Probabilities of Diagonal and Non-Diagonal Couplings between $d$ Electrons in Transition Metal

I. The $d$-Band Energy

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Abstract

It is shown that the full account of the non-diagonal couplings between $d$ electrons sited on different atoms in a transition metal implemented within the framework of the Wills-Harrison model leads to vanishing the $d$-band contribution to the internal energy.

Keywords: Transition metal, Wills-Harrison model, $d$-state coupling

In the Wills-Harrison (WH) model [1] for the transition-metal internal energy, the $d$-band energy, $E_{b}$, is represented as follows (hereafter, per atom):

$$E_{b} = -\frac{1}{2} z_{d} \left(10 - \frac{z_{d}}{10}\right) W, \quad \text{(1)}$$

where $z_{d}$ is the effective $d$-electron valence, $W$ - $d$-band width:

$$W = \left(\frac{12}{N^{2}} \sum_{m=1}^{N} \sum_{l=1}^{N} V_{d}^{2}(r_{ml})\right)^{1/2}, \quad \text{(2)}$$

where $N$ is the number of atoms, $V_{d}(r)$ - effective potential of the $d$-$d$ interaction (hereafter, in atomic units):

$$V_{d}(r) = \frac{r_{d}^{3}}{r^{2}} K_{b}. \quad \text{(3)}$$
Here, \( r_d \) is the \( d \)-state radius, \( K_b \) - combinatoric coefficient, which in the WH approximation depends on diagonal only couplings between \( d \) electrons sited on different atoms:

\[
K_b^{WH} = \left( \sum_{m=-2}^{2} \frac{y_m^2}{5} \right)^{1/2}, \tag{4}
\]

where \( m \) is the magnet quantum number,

\[
y_m = |y_m| = -\frac{(-1)^{|m|} 180}{\pi (2 + |m|)! (2 - |m|)!}. \tag{5}
\]

From (4), (5)

\[
K_b^{WH} = 28.06 / \pi. \tag{6}
\]

In [2] was introduced the probability \( p \) that all 25 \( d-d \) couplings between two different atoms in a metal are equiprobable. Then, the probability of the WH limit case that only 5 equiprobable diagonal couplings are possible is \( (1 - p) \). From this assumption, the probability of a non-diagonal coupling is \( 0.8p \), probability of a diagonal coupling is \( (1 - 0.8p) \) and

\[
K_b = \left[ \frac{1}{5} \left( \frac{1 - 4p}{5} \right) y_0^2 + \left( 2 - \frac{6p}{5} \right) (y_1^2 + y_2^2) + \frac{4p}{5} y_0 (y_1 + y_2) + \frac{8p}{5} y_1 y_2 \right]^{1/2}. \tag{7}
\]

Now, allow us to apply (5) to (7). As a result,

\[
K_b = K_b^{WH} / \sqrt{1 - p}. \tag{8}
\]

This surprising result denotes that at full account of the non-diagonal couplings between \( d \) electrons sited on different atoms \( (p = 1) \), the \( d \)-band energy in a transition metal is being become equal to zero.

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**References**


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