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THRESHOLD EXONENTS IN ANOMALOUS ABSORPTION SPECTRA OF HEAVY ALKALI METALS

Y. OHMURA, A. OGIWARA and S. SATÔ

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Abstract - Threshold exponents of soft X-ray absorption and emission spectra of heavy alkali metals (K, Rb and Cs), in the theory of Nozières and De Dominicis are calculated. The phase shifts are obtained in the Born approximation by taking account of: (1) the effect of characteristic features of the Bloch electrons in the effective mass, (2) structures of the hole in the hole potential and (3) the effect of the screening on the hole potential. For Cs, pulling-in of the localized 4f-orbital which results in the screening of the 5p-hole potential in the final state is proposed.

I - INTRODUCTION The X-ray absorption and emission spectra of metals near the threshold energy \( \omega_F \) have been shown by Nozières and De Dominicis (ND) to be given approximately as

\[
\omega_\ell (\omega) = A_{\ell-1} (\omega) \exp\left(-\alpha_{\ell-1} \ln|\omega - \omega_F|/D\right) \\
+ A_{\ell+1} (\omega) \exp\left(-\alpha_{\ell+1} \ln|\omega - \omega_F|/D\right),
\]

(1)

\[
\alpha_\ell = \frac{2\delta_\ell}{\pi} - 2\sum_j (2j+1)(\delta_j/\pi)^2.
\]

Here, \( \delta_\ell \) is the angular momentum of the inner-shell electron that is involved in the transition, and \( A_{\ell-1} \) and \( A_{\ell+1} \) are functions including the product of a step function and the square of the transition matrix element for the transition of the electron state \( \ell \) to \( \ell+1 \) at the threshold. \( D \) is a constant of an energy with a magnitude of the order of the width of the conduction band. \( \alpha_{\ell-1} \) and \( \alpha_{\ell+1} \) are exponents obtained through eq. (2) by the phase shifts \( \delta_\ell \) which describe the scattering of conduction electrons by the core hole. Experimental/2,3/ and theoretical/4/ results on exponents \( \alpha_0 \) for absorption of \( p \)-shell electrons for K, Rb and Cs are shown in Table I.
Table I. Experimental and Theoretical Results on Exponents $\alpha_0$

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. I</td>
<td>0.23</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>Exp. II</td>
<td>0.28±0.02</td>
<td>0.26±0.02</td>
<td>0.07±0.02</td>
</tr>
<tr>
<td>Theory</td>
<td>0.28</td>
<td>0.29</td>
<td>0.23</td>
</tr>
</tbody>
</table>


Though the values of Exp.I and Exp.II are considerably different with each other, Table I seems to show that the theoretical result is still qualitatively different from the experimental result in the following points: (1) Theoretical values of $\alpha_0$ are not descending in the order of K, Rb and Cs. (2) The exponent $\alpha_0$ of Cs obtained experimentally is almost 0, while the theoretical value is far from it. In this paper, we try to revise the theoretical values of $\alpha_0$ taking into account of 3 points denoted in abstract in the belief that the ND theory is still working well as a first approximation in the problem of absorption near threshold for heavy alkali metals.

II - Theory

We calculate phase shifts based on a simple model following the prescription of ref.5. Since the inner-shell hole is formed by removing a core electron, the hole potential is given, in the usual notations/5/ as

$$v_{dc}(r) = -k_s |r-r'| \int dr' \frac{\rho_c(r')}{|r-r'|}$$

(3)

where $\rho_c(r')$ is the density of the core electron at $r'$ and $k_s$ is the screening constant. Fig.1 shows the hole potential thus obtained for Li Is-hole, Na 2p-hole and K 3p-hole. We find that the hole potential becomes more shallow and more flat in the order of Li, Na and K. We include the exchange interaction of the conduction electrons with the core-hole in addition to the direct Coulomb interaction given by eq.(3). This is done by the $X_-$-method. If the hole is born, for example, by the transition of the core electron with the spin upward, the exchange potential due to the hole is effective only on conduction electrons with the spin upward. The extra potential for the electrons with the spin upward is thus given by

$$v_{ex,\uparrow}(r) = -6\alpha (3/4\pi)^{3/2} \int [\rho_0,\uparrow(r) - \rho_c(r)] \frac{1}{\rho_c(r)} - (\rho_0,\uparrow(r))^\dagger$$

(4)

where $\rho_0,\uparrow(r)$ is the density of electrons at $r$ with the spin upward and $\alpha$ is a constant taken to be 0.7.

The exchange effect, of which Girvin and Hopfield/6/ first took into account in the exponent in the ND theory, must be treated carefully since it is claimed to have no effect on the threshold exponent if it is treated similarly as in the s-d problem/7-9/. The final state, however, is in the excited state and this could make the present problem different from the case of s-d problem where the ground state is concerned. The crucial parameter in the present problem, $-JpF \ln[(\omega-\omega_p)/|D|]$, where $J$ is the coupling constant of the exchange potential($J>0$) and $p_F$ is
the constant density of states of the conduction electrons per atom per spin, is thought very large near threshold, and the less divergent terms are required to be equally summed leading to the renormalization of the coupling constant. If we consider the lifetime \( t \) of the final state, \((\omega - \omega_p) 2t \) is required for the frequency range. The imaginary part of the self energy in this frequency range could become large. In that case, the sum of the divergent terms to an infinite orders could be meaningless. If this is true, we will be allowed to use the perturbation theory taking only a few terms in the expansion. In the present problem, this means to introduce the exchange potential as the first correction to the hole potential given by eq.(3).

Thus, the hole potential (by the transition of the core electron with spin upward) to the conduction electrons could be

\[ v_c = v_{dc} + v_{ex}, \]

for the spin upward electron

\[ v_{dc}, \]

for the spin downward electron.

The phase shifts for spin upward (\( \uparrow \)) and spin downward (\( \downarrow \)) electrons are calculated using the potential given by eq.(5) following the prescription given in ref.5. We have the relation

\[ \delta_{\uparrow \uparrow} = \delta_{\downarrow \downarrow} + \Delta \delta_{\uparrow \downarrow}, \]

where the second term of eq.(6) is from the exchange part of the hole potential. The Friedel sum rule and the threshold exponents are given by the following formula:

Fig.1 The hole potential of Li, Na and K.

Fig.2 The hole potential of K.

Fig.3 The hole potential of Rb.

Fig.4 The hole potential of Cs.
We used the double $\zeta$-functions of atomic orbitals proposed by Clementi and Roetti/10/ for the wave functions of the core parts. A single orthogonalized wave function is used for the electron in the conduction band.

III - RESULTS

Figure 2 and Fig.4 show the potentials obtained by eq. (3), (4) and (5). Absolute magnitude of the potentials decreases in the order of K, Rb and Cs. Table II gives the result of the calculation for $\alpha_0$.

IV - Discussion

Table II shows that the inclusion of the exchange potential in our calculation made the values of $\alpha_0$ close to that of Exp. I in Table I. Decrease of the hole potential by the exchange interaction made the values of $\alpha_0$ descending in the order of K, Rb and Cs. We are not convinced if the inclusion of the exchange interaction is reasonable. Present study shows, however, that the decrease of the hole potential by any other reasons will also decrease the values of $\alpha_0$.

For Cs, our result does not agree even qualitatively with the experimental results. It is theoretically difficult to obtain $\alpha_0 \leq 0$ in the reasonable approximation to the core hole potential. Since the 4f-orbitals of Cs lie close to the Fermi energy, we could expect that the localized 4f-orbital is pulled in by the 5p-hole potential allowing, afterwards, one electron occupy this localized 4f-orbital: This could result in the screening of the 5p-hole potential considerably. The Friedel sum rule(7) is then changed to meet the new situation where the net charge of the hole potential is zero. Problems in threshold absorption of rare-gas impurities in metals/11/, where $\alpha_0$=-1 are observed, could also be solved by taking account of similar effects. The result of our calculation will be published elsewhere.

Table II. Threshold Exponents $\alpha_0$ Obtained in the Present Paper

<table>
<thead>
<tr>
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<th>Cs</th>
</tr>
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<tbody>
<tr>
<td>Theor.I</td>
<td>0.31</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td>Theor.II</td>
<td>0.22</td>
<td>0.19</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Theor.I ; Result without the exchange potential.

Theor.II ; Result with the exchange potential.

References