density of unoccupied electronic states in the Au 5d level due to partial incorporation of the 5d electrons into chemical bonding. The area of this peak also increases with increasing oxidation state of gold. This represents further evidence that the Au in the ternary oxides is negatively charged. With regard to the observed peak, and the energy position of the rising edges, the number of vacancies seems to increase in the order Cs_3AuO, CsAu, and Rb_3AuO. This means that the bonding in Rb_3AuO is mainly ionic but with a metallic tendency, whereas the anionic character in Cs_3AuO is the same as, or slightly more pronounced than, in CsAu. These results prove that the L_{III} spectra of transition metal compounds may well be suitable for the investigation of oxidation states, and that they contain even more information (e.g. about the degree of covalent bonding) than the L_I spectra.

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