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

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

According to Jaccarino et al. [3] we neglect K_{VV} and K_{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 α, β and partial susceptibilities $\chi_{\text{p}}{}^{\lambda}$ for s-, p- and d-electrons on the Fermi surface:

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

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_{F}, enhancement factors S^{λ} and the Bohr magneton μ_{B}:

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

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

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

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

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

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_{λ} 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_{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

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

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

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

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_{k_f}	0.10	0.020	0.023	0.041	0.115	0.072	0.181
p_{k_f}	0.01	−0.001	−0.000	0.000	0.003	0.000	
d_{k_f}	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	

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

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

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

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 1 s-, 2 s-, 3 s- and 4 s-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 5 s-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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