Calculation of the Knight Shift in Palladium

R. Krieger and J. Voitländer
Institut für Physikalische Chemie
der Universität München

Z. Naturforsch. 34a, 523—524 (1979);
received March 10, 1979

The direct and core-polarization contributions to the Knight shift in palladium metal have been calculated taking an enhancement factor of 10 for d- and 1.28 for s-electrons. We found a large negative contribution of \(-3.88\%\) for the core electrons and a comparatively small direct contribution of \(0.18\%\) for s-electrons on the Fermi surface. Together with an estimated contribution of \(0.36\%\) for conduction electrons in s-orbitals, but not on the Fermi surface, the calculated total amount of \(-3.34\%\) is in good agreement with the experimental value of \(-4\%\) obtained by the Jaccarino plot for palladium at 0 K.

Knight shift calculations of Das et al. [1] for simple metals like alkali metals have shown that the direct contribution of the s-electrons on the Fermi surface has to be corrected by the core-polarization contribution which for these metals is never larger than about 10% of the total shift. In transition metals with an incompletely filled d-shell, however, the d-electrons on the Fermi surface through core-polarization can lead to a large negative core-contribution which — following Watson et al. [2] — outweighs the positive direct contribution. The negative Knight shift in palladium observed by Jaccarino et al. [3] and later on by Brill and Voitländer [4] is an example for this case.

In order to get a better insight into the mechanism of the core-polarization in transition metals with a partially filled d-band we performed this Knight shift calculation for palladium.

The total Knight shift may be written as

\[
K^{\text{total}} = K^{\text{direct}} + K^{\text{core}} + K^{\text{VV}} + K^{\text{dia}}. \quad (1)
\]

According to Jaccarino et al. [3] we neglect \(K^{\text{VV}}\) and \(K^{\text{dia}}\), the contributions of the Van Vleck orbital paramagnetism and the diamagnetism, respectively, and express the direct and core-contribution of the Fermi contact by hyperfine fields \(x\), \(\beta\) and partial susceptibilities \(\chi^\lambda\) for s-, p- and d-electrons on the Fermi surface:

\[
\begin{align*}
K^{\text{direct}} &= \alpha_s \chi_s^s, \\
K^{\text{core}} &= \sum_{\lambda} \beta_{\lambda} \chi_p^\lambda, \quad (\lambda = s, p, d). \quad (2)
\end{align*}
\]

The susceptibilities \(\chi^\lambda\) are determined by the product of partial densities of states \(N_\lambda(E_F)\) at the Fermi energy \(E_F\), enhancement factors \(S^\lambda\) and the Bohr magneton \(\mu_B\):

\[
\chi^\lambda = \mu_B^2 N_\lambda(E_F) S^\lambda \quad (\lambda = s, p, d). \quad (3)
\]

An enhancement factor \(S^d = 10\) for d-electrons was found by an analysis of the temperature dependence of the total susceptibility of palladium by Sänger and Voitländer [5]. The same authors estimated an enhancement factor \(S^s = 1.28\) for s-electrons from silver, and a factor \(S^p = 1\) will be assumed for p-electrons. The partial densities of states are given by

\[
N_\lambda(E_F) = \langle c_{\lambda}^2 \rangle_{E_F} N(E_T) \quad (\lambda = s, p, d), \quad (4)
\]

where \(N(E_F)\) is the total density of states at \(E_F\). The coefficients \(c_{\lambda}\) of the wave functions on the Fermi surface are defined by

\[
\psi_{\lambda \mathbf{k}} = \sum_{\mathbf{r}} c_{\lambda, \mathbf{k}} \varphi_{\lambda \mathbf{r}} \quad (\lambda = s, p, d). \quad (5)
\]

To obtain the wave functions for the conduction electrons near the Fermi surface we performed a KKR energy band calculation for palladium. The coefficients \(c_{\lambda}\) were calculated at 8282 points on the Fermi surface and the average \(\langle c_{\lambda}^2 \rangle_{E_F}\) was taken. The radial parts of \(\psi_{\lambda \mathbf{k}}\) are determined by the radial Schrödinger equation for electrons moving in the muffin tin potential of the band calculation with energy \(E_F\). The average values \(\langle c_{\lambda}^2 \rangle_{E_F}\) of the coefficients are given in Table 1. They show that on the Fermi surface there are 90% d-electrons and only 10% s-electrons.

The hyperfine field of the direct contribution is easily derived from the well known Knight formula

\[
\alpha_s = (8\pi/3) \langle |\varphi_{s \mathbf{k}}(0)|^2 \rangle_{E_F}. \quad (6)
\]

The contribution of the core-electrons was determined using the momentum perturbation method developed by Das et al. [1]. A one-electron exchange operator

\[
\hat{H}^{\lambda}_{E_S} = - \frac{\psi_{s \mathbf{k}}(r_1)}{\psi_{s}(r_1)} \int \frac{\psi^*_{s \mathbf{k}}(r_2)}{r_{12}} \frac{e^2}{r_2} \psi_{s}(r_2) \, dr_2 \quad (7)
\]

is needed for each core electron in the state \(ns\) to calculate the hyperfine fields for the core contri-
Table 1. Direct and core-contributions to the Knight shift in palladium (in %)

<table>
<thead>
<tr>
<th>$\delta k_t$</th>
<th>K$_{core}$ $(T = 0)$</th>
<th>K$_{contact}$</th>
<th>$K_{direct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 s</td>
<td>2 s</td>
<td>3 s</td>
</tr>
<tr>
<td>0.10</td>
<td>0.020</td>
<td>0.023</td>
<td>0.041</td>
</tr>
<tr>
<td>0.01</td>
<td>-0.001</td>
<td>-0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.89</td>
<td>-0.201</td>
<td>-1.841</td>
<td>-0.185</td>
</tr>
<tr>
<td>1.00</td>
<td>-0.182</td>
<td>-1.818</td>
<td>-0.144</td>
</tr>
</tbody>
</table>

$K_{contact} (T = 0) = -3.34 \quad K_{exp} (T \rightarrow 0) = -4.$

The results of the calculation of the Knight shift contributions, especially the details for the 1s-, 2s-, 3s- and 4s-electrons, are given in Table 1. We found a large negative contribution of $-3.88\%$ for the core electrons and a small direct contribution of $0.18\%$. Conduction electrons in s-orbitals, but not on the Fermi surface, may also be polarized by Fermi electrons. For these electrons we estimated a contribution of $0.36\%$ using a Clementi atomic orbital for the 5s-state and reducing the result of 2% by the factor 0.18 because the s-band in palladium is occupied with 0.18 electrons with the spin parallel to the Fermi electrons. For the calculation of the core-contribution we also used Clementi atomic orbitals as wave functions of the core electrons. The calculated total amount of $-3.34\%$ is in good agreement with the experimental value of $-4\%$ obtained by the Jaccarino plot [3] for palladium extrapolated to 0 K. In particular, our calculations show that — as already expected by Watson et al. [2] — the exchange-polarization between d-electrons on the Fermi surface and s-electrons in core orbitals alone leads to the observed large negative Knight shift in palladium [*].

A grant to one of us (R.K.) from the Deutsche Forschungsgemeinschaft as well as computer facilities by the Leibniz Rechenzentrum, Bayerische Akademie der Wissenschaften, are gratefully acknowledged.