## Calculation of the Knight Shift in Palladium

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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

$$K^{\text{total}} = K^{\text{contact}}_{\text{direct}} + K^{\text{contact}}_{\text{core}} + K_{\text{VV}} + K_{\text{dia}} . \quad (1)$$

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 $\alpha$, $\beta$ and partial susceptibilities $\chi_{\text{p}}{}^{\lambda}$ for s-, p- and d-electrons on the Fermi surface:

$$K^{\text{contact}}_{\text{direct}} = \alpha_{\text{s}}\, \chi_{\text{p}}{}^{\text{s}} ,$$
$$K^{\text{contact}}_{\text{core}} = \sum_{\lambda} \beta_{\lambda}\, \chi_{\text{p}}{}^{\lambda} , \quad (\lambda = \text{s, p, d}) . \quad (2)$$

The susceptibilities $\chi_{\text{p}}{}^{\lambda}$ are determined by the product of partial densities of states $N_{\lambda}(E_{\text{F}})$ at the Fermi energy $E_{\text{F}}$, enhancement factors $S^{\lambda}$ and the Bohr magneton $\mu_{\text{B}}$:

$$\chi_{\text{p}}{}^{\lambda} = \mu_{\text{B}}{}^{2}\, N_{\lambda}(E_{\text{F}})\, S^{\lambda} \quad (\lambda = \text{s, p, d}) . \quad (3)$$

An enhancement factor $S^{\text{d}} = 10$ 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 $S^{\text{s}} = 1.28$ for s-electrons from silver, and a factor $S^{\text{p}} = 1$ will be assumed for p-electrons. The partial densities of states are given by

$$N_{\lambda}(E_{\text{F}}) = \langle c_{\lambda}{}^{2} \rangle_{E_{\text{F}}}\, N(E_{\text{F}}) \quad (\lambda = \text{s, p, d}) , \quad (4)$$

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

$$\psi_{k_{\text{F}}} = \sum_{\lambda} c_{\lambda,\, k_{\text{F}}}\, \psi_{\lambda,\, rk} \quad (\lambda = \text{s, p, d}) . \quad (5)$$

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 $\langle c_{\lambda}{}^{2} \rangle_{E_{\text{F}}}$ was taken. The radial parts of $\psi_{\lambda,\, k_{\text{F}}}$ are determined by the radial Schrödinger equation for electrons moving in the muffin tin potential of the band calculation with energy $E_{\text{F}}$. The average values $\langle c_{\lambda}{}^{2} \rangle_{E_{\text{F}}}$ 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

$$\alpha_{\text{s}} = (8\pi/3) \langle |\, \psi_{\text{s},\, k_{\text{F}}}(0) \,|^{2} \rangle_{E_{\text{F}}} . \quad (6)$$

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

$$\hat{H}^{\lambda}_{E,\,\text{ns}} = - \frac{\psi_{\lambda,\, k_{\text{F}}}(r_1)}{\psi_{\text{ns}}(r_1)} \int \psi^{*}_{\lambda,\, k_{\text{F}}}(r_2)\, \frac{e^{2}}{r_{12}}\, \psi_{\text{ns}}(r_2)\, \text{d}\tau_2 \quad (7)$$

is needed for each core electron in the state ns to calculate the hyperfine fields for the core contri-

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Table 1. Direct and core-contributions to the Knight shift in palladium (in %)

| | $\langle c_\lambda^2 \rangle_{E_F}$ | $K_{\text{core}}^{\text{contact}}$ $(T=0)$ | | | | | $K_{\text{direct}}^{\text{contact}}$ |
|---|---|---|---|---|---|---|---|
| | | 1 s | 2 s | 3 s | 4 s | (5 s) | |
| $s_{kt}$ | 0.10 | 0.020 | 0.023 | 0.041 | 0.115 | 0.072 | 0.181 |
| $p_{kt}$ | 0.01 | −0.001 | −0.000 | 0.000 | 0.003 | 0.000 | |
| $d_{kt}$ | 0.89 | −0.201 | −1.841 | −0.185 | −1.858 | 0.286 | |
| $\sum =$ | 1.00 | −0.182 | −1.818 | −0.144 | −1.740 | 0.358 | |

$K_{\text{total}}^{\text{contact}}\,(T=0) = -3.34 \qquad K_{\text{exp}}\,(T \to 0) = -4.$

butions

$$\beta_\lambda = (8\pi/3) \sum_{\text{ns}} 2 \cdot \langle \delta\psi_{\text{ns},N} | \hat{H}^{\lambda}_{E,\text{ns}} | \psi_{\text{ns}} \rangle \qquad (8)$$

$$(\lambda = \text{s, p, d}) .$$

Here $\delta\psi_{\text{ns},N}$ is the perturbation of the wave function of the core state ns by the Fermi contact [1].

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 [*].

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