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PARAMAGNETIC RESONANCE SPECTRA
OF 4d AND 5d TRANSITION ELEMENTS

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Abstract. — The paramagnetic resonance spectra of Nb$^{4+}$, W$^{5+}$, Mo$^{3+}$, and Tc$^{4+}$ and Re$^{4+}$ in the cubic field in K$_2$PtCl$_6$, Cs$_2$ZrCl$_6$ and (NH$_4$)$_2$PtCl$_6$ was measured in detail. The spectrum of $\Gamma_8$ state was carefully plotted out and compared with theory.

We briefly report measurements on the 4d and 5d transition elements in the crystal field of Cs$_2$ZrCl$_6$. Among the elements that were studied in detail are Nb$^{4+}$ and W$^{5+}$, Mo$^{3+}$, Tc$^{4+}$ and Re$^{4+}$. Some of these elements were studied in similar crystal fields such as K$_2$PtCl$_6$ and (NH$_4$)$_2$PtCl$_6$ as well as Cs$_2$HfCl$_6$.

The ions Nb$^{4+}$ and W$^{5+}$ have similar electronic structure, 4d$^1$ and 5d$^1$ respectively. Their spectra were studied in the crystal field of Cs$_2$ZrCl$_6$. Both spectra can be explained to arise from the paramagnetic ion taking the place of the Zr$^{4+}$ ion. However, the spectrum consists of the superposition of three spectra corresponding to three ions per unit cell, with a tetragonal distortion along the cubic axes.

The spectrum can be described by the spin Hamiltonian:

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + AS I_z + B(S, I_x + S_y I_y)$$

with parameters:

- Nb$^{4+}$: $g_{\parallel} = 1.9184 \pm 0.0006$
- W$^{5+}$: $g_{\parallel} = 1.8113 \pm 0.0005$

$$|A| = 124.7 \pm 0.5 \times 10^{-4} \text{ cm}^{-1}$$
$$|B| = 63.1 \pm 1.5 \times 10^{-4} \text{ cm}^{-1}$$
$$S = 1/2, \quad I = 1/2.$$
\[ \mathcal{H} = \beta \left[ S^{(1)} H^{(1)} + S^{(1)} H_0^{(1)} - S_0^{(1)} H_0^{(1)} \right] + 
+ u \beta \left[ H_0^{(1)} \left( \frac{1}{2} S_3^{(1)} + \frac{1}{2} \sqrt{\frac{3}{5}} S_1^{(3)} \right) \right] + H_1^{(1)} \left( \frac{1}{2} S_3^{(3)} + \frac{1}{2} \sqrt{\frac{3}{5}} S_1^{(3)} \right) \right] + \sqrt{\frac{2}{5}} H_0^{(1)} S_0^{(3)} \right] \]

Where the \( S^{(m)}, I^{(m)} \) and \( H^{(m)} \), are the \( n \)-th components of the irreducible operators of order \( m \), constructed from the vector operators \( S, I \) and \( H \) \[^3\].

In the case of \( Cr^{3+} \) and \( V^{2+} \), \( |A| > |U| \), \( |g| > |u| \) and the angular dependence is very small \[^4\]. In the case of \( Re^{4+} \) and \( Tc^{4+} \), \( |A| > |U| \), \( |g| > |u| \), and the angular dependence is more prominent \[^2\].

The spectrum of \( Tc^{4+} \) in \( K_2PtCl_6 \) was studied in detail. The angular dependence was determined and the relative intensities of the lines were measured. The following parameters were found:

**Table I**

*Comparison between the parameters of the \( \Gamma_3 \) Hamiltonian for \( Re^{4+} \) (5d\(^3\)), \( Tc^{4+} \) (4d\(^3\)), and \( Cr^{3+} \) (3d\(^3\)) for octahedral symmetry*

<table>
<thead>
<tr>
<th>Host and ion</th>
<th>( T (\text{K}) )</th>
<th>( g )</th>
<th>( u/g )</th>
<th>( U/A )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_2PtCl_6 ): ( Re^{4+} )</td>
<td>...</td>
<td>1.815 ± 0.001</td>
<td>(-7.2 \pm 0.5) \times 10(^{-3})</td>
<td>(-9.8 \pm 0.3) \times 10(^{-2})</td>
<td>(a)</td>
</tr>
<tr>
<td>( K_2PtCl_6 ): ( Tc^{4+} )</td>
<td>4.2</td>
<td>1.989 ± 0.005</td>
<td>(-1.0 \times 10^{-4})</td>
<td>(-8.9 \sim 0.1) \times 10(^{-3})</td>
<td>(b)</td>
</tr>
<tr>
<td>( MgO ): ( Cr^{3+} )</td>
<td>290</td>
<td>1.980 ± 0.005</td>
<td>\sim 0</td>
<td>\sim 0</td>
<td>(c)</td>
</tr>
</tbody>
</table>


\(^{(b)} \) This work.

\(^{(c)} \) W. Low, *Phys. Rev.*, 101, 1827 (1956), and also other data (to be published).

**References**