Nuclear Spin Relaxation in Transition Metals; Core Polarization

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The nuclear relaxation induced by core polarization (c.p.) in a transition metal is calculated in the tight-binding limit. It is shown that a Korringa-like relation exists between the c.p. Knight shift and the c.p. relaxation rate, but with a factor that inhibits relaxation, the numerical value of which depends on the relative weight of Γ_5 and Γ_3 orbitals at the Fermi surface. Using estimates of the hyperfine fields, the relaxation rates associated with the contact, c.p., and orbital interactions are calculated for three transition metals. It is found that all three processes make significant contributions. The agreement with the measured relaxation rates is satisfactory considering the uncertainties in the estimated numbers.

1. INTRODUCTION

THE Knight shift in metals is the sum of several contributions resulting from:

(a) The contact interaction with the unpaired electron spins at the Fermi surface.

(b) The contact interaction with closed-shell electrons which, as a result of configuration interaction, have a nonvanishing spin density at the nucleus (core polarization).

(c) The orbital and spin-dipolar interactions with electrons in partly filled $l\neq0$ shells.

The relative importance of these contributions depends upon the electronic structure of the metal. In the alkalis the first is dominant,[1] in platinum the second,[2] and in vanadium the third.[3]

On general grounds, it is expected that each of these interactions will also lead to a relaxation process for the nuclear spin. The relaxation due to the first was calculated by Korringa[4] and is well known; the relaxation due to the third was recently calculated by Obata.[5] It is the purpose of this work to study the relaxation process connected with the core polarization.

Our aim is not to obtain an absolute magnitude for the relaxation rate, but only to relate it to the core polarization Knight shift. To this end the method of configuration interaction[6] is well suited. As explained in the next section, the unrestricted Hartree-Fock method[1,7–9] is not convenient for relaxation calculations. We now outline our main results.

Since the exchange energies responsible for core polarization are small compared to promotion energies, we do a first-order perturbation calculation. The expression for the matrix elements leading to relaxation

which we find can be simplified in the tight binding limit. This simplification is a result of retaining only those configurations that keep the excited core electron on the same atom. As a consequence we obtain a relation similar to Korringa's,[4] but with a numerical reduction factor arising from the degeneracy of the d bands. Thus relaxation by core polarization is less effective than relaxation by ordinary contact interaction, the reduction factor ranging from one-half when only the twofold (Γ_3) d states are present at the Fermi surface, to one-fifth when all d orbitals are equally represented. In the same approximation and allowing for the mixing of s and d orbitals in a given Bloch state at the Fermi surface, the total relaxation rate is found to be the *sum* of the contact and core polarization relaxation rates. The absence of any interference terms simplifies the interpretation of nuclear relaxation data.

2. CORE POLARIZATION IN THE LITHIUM ATOM

In order to exhibit the relation between the Knight shift and the nuclear relaxation induced by core polarization, we first consider the lithium atom. We neglect spin-orbit coupling so that the spin and orbital angular momenta are separately good quantum numbers. The Hamiltonian is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}',\tag{1}$$

where $\mathcal{H}_0$ is the sum of the kinetic and electrostatic energies, and $\mathcal{H}'$ is the contact interaction,

$$\mathcal{H}'=\frac{8\pi}{3}\beta\sum_{i=1}^{3}\mathfrak{y}\cdot\sigma_i\delta(r_i-R),\tag{2}$$

where β is the Bohr magneton, $\mathfrak{y}$ the nuclear moment, σ_i the Pauli spin operator for electron i, R the position of the nucleus, and the sum is over the three electrons on the lithium atom. The magnetic field at the nucleus is given by the matrix elements of the operator

$$H=-\frac{8\pi}{3}\beta\sum_{i}\sigma_i\delta(r_i-R).\tag{3}$$

[1] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **A73**, 811 (1959).

[2] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. (to be published).

[3] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

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[5] Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

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[7] W. Marshall, Proc. Phys. Soc. (London) **78**, 113 (1961).

[8] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[9] K. F. Berggren and R. F. Wood, Phys. Rev. **130**, 198 (1963).

H is an irreducible tensor operator of the first rank[10]; it obeys the required commutation rules both with respect to the total angular momentum J and the total spin S, i.e.,

$$[S_\pm,H_z]=\mp 2H_\pm;\quad [S_\pm,H_\mp]=\mp H_z$$
$$[S_z,H_\pm]=\pm H_\pm;\qquad [S_z,H_z]=0,\qquad (4)$$

where $S_\pm=(S_x\pm iS_y)$ and $H_\pm=\frac{1}{2}(H_x\pm iH_y)$. Hence we can apply the Wigner-Eckart theorem[10] to the matrix elements of H taken between stationary states of $\mathfrak{K}_0$ having quantum numbers S and m_S. (If spin-orbit coupling had not been neglected, the theorem would still hold provided J, m_J were used instead of S, m_S.) Thus, for the ground-state doublet $|g,S,m_S\rangle$, where g is the set of orbital quantum numbers and $S=\frac{1}{2}$, we obtain

$$(g,\tfrac{1}{2},\tfrac{1}{2}|H_z|g,\tfrac{1}{2},\tfrac{1}{2})=(g,\tfrac{1}{2},\pm\tfrac{1}{2}|H_\pm|g,\tfrac{1}{2},\mp\tfrac{1}{2}).\quad (5)$$

This relation is significant because, when the atom is part of a solid, the diagonal and off-diagonal (in m_S) matrix elements of H are closely related to the Knight shift and the relaxation rate, respectively. It is obeyed, whether core polarization is taken into account or not, provided the wave functions used are eigenfunctions of S^2. The unrestricted Hartree-Fock solutions are not eigenfunctions of S^2 and hence, are not a useful starting point for a calculation of the relaxation.

We shall treat the core polarization by perturbation theory, using Nesbet's method[6] of configuration interaction. The unperturbed wave functions are solutions to the Hartree-Fock (HF) equations obtained under symmetry and equivalence restrictions. To illustrate the method we apply it to lithium.

The outer electron is assumed to be in a p_z state and to have up ($\uparrow$) spin. The unperturbed solution is $\Psi_0{}^\uparrow$ $=[1s\alpha,1s\beta,2p_z\alpha]$, where the square bracket around the one-electron states is used to denote the Slater determinant constructed from these states. The symmetry orbitals $1s$ and $2p_z$ are the best solutions of that symmetry which satisfy the Hartree-Fock equations for up-spin (they are not variational solutions for the energy but this is unimportant for our purpose). The matrix elements of H over the $\Psi_0{}^\uparrow$, $\Psi_0{}^\downarrow$ manifold vanish so that the hyperfine field results entirely from core polarization. To calculate it we form a complete and orthonormal set of one-electron functions (n,l,m_l), which includes our $1s$ and $2p$ orbitals. In principle, the true wave function is an infinite sum of determinants constructed from these orbitals. In perturbation theory, we restrict ourselves to those admixtures to $\Psi_0{}^\uparrow$ which are of the order of the ratio of an exchange integral to the difference in energy between two configurations. We consider only admixtures of the type $[1s,ns,2p_z]$ since these are responsible for the nonvanishing of H.

The three determinantal wave functions based on $1s$, ns, and $2p_z$ that can mix with $\Psi_0{}^\uparrow$ are:

$$\Psi_{1n}{}^\uparrow=[1s\alpha,ns\beta,2p_z\alpha],$$
$$\Psi_{2n}{}^\uparrow=[ns\alpha,1s\beta,2p_z\alpha],\qquad (6)$$
$$\Psi_{3n}{}^\uparrow=[1s\alpha,ns\alpha,2p_z\beta].$$

However, the matrix element $(\Psi_{2n}{}^\uparrow|\mathfrak{K}_0|\Psi_0{}^\uparrow)$ vanishes by construction.[6] This is because $(1s)$ is the best s orbital that satisfies the HF equations for up-spin; since $\Psi_{2n}{}^\uparrow$ differs from $\Psi_0{}^\uparrow$ in the substitution of a single orbital, the matrix element vanishes. $\Psi_{1n}{}^\uparrow$ also differs from $\Psi_0{}^\uparrow$ in a single orbital, but this is substituted in the down spin. As $(1s)$ does not satisfy the HF equations for down spin, the matrix element $(\Psi_{1n}{}^\uparrow|\mathfrak{K}_0|\Psi_0{}^\uparrow)$ does not vanish; it differs from $(\Psi_{2n}{}^\uparrow|\mathfrak{K}_0|\Psi_0{}^\uparrow)$ by an exchange integral. We denote the Coulomb interaction between two electrons by g, and the matrix element $(u_l(\mathbf{r}_1)u_m(\mathbf{r}_2),g(\mathbf{r}_1,\mathbf{r}_2)u_n(\mathbf{r}_1)u_p(\mathbf{r}_2))$ by $(l,m|g|n,p)$ in which case

$$(\Psi_{1n}{}^\uparrow|\mathfrak{K}_0|\Psi_0{}^\uparrow)=(ns,2p_z|g|2p_z,1s),$$
$$(\Psi_{3n}{}^\uparrow|\mathfrak{K}_0|\Psi_0{}^\uparrow)=-(ns,2p_z|g|2p_z,1s).\qquad (7)$$

Let $c_n=(ns,2p_z|g|2p_z,1s)/(E_{1s}-E_{ns})$, where $E_{1s}-E_{ns}$ is the energy difference between the configurations $(1s,1s,2p_z)$ and $(1s,ns,2p_z)$. Consistent with treating the exchange terms to first order we neglect the exchange splitting of E_{ns}. To first order in c_n the wave function is

$$\Psi^\uparrow=\Psi_0{}^\uparrow+\sum_n c_n[\Psi_{1n}{}^\uparrow-\Psi_{3n}{}^\uparrow]\qquad (8)$$

and it is easily verified that it is a spin doublet, $S=\frac{1}{2}$.[11] Within this doublet, the magnetic field at the nucleus is proportional to the electron spin and is given by

$$\mathbf{H}=\frac{8\pi}{3}\beta\boldsymbol{\sigma}\sum_n [c_n\varphi_{1s}{}^*(0)\varphi_{ns}(0)+\text{c.c.}],\qquad (9)$$

where $\varphi_{ns}(0)$ is the value of the ns orbital at the nucleus. It is seen that the admixture of Ψ_{1n} contributes to H_z and the admixture of Ψ_{3n} contributes to $H_\pm$.

3. RELAXATION BY CORE POLARIZATION IN A TRANSITION METAL

The treatment of the wave functions in the transition metal parallels that of the preceding paragraph. The unperturbed orbitals are (in principle) HF solutions obtained under symmetry and equivalence restrictions. The exchange integrals responsible for core polarization are treated to first order in perturbation theory. The exchange integrals between two conduction band orbitals are neglected. It is plausible that consideration of

[10] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. 5. E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap. 3.

[11] This wave function appears to be different from that used in Ref. 7. This is because our unperturbed Ψ_0 differs from Marshall's in first order in c_n. Our total wave function agrees with his.

these exchange terms would not alter significantly the reduction factor that is obtained below.

The true eigenstates of $\mathfrak{IC}_0$ [Eq. (1)] are eigenfunctions of $\mathbf{S}^2$, but because we neglect exchange between valence orbitals, the spin degeneracy of the Slater determinants constructed from a given set of orbitals is not lifted. Hence we may take single Slater determinants as unperturbed wave functions. In this approximation each valence state occupied by an electron contributes independently to the core polarization and it is sufficient to consider first a single valence electron, and then to sum over the occupied states.

The self-consistent Bloch functions of the partly filled bands, denoted by $(\nu\mathbf{k})$ or $\varphi_{\nu k}$, are mixtures of s, p, and d atomic orbitals. The unperturbed HF solution for a system with a single $(\nu\mathbf{k})$ electron outside of the filled bands is written schematically as

$$\Psi_{\nu k\uparrow}{}^0=[\cdots,1s\kappa\alpha,1s\kappa\beta,\cdots,\nu k\alpha], \qquad (10)$$

where for simplicity only one of the occupied s shells has been indicated; the contributions from different s shells are additive and the relation between the Knight shift and the relaxation is not affected by this simplification. The orbitals in (10) are solutions to the HF equations for up spin, so there are no admixtures to (10) that differ only in the substitution of one up-spin orbital. In analogy to Eq. (6), the states that mix with

(10) and contribute to core polarization are

$$\Psi_{\nu k\uparrow}{}^1(n,\kappa,0)=[\cdots,1s\kappa\alpha,ns\kappa\beta,\cdots,\nu k\alpha]$$
$$\Psi^3{}_{\nu' k\uparrow}(n,\kappa,\mathbf{q}) \qquad (11)$$
$$=[\cdots,1s\kappa\alpha,ns(\kappa-\mathbf{q})\alpha,\cdots,\nu'(\mathbf{k}+\mathbf{q})\beta].$$

The admixtures of Ψ^1 and Ψ^3 contribute to the Knight shift and to the relaxation, respectively. The matrix elements that determine these admixtures are

$$(\Psi_{\nu k\uparrow}{}^1(n,\kappa,0)|\mathfrak{IC}_0|\Psi_{\nu k\uparrow}{}^0)=(ns\kappa,\nu k|g|\nu k,1s\kappa),$$
$$(\Psi_{\nu' k\uparrow}{}^3(n,\kappa,\mathbf{q})|\mathfrak{IC}_0|\Psi_{\nu k\uparrow}{}^0) \qquad (12)$$
$$=-(ns(\kappa-\mathbf{q}),\nu'(\mathbf{k}+\mathbf{q})|g|\nu k,1s\kappa),$$

and the wave functions, to first order, are

$$\Psi_{\nu k\uparrow}=\Psi_{\nu k\uparrow}{}^0+\Sigma(n,\kappa)e_{1\nu\nu}(n,\kappa,0;\mathbf{k})\Psi_{\nu k\uparrow}{}^1(n,\kappa,0)$$
$$+\Sigma(n,\kappa,\mathbf{q},\nu')e_{3\nu'\nu}(n,\kappa,\mathbf{q};\mathbf{k})\Psi_{\nu' k\uparrow}{}^3(n,\kappa,\mathbf{q}), \qquad (13)$$

where

$$e_{1\nu\nu}(n,\kappa,0;\mathbf{k})=\frac{(ns\kappa,\nu k|g|\nu k,1s\kappa)}{E_{1s}(\kappa)-E_{ns}(\kappa)}, \qquad (14)$$

and similarly for $e_{3\nu'\nu}$. κ and $\mathbf{q}$ are summed over the reduced zone and ν' over the partly filled bands. We consider a nucleus situated at the origin of the coordinates. The operator $\mathbf{H}$ [Eq. (3)] has the matrix elements

$$(\Psi_{\nu k\uparrow}|H_z|\Psi_{\nu k\uparrow})=\frac{8\pi}{3}\beta\{-|\varphi_{\nu k}(0)|^2+\sum_{n,\kappa}[e_{1\nu\nu}(n,\kappa,0;\mathbf{k})\varphi_{1s\kappa}{}^*(0)\varphi_{ns\kappa}(0)+\text{c.c.}]\}, \qquad (15a)$$

$$(\Psi_{\nu' k+q\downarrow}|H_-|\Psi_{\nu k\uparrow})=\frac{8}{3}\pi\beta\{-\varphi_{\nu' k+q}{}^*(0)\varphi_{\nu k}(0)-\sum_{n,\kappa}[e_{3\nu'\nu}(n,\kappa,\mathbf{q};\mathbf{k})\varphi_{1s\kappa}{}^*(0)\varphi_{ns\kappa-q}(0)$$
$$+e_{3\nu\nu'}(n,\kappa,-\mathbf{q};\mathbf{k}+\mathbf{q})\varphi_{1s\kappa}(0)\varphi_{ns\kappa+q}{}^*(0)]\}, \qquad (15b)$$

and the Knight shift and the relaxation rate are, respectively:

$$\frac{\Delta H}{H}=-\frac{V}{(2\pi)^3}\gamma_e\hbar\sum_\nu\int(\Psi_{\nu k\uparrow}|H_z|\Psi_{\nu k\uparrow})\frac{dS_{\nu k}}{|\boldsymbol{\nabla}_k E_\nu|}, \qquad (16a)$$

$$\frac{1}{\tau}=\frac{V^2}{(2\pi)^6}\frac{4\pi}{\hbar}(\gamma_n\hbar)^2k_BT\sum_{\nu,\nu'}\int|(\Psi_{\nu' k'\downarrow}|H_-|\Psi_{\nu k\uparrow})|^2\frac{dS_{\nu k}}{|\boldsymbol{\nabla}_k E_\nu|}\frac{dS_{\nu' k}}{|\boldsymbol{\nabla}_k E_{\nu'}|}, \qquad (16b)$$

where V is the volume, γ_e and γ_n the electron and nuclear gyromagnetic ratios, respectively, k_B the Boltzmann constant, T the temperature, $\boldsymbol{\nabla}_k E_\nu$ the gradient of the energy of band ν, and $dS_{\nu k}$ is integrated over the Fermi surface. Equations (16a) and (16b) are valid for temperatures low enough that the variation of the integrands within $k_B T$ of the Fermi surface can be neglected.

In order to obtain a relation between (16a) and (16b) we express the core polarization part of Eq. (15) in terms of Wannier functions,

$$a_{ns}(\mathbf{r}-\mathbf{R}_l)=\frac{1}{N^{1/2}}\sum_\kappa\exp(-i\kappa\cdot\mathbf{R}_l)\varphi_{ns\kappa}(\mathbf{r}). \qquad (17)$$

We make the approximation that the energy denominator of Eq. (14) is constant. This is obviously justified for the energy of the core state, but it is also a good approximation for E_{ns}. For, if (ns) is a low-lying excited state, the variation of E_{ns} is small compared to the energy difference with the deep-lying core state while if (ns) is a high-lying excited state the variation is small compared to E_{ns} itself. Let S_1 and S_3 refer respectively to the core polarization sums in Eqs. (15a) and (15b). We assume $\varphi_{1s\kappa}$ and $\varphi_{ns\kappa}$ to be real at the origin. Using (17) we find

$$S_1=\sum_{n,R_l,R_\alpha}(ns0,\nu k|g|\nu k,1s R_\alpha)$$
$$\times a_{1s}(-\mathbf{R}_l)a_{ns}(-\mathbf{R}_l+\mathbf{R}_\alpha), \qquad (18a)$$

$$S_3 = - \sum_{n,\mathbf{R}_l,\mathbf{R}_\alpha} e^{-i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_\alpha)}[(ns0,\nu'(\mathbf{k}+\mathbf{q})|g|\nu\mathbf{k},1s\mathbf{R}_\alpha)$$

$$+ (1s0,\nu'(\mathbf{k}+\mathbf{q})|g|\nu\mathbf{k},ns\mathbf{R}_\alpha)]$$
$$\times a_{1s}(-\mathbf{R}_l)a_{ns}(-\mathbf{R}_l+\mathbf{R}_\alpha), \quad (18b)$$

where the notation $(ns\mathbf{R}_\alpha)$ in the matrix elements of g refers to the corresponding Wannier functions.

We now make two approximations: First we retain only the core orbitals with $\mathbf{R}_l=0$, which is well justified; second, we retain only those excited states with $\mathbf{R}_\alpha=0$, which means that only those configurations for which a core electron remains on the same atom are included. This approximation is not as good as the former but there is a saving grace: If $\varphi_{ns\mathbf{k}}(0)$ is independent of $\mathbf{k}$, then it can easily be shown that $a_{ns}(0-\mathbf{R}_\alpha)$ vanishes for $\mathbf{R}_\alpha \neq 0$. Since in s bands $\varphi_\mathbf{k}(0)$ does not vary rapidly with $\mathbf{k}$, $a_{ns}(0-\mathbf{R}_\alpha)$ will be small.

To evaluate the exchange integral in Eq. (18) we assume that $\varphi_{\nu\mathbf{k}}$ is the sum of two parts,

$$\varphi_{\nu\mathbf{k}} = u_{\nu s \mathbf{k}} + \sum_{\mathbf{R}_l}\left[\sum_{\epsilon=1}^{3} b_{\nu\epsilon}(\mathbf{k})u_\epsilon(\mathbf{r}-\mathbf{R}_l)\right.$$

$$\left. + \sum_{\gamma=1}^{2} c_{\nu\gamma}(\mathbf{k})u_\gamma(\mathbf{r}-\mathbf{R}_l)\right], \quad (19)$$

$u_{\nu s \mathbf{k}}$ being the contribution of the s band (which, near the zone edge, may have a strong p character), and the remainder being that of the d bands which we treat in the tight-binding approximation. The functions u_ϵ and u_γ belong to the Γ_5 and Γ_3 representations, respectively (we are dealing with a cubic crystal) and are normalized to unity. The s and d parts of $\varphi_{\nu\mathbf{k}}$ both contribute to core polarization, but as the contact term from a pure s state is an order of magnitude larger[8] than the core polarization term from a pure d or s state, the core polarization due to the s part can be neglected—it would represent at most a small correction to the contact term. In the matrix element $(1s0,\nu'\mathbf{k}'|g|\nu\mathbf{k},ns0)$, the interaction g is invariant under rotations and since $(1s0)$ and $(ns0)$ are also invariant under the cubic operations, only the terms that have the same u_ϵ or u_γ in the expansions of $\varphi_{\nu\mathbf{k}}$ and $\varphi_{\nu'\mathbf{k}'}$ contribute to the integral. We obtain

$$(1s0,\nu'\mathbf{k}'|g|\nu\mathbf{k},ns0)$$

$$= \sum_{\epsilon,\gamma} [b_{\nu'\epsilon}^*(\mathbf{k}')b_{\nu\epsilon}(\mathbf{k})+c_{\nu'\gamma}^*(\mathbf{k}')c_{\nu\gamma}(\mathbf{k})]J_n, \quad (20)$$

where it has been assumed that the radial dependence of u_ϵ and u_γ are the same, resulting in a common exchange integral J_n.

We substitute Eq. (20) into (18), (15), and the resulting expression into (16), to obtain

$$\frac{\Delta H}{H} = \frac{V}{(2\pi)^3}\frac{4\pi}{3}(\gamma_e\hbar)^2\sum_\nu \int \left\{ |\varphi_{\nu\mathbf{k}}(0)|^2 + \left[\sum_n \frac{2J_n}{\langle E_n\rangle-\langle E_1\rangle}a_{1s}(0)a_{ns}(0)\right]\left[\sum_{\epsilon,\gamma}(|b_{\nu\epsilon}(\mathbf{k})|^2+|c_{\nu\gamma}(\mathbf{k})|^2)\right]\right\}\frac{dS_{\nu\mathbf{k}}}{\nabla_\mathbf{k}E_\nu}, \quad (21a)$$

$$\frac{1}{\tau} = \frac{V^2}{(2\pi)^6}\frac{4\pi}{\hbar}\left(\frac{4\pi}{3}\right)^2(\gamma_e\gamma_n\hbar^2)^2k_BT\sum_{\nu,\nu'}\int\int\left|\varphi_{\nu'\mathbf{k}'}^*(0)\varphi_{\nu\mathbf{k}}(0)+\left[\sum_n\frac{2J_n}{\langle E_n\rangle-\langle E_1\rangle}a_{1s}(0)a_{ns}(0)\right]\right.$$

$$\left.\times\left[\sum_{\epsilon,\gamma}(b_{\nu'\epsilon}^*(\mathbf{k}')b_{\nu\epsilon}(\mathbf{k})+c_{\nu'\gamma}^*(\mathbf{k}')c_{\nu\gamma}(\mathbf{k}))\right]\right|^2\frac{dS_{\nu\mathbf{k}}}{|\nabla_\mathbf{k}E_\nu|}\frac{dS_{\nu'\mathbf{k}'}}{|\nabla_{\mathbf{k}'}E_{\nu'}|}. \quad (21b)$$

Using the cubic symmetry operations, it is easily shown that

$$\int \varphi_{\nu\mathbf{k}}(0)c_{\nu\epsilon}^*(\mathbf{k})dS_{\nu\mathbf{k}} \equiv 0,$$

and

$$\int b_{\nu\epsilon}(\mathbf{k})b_{\nu\epsilon'}^*(\mathbf{k})dS_{\nu\mathbf{k}} = 0 \quad \text{for} \quad \epsilon \neq \epsilon'.$$

Thus there are no cross terms in the modulus square of the matrix element in (21b).

This is a useful result which simplifies the interpretation of the relaxation data when the relaxation rates due to the contact interaction of the valence s electron and to the core polarization are both significant. It shows that there are no interference terms between the two processes and hence that they are additive, even when s–d mixing in the wave functions is taken into account. Although one expects a given band to have primarily s or d character at the Fermi surface, a small s admixture in the wave function may result in comparable contributions to the contact and core polarization hyperfine fields. It may be noted that if core polarization is due to an s conduction electron as in the alkali metals, the contribution to the matrix element that is due to the part of the wave function that has s character *will* interfere with the contact term. This means that, e.g., in lithium it is immaterial, as far as the relaxation time is concerned, whether the departure of the Knight shift from the one-electron value is a result of core polarization,[1] or of correlation between a symmetrical core and the outer electron.[9]

We assume that the core polarization and contact hyperfine fields are of opposite signs and define

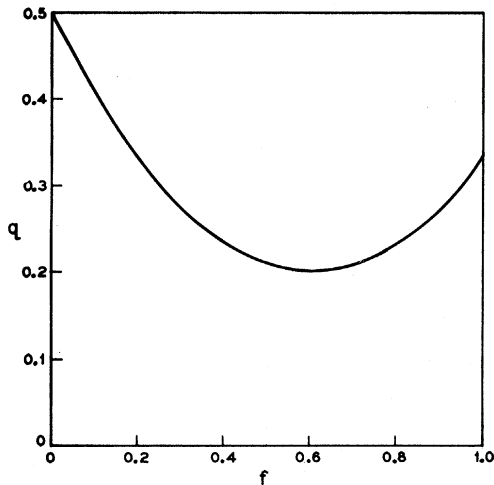$$\sum_n \frac{2J_n}{\langle E_n\rangle-\langle E_1\rangle}a_{1s}(0)a_{ns}(0) \equiv -|\varphi_{cp}(0)|^2. \quad (22)$$

FIG. 1. Reduction factor of the Korringa relation for core polarization, $q=\frac{1}{3}f^2+\frac{1}{2}(1-f)^2$, plotted as a function of f, the fractional character of Γ_5 d orbitals at the Fermi surface.

We further define

$$\sum_\nu \frac{V}{(2\pi)^3}\int \frac{dS_{\nu k}}{\boldsymbol{\nabla}_k E_\nu}\equiv\eta(\zeta_0), \qquad (23a)$$

$$\sum_\nu \frac{V}{(2\pi)^3}\int |\varphi_{\nu k}(0)|^2\frac{dS_{\nu k}}{\boldsymbol{\nabla}_k E_\nu}\equiv\langle\varphi_s^2(0)\rangle\eta(\zeta_0), \quad (23b)$$

where $\eta(\zeta_0)$ is the density of states for one direction of the spin at the Fermi level ζ_0.

Let Kf and $K(1-f)$ be, respectively, the probability amplitudes squared of the Γ_5 and Γ_3 orbitals in the wave functions, averaged at ζ_0. Thus K is the fractional d character and f the relative weight of the Γ_5 representation at the Fermi surface. In terms of the newly defined quantities Eqs. (21a) and (21b), simplify to

$$\frac{\Delta H}{H}=\frac{4\pi}{3}(\gamma_e\hbar)^2(\langle\varphi_s^2(0)\rangle-|\varphi_{cp}(0)|^2K)\eta, \qquad (24a)$$

$$\frac{1}{\tau}=\frac{4\pi}{\hbar}\left(\frac{4\pi}{3}\right)^2(\gamma_e\gamma_n\hbar)^2k_BT[\langle\varphi_s^2(0)\rangle^2$$
$$+|\varphi_{cp}(0)|^4K^2(\tfrac{1}{3}f^2+\tfrac{1}{2}(1-f)^2)]\eta^2. \quad (24b)$$

It is seen from (24) that the contact and core polarization terms separately obey a Korringa-like relation. However the Korringa relation for the core polarization has a reduction factor $\frac{1}{3}f^2+\frac{1}{2}(-1f)^2$, i.e.,

$$\left(\frac{1}{\tau}\right)_{cp}=\frac{4\pi}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2\left(\frac{\Delta H}{H}\right)_{cp}^2k_BT[\tfrac{1}{3}f^2+\tfrac{1}{2}(1-f)^2]. \quad (25)$$

The reduction factor has the minimum value of one-fifth for $f=3/5$, corresponding to an equal population of all the d orbitals, and a maximum value of one-half for $f=0$, corresponding to a population of only Γ_3 orbitals; it is plotted on Fig. 1.

The origin of the reduction factor lies in the fact that the matrix elements of H involved in the Knight shift and in relaxation are not the same. Thus the Knight shift is given by the average (at the Fermi surface) of the matrix element of H that is *diagonal* in k, while the relaxation rate is given by the modulus-square of the *off-diagonal* matrix element. Because of the degeneracy of the d bands there are cancellations in the latter while not in the former, resulting in a reduction factor equal to the reciprocal of the degeneracy. In the case of s bands this factor is unity and one regains the Korringa relation.

4. TEMPERATURE DEPENDENCE OF τT

In the next section we will compare the experimental results on τT for the transition metals vanadium, niobium, and platinum. For V and Nb, τT (as well as the susceptibility χ) are temperature-independent in the range 0–300°K. For Pt however both τT and χ change measurably in this range.

As expected, when k_BT becomes comparable with the energy range over which the density of states or the matrix element of H_- vary significantly, the product τT shows a temperature dependence. Equation (16b) is replaced by the more general expression

$$\frac{1}{\tau}=\frac{4\pi}{\hbar}\frac{V^2}{(2\pi)^6}(\gamma_n\hbar)^2k_BT\int F(E)\left(-\frac{dg}{dE}\right)dE, \quad (26)$$

where $g(E)$ is the Fermi function and $F(E)$ is given by

$$F(E)=\sum_{\nu,\nu'}|(\Psi_{\nu'k'\downarrow}|H_-|\Psi_{\nu k\uparrow})|^2\frac{dS_{\nu k}}{\boldsymbol{\nabla}_k E_\nu}\frac{dS_{\nu'k'}}{\boldsymbol{\nabla}_{k'}E_{\nu'}} \quad (27)$$
$$\equiv H_1^2(E)\eta^2(E).$$

The temperature dependence of (26) is then obtained from the relations[12]

$$\int F(E)\left(-\frac{dg}{dE}\right)dE=F(\zeta)+\frac{\pi^2}{6}(k_BT)^2\left(\frac{d^2F}{dE^2}\right)_\zeta \quad (28a)$$

and

$$\zeta=\zeta_0-\frac{\pi^2}{6}(k_BT)^2\left(\frac{1}{\eta}\frac{d\eta}{dE}\right)_{\zeta_0}. \quad (28b)$$

If in $F(E)$, $H_1^2(E)$ is assumed to be independent of E, then upon using (28) one obtains

$$\frac{1}{\tau T}=1+\frac{\pi^2}{3}(k_BT)^2\left(\frac{1}{\eta}\frac{d^2\eta}{dE^2}\right)_{\zeta_0}. \quad (29)$$

In the cubic transition metals this assumption of the constancy of $H_1^2(E)$ cannot be made, mainly because f, the fraction of Γ_5 orbitals, is expected to vary with

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[12] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), Chap. VI.

the energy. Hence the coefficient of T^2 will not be given by (29), but will involve df/dE.

These considerations also apply to the relaxation induced by the orbital interaction; the latter depends on the density of d states at the Fermi surface, which is very close to the total density of states η (see also next section). The existence of a significant temperature dependence in τT indicates that an appreciable contribution to relaxation must come from core polarization and/or orbital interactions. However, because of the dependence of f on E, it is not necessarily warranted to compare the temperature dependence of τT with that of the susceptibility and to expect that these dependences will be similar.

5. COMPARISON WITH EXPERIMENT

The nuclear relaxation time has been measured in vanadium,[13] niobium,[14] and platinum.[15] We shall now estimate the relaxation rates associated with each of the four processes, i.e., (a) contact interaction with the valence s function, (b) core polarization (cp), (c) orbital interaction (orb), and (d) spin dipolar interaction (dip), and then compare the sum of the rates with the experimental value. It was shown above that processes (a) and (b) give no interference terms. Likewise the orbital interaction gives no interference terms because, unlike the other processes, it leaves the electron spin unchanged. Process (d) does interfere with processes (a) and (b). However, if the band states at the Fermi surface can be separated into s-p bands and d bands, the interference terms vanish. Since very little is known about the degree of s-d mixing except that it is believed to be small, we shall neglect it. Our model is then the usual one of separate s and d bands with the mass of the s electron assumed to be that of the free electron.

We shall express the relaxation rates for the contact, core polarization, and orbital processes directly in terms of the appropriate hyperfine fields and the density of states. We do this rather than use Eq. (25) for two reasons: (1) No Korringa-like relation exists for the orbital interaction and (2) even for the contact and core polarization processes a Korringa relation loses its usefulness whenever an unambiguous separation of the contributions to the Knight shift cannot be effected.

The relaxation rates due to the four processes are

$$\frac{1}{\tau_s} = \frac{4\pi}{\hbar}[\gamma_n \hbar H_{hf}(s)]^2\left(\frac{\eta_s}{A}\right)^2 k_B T \equiv R_s T, \qquad (30a)$$

$$\frac{1}{\tau_{cp}} = \frac{4\pi}{\hbar}[\gamma_n \hbar H_{hf}(d)]^2\left(\frac{\eta_d}{A}\right)^2 k_B T[\tfrac{1}{3}f^2 + \tfrac{1}{2}(1-f)^2]$$

$$\equiv R_{cp}T[\tfrac{1}{3}f^2 + \tfrac{1}{2}(1-f)^2], \qquad (30b)$$

[13] J. Butterworth, Phys. Rev. Letters **5**, 305 (1960).
[14] K. Asayama and J. Itoh, J. Phys. Soc. Japan **17**, 1065 (1962).
[15] J. Butterworth, Phys. Rev. Letters **8**, 423 (1962).

TABLE I. The atomic hyperfine fields of the s and d electrons of V, Nb, and Pt. Columns 1 and 2 give the hyperfine field *per spin* resulting from the s contact and d core polarization interactions, respectively. (To obtain the corresponding hyperfine fields per electron spin multiply by $\tfrac{1}{2}$.) Column 3 gives the hyperfine field per unit angular momentum resulting from the orbital interaction. Appropriate reduction factors for the fields in the metals are given in the text. The sources of the following values are specified in the lettered references.

	$2H_{hf}(s)$	$2H_{hf}(d)$	$H_{hf}(\text{orb})$
	in 10^6 Oe		
V	3.2ᵃ	−0.234ᶜ	0.25ᵉ
Nb	7.1ᵃ	−0.42ᵈ	0.38ᵉ
Pt	33.9ᵇ	−2.36ᵇ	1.47ᵇ

ᵃ Use was made of the Fermi-Segré formula (E. Fermi and E. Segré, Z. Physik **82**, 72, 9 (1933) and the term values for the V configurations $3d^44s_1$ and $3d^45s_1$ and for Nb $4d^45s_1$ and $4d^46s_1$.
ᵇ All fields for Pt are given in Ref. 2.
ᶜ The electron paramagnetic resonance measurements of the hfs of V^{2+}; $3d^3$ in ionic crystals was used. K. D. Bowers and J. Owen, Rep. Progr. Phys. **18**, 304 (1955).
ᵈ No measurements comparable to c exist for Nb^{2+}. The value given is for the isoelectronic ion Tc^{4+}; $4d^3$ and the sign has not been determined. W. Low and P. M. Lewellyn, Phys. Rev. **110**, 842 (1958).
ᵉ Hartree-Fock calculated values by A. J. Freeman and R. E. Watson were used to obtain $\langle 1/r^3\rangle$. We are indebted to these authors for private communication of their work prior to publication.

$$\frac{1}{\tau_{orb}} = \frac{4\pi}{\hbar}[\gamma_n \hbar H_{hf}(\text{orb})]^2\left(\frac{\eta_d}{A}\right)^2 k_B T\left[\frac{2}{3}f\left(2-\frac{5}{3}f\right)\right]$$

$$\equiv R_{orb}T\left[\frac{2}{3}f\left(2-\frac{5}{3}f\right)\right], \qquad (30c)$$

$$\frac{1}{\tau_{dip}} \simeq R_{orb}T\left(\frac{1}{25}\right), \qquad (30d)$$

where

$$H_{hf}(s) = (8/3)\pi\beta\langle\varphi_s(0)^2\rangle, \quad H_{hf}(d) = (8/3)\pi\beta\langle\varphi_{cp}(0)^2\rangle,$$

and $H_{hf}(\text{orb}) = 2\beta\langle 1/r^3\rangle$ are the averages at the Fermi surface of the hyperfine fields produced by the spin of one unpaired s electron, one unpaired d electron, and by one unit of orbital angular momentum, respectively. A is Avogadro's number and η_s and η_d are the density of states per mole (for one direction of the spin) of the s and d bands. To calculate the relaxation rates we need to know, aside from the fraction f, only the three hyperfine fields and the two densities of states.

The atomic hyperfine fields of the s and d electrons are given in Table I. In every case except that in which $H_{hf}(d)$ is obtained from the temperature dependences of the Knight shift and the susceptibility[2] a major uncertainty enters insofar as one does not know the amount by which the field in the atom (or ion) differs from that in the metal. This question has been given some consideration for the contact interaction term.[16] We have arbitrarily taken $\xi_s \equiv [H_{hf}(s)_{\text{metal}}/H_{hf}(s)_{\text{atom}}] = 0.7$, the measured value for silver, and

$$\xi_d \equiv [H_{hf}(d)_{\text{metal}}/H_{hf}(d)_{\text{atom}}] = 1.$$

[16] W. D. Knight, Solid State Phys. **2**, 93 (1956).

TABLE II. The nuclear relaxation rates in V, Nb, and Pt. The first three columns give the estimated hyperfine fields in the metals. The fourth column gives the calculated s density of states for one direction of the spin assuming one s electron/atom in V and Nb and 0.2 s electron/atom in Pt. The fifth column lists the difference between η_{sp-ht}, the value deduced from the measured specific heat, and η_s. The values of γ_n are from W. D. Knight, Solid State Phys. 2, 93 (1956). The next three columns give the calculated values of R_s, R_{cp}, and R_{orb}. Columns 10 and 11 list calculated values of $R=1/\tau T$ for 2 values of f, and the last the measured values (all in sec^{-1} °K^{-1}).

	$H_{hf}(s)$	$H_{hf}(d)$	$H_{hf}(\text{orb})$	$\dfrac{\eta_s}{A}$	$\dfrac{\eta_{sp-ht}-\eta_s}{A}$	$\gamma_n\hbar$	R_s	R_{cp}	R_{orb}	R_{calc}		R_{exp}
	— in 10^6 oersteds			in 10^{11} cgs/atom		in 10^{-24} cgs	in sec^{-1} °K^{-1}			$f=\frac{3}{5}$	$f=1$	$=1/\tau T$
V	1.12	−0.117	0.19	0.75	11.5[a]	7.43	0.642	1.65	4.35	2.86	2.33	1.27[d]
Nb	2.48	−0.21	0.285	0.89	10.4[b]	6.91	3.76	3.74	6.9	7.55	6.80	5.26[e]
												2.8[g]
Pt	11.9	−1.19	1.1	0.45	8.05[c]	6.06	17.5	54.2	47.5	49.2	48.1	34[f]

[a] W. S. Corak, B. B. Goodman, C. B. Satterwaite, and A. Wexler, Phys. Rev. 102, 656 (1956).
[b] A. Brown, M. W. Zemansky, and H. A. Boorse, Phys. Rev. 92, 52 (1953).
[c] D. W. Budworth et al., Proc. Roy. Soc. (London) A257, 250 (1960).
[d] See Ref. 13.
[e] See Ref. 14.
[f] See Ref. 15.
[g] This is a recent unpublished value obtained for very high purity Nb by J. Butterworth. We thank Dr. Butterworth for communicating this result to us prior to publication.

For $\xi_{orb}\equiv(\langle r^{-3}\rangle_{metal}/\langle r^{-3}\rangle_{atom})$, we have taken the value $\frac{3}{4}$ previously used in the orbital Knight shift analysis of V and Pt.[2] It should be remarked that the $\langle r^{-3}\rangle$ to be used in the orbital Knight shift differs from that which enters into the orbital relaxation; the former is to be averaged over all the occupied states of the d band whereas the latter involves only the average over states at the Fermi surface. Obviously if the radial extent of the wave functions is strongly energy dependent the two averages need not be the same.

The density of states which appears in the expression of the relaxation rate would seem to be that which is determined from a measurement of the electronic specific heat. The latter quantity reflects the spectrum of the quasiparticles which has contributions from the self-energy of the electron (arising from the electron-phonon and Coulomb interactions). However recent theoretical work[17] has shown that the self-energy makes no contribution to the relaxation rate, the latter being determined by the density of states of the "bare" electrons. This quantity is not known experimentally but theory[18] supported by some experimental evidence[19] indicates that the electron-phonon interaction by itself leads to an increase in the density of states over the "bare" electron value. The Coulomb interaction seems[20] to have an effect in the same direction. For lack of a measured value we shall make use of the density of states as determined from the specific heat, expecting that the relaxation rates thus calculated will probably be too large.

As the measured specific heat is the sum of the contributions from the s and d bands we must estimate the fraction that is associated with the s band. For the number of s electrons per atom we arbitrarily take 1 for V and Nb, while in Pt we take 0.2 as calculated in Ref. 2.

The factors R_s, R_{cp}, and R_{orb} of Eqs. (30) calculated in this manner are shown in Table II. In order to obtain the total relaxation rate

$$RT\equiv(1/\tau_s+1/\tau_{cp}+1/\tau_{orb}+1/\tau_{dip}),$$

it would be necessary to know the value of f, which is not available for any transition metal. A calculation in nickel[21] suggests that Γ_3 and Γ_5 occur in comparable amounts at the Fermi surface. We made two estimates of R, one for $f=3/5$ and one for $f=1$ or equivalently $f=1/5$ (see Fig. 2); it is very likely that f is actually
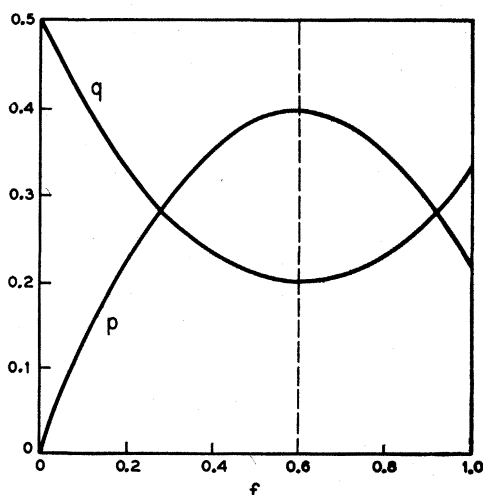

FIG. 2. The factors $p=(2/3)f[2-(5/3)f]$ (from Ref. 5) and $q=\frac{1}{3}f^2+\frac{1}{2}(1-f)^2$ occurring in $1/\tau_{orb}$ and $1/\tau_{cp}$ plotted as a function of f. The two parabolas have their maximum and minimum at the value $f=3/5$ corresponding to equal probability for each d orbital at the Fermi surface.

[17] L. P. Kadanoff, Phys. Rev. 132, 2073 (1963). We are indebted to Dr. Kadanoff for sending a preprint of this work to us.
[18] M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) 67, 828 (1954).
[19] K. Krebs, Phys. Letters 6, 31 (1963).
[20] E. A. Stern, Phys. Rev. 121, 397 (1961).
[21] J. G. Hanus, Quarterly Progress Report, Solid State and Molecular Theory Group MIT, April 1962, p. 29 (unpublished).
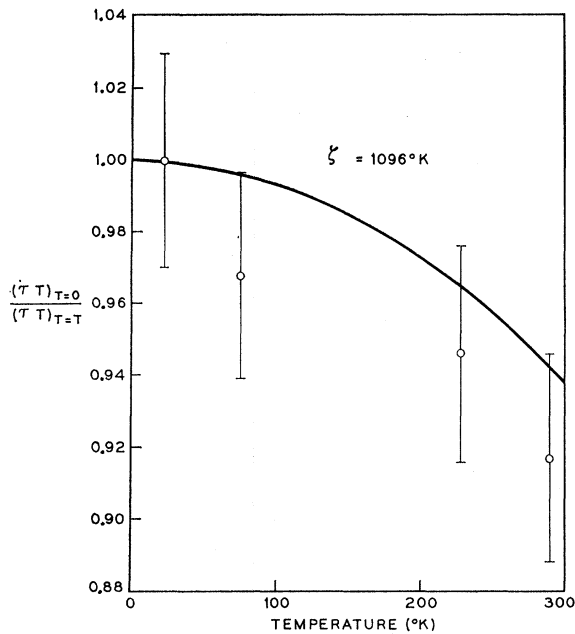
FIG. 3. The temperature dependence of $1/\tau T$. The circles show the values measured by Butterworth (Ref. 5). The solid line is a theoretical curve for a parabolic band with a Fermi temperature of 1096°K.

in the range $1/5$ to 1. For the particular values $R_{orb} = \frac{3}{4}R_{cp}$ the sum $1/\tau_{cp}+1/\tau_{orb}$ would be independent of f, which is reflected in the insensitivity of R to the value of f in platinum. The experimental values of $1/\tau T$ are given in the last column. They are consistently smaller than the calculated R values.

For all three metals, the d electrons contribute significantly to the relaxation. Because of this, as mentioned in Sec. 4, $1/\tau T$ is expected to vary with temperature if the susceptibility is itself temperature-dependent. This was found to be the case in Pt[15] as is shown on Fig. 3. Although the accuracy of the measurements is not sufficient to warrant a detailed comparison with theory, we have, for the purpose of reference, indicated by the solid line, the predicted variation of $1/\tau T$ for a *parabolic d* band having a Fermi temperature of $\zeta = 1096$°K (see Ref. 2). The matrix element of the hyperfine interaction has been assumed to be constant, independent of the electron's energy.

This comparison between experiment and theory should not be taken very seriously because (a) only a fraction of the relaxation rate, probably $\frac{1}{2}$ to $\frac{2}{3}$, is associated with d electrons, (b) the change in the fraction f

with energy was not considered, and (c) the parabolic band approximation has only qualitative significance. For a general band shape, $(\tau T)^{-1}/(\tau T)_{0°K}^{-1}$ and $\chi(T)/\chi(0)$ have different coefficients in front of the T^2 terms that determine their temperature variations. For a parabolic band of *noninteracting* electrons, these coefficients are fortuitously identical and the temperature variation is given by

$$\frac{\chi_0(T)}{\chi_0(0)}=1-\frac{\pi^2}{12}\left(\frac{T}{\zeta}\right)^2. \qquad (31)$$

However even in a parabolic band the modification of χ_0 by the exchange terms destroys this similarity and to compare the temperature dependences of $1/\tau T$ and χ it is necessary to know the contribution of exchange to χ and to correct for it.

6. CONCLUSIONS

We have shown that the contribution of the core polarization hyperfine field to the nuclear relaxation is considerably reduced with respect to that which the Korringa relation would have predicted. Furthermore there are no interference terms between the contact and core polarization. Thus the total relaxation rate is given by the sum of the contributions of the contact, core polarization, and orbital interactions. It is found that there are substantial contributions to the relaxation rate from all three processes and no single one is dominant in all metals. Qualitative agreement with experiment is obtained for the cases examined.

As to detailed agreement it was noted that the calculated rates for V, Nb, and Pt somewhat exceed the measured ones. Possible reasons for this are as follows: (1) Uncertainties in the ξ_s factor which arise from two sources; (a) the normalization of s function in the solid and (b) the degree of s–p mixing at the Fermi surface, (2) uncertainties in $\langle 1/r^3\rangle$ in the metal, (3) uncertainties in the core polarization hyperfine field in the metal, except for Pt where it is obtained directly from the temperature dependence of the Knight shift and susceptibility and (4) the use of the electronic specific-heat density of states rather than that of the noninteracting electron gas. As noted in the text, the former is larger than the latter, which should result in our having overestimated the relaxation rates.