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X-RAY RAMAN SPECTRUM OF A Be THIN FILM
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SURFACE CORE LEVEL SHIFT OF BERYLLIUM. X-RAY RAMAN SPECTRUM OF A Be THIN FILM

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Abstract - The bonding characteristics and the inner core Is binding energy of an one-dimensional Be film is studied in comparison to the bulk Be metal. The difference in the Is binding energy is calculated very accurately together with the variation of the bonding characteristics responsible for the appearance of anomalous peaks in the x-ray Raman spectrum of Be metal.

The calculated core level shift between the bulk and the film after the adjustment of the Fermi level provides the chemical shift for the Is core binding energies between bulk and surface atoms in Be metal. The calculated value for the core surface chemical shift is 0.55eV in excellent agreement with the experimental value of 0.5eV.

Earlier calculation based on the small cluster unrestricted Hartree-Fock (UHF) method have provided a very good picture of the bonding characteristics and inner core electron properties of Be metal [1,2]. In addition to some standard bonding and binding properties, the nature of the anomalous peaks in the x-ray Raman spectrum [1] and the Is core binding energy [2] were given an excellent description. Based on the success of these earlier UHF calculations, the present work extends this method to the description of the Is core binding energy and x-ray Raman spectrum of a Be thin film for which several controversies still exist [3]. At the same time this work illustrates a very successful scheme for calculating accurately the chemical shift observed in electronic binding energies between bulk and surface atoms in a metal; Be in the present case [4].

The choice of Be for this study is based on its simplicity and peculiarity in the physical properties. This simplicity (Be atom is light and has a closed shell 1s^22s^2 configuration) and peculiarity, due mainly to its large departure from free electron behavior, makes Be more amenable to a UHF small cluster type of calculation. This type of calculation for Be metal has been proven very successful not only in computing the bonding characteristics and their signature in the x-ray Raman spectrum [1], but also in very accurately calculating inner core (Is) electron binding energies [2] and phonon properties as well [5].
Depending on the property under study, a small atomic cluster comprised of a reference atom and its near and at least next near neighbors can be satisfactory for simulating the infinite crystal. One then should be careful enough to correctly distinguish the realistic characteristics from the spurious effects resulting from the finite surface of the cluster. Questions about the suitability and limitations of small clusters calculations have been discussed elsewhere [5,6]. Bulk Be metal and Be thin film are described in this calculation by a 13-atom cluster comprised of a reference atom and its 12 nearest neighbors, in hexagonal closed packed (hcp) geometry. Seven atom clusters, including only the absolutely nearest neighbors were also quite successful in describing most of the electronic properties (except total binding energies) of both bulk and planar systems. Details about the exact cluster geometry and the basis set are given in Ref. 1 and in a forthcoming publication by this author. The geometry of the Be$_7$ planar cluster can be seen in figure 1 which also displays in a constant amplitude contour, the wave function at the Fermi level.

![Figure 1](image_url)

Constant amplitude contours for the state at the Fermi level of the Be$_7$ thin film cluster. Solid curves represent positive amplitudes, dotted curves represent negative amplitudes and dashed curves zero amplitudes. The positions of the Be nuclei can be easily seen as large dots.

This wave function was calculated ab initio by the UHF method, which has been recognized as the most accurate simple Hartree-Fock type of method for metal clusters [7]. The standard POLYATOM computer code was used in evaluating the integrals and a modified version of the program UHFABK of A.B. Kunz was employed to perform the UHF calculations. This last program is capable of selectively depopulating occupied orbitals, so that state specific self-consistent-field differences (ΔSCF) in total energies can be calculated to obtain specific one-electron binding energies ($\varepsilon_b$). These binding energies are given as:

$$\varepsilon_b = E_t(N-1) - E_t(N)$$  \hspace{1cm} (1)

where $E_t(N-1)$ and $E_t(N)$ are the total energies of the final and initial states of the $N$ electron system. $N$ in the Be$_{13}$ clusters is equal to 52. This cluster ΔSCF value accounts for symmetry, exchange and complete relaxation of the orbitals. It has been argued [2,7] that to a good approximation contributions of atomic-like electron correlation and relativity effects, $\Delta E_a$, can be incorporated separately by simple superposition to the cluster ΔSCF results. The final correlated binding energy $\varepsilon_b^c$, is thus given by

$$\varepsilon_b^c = \varepsilon_b + \Delta E_a$$  \hspace{1cm} (2)

The results for Be bulk metal are in excellent agreement with experiment, as can be seen in the second raw of table I. For the thin film, since the atomic correlation is the same, it is expected that the absolute value, and not only the relative magnitude, of the $1s$-binding energy should be very accurate as it is for the bulk. Of course, this implies that the planar cluster is properly describing
the 2D film so well as the bulk cluster describes the solid.

**TABLE I**

Comparison of the calculated physical quantities for the one monolayer thin film and bulk Be systems. The fist value for the Fermi energy and work function is simply the Koopman's value. The second value is obtained by $\Delta$SCF differences.

<table>
<thead>
<tr>
<th></th>
<th>Thin film calculated</th>
<th>Bulk calculated</th>
<th>Bulk observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s binding energy (eV) (relative to vacuum)</td>
<td>114.7</td>
<td>115.4</td>
<td>115.6</td>
</tr>
<tr>
<td>Fermi energy (eV)</td>
<td>9.7</td>
<td>14.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td>5.60</td>
<td>2.25</td>
<td>7.10</td>
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<td></td>
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As can be seen in the table I, not only the 1s binding energy, but also the $\Delta$SCF values of the work function, $\phi$, and of the Fermi energy, $\epsilon_F$, are in good agreement with experiment for the bulk Be metal. The corresponding values for the thin film are expected to be of the same accuracy, since the same basis set, number of near neighbors and method of calculation were employed. The Koopman's values for the same quantities are well overestimated as is expected, due to poor screening.

The 0.7eV 1s binding energy difference between the bulk and the thin film is an important quantity on its own merit. However, the same quantity properly referred to the Fermi level difference, can provide the surface core level shift between bulk and surface atoms of the same crystal. This last quantity, which has attracted a lot of interest recently, is considered as a very important and useful measure of the difference in chemical environment between bulk and surface atoms of a given material [8]. Within the framework of equations (1) and (2), the core level shift $\Delta\epsilon_{bs}$, can be expressed as $\Delta\epsilon_{bs} = \epsilon_{bs}^B - \epsilon_{bs}^S$ (3), where $\epsilon_{bs}^B$ and $\epsilon_{bs}^S$ represent the binding energies $\epsilon_b$ for the bulk (B) and surface (S) atoms respectively with respect to the Fermi level $E(F)$. The corresponding quantities with respect to the vacuum (V) are designated $\epsilon_{bs}^B,V$ and $\epsilon_{bs}^S,V$ respectively. The binding energies with respect to vacuum $b$ are the quantities coming out of the calculation, whereas the energies with respect to the Fermi level are the experimentally measured binding energies. The two are connected through the work function $\phi$ (or $\phi^B$ and $\phi^S$ for bulk and surface respectively. Equation (3) can then be rewritten as:

$$\Delta\epsilon_{bs}^B = \epsilon_{bs}^B,V - \epsilon_{bs}^S,V - (\phi^B - \phi^S)$$  (4)

Using the results of table I, equation (4) gives $\Delta\epsilon_{bs}^B = -0.50eV$, in excellent agreement with the experimental value of -0.55eV [4].

Another inner core characteristic of Be metal which has been described quite well by the UHF cluster technique, is the nature of the anomalous peaks in the x-ray Raman spectrum [1]. These peaks are not present in the thin film theoretical x-ray Raman spectrum. This is in accord with the predicted origin of these peaks, as due to the quite large 3spX3p$\nu_4$ splitting of the 3sp band [1]. A similar splitting of the 2sp orbital was considered responsible for the dip in the density of states curve at the Fermi level [1]. This type of splitting is not present in the two dimensional (2D) film and as a consequence, the x-ray Raman spectrum of a 2D Be film is predicted here to have no anomalous peaks, similar to those observed in bulk Be.
metal. Similarly this calculation predicts a good metallic character for the Be 2D film as suggested also by more elaborated Local Density Approximation (LDA) calculations [3].

Concluding this presentation, in order to gain more insight in the surface core level shift results, a short comparison with other calculations is given. The LDA calculation based on Koopman's values for a three layers Be film predicts a shift of -0.21eV [3], whereas Miedema's estimate procedure [9] gives only -0.15eV. The shift of -0.50eV predicted here is in excellent agreement with the experimental value of -0.55eV. Preliminary calculations for other light metals have given results of similar quality, indicating that this type of agreement is not purely fortuitous. It appears that a predominance of initial state effects and an almost lack of significant post-collision events could be mainly responsible for the success of the proposed method here. An examination of the physical and mathematical factors influencing the success and the possible limitations of the present method, together with additional details and complete calculations for several simple metals will be given in a forthcoming publication.

References