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Nuclear-Spin Relaxation and Knight Shift in Transition Metals*

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The electron-phonon enhancement of electronic specific heat and the effective Coulomb enhancement of spin susceptibility are taken into account, the former through the Eliashberg-McMillan theory of superconductivity for transition metals and the latter through gyromagnetic effect experiment, in calculating the nuclear-spin relaxation rates in transition metals. The nuclear-spin relaxation rate of vanadium determined experimentally is found to be consistent with the conjecture that the observed Knight shift is almost entirely due to orbital paramagnetism. Inclusion of the above corrections gives better qualitative agreement with observed relaxation rates for V, Nb, and Pt.

I. INTRODUCTION

The relative importance of three distinct nuclear relaxation processes, namely, contact interaction,[1] core polarization,[2] and orbital and spin-dipolar[3] interaction in different metals has been clearly demonstrated in the past. It has also been realized[2] that the existing discrepancies among theoretical and experimental values of nuclear-spin relaxation rates in many transition metals may be rectified by taking proper account of the electron-phonon enhancement factor of electronic specific heat and the "effective Coulomb" enhancement factor of the spin susceptibility. In a superconductor, BCS theory[4] predicts that the spin susceptibility should decrease exponentially with temperature, falling to zero at absolute zero.[5] An indirect way of testing this prediction is the Knight-shift experiment in which one expects that, like the spin susceptibility, the Knight shift (K) for a superconductor should also vanish exponentially at absolute zero. The non-transition-metal superconductors (Hg, Sn, Al) do show a decrease in K with temperature though not in perfect agreement with BCS prediction.[6] On the contrary, the Knight-shift result in a transition metal is quite anomalous.[7] For vanadium no change in the Knight-shift value from normal to superconducting state could be detected.[7] A number of theoretical attempts to explain this anomaly invoked the idea that in the presence of an external magnetic field the electronic ground state of superconductors is not a spin-zero singlet state. It was pointed out that the spin-orbit scattering at surface atoms,[8] spin-orbit scattering with the periodic lattice,[9] or triplet-state pairing[10] may result in a nonzero-spin electronic ground state. For vanadium the spin-orbit effects are quite small[11] and there is no experimental indication of the striking consequence of a triplet-state pairing theory of superconductivity in any system. The role of orbital paramagnetism in explaining this Knight-shift anomaly in superconducting vanadium has been pointed out independently, by Orgel,[12] by Clogston *et al.*,[13] and by Noer and Knight.[7] Narath *et al.*[14] have calculated various contributions to normal-state Knight shift and nuclear-spin relaxation rate for many transition metals and found that although the largest contribution to the relaxation arises from the contact interaction, the normal-state Knight shift is dominated by the orbital interaction.

The purpose of this paper is to indicate that once the electron-phonon enhancement factor of electronic specific heat and the "effective Coulomb" enhancement factor of the spin susceptibility are properly taken into account—the former through the Eliashberg-McMillan (EM) theory of superconductivity for strong-coupling superconductors[15] and the latter through the gyromagnetic-effect theory[16] and experiment[17]—there is a marked improvement in agreement between theory and experiment of nuclear-spin relaxation rate in many transition metals. The calculated relaxation rate is also consistent with the conjecture that the experimentally observed Knight shift in the superconducting state is *mainly* due to the orbital paramagnetism. The paper is organized in the following way: In Sec. II we give briefly the procedures and the relevant equations for calculating the electron-phonon enhancement factor and "effective Coulomb" enhancement factor. We also indicate how the nuclear relaxation rate and the Knight shift are calculated in a self-consistent way. In Sec. III we perform numerical calculations of the nuclear-spin relaxation rate and the Knight shift for vanadium, niobium, and platinum and compare them with available experiments. Finally, we discuss the results of our calculation in view of the uncertainties in many parameters.

II. THEORY

A. Calculation of Electron-Phonon Enhancement Factor $(1+\lambda)$ and "Bare Coulomb" Factor $N(0)V_C$

Using theoretical work of Eliashberg for strong-coupling superconductor, McMillan in his pioneering paper[15] has provided the prescription for calculating the electron-phonon coupling parameter $\lambda\,[\equiv N(0)V_{\text{Ph}}]$ and the Coulomb parameter $N(0)V_C$ through experimentally determined superconducting transition temperature (T_c), the Debye temperature (Θ), and coefficient of isotope effect (α). We will give a few relevant equations for the benefit of the reader. The transition temperature in EM theory is given by the expression

$$T_c=\frac{\Theta}{1.45}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right), \tag{1}$$

where μ^* is the Coulomb pseudopotential given by

$$\mu^*=N(0)V_C[1+N(0)V_C\ln(E_B/\omega_0)]^{-1}. \tag{2}$$

Here V_C is the matrix element of the screened Coulomb interaction averaged over the Fermi surface, $N(0)$ is the electronic density of states at the Fermi surface, E_B is the electronic bandwidth, and ω_0 is the maximum phonon frequency. The coefficient α of the isotope effect ($T_c\propto M^{-\alpha}$, M being the ionic mass) is given by

$$\alpha=\frac{1}{2}\left[1-\left(\mu^*\frac{\Theta}{1.45T_c}\right)^2\left(\frac{1+0.62\lambda}{1+\lambda}\right)\right]. \tag{3}$$

McMillan's procedure for calculating $(1+\lambda)$ and μ^* from Eqs. (1) and (3) is as follows: Neglecting, as a first approximation, the "strong-coupling parameter" $[(1+0.62\lambda)/(1+\lambda)]$ in Eq. (3) and from known experimental values of α, Θ, and T_c one calculates μ^* from Eq. (3). Then using this μ^* and known values Θ and T_c one calculates λ from Eq. (1). Once μ^* is known one can calculate $N(0)V_C$ from Eq. (2) using known values of E_B and ω_0. In Table I we have given the values of $(1+\lambda)$ and other relevant quantities for transition metals of our interest. Recently Bennemann and Garland[18] have generalized the McMillan equation [Eq. (1)] by taking into account the electron-spin-excitation coupling. This effect may have some importance for the metals near the end of the transition series, viz., Pd, Pt, Zr, Ru, etc.

TABLE I. Empirical value of electron-phonon enhancement factor $(1+\lambda)$ along with Debye temperature Θ, transition temperature T_c, and the electronic specific heat γ. The "bare" Coulomb parameter $N(0)V_C$ is taken as 0.34 (calculated for V) for all transition metals. $\mu^*=0.13$.

Metal	T_c (°K)	Θ (°K)	$(1+\lambda)$	γ (mJ/mole °K^2)
V	5.30[a]	399[a]	1.60[a]	9.9[a]
Nb	9.22[a]	277[a]	1.82[a]	7.8[a]
Pt	<0.01[b]	234[b]	1.20[c]	6.68[b]
Pd	<0.01[b]	270[b]	1.35[c]	10.0[b]

[a] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[b] G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, N. Y., 1969), p. 734.

[c] See Ref. 17, p. 288. These values should include $N(0)V_{\text{Pm}}$.

B. Calculation of "Effective Coulomb" Enhancement Factor $N(\bar{0})V_C$

The paramagnetic spin susceptibility χ_s is the Coulomb enhanced "bare" spin susceptibility. Physically, the Coulomb interaction enhances the spin susceptibility owing to the fact that under an external magnetic field more electrons, coupled through Coulomb field, will line up than if they were noninteracting. In calculating the Coulomb enhancement factor for the spin susceptibility one should use "effective" Coulomb potential $\bar{V}_C$ instead of "bare" Coulomb potential V_C by taking into account the short-range correlation effect which keeps electrons apart regardless of their spin orientation. Such correlation effects can be included, in principle, in calculating static spin susceptibility through Landau Fermi-liquid theory in order to estimate the reduction in "bare" Coulomb potential.[19] In what follows we outline an alternate procedure for calculating $N(0)\bar{V}_C$ from known experimental information. The spin susceptibility is expressed as

$$\chi_s=\frac{\chi_{\text{sp ht}}}{(1+\lambda)[1-N(0)\bar{V}_C]}, \tag{4}$$

where $\chi_{\text{sp ht}}$ is the susceptibility calculated from the specific heat using the relation

$$\chi_{\text{sp ht}}=\tfrac{3}{4}(\gamma_e\hbar)^2(\pi K_B)^{-2}\gamma. \tag{5}$$

The values of γ for different transition metals are given in Table I. A knowledge of χ_s in conjunction with experimental values of $\chi_{\text{sp ht}}$ and $(1+\lambda)$ should determine $N(0)\bar{V}_C$. But, in practice, it is not possible experimentally to separate the spin part of the susceptibility from total spin susceptibility, which is a sum of paramagnetic and diamagnetic contributions:

$$\chi_t=\chi_{\text{para}}+\chi_{\text{dia}}, \tag{6a}$$

$$\chi_{\text{para}}=\chi_s+\chi_{\text{so}}+\chi_{\text{VV}}+\alpha(\tfrac{1}{2}\chi_{\text{so}}+\chi_s)/(1-\alpha\chi_s), \tag{6b}$$

$$\chi_{\text{dia}}=\chi_L+\chi_{\text{od}}. \tag{6c}$$

χ_s, χ_{so}, and χ_{VV} are the spin, spin-orbit, and orbital (Van Vleck paramagnetism) contributions to paramagnetic susceptibility, respectively, whereas χ_L and χ_{od} are Landau diamagnetic and orbital diamagnetic (of the filled core) contributions to diamagnetic susceptibility. A way of separating χ_{para} from χ_t is to make use of theoretical[16] and experimental[17] information on gyromagnetic effect in transition metals. The gyromagnetic ratio, determined experimentally, is given by[17]

$$g' = \chi_t \Big/ \tfrac{1}{2}\, \chi_s \left(\frac{1}{1-\alpha\chi_s}\right) + \tfrac{3}{4}\, \chi_{\text{so}} \left(\frac{1+\frac{1}{3}\alpha\chi_{\text{so}}}{1-\alpha\chi_3}\right) + \chi_{\text{VV}} + \chi_L - \left(\frac{m_p}{m_0}\right)\frac{1}{g_n}\, \chi_n \,. \tag{7}$$

α is the molecular field coefficient,[16] χ_n is the nuclear susceptibility enhanced by the proton to electron mass ratio (m_p/m_0), and g_n is the nuclear Lande g factor. The paramagnetic part of the susceptibility can be expressed in terms of experimentally known quantities χ_t and g' as

$$\chi_{\text{VV}} + \tfrac{1}{2}\, \chi_{\text{so}} \left(\frac{1+\frac{1}{2}\alpha\chi_{\text{so}}}{1-\alpha\chi_s}\right) = \chi_t \left(\frac{2-g'}{g'}\right) + \chi_{\text{od}} - \chi_L + 2\left(\frac{m_p}{m_0}\right)\left(\frac{\chi_n}{g_n}\right) \tag{8}$$

and

$$\chi_s \left(\frac{1}{1-\alpha\chi_s}\right) + \tfrac{1}{2}\, \chi_{\text{so}} \left(\frac{1}{1-\alpha\chi_s}\right) = \chi_t \, \frac{2(g'-1)}{g'} - 2\left[\chi_{\text{od}} + \left(\frac{m_p}{m_0}\right)\left(\frac{\chi_n}{g_n}\right)\right] . \tag{9}$$

Huguenin *et al.*[17] have estimated the values of

$$\frac{\chi_s + \frac{1}{2}\chi_{\text{so}}}{1-\alpha\chi_s}$$

and

$$\chi_{\text{VV}} + \tfrac{1}{2}\, \chi_{\text{so}} \left(\frac{1-\frac{1}{2}\alpha\chi_{\text{so}}}{1+\alpha\chi_s}\right)$$

in Table 3 of their paper. It is noted that for metals like V, Cr, Nb, and Ta the spin-orbit susceptibility is quite small and the exchange enhancement of the spin susceptibility (so called "paramagnon effect") can be neglected, providing us with the magnitudes of χ_s and χ_{VV} for these metals. The paramagnon effect may become quite important for metals at the end of the transition series such as Pd. Fortunately for these metals a fair estimate of spin paramagnetism, orbital paramagnetism, and core diamagnetism can be obtained from experimentally determined magnitude, sign, and temperature dependence of Knight shift and total susceptibility.[2]

C. Nuclear-Spin Relaxation and Knight-Shift Calculation

The expressions for nuclear-spin-lattice relaxation[2] rate $(TT_1)^{-1}$ and normal-state Knight shift[3] K_n for transition metals are given as

$$1/TT_1 = 4\pi\gamma_n^2 \hbar K_B [N(0)]^2 \{[\rho H^s_{\text{hf}}]^2 + [(1-\rho)H^d_{\text{hf}}]^2 q + [(1-\rho)H^0_{\text{hf}}]^2 p\}, \tag{10}$$

$$K_n = -(2/\gamma_e \hbar)[H^s_{\text{hf}}\chi_s + H^d_{\text{hf}}\chi_d + H^0_{\text{hf}}\chi_{\text{VV}}] . \tag{11}$$

The hyperfine fields H^s_{hf}, H^d_{hf}, and H^0_{hf} in transition metals result from paramagnetic polarization of the s electrons at the nucleus (so-called "contact interaction"), d electrons polarizing filled s-shell electrons causing a *negative* polarization at the nucleus (so-called "core polarization"), and the orbital paramagnetism, respectively. ρ is the ratio of s-like electronic density of states to the total electronic density of states $N_s(0)/N(0)$, and parameters p and q are expressed in terms of relative weights of Γ_5 to Γ_3 representation at the Fermi surface $f(\Gamma_5)$,

$$p = \tfrac{2}{3} f(\Gamma_5)[2 - \tfrac{5}{3} f(\Gamma_5)] , \tag{12a}$$

$$q = \tfrac{1}{3}[f(\Gamma_5)]^2 + \tfrac{1}{2}[1 - f(\Gamma_5)]^2 , \tag{12b}$$

and χ_s, χ_d, and χ_{VV} are s-spin, d-spin, and orbital paramagnetic susceptibilities, respectively.

Kadanoff[20] has shown that for Migdal's description of electron-phonon interaction in normal metal [correct to the order of $(M/m_0)^{1/2}$] the electronic density of states occurring in the expression for $(TT_1)^{-1}$ should be the "bare" density of states, i.e.,

$$N(0) = N_\gamma(0)[1 + N(0)V_{\text{Ph}} + N(0)V_{\text{Pm}}]^{-1} , \tag{13}$$

where $N_\gamma(0)$ is the density of states derived from electronic specific heat γ,

$$N_\gamma(0) = \tfrac{3}{2}\gamma(\pi K_B)^{-2} , \tag{14}$$

and V_{Ph} and V_{Pm} are the matrix elements of electron-electron interactions mediated by phonons and dynamic spin fluctuations (paramagnons), respectively. Moreover, the spin susceptibilities occuring in Eq. (11) should be corrected for the Coulomb enhancement factor $1 - N(0)\overline{V}_C$ from its "bare" value.

Even after taking due considerations for the electron-phonon enhancement factor for specific heat and the "effective Coulomb" enhancement factor for spin susceptibility, there are two unknown parameters in Eq. (10), namely, ρ and $f(\Gamma_5)$. It should be possible to extract these quantities in the course of band structure calculations but, unfortunately, they are not available at the present time.[21] We propose a way of estimating ρ as follows. The orbital paramagnetism should be unaffected by superconducting transition.[7,13] For vanadium, because $K_s \cong K_n$ we conjecture that in the normal state there is approximately an *accidental cancellation* of the spin part of the Knight shift, i.e.,

$$H^s_{\text{hf}}\chi_s \cong H^d_{\text{hf}}\chi_d \,. \tag{15}$$

Equation (15) provides a way of estimating ρ needed for calculating $(TT_1)^{-1}$ through the equation

$$\frac{H^s_{\mathrm{hf}}}{H^d_{\mathrm{hf}}} \cong \frac{(1-\rho)[1-\rho N(0)\overline{V}_C]}{\rho[1-(1-\rho)N(0)\overline{V}_C]} = \frac{\chi_d}{\chi_s} . \qquad (16)$$

Equation (16) assumes that the effective Coulomb interaction $\overline{V}_C$ is the same for s and d electrons and that the susceptibility enhancement of two types of electrons depends upon their respective densities of states. This may not be a very good approximation as the effective Coulomb interaction $\overline{V}_C$ depends upon screening effect which, in turn, is dependent on electronic density. For transition metals with $N(0)\overline{V}_C \sim 0.2$ and $\rho \sim 0.1$, the middle part of Eq. (16) can be replaced by $(1-\rho)/\rho$. The knowledge of hyperfine fields and $N(0)\overline{V}_C$ gives us a way of estimating ρ. To the author's knowledge K_s is known only for vanadium. For the metals for which K_s is not known, we assume that

$$K_s = -\frac{2}{\gamma_e\hbar} H^0_{\mathrm{hf}}\chi_{\mathrm{vv}}, \qquad (17)$$

so that we may write the equation

$$K_n - K_s \equiv \Delta K = (H^s_{\mathrm{hf}}\chi_s + H^d_{\mathrm{hf}}\chi_d)(-2/\gamma_e\hbar) . \qquad (18)$$

Equation (18) leads to the following quadratic equation in ρ:

$$\rho^2[XY+Y+ZY^2]+\rho[X-XY-Y+ZY^2-1] + 1 + Z(1-Y) = 0 , \qquad (19)$$

where

$$X = H^s_{\mathrm{hf}}/H^d_{\mathrm{hf}} , \qquad (20a)$$

$$Y = N(0)\overline{V}_C , \qquad (20b)$$

$$Z = \Delta K/(\gamma_e\hbar)N(0)H^d_{\mathrm{hf}} . \qquad (20c)$$

The positive root of Eq. (19) is accepted as a physical value of ρ.

III. NUMERICAL CALCULATIONS

In this section we give details of numerical results for V, Nb, and Pt based on the theories outlined in Sec. II. Incomplete experimental information precludes us from making a complete analysis of the theory except for the case of vanadium. However, we have tried to calculate the nuclear-spin relaxation rates for Nb and Pt after making some reasonable assumptions. We have tabulated in Table II the available informations for V, Nb, and Pt.

A. Vanadium

Using Eq. (4) and values of γ, $(1+\lambda)$, and X_s from Tables I and II we have obtained $N(0)\overline{V}_C$ for V to be 0.13. It is apt to point out here that the "bare" Coulomb potential V_C seems to be reduced considerably owing to correlation effect. Now, Eq. (16) along with known values of hyperfine fields

TABLE II. Experimental values of gyromagnetic ratio g', the total susceptibility χ, paramagnetic susceptibilities, the normal- and superconducting-state Knight shifts K_n and K_s, nuclear-spin relaxation rates $(TT_1)^{-1}$, $\gamma_n\hbar$, and the hyperfine fields H^s_{hf}, H^d_{hf}, and H^0_{hf} for V, Nb, and Pt.

Metal	g'	χ (10^{-6} emu/mole)	$\frac{\chi_s+\frac{1}{2}\chi_{so}}{1-\alpha\chi_s}$ (10^{-6} emu/mole)	$\chi_{\mathrm{vv}}+\frac{1}{2}\chi_{so}\frac{1-\frac{1}{2}\alpha\chi_{so}}{1-\alpha\chi_s}$ (10^{-6} emu/mole)	$K_n(\%)^{a}$	$K_s(\%)^{a}$	$(TT_1)^{-1}$ (sec °K)$^{-1}$	$\gamma_n\hbar$ (10^{-24} cgs)^{b}	H^s_{hf} (10^6 Oe)^{b}	H^d_{hf} (10^6 Oe)^{b}	H^0_{hf} (10^6 Oe)^{b}
V	1.18 ± 0.10	291	98 ± 25	203 ± 23	0.58 ± 0.001	0.58	1.27^{a}	7.43	1.12	−0.117	0.19
Nb	1.05 ± 0.07	212	44 ± 19	188 ± 17	0.875 ± 0.01	···	2.8^{a}	6.91	2.48	−0.21	0.285
Pt	1.62 ± 0.08	189	200 ± 13	19 ± 10	−3.53	···	34^{a}	6.06	11.9	−1.19	1.1

[a] Review by L. E. Drain. See Ref. 14.

[b] The second paper in Ref. 2. All the other data from Ref. 17.

(see Table II) yields the value of ρ to be 0.104. This value of ρ seems to be reasonable for a transition-metal system.[32] We do not expect the value of ρ to change very much from one transition-metal system to another. We have tabulated $(TT_1)^{-1}$ for $f(\Gamma_5)=0.6$ and 1.0 in Table III for $\lambda\neq 0$, $\overline{V}_C\neq 0$, for $\lambda\neq 0$, $\overline{V}_C\equiv V_C$, and for $\lambda=0$, $\overline{V}_C=0$ in order to point out the electron-phonon and the Coulomb enhancement effects in the nuclear-spin-lattice relaxation rate. Noting the uncertainties in the values of hyperfine fields, g value, $\langle 1/r^3\rangle$, and diamagnetic susceptibilities we do not take the agreement between calculated [1.67 at $f(\Gamma_5)=0.6$] and observed (1.27) values of $(TT_1)^{-1}$ too seriously. But it is comforting to note that proper consideration of physical effects tends to improve the qualitative agreement between theory and experiment. We would like to mention, in passing, that χ_{VV} calculated on the assumption of approximate cancellation of spin part of the Knight shift in normal state of vanadium turns out to be 170×10^{-6} emu/mole which is about 15% smaller than χ_{VV} (203×10^{-6} emu/mole) from gyromagnetic effect ($g'=1.18$) and total susceptibility measurements. Neglect of negative diamagnetic contribution to K_n and χ_{so} may be partly responsible for this discrepancy. If $(1+\lambda)$ is taken as 1.94 (Ref. 18) the values of ρ and $N(0)\overline{V}_C$ become 0.119 and 0.28, respectively, giving $(TT_1)^{-1}$ at $f(\Gamma_5)=0.6$ as 1.28.

B. Niobium

The strikingly small value of χ_s determined from gyromagnetic ratio experiment leads to an unphysical negative $N(0)\overline{V}_C$ from Eq. (4) for Nb. This, we believe, is due to the uncertainty in the value of g', because we feel that the values of $(1+\lambda)$ and γ are known quite accurately for Nb. The other consequence of this low value of g' is the anomalously large contribution of orbital paramagnetism to Knight shift which turns out to be larger than the experimental value for normal state (see Table III). Moreover, the value of ρ calculated for $g'=1.05$ seems to be much smaller (0.06) than one expects from band structure calculations.[22] We have assumed the upper value of g' for Nb, viz., 1.12. Since K_s is not known experimentally for Nb we have assumed that K_s is entirely due to orbital paramagnetism [cf. Eq. (17)]. Thus, knowing K_s and K_n we have determined ρ from Eq. (19); it turns out to be 0.10. Again, in the case of Nb, we observe that there is an improvement in agreement between theoretical (2.44) and experimental (2.8) values of the nuclear-spin relaxation rate if one accounts for proper physical effects.

C. Platinum

In this system the magnetic susceptibility is strongly enhanced by exchange effects and is tem-

TABLE III. Calculated values of "effective" Coulomb parameter $N(0)\overline{V}_C$ and ratio of density of states $N_s(0)/N(0)$ ($\equiv\rho$) for different values of g', and $\overline{V}_C\neq 0$, $\lambda\neq 0$, K_s, and $(TT_1)^{-1}$ for different λ, $\overline{V}_C$, and $f(\Gamma_5)$. Experimental values of $(TT_1)^{-1}$ and K_n are also given.

				$(TT_1)^{-1}$ (sec °K)$^{-1}$ (theory)								
				$\overline{V}_C\neq 0$, $\lambda\neq 0$		$\overline{V}_C=V_C$, $\lambda\neq 0$		$\overline{V}_C=0$, $\lambda=0$				
Metal	g'	$N(0)\overline{V}_C$	ρ	$f(\Gamma_5)=0.6$	$f(\Gamma_5)=1.0$	$f(\Gamma_5)=0.6$	$f(\Gamma_5)=1.0$	$f(\Gamma_5)=0.6$	$f(\Gamma_5)=1.0$	$(TT_1)^{-1}$ (sec °K)$^{-1}$ (expt.)	K_n(%) (expt.)	K_s(%) (theory)
V	1.18	0.13	0.104	1.67	1.32	1.98	1.77	3.93	3.35	1.27	0.58 ± 0.001	0.58
Nb	1.05	−0.34	0.06	1.50	1.31	2.55	2.37	6.06	5.45	2.8	0.875 ± 0.01	0.959
	1.12	+0.29	0.10	2.44	2.26	2.55	2.37	6.06	5.45			0.806
Pt	1.62	0.6[a]	0.053[b]	35.6	34.8	...	...	51.3	50.2	34	−3.53	0.374

[a] Reference 16.

[b] Reference 2.

perature dependent owing to a peak in d-state density of states near the Fermi surface. Because of the large d-spin susceptibility the Knight shift is dominated by the core polarization interaction and is negative[2] (see Table II). There is no estimate of electron-phonon enhancement factor for Pt from superconductivity data. In Ref. 17 $N(0)\overline{V}_C$ for Pt is estimated to be 0.6, which leads to the value of $(1+\lambda)$ as 1.20. The large spin-orbit coupling in Pt prevents us from determining ρ under simplified assumptions made for V and Nb. We have taken ρ as 0.053 as indicated in Ref. 2. The calculated values of $(TT_1)^{-1}$ are given in Table III, which agree fairly well with the experimental value. The improved agreement is mainly due to consideration of the electron-phonon enhancement factor for the density of states.

IV. DISCUSSION

We have made necessary corrections for electron-phonon enhancement of electronic specific heat and Coulomb enhancement (including exchange effect) of spin susceptibility in calculating nuclear-spin relaxation rate. The calculations for these corrections are possible owing to recent advances in the theory of superconductivity of transition metals[15] and measurements of gyromagnetic ratio in some transition metals.[17] The conjecture that the experimentally observed Knight shift in superconducting state is *mainly* because of orbital paramagnetism is used to determine the density of states ratio ρ, and in turn, the nuclear spin relaxation rate $(TT_1)^{-1}$. The magnitude of ρ thus determined was found to be of the right order of magnitude and gave reasonable values of $(TT_1)^{-1}$, leading to some self-consistency in our calculation. The above procedure is not applicable for heavy transition metals (Pt, Pd) with large spin-orbit coupling. Some minor differences in the magnitudes of $(TT_1)^{-1}$ for $\lambda=0$, $\overline{V}_C=0$ between ours and those of Ref. 2 are due to slightly different values of electronic specific heats and density of states ratios used in the two calculations.

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