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# X-ray Photoelectron Spectroscopy of Ga Metal and Ga Chalcogenides

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## Introduction

Gallium is an element that can exist in different oxidation states [1] $Ga^0$, $Ga^{+1}$, $Ga^{+2}$ and $Ga^{+3}$. As the B(inding) E(nergy) of core electrons in an atom can be correlated with the charge [2, 3] on the atom, a wide variety of B.E.'s for the Ga core levels in compounds with different oxidation states is expected. Therefore we have measured the Ga B.E. in the metal and in a number of its chalcogenides (S, Se, Te) with Ga in different oxidation states. The B.E. for the core levels of the chalcogens were not measured as their oxidation state remains –2 throughout the whole series of compounds studied.

## Experimental

All the compounds were synthesized [1, 4, 5] by heating the stoichiometric amounts of both components under vacuum in a sealed quartz tube at high temperature.

The Ga metal sample for ESCA spectroscopy was prepared by vacuum deposition of the metal either on a gold plate or on a graphite pellet. Successive evaporations were made in both cases to see the influence of the layer thickness on the B.E.

The evaporation technique onto a gold plate was also used for the chalcogenides. Care was taken to hold the evaporation temperature in the cross probe as low as possible in order to prevent decomposition. A second method of sample preparation which excluded decomposition was also used. Herein the compound is mixed with graphite and then pressed into a pellet.

The instrument was a 5950 A Hewlett–Packard Electron Spectrometer using the monochromatised $AlK_\alpha$ line (1486.7 eV) as X-ray excitation source. The reproducibility is ± 0.2 eV for all the measurements.

## Results and Discussion

For all the compounds the B.E. of the Ga 3d line was measured as this is the most intense line. The spin–orbit splitting $3d_{5/2}$–$3d_{3/2}$ cannot be resolved with this instrument. For some compounds the B.E. of the Ga $3p_{3/2}$ levels was also taken but the variations in chemical shift are the same as those for the Ga 3d level within the experimental error. As an internal standard the Au $4f_{7/2}$ or the $C_{1s}$ line of graphite was taken with a B.E. of 84 or 283.4 eV respectively. The results for the Ga metal are tabulated in Table I.

The B.E. value for the evaporated metal on a graphite substrate remains constant and is independent of the layer thickness. The value is in good agreement with those obtained by Schön [6] and Siegbahn [7]. However, deposition of Ga metal on a gold plate gives a significant increase in Au B.E. after each evaporation while the Ga B.E. is slightly decreasing. The formation of discrete compounds or of an alloy could explain the increase in Au B.E. for the electronegativity [8] of Ga is higher than that of Au. An electron flow from Au to Ga has to be expected. In that case also the Ga B.E. has to increase in function of the Ga layer thickness. As this is not true, clearly some other effect is also playing a role.

The B.E.'s ascertained for the chalcogenides are presented in Table II. It is obvious that the Ga B.E. for the compounds in one column do not change within the experimental error. On successive evaporations of chalcogenides $Ga_nX_m$ into the gold substrate no change of the Ga B.E.'s was found. This is accepted as a proof that the evaporation technique

TABLE I. Binding Energies.

| Number of Evaporation | Binding Energy | | B.E. (standard $C_{1s}$ line of graphite) | | | |
|---|---|---|---|---|---|---|
| | Au $4f_{7/2}$ (eV) | Ga 3d (eV) | $C_{1s}$ (eV) | Ga 3d (eV) | Gunar and Schön [6] | Siegbahn [7] |
| Zero | 83.8 | – | 284.3 | – | | |
| First | 83.9 | 19.0 | 284.3 | 18.3 | 18.6 ± 0.2 | 18.0 |
| Second | 84.5 | 18.8 | 284.3 | 18.3 | | |
| Third | 85.5 | 18.6 | 284.3 | 18.3 | | |

TABLE II. B.E. of the Ga 3d Level in Gallium Chalcogenides.

| Composition | Sample Prepn. | X = S | X = Se | X = Te |
|---|---|---|---|---|
| $Ga_2X$ | Fl. | 20.1 | 19.7 | |
| | Pellet | | | 20.3 |
| GaX | Fl. | 20.2 | 19.9 | |
| | Pellet | 19.9 | 19.7 | 20.2 |
| $Ga_2X_3$ | Fl. | 20.2 | 19.9 | 19.8 |
| | Pellet | | 19.8 | 20.0 |

does not yield decomposition. Moreover, the B.E. shifts found on pelletted samples and on flashed samples are always parallel as well in a row as in a column. This again proves that there is no decomposition on evaporation.

For GaS and $Ga_2S_3$ the crystal structures are known [9, 10]. In both compounds each Ga atom is in a tetrahedral configuration. In $Ga_2S_3$ the four corners of the tetrahedron are sulphur atoms while in GaS each gallium atom is surrounded by three sulphur and one gallium atom. Here there are Ga–Ga bonds which give rise to a change of the formal oxidation state without changing the spacial configuration. Furthermore, on the basis of the electronegativity difference, an increase in Ga B.E. would be expected by replacing a Ga–Ga bond by a Ga–S bond. However, taking into account the potential term into the equation $EB = hq + V + l$ [11] the expected increase in B.E. is seen to be counterbalanced by a negative potential produced by the sulphur atoms. Both arguments – the configuration together with the potential term – can explain the almost constant Ga B.E. in those two compounds. An extension of these arguments to the data for $Ga_2S$ and also the selenide and telluride compounds seems to be acceptable.

The decrease found in Ga B.E. by changing sulphur by selenium and the subsequent increase in going from the selenides to the tellurides cannot be explained by an electronegativity effect only. In the series S, Se, Te the electronegativity is decreasing even if the orbital electronegativity is taken into account. Here again the contribution of the potential term has to be considered. Two factors are changing this term. Firstly, the decreasing electronegativity influences the charge $q'$ and secondly the covalent radius is increased. Both effects reduce the negative potential term. The exact distances between the atoms and the hybridization are needed before we can calculate the potential term. Another effect that can also play an important role is the relaxation energy.

A complete crystal structural analysis of all the compounds studied is needed before a decision can be made.

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11 k and l are constants; q is the charge on the Ga atom; V, the potential term, is expressed as $\Sigma(q'/r)$ where $q'$ is the charge and r the distance from the Ga atom of the atoms surrounding it.