The Madelung Energy for the Structure $Y_2HfS_5$.

The Madelung energy for the compound $Y_2HfS_5$ is calculated. The results are given as a function of the effective charge, $w_F$, on the sulfur ion, $q_S$, as $w_F = -56.495 - 59.420 q_S - 34.167 q_S^2$ with the normal valence of sulfur at $q_S = -2$. Assuming that the exponent in the Born potential is 10, the binding energy, $W$, of $Y_2HfS_5$ is found to be $W = -4222.8 - 4441.4 q_S - 2553.8 q_S^2$ kcal/mole.
CONTENTS

1. INTRODUCTION ........................................ 5
2. CRYSTAL STRUCTURE .................................... 5
3. COMPUTATION ........................................... 6
   ACKNOWLEDGEMENT ........................................ 12
   LITERATURE CITED ...................................... 12
   DISTRIBUTION ........................................... 13

TABLES

I Atomic Positions of Constituent Ions in Y_2HfS_5 ........ 6
II Atomic Positions of All Ions in Unit Cell of Solid Y_2HfS_5 7
III Electric Potential at Various Sites in Y_2HfS_5 ........ 8
1. INTRODUCTION

In the theory of the cohesive energy of ionic or nearly ionic crystals, the electrostatic energy, or Madelung energy, is important. Generally, the electrostatic cohesive force persists, despite the presence of strong repulsive forces of ions of similar charge among the constituent ions. Because of the magnitude of the Madelung energy, it dominates the energy of formation of most ionic solids and therefore is of interest to chemists who are attempting to grow single crystals larger than microscopic powders.

The amount of literature on the various methods of calculating the electrostatic energy of an ionic solid is absolutely overwhelming, but a methodical compilation of the results of these calculations does not seem to exist. Practically every textbook of physical chemistry or solid-state physics lists a number of references to original papers on this subject. Consequently, we list here only references pertinent to the problem at hand: the calculation of the Madelung energy for Y_2HfS_5. The technique used here is elementary; however, it seems not to be in any of the textbooks.

2. CRYSTAL STRUCTURE

The crystal structure of Y_2HfS_5 is, according to Jeitschko and Donohue,\(^1\) orthorhombic, Pnma, which is space group No. 62 in the International Tables of Crystallography.\(^2\) As reported by Jeitschko and Donohue, the cell dimensions and the atomic position of each independent constituent ion are given in table I. The symmetry operations necessary to develop the position of the ions in a single cell are taken from the International Tables of Crystallography.\(^2\) The number of molecular units, Z, in a cell is 4 so that there are 32 independent \(x, y,\) and \(z\) coordinates necessary to specify the position of all the ions in a single cell. The position of each of the atoms is shown in table II in a coordinate system so that the yttrium ion in position 1 is chosen as the origin and the ions are listed in the sequence chosen by Jeitschko and Donohue.\(^1\) By translation, any lattice point is equivalent to any other point obtained from that point by adding an integer to any or all of its \(x, y,\) and \(z\) coordinates. Using this rule, one can choose a coordinate system so that \(-1/2 < x \leq 1/2\), \(-1/2 < y \leq 1/2\), and \(-1/2 < z \leq 1/2\), and this system has been chosen in table II (p. 7).

\(^1\)W. Jeitschko and P. C. Donohue, Acta Crystallogr., B31 (1975), 1890.
TABLE I. ATOMIC POSITIONS OF CONSTITUENT IONS IN $Y_2HfS_5$~

<table>
<thead>
<tr>
<th>Ion</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>8(d)</td>
<td>0.1778</td>
<td>0.9974</td>
<td>0.0251</td>
</tr>
<tr>
<td>Hf</td>
<td>4(m)</td>
<td>0.0060</td>
<td>1/4</td>
<td>0.5742</td>
</tr>
<tr>
<td>$S_1$</td>
<td>8(d)</td>
<td>0.4081</td>
<td>0.0367</td>
<td>0.1630</td>
</tr>
<tr>
<td>$S_2$</td>
<td>4(m)</td>
<td>0.1822</td>
<td>1/4</td>
<td>0.3331</td>
</tr>
<tr>
<td>$S_3$</td>
<td>4(m)</td>
<td>0.5032</td>
<td>1/4</td>
<td>0.5522</td>
</tr>
<tr>
<td>$S_4$</td>
<td>4(m)</td>
<td>0.2921</td>
<td>1/4</td>
<td>0.8152</td>
</tr>
</tbody>
</table>


Note: The x, y, and z coordinates are in units of $a$, $b$, and $c$, respectively, with $a = 11.4585$ Å, $b = 7.7215$ Å, and $c = 7.2207$ Å.

The symmetries of the various positions are:

- $8(d)$, $\pm(x, y, z)$, $\pm(1/2 + x, 1/2 - y, 1/2 - z)$,
- $4(m)$, $\pm(x, 1/4, z)$, $\pm(1/2 - x, 3/4, 1/2 - z)$.

3. COMPUTATION

The electrostatic potential, $\phi$, at a site, $\nu$, due to ions of charge, $q_\nu$, in the crystal is given by

$$\phi(\nu) = \sum_{l,m,n} \sum_{\nu=1}^{32} \frac{q_\nu}{R_{l,m,n,\nu}^2},$$

where

$$R_{l,m,n,\nu}^2 = (x_\nu - x_\nu + l)^2a^2 + (y_\nu - y_\nu + m)^2b^2 + (z_\nu - z_\nu + n)^2c^2,$$

with $l$, $m$, and $n$ integers ranging from positive to negative values large enough so that the sum converges to a unique limit ($\sim 10$ for four significant digits). The charge on each ion, $Z_\nu$, is in units of the electronic value so that $Z_\nu = e\nu$. For the normal valence,
TABLE II. ATOMIC POSITIONS OF ALL IONS IN UNIT CELL OF SOLID Y₂HfS₅

<table>
<thead>
<tr>
<th>Ion No.</th>
<th>Ion</th>
<th>Coordinate</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>xᵢ</td>
<td>yᵢ</td>
</tr>
<tr>
<td>1</td>
<td>Y</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
<td>Y</td>
<td>0.5000</td>
<td>-0.4948</td>
</tr>
<tr>
<td>3</td>
<td>Y</td>
<td>-0.3556</td>
<td>-0.5000</td>
</tr>
<tr>
<td>4</td>
<td>Y</td>
<td>0.1444</td>
<td>0.0052</td>
</tr>
<tr>
<td>5</td>
<td>Y</td>
<td>-0.3556</td>
<td>0.0052</td>
</tr>
<tr>
<td>6</td>
<td>Y</td>
<td>0.1444</td>
<td>-0.5000</td>
</tr>
<tr>
<td>7</td>
<td>Y</td>
<td>0.0000</td>
<td>-0.4948</td>
</tr>
<tr>
<td>8</td>
<td>Y</td>
<td>0.5000</td>
<td>0.0000</td>
</tr>
<tr>
<td>9</td>
<td>Hf</td>
<td>-0.1718</td>
<td>0.2526</td>
</tr>
<tr>
<td>10</td>
<td>Hf</td>
<td>-0.1838</td>
<td>-0.2474</td>
</tr>
<tr>
<td>11</td>
<td>Hf</td>
<td>0.3162</td>
<td>-0.2474</td>
</tr>
<tr>
<td>12</td>
<td>Hf</td>
<td>0.3282</td>
<td>0.2526</td>
</tr>
<tr>
<td>13</td>
<td>Si</td>
<td>0.2303</td>
<td>0.0393</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>-0.2697</td>
<td>0.4659</td>
</tr>
<tr>
<td>15</td>
<td>Si</td>
<td>0.4141</td>
<td>-0.4607</td>
</tr>
<tr>
<td>16</td>
<td>Si</td>
<td>-0.0859</td>
<td>-0.0341</td>
</tr>
<tr>
<td>17</td>
<td>Si</td>
<td>0.4141</td>
<td>-0.0341</td>
</tr>
<tr>
<td>18</td>
<td>Si</td>
<td>-0.0859</td>
<td>-0.4607</td>
</tr>
<tr>
<td>19</td>
<td>Si</td>
<td>0.2303</td>
<td>0.4659</td>
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<tr>
<td>20</td>
<td>Si</td>
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<td>0.0393</td>
</tr>
<tr>
<td>21</td>
<td>Si</td>
<td>0.0044</td>
<td>0.2526</td>
</tr>
<tr>
<td>22</td>
<td>Si</td>
<td>-0.3600</td>
<td>-0.2474</td>
</tr>
<tr>
<td>23</td>
<td>Si</td>
<td>0.1400</td>
<td>-0.2474</td>
</tr>
<tr>
<td>24</td>
<td>Si</td>
<td>-0.4956</td>
<td>0.2526</td>
</tr>
<tr>
<td>25</td>
<td>Si</td>
<td>0.3254</td>
<td>0.2526</td>
</tr>
<tr>
<td>26</td>
<td>Si</td>
<td>0.3150</td>
<td>-0.2474</td>
</tr>
<tr>
<td>27</td>
<td>Si</td>
<td>-0.1810</td>
<td>-0.2474</td>
</tr>
<tr>
<td>28</td>
<td>Si</td>
<td>-0.1746</td>
<td>0.2526</td>
</tr>
<tr>
<td>29</td>
<td>Si</td>
<td>0.1143</td>
<td>0.2526</td>
</tr>
<tr>
<td>30</td>
<td>Si</td>
<td>-0.4699</td>
<td>-0.2474</td>
</tr>
<tr>
<td>31</td>
<td>Si</td>
<td>0.0301</td>
<td>-0.2474</td>
</tr>
<tr>
<td>32</td>
<td>Si</td>
<td>-0.3587</td>
<td>0.2526</td>
</tr>
</tbody>
</table>

Note: The x, y, and z coordinates are in units of a, b, and c so that the actual distance from ion 1 to any ion, i, is \( (a^2x_i^2 + b^2y_i^2 + c^2z_i^2)^{1/2} \).
$q_v = 3, \ 1 \leq v \leq 8 \quad (Y^{3+}),$
$q_v = 4, \ 9 \leq v \leq 12 \quad (Hf^{4+}),$
$q_v = -2 \ 13 \leq v \leq 32 \quad (S^{2-}),$

and $\sum_{v=1}^{32} q_v = 0$ for neutrality of the entire solid. The sum given by equation (1) was calculated for each of the different ions (Y, Hf, S1, S2, S3, and S4) given in table I. The sum was done so that, for each value of $l$, $m$, and $n$, the sum over all the constituent ions in a cell was done first. The results of this calculation are shown in table III. As a check on the convergence of the sum for a given site, $\mu$ was computed and compared to a site that is identical, that is, $\phi(l)$

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>$\phi(\mu)$, $q_S = -2$</th>
<th>$\phi(\mu)$, $q_S = 0$</th>
<th>$\phi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>-2.2256</td>
<td>-1.7304</td>
<td>0.24760</td>
</tr>
<tr>
<td>Y</td>
<td>-2.2256</td>
<td>-1.7302</td>
<td>0.24770</td>
</tr>
<tr>
<td>Hf</td>
<td>-2.4535</td>
<td>2.9775</td>
<td>2.71555</td>
</tr>
<tr>
<td>S1</td>
<td>1.4336</td>
<td>-0.72753</td>
<td>-1.08057</td>
</tr>
<tr>
<td>S1</td>
<td>1.4337</td>
<td>-0.72777</td>
<td>-1.08074</td>
</tr>
<tr>
<td>S2</td>
<td>1.4088</td>
<td>0.13992</td>
<td>-0.63444</td>
</tr>
<tr>
<td>S3</td>
<td>1.1192</td>
<td>1.1824</td>
<td>0.03160</td>
</tr>
<tr>
<td>S4</td>
<td>1.6004</td>
<td>0.11696</td>
<td>-0.74172</td>
</tr>
</tbody>
</table>

Note: The charge on yttrium ion $q_Y$ is +3, while the charge on the hafnium ion is $q_{Hf}$ chosen so that $q_{Hf} + 5q_s = -6$, where $q_s$ is the charge on the sulfur ion. The last column is the constant in the expression $\phi(\mu) = \phi_0(\mu) + q_s \phi_1$. 

TABLE III. ELECTRIC POTENTIAL AT VARIOUS SITES IN Y$_2$HfS$_5$; UNITS ARE (Å)$^{-1}$
and \( \phi(2) \) or \( \phi(9) \) and \( \phi(10) \), and the sum was extended until the agreement was satisfactory. A limit of \( \pm 10 \) on the \( l, m, \) and \( n \) sums gave agreement to four digits. The total electrostatic energy, \( U_E \), for a cell is given by

\[
U_E = \frac{e^2}{2} \sum_{i=1}^{6} q_i N_i \phi_i(u_1),
\]

where \( N_i \) is the number of each type of ion (such as \( q_1 = 3, N_1 = 8 \) for \( Y \) and \( q_1 = 4, N_1 = 4 \) for \( Hf \)) and \( u \) covers the distinct types of ions.

In the discussion of the structure, Jeitschko and Donohue\(^1\) state that the compound \( Y_2HfS_6 \) is semi-ionic. That is, the yttrium site is ionic along with the complex \( (HfS_6)_6 \), but within this latter complex the hafnium and sulfur may be covalent. To account partially for this covalency, one can choose an effective charge on the sulfur ion, \( q_s \), so that

\[
q_{Hf} + 5q_s = -6,
\]

which retains the ionic character of the \( HfS_6 \) complex. Also, the lattice sum was performed by using \( q_s = -0 \) (\( q_{Hf} = -6 \), not realistic), and the results are given in table III. Since the electrostatic potential is linear in the charge, each potential can be written in the form

\[
\phi(u) = \phi_0(u) + q_s \phi_1(u)
\]

for each distinct site. In the simple compounds where the x-ray data depend on only one parameter such as "\( a \)" the cell size in a simple cubic material, the electrostatic potential is generally expressed as

\[
\phi = -\frac{eM}{a},
\]

where \( M \) is the Madelung constant, which has been tabulated for most of the simpler cubic structures.\(^3\) In the more complicated structures, an effective Madelung constant can be defined by

\(^1\)W. Jeitschko and P. C. Donohue, Acta Crystallogr., B31 (1975), 1890.
\[ M_\mu = \phi(\mu) v^{1/3} , \]  

(6)

where \( \phi(\mu) \) is given by Jeitschko and Donohue,\(^1\) and \( v \) is the volume of the unit cell. We do not use this definition here.

If one chooses a solid of dimension \( A, B, \) and \( C \) lengths in the \( x, y, \) and \( z \) dimensions, respectively, then the number of cells in its volume is given by

\[ N = \left( \frac{A}{a} \right) \left( \frac{B}{b} \right) \left( \frac{C}{c} \right) , \]  

(7)

and the total energy per unit volume, \( w_\varepsilon \), is

\[ w_\varepsilon = \frac{U}{v} , \]  

(8)

where we have used equation (2) and \( v = abc \).

In many calculations, where the complete binding energy is required, one must assume some form of a repulsive force. Many different types are assumed in the literature with various degrees of sophistication. We assume the simple Born potential, \( B/r^n \), where \( B \) is a constant and \( n \) is determined from experimental data.\(^4\) If the material is assumed isotropic, then both the electrostatic energy and the repulsive energy can be written in terms of a single variable such as \( v^{1/3} \), where \( v \) is the volume of the unit cell. The condition that the energy is a minimum then requires that the derivative of the energy vanish at the equilibrium value of \( v \). If it does, then

\[ w = w_\varepsilon \left( 1 - \frac{1}{n} \right) , \]  

(9)

with \( w_\varepsilon \) given by equation (8).

It is customary to express the energy in kilocalories per mole, \( W_E \), for \( Y_2HfS_5 \), this conversion of the various constants gives

\(^1\)W. Jeitschko and P. C. Donohue, Acta Crystallogr., B31 (1975), 1890.

\[ W_E = 83.05 \omega_E \quad (10) \]

if \( W_E \) is in reciprocal angstroms. Using the results given in table III, one can write electrostatic energy as

\[ W_E(q_s) = -56.495 - 59.420q_s - 34.167q_s^2. \quad (11) \]

The result given in equation (11) for several values of \( q_s \) is \( W_E(-2) = -74.325 \), \( W_E(-1) = -32.240 \), and \( W_E = -40.275 \), all in reciprocal angstroms. With the result of equation (11) substituted in equations (10) and (9), one finally has for \( W \), the total energy,

\[ W = 83.05 \left( 1 - \frac{1}{n} \right) (-56.495 - 59.420q_s - 34.167q_s^2) \text{ kcal/mole.} \quad (12) \]

Generally, the best fit value of \( n \) is obtained by matching the theoretical and experimental values, and in simple compounds the resulting value of \( n \) varies from 6 to 12. Choosing a value of \( n = 10 \) in equation (12), one obtains

\[ W = -4222.8 - 4441.4q_s - 2553.8q_s^2 \text{ kcal/mole.} \quad (13) \]

This gives the lattice energy frequently used in the Born-Haber cycle calculations.\(^5\)

Occasionally, the lattice energy is calculated by assuming that the solid is formed from preexisting ionic complexes.\(^6\) A reasonable approach from this assumption is \( 2Y^{3+} + (\text{HfS}_5)^6^- \), which forms the solid. In this approach, one needs the energy of formation, \( U \), of a single \((\text{HfS}_5)^6^-\). This energy as a function of \( q_s \) is

\[ U[(\text{HfS}_5)^6^-] = -46.709q_s - 28.332q_s^2(\text{A}^{-1})^{-1}. \quad (14) \]

---


If this result is subtracted from equation (11) and the result is multiplied by 83.05[1 - (1/n)], then the energy of formation of the solid $Y_2\text{HfS}_5$ from the constituent ionic complexes $2Y^{3+}$ and $(\text{HfS}_5)^{6-}$ is

$$U = -4222.8 - 948.74q_S - 436.14q_S^2 \text{ kcal/mole}.$$  \hspace{1cm} (15)

---

ACKNOWLEDGEMENT

I thank Richard P. Leavitt for his help in the conversion of units and Herbert Curchack and Robert Rosen for helpful guidance through the necessary steps in the computer programming.

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15