Journal of

The Chemical Society,

Chemical Communications

NUMBER 21/1978 1 NOVEMBER

ESCA Study of Compounds of Gold in the Oxidation State −1

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Summary ESCA measurements on a series of gold compounds reveal a monotonic relationship between binding energies of the Au $4f$ levels and formal oxidation states, and provides first evidence for the oxidation state −1 of gold in CsAu and RbAu.

THE report of ionic conduction in the liquid intermetallic compound CsAu[1] has increased the interest in alkali metal–gold alloys in the solid state. Several spectroscopic studies[2,3] and band-structure calculations[3,4] have been carried out in order to obtain an insight into the electronic structure of the crystalline alloys. The UPS (u.v.-photoelectron spectroscopy) photoemission valence-band data compare well with the relativistic KKR (Korringer–Kohn–Rostoker) band-structure calculations.[3] In these calculations a significant charge-transfer from the alkali metal to the gold site has been found. The latter is consistent with the electronegativity scale of Pauling,[5] which assigns to gold the greatest electronegativity amongst the metallic elements. Taking the Pauling scale as a means of comparison, we find that the ionicity of CsAu, *ca.* 50%, is comparable with that of CsCl (56%) on the same scale.

X-ray photoelectron spectroscopy has shown that the binding energies of core electrons in an atom or ion depend on the valence charge distribution and thus contain information about the ionicity of a material.[6] We have, therefore, studied the gold core level spectra of crystalline CsAu and RbAu. Through a careful study of metallic gold, CsAu, RbAu, and $KAuCl_4$, reliable Au($4f_{7/2}$) binding energies, from which chemical shifts should be referred, have been obtained.

The experiments were carried out on an ESCA III system, manufactured by Vacuum Generators, employing Al-K_α and Mg-K_α radiations. The residual pressure within the sample chamber during the measurements was *ca.* 5×10^{-9} Torr. The spectrometer was operated in the computer-controlled scanning mode. Each spectrum was scanned for a preselected period of time during each cycle with multiple repetition until a sufficiently large number of counts had been accumulated.

The CsAu and RbAu samples were prepared under vacuum by mixing accurately weighed amounts of high purity constituents at a temperature above the melting point of CsAu (590 °C). After cooling, the highly reactive solid samples were transferred to the analysing chamber of the spectrometer under dry argon at liquid nitrogen temperature. The samples were d.c. sputtered in a high-purity argon atmosphere for 60 to 120 min. They were considered to be free from chemical contamination when the peaks due to oxygen and carbon core levels were absent within the detectability of the X-ray photoemission spectra. There was no change of the shape and the shift of the Au $4f$ level signals due to the sputtering procedure.

The difference between the binding energy of an atom with no net effective charge and that of the same atom in a compound with unlike atoms is a direct measure of the effective charge-transfer that occurs upon compound formation. Therefore, both types of samples should be studied to accurately evaluate the chemical shifts. We have used the following procedure. The binding energies for the Au($4f_{7/2}$) level of the CsAu and RbAu samples were calibrated *vs.* the Au($4f_{7/2}$) line of a metallic gold dot evaporated on to the surface of the samples. For the binding energy of the Au($4f_{7/2}$) line in the metal a value of 83·8 eV relative to the Fermi level was used. The C($1s$) line from the surface contamination was then found at 285·0 eV.

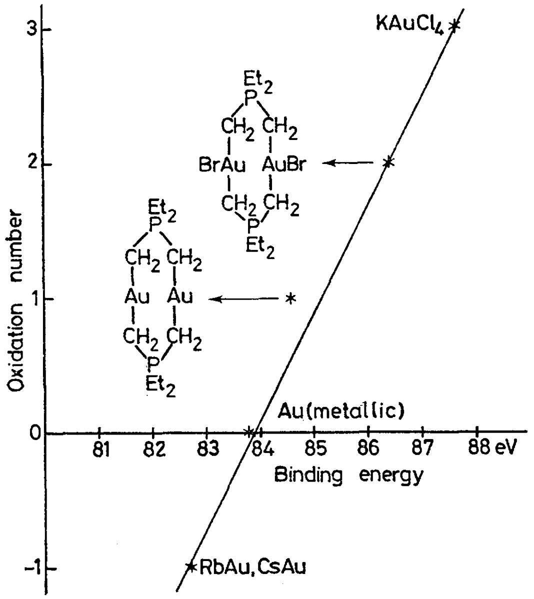

FIGURE. Binding energy of the Au($4f_{7/2}$) level in compounds with different oxidation states.

Between the alkali metal–gold compound and pure gold, a difference in binding energy of the Au($4f_{7/2}$) level of −1·1 eV is observed. The results of the core-level measurements are identical for RbAu and CsAu within experimental accuracy.

The primary object of our study is to establish that a negatively charged gold ion exists in CsAu and RbAu. For this purpose we have correlated in the Figure the experimentally observed chemical shifts for the Au($4f_{7/2}$) levels in gold-containing materials as measured in this work and by Schmidbauer *et al.*[7] with oxidation states ranging from 1− to 3+. In ref. 7 the oxidation states were determined using ESCA and Mössbauer spectra. The photoelectron spectra of CsAu, RbAu, gold metal, μ-bis(diethylphosphoniodimethylene)-digold, μ-bis(diethyl-phosphoniodimethylene)-bis(bromogold)(*Au–Au*), and KAuCl$_4$ (Figure) show the $4f_{7/2}$ electron levels of gold progressively shifted to higher energy in the sequence Au^0, Au^{I}, Au^{II}, and Au^{III}. From the Figure the oxidation number of gold is found to be 1− for CsAu and RbAu.

We thank the Deutsche Forschungsgemeinschaft for financial support.

(*Received*, 12*th May* 1978; *Com.* 512.)

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