

First-principles study of spin-orbit effects and NMR in Sr_2RuO_4

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We present a first principles study of nuclear magnetic resonance (NMR) and spin orbit effects in the unconventional superconductor Sr_2RuO_4 . We have calculated the uniform magnetic susceptibility, which agrees rather well with the experiment in amplitude, but, as in an earlier model result we found the calculated hard axis to be z , opposite to the experiment. We have also calculated the Knight shifts and the NMR relaxation rates for all atoms, and again found an overall good agreement, but with important deviations from the experiment in the same particular characteristics, such as the Knight shift anisotropy. Our results suggest that correlations in Sr_2RuO_4 lead to underestimations of the orbital effects in density-functional-based calculations. We also argue that the accepted “experimental” value for the relative contribution of orbital polarization in susceptibility, 10–15 %, is also an underestimation. We discuss the puzzling invariance of the O and Ru Knight shifts across the superconducting transition for all directions of the applied field. We show that this fact cannot be explained by accidental cancellations or spin-flip scattering, as it happens in some elemental superconductors. We also point out that a large contribution of the dipole and orbital hyperfine field into the Knight shifts in Sr_2RuO_4 , combined with the possibility of an orbital-dependent superconductivity, calls for a revision of the standard theory of the Knight shift in the superconducting state.

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I. INTRODUCTION

The layered perovskite Sr_2RuO_4 is often considered to be one of the rare cases of spin-triplet superconductors¹ (see, however, Ref. 3). While there is convincing evidence against a conventional s -wave state,² the evidence for a spin-triplet p -wave superconductivity rests exclusively³ on the NMR experiments. Specifically, the main (and, arguably, the only) argument in favor of a (particular) p -wave state is the fact that the NMR Knight shift for a magnetic field parallel to the RuO_2 layers does not decrease in the superconducting state. Indeed, in a singlet superconductor the Cooper pairs have no net spin and cannot produce any Knight shift, so for applied fields smaller in energy units than the superconducting gap, as the number of unpaired electrons at the Fermi level decreases so does the Knight shift. On the contrary, among the p -wave states allowed in a tetragonal symmetry, there is one where the spins of the pairs lie in the ab plane and are capable of screening an external in-plane field. Indeed, a simple theory⁴ predicts that the Knight shift for such fields remains constant across the superconducting transition. The latter appears to be well established, being confirmed for the ^{17}O shift,⁵ for the ^{101}Ru shift,⁶ and for the spin susceptibility as probed by neutrons.⁷

The superconducting state in question, sometimes called a chiral p -wave state, is described by a vector order parameter $\mathbf{d} \propto (k_x \pm ik_y)\hat{z}$, and is also compatible with the μSR relaxation experiments⁸ which indicate the appearance of spontaneous magnetic moments below T_c that is usually interpreted in terms of a superconducting state with Cooper pairs having nonzero orbital moments. On the other hand, it is not readily compatible with multiple indications of line nodes of the

order parameter,¹ since such lines are not required by symmetry in this chiral p -wave state and can appear only accidentally. While such an accident is always possible, no superconductors are known so far where the order parameter would have nodes not required by symmetry, for the obvious reason that such nodes strongly reduce the total pairing energy.

Confidence in the chiral p -wave state has been further shaken by the fact that the Knight shift in Sr_2RuO_4 remains constant not only for the in-plane fields, but in fact for *any* direction of the applied field.⁹ According to the existing theory, no superconducting state allowed for tetragonal crystals can have such a property. The suggested explanation was that the direction of \mathbf{d} in a magnetic field of 0.02 T changes,⁹ creating a state with the symmetry $\mathbf{d} = k_z\hat{x}$ [a “rotated” state $\mathbf{d} = (k_z + ik_y)\hat{x}$ is not allowed in a tetragonal symmetry¹⁰ and can appear only as a second phase transition]. This explanation, however, is rather doubtful for the following reasons: (i) such a state would have an additional node line and therefore lose a good deal of pairing energy, (ii) although in this state the spins of the pairs lie in the yz plane, there is no y - z symmetry (as opposed to the xy plane) and it is not *a priori* clear whether the magnetic susceptibility of the Cooper pair will be the same as for the normal electrons, and finally, (iii) the spin-orbital part of the pairing interaction, which keeps the spins in the xy plane, despite z being the easy magnetization axis,¹¹ is rather strong in this material, and the field of 0.02 T (1.1 μeV or 0.013 K) seems to be way too small to overcome it.

These considerations have spawn several alternative suggestions for the pairing symmetry in Sr_2RuO_4 , such as a chiral d -wave state³ or a mixture of nearly degenerate planar

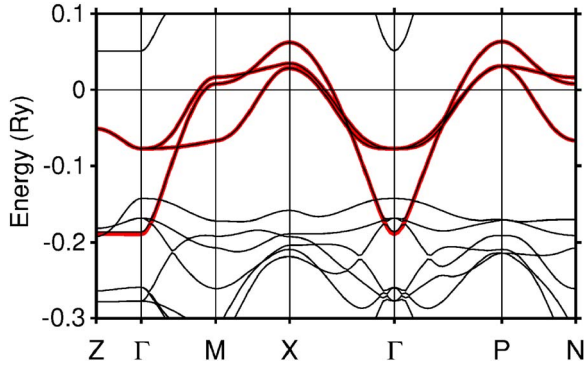


FIG. 1. (Color online) LDA (NMTO) band structure (thin line) and pure t_{2g} bands (thick line), obtained by integrating out all other states (see Table I). The Fermi level is set to zero.

p -wave states.¹² On the other hand, examples are known where the magnetic susceptibility and the Knight shift do not vanish at $T=0$ even in conventional superconductors: mercury,¹³ tin,¹⁴ or vanadium.¹⁵ Such cases are traditionally attributed to either spin-flip scattering due to spin-orbit coupling on point defects^{16,17} or sample boundaries,¹⁸ or to accidental cancellations of the Fermi contact and core polarization contributions due to peculiarities of the electronic structure.¹⁹

It is clear at this point that first principles calculations of the NMR Knight shift and the relaxation rate are highly desirable in order to gain a better understanding of the physics of the NMR in this compound. Similarly, to access the applicability of alternative interpretations it is important to understand spin-orbit effects better (note that the selection between different p -wave states is entirely controlled by spin-orbit coupling; see Refs. 1 and 20). In this paper we present full-potential highly accurate calculations of the spin-orbit effects in Sr_2RuO_4 within the local density approximation (LDA) with and without external magnetic field, as well as first principles calculations of the NMR Knight shifts and the NMR relaxation rates, and analyze the possible ramifications. In particular, we analyze the possibility of accidental cancellations due to electronic structure peculiarities, the possible dominance of the van-Vleck term, and the effects of spin-orbit coupling and correlations beyond LDA.

II. ELECTRONIC STRUCTURE

Sr_2RuO_4 has the perovskite crystal structure of the cuprate superconductor La_2CuO_4 (space group $I4/mmm$).²¹ The primitive cell is tetragonal body centered (lattice constants $a=b=3.87$ Å and $c=12.74$ Å); Ru is located at (0,0,0) and Sr at (0,0,0.353), while the two nonequivalent oxygens are O1 at (1/2,0,0) and O2 at (0,0,0.1615) respectively.

The electronic structure of Sr_2RuO_4 has already been studied by several authors^{22–24} by means of density functional theory (DFT) in the LDA or in the generalized gradient approximation (GGA). In the present work we adopt different LDA approaches: the linear muffin-tin orbitals (LMTO) method in the atomic spheres approximation (Stuttgart LMTO47 code),²⁵ the N th order muffin tin orbitals²⁶

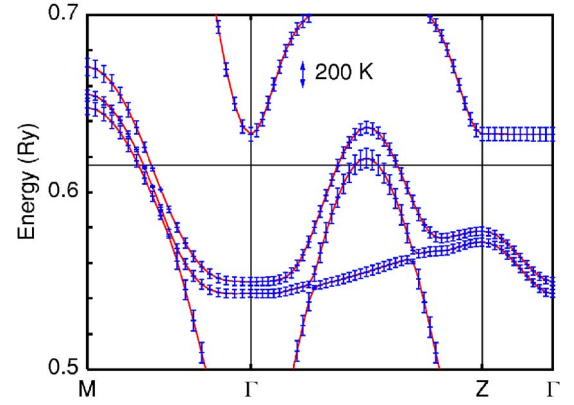


FIG. 2. (Color online) LDA (LAPW) band structure with spin-orbit effects. The lines represent the actual band structure (spin-orbit splitting is too small on this scale; the “error bars” indicate the size of the spin-orbit splitting of each state. In the central panel we show the length of an “error bar” corresponding to a splitting of 200 K (≈ 17 meV). The horizontal line is the Fermi energy.

(NMTO) method and the NMTO-based downfolding approach (Stuttgart NMTO47 code), which allows us to calculate hopping integrals and Wannier functions, and the linear augmented plane wave (LAPW) method (WIEN2k code).²⁷ Our results for the band structure (Figs. 1 and 2) are consistent with previous calculations. The NMTO bands (Fig. 1) are obtained from the self-consistent LMTO potential, following a standard procedure.²⁶

The tetravalent Ru has four electrons in the d shell. The cubic crystal field splits the d levels into three-fold degenerate t_{2g} and two-fold degenerate e_g states; the bands at the Fermi level are thus t_{2g} bands 2/3 filled. DFT calculations show that these three t_{2g} bands can be divided into a wider xy band, almost two-dimensional, and two narrower almost one-dimensional xz and yz bands. In Fig. 1 we show the band structure obtained by using the NMTO method. The t_{2g} bands (thick line) were obtained by integrating out all the degrees of freedom except for the t_{2g} ; by means of this first-principles downfolding procedure²⁶ we could construct Wannier functions and a real space Hamiltonian for these bands.²⁸ The corresponding hopping integrals are tabulated in Table I up to the fourth nearest neighbors; farther hoppings are tiny and can be neglected. The tables show that the interorbital hybridization is very small; thus the bare band dispersion can be written as

$$\begin{aligned} \epsilon(\mathbf{k}) = & \epsilon_0 + 2t^{100} \cos k_x + 2t^{010} \cos k_y + 4t^{110} \cos k_x \cos k_y \\ & + 8t^{\frac{1}{2}\frac{1}{2}\frac{1}{2}} \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2} + 2t^{200} \cos 2k_x \\ & + 2t^{020} \cos 2k_y \end{aligned} \quad (1)$$

for each band. These bare bands are slightly modified by the hybridization terms that take the form

TABLE I. Hopping integrals t^{lmn} in mRy. The connecting vector is $\mathbf{T}=la\hat{x}+ma\hat{y}+nc\hat{z}$, where a and c are the lattice constants; the hopping integrals are tabulated up to the fourth neighbors.

	ϵ_0	t^{100}	t^{010}	t^{110}	$t^{1/2\ 1/2\ 1/2}$	t^{020}	t^{200}
$yz-yz$	-26.80	-3.03	-22.59	0.94	-1.18	2.88	0.06
$xz-xz$	-26.80	-22.59	-3.03	0.94	-1.18	0.06	2.88
$xy-xy$	-25.21	-27.73	-27.73	-8.18	0.09	0.44	0.44
$yz-xz$	0	0	0	0.46	-0.76	0	0
$yz-xy$	0	0	0	0	0.39	0	0
$xz-xy$	0	0	0	0	0.39	0	0

$$H_{xz,yz}(\mathbf{k}) = 4t^{110} \cos k_x \cos k_y + 8t^{\frac{1}{2}\frac{1}{2}\frac{1}{2}} \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2},$$

$$H_{xz,yz}(\mathbf{k}) = H_{yz,xy}(\mathbf{k}) = +8t^{\frac{1}{2}\frac{1}{2}\frac{1}{2}} \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2},$$

where t^{lmn} are the hopping integrals tabulated in Table I. This Hamiltonian yields a Fermi surface consisting of an electron-like sheet (γ), which is nearly cylindrical in shape, and four crossing planes, reconnected into a holelike (α) and an electronlike (β) tetragonal prism by the weak hybridization $xz - yz$. The Fermi surface obtained with the NMTO method is in good agreement with previously reported results based on LAPW (Ref. 24). The LAPW Fermi surface is also displayed in Fig. 3; qualitatively it is very similar to the results obtained in Ref. 24. Differently from previous calculations, here we include spin-orbit effects; these results will be discussed in Sec. V.

Since the bands at the Fermi level have mostly Ru t_{2g} character with some admixture of O p , it is likely that NMR is also dominated by Ru d and O p contributions. In addition, the polarization of the core electrons due to the d shell will be sizable for Ru. NMR results will be discussed in Sec. IV.

III. STONER FACTOR AND SPIN-ORBIT INTERACTION

In the spin DFT, the static spin susceptibility is formally exact and can be calculated as

$$\chi_s = dM_s(H)/dH, \quad (2)$$

where $M_s(H)$ is the spin magnetic moment induced by an external field H . This is related to the *noninteracting* spin susceptibility, which is simply the density of states (DOS) in appropriate units, $\chi_0 = \mu_B^2 N(0)$, where μ_B is the Bohr magneton. The renormalization is quantified in terms of the Stoner factor I :

$$\chi_s = \chi_0 / (1 - I\chi_0/2) \quad (3)$$

(in the literature one can also find an alternative definition of the Stoner factor, per two spin instead of one, which differs from ours by the factor 1/2 in the denominator). One can also calculate the orbital part of the magnetic susceptibility as

$$\chi_L = dM_L(H)/dH, \quad (4)$$

as long as the spin-orbit interaction is included in the calculations.

The most straightforward and the most accurate way to compute I is by performing self-consistent LDA calculations in an external field. For this purpose we have selected the full-potential linear augmented plane wave method as implemented in the WIEN2k+lo package.²⁷ This package allows for self-consistent calculations in an external field, including the interaction of the field with the orbital moment. Two sets of calculation were performed for a field along z or x axes. Particular care has been taken to provide a high level of convergence: up to 729 inequivalent k points ($17 \times 17 \times 17$ mesh), RKMAX up to nine, and states up to 3.5 Ry included in the second-variational diagonalization of the spin-orbit Hamiltonian. Local orbitals were included in the basis for both Ru and O, and a relativistic local p -orbital was added for Ru, to ensure the convergence of the spin-orbit calculations. The results are shown in Fig. 4 and Table II. The following observations are in place: (1) the spin susceptibility is anisotropic, with z being the *hard* axis, (2) the orbital susceptibility is nearly isotropic, and (3) there is a metamagnetic transition at a field between 75 and 100 T to a state

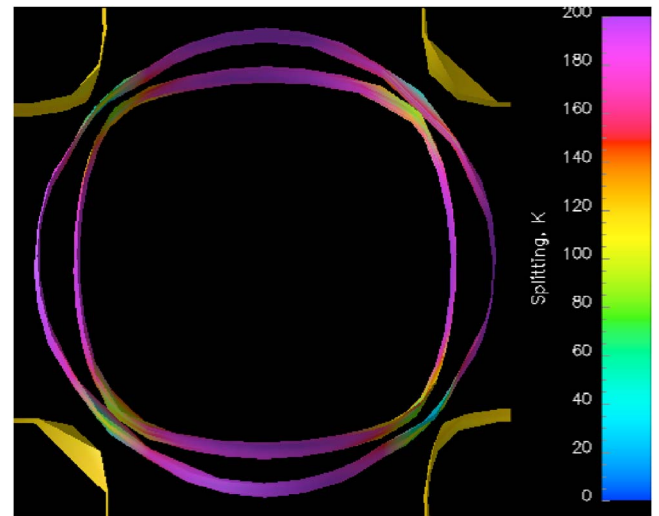


FIG. 3. (Color online) LAPW Fermi surface, painted according to the spin-orbit splitting at each point (see the color bar for the scale in the temperature units).

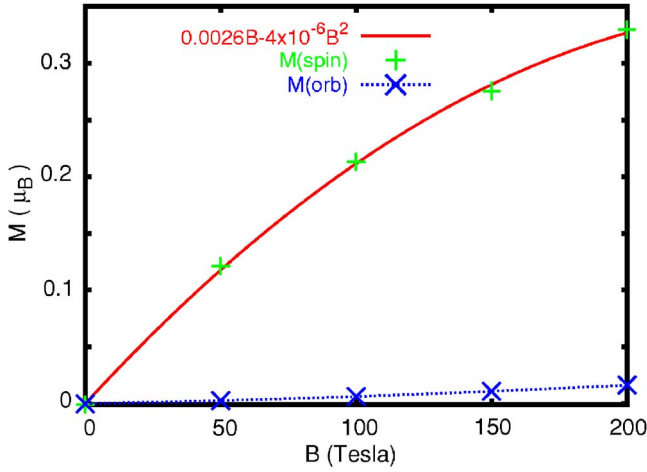


FIG. 4. (Color online) Orbital and spin magnetization (LAPW).

with a magnetic moment that extrapolates to $\approx 0.1 \mu_B/\text{Ru}$ in zero field. While this metamagnetism is obviously inobservable, it is probably related to the metamagnetism observed in some Sr_2RuO_4 -based alloys. In this paper we will not discuss this metamagnetism and will concentrate on the susceptibility. The low-energy slopes of $M(T)$ curves yield the results (in 10^{-4} esu/mol) listed in Table II.

We see that the calculations reproduce well the overall scale of the susceptibility but predict an opposite anisotropy compared to the experiment, albeit of the same scale (6% vs -11%). Note that a similar problem was encountered by Ng and Sigrist in their model calculation.²⁰ They ascribed the discrepancy to anisotropy of the orbital susceptibility, which, they pointed out, should be larger in the z direction because of the possibility to form an $xz+iyz$ state out of degenerate xy and yz orbitals. Indeed, we find such an anisotropy in our calculated orbital susceptibility, but it is way too small. Yet we believe that Ng and Sigrist's conjecture was right and the reason we do not see this effect is due to the fact that the density functional calculations routinely underestimate orbital effects (overestimate orbital moment quenching). In the experimental literature one can find a variety of estimates for the ratio χ_{orb}/χ_{tot} , from 10% (Ref. 1) to 17% (Ref. 29), while our result is 6%. Increasing our orbital susceptibility by a factor of two or three, however, still does not reproduce the experimental anisotropy. This strongly suggests, in accord with Ref. 20, that the separation of the orbital and spin parts in the experiment was inaccurate and in reality the orbital susceptibility is larger than usually quoted. Indeed, the separation of the orbital and spin susceptibilities in the experiment is based on the assumption that the orbital part is totally temperature independent, which is not true for metallic systems where a non-negligible orbital susceptibility comes from the states at the Fermi level (see, e.g., Ref. 31). Note that the anisotropy of χ_{orb} extracted in this way is 0.40×10^{-4} emu/mol,⁶ 2.5 times smaller than the observed anisotropy of the total susceptibility.¹¹ We will return to this issue again later when discussing the NMR experiments.

The calculation reported in this section yields a DOS of 50 states/Ry/cell. If interpreted in terms of Eq. (3), this re-

TABLE II. Static susceptibility in 10^{-4} emu/mol, as obtained from LAPW band structure.

	χ_s (calc)	χ_L (calc)	χ (exp) (Ref. 11)
z	7.26	.48	9.8
xy	7.67	.43	8.8

sults in the Stoner factor $I=0.46$ eV, and the renormalization coefficient $R=\chi_s/\chi_0=6.2$. In the next section we will be using LMTO calculation which give slightly smaller DOS, namely 45.6 states/Ry/cell. We will therefore use such R that renormalizes the LMTO DOS to the accurate LDA χ_s , that is, $R=6.8$. We point out that this value is about twice as large as the Stoner enhancing factor we obtained directly from self-consistent LMTO calculations in a magnetic field. This is not surprising; in our experience,³² allowing nonspherical variations of the spin density practically always results in more magnetic solutions.

IV. NMR KNIGHT SHIFTS

Next we calculate the NMR Knight shifts. These shifts originate from the hyperfine interaction $-\gamma_n \mathbf{I} \cdot \mathbf{H}$, between the nuclear magnetic moment $-\gamma \mathbf{I}$ and the hyperfine field \mathbf{H} produced at the nucleus site by the electrons. The hyperfine field operator \mathbf{H} is the sum of a core (\mathbf{H}^{core}), a contact (\mathbf{H}^c), a dipole-dipole (\mathbf{H}^d) and an orbital (\mathbf{H}^o) term. In order to calculate the NMR shifts we used two different approaches.

The first is described in Ref. 33 and based on the LMTO-atomic sphere approximation (ASA) method. Here we just summarize the most important steps. The bare Knight shifts are calculated from the LDA band structure by using linear response theory and without introducing any external magnetic field. This means, e.g., for the spin terms, $K \equiv 2\mu_B \text{Tr}(\uparrow|N\mathbf{H}|\uparrow)$, where we introduced the density-of-states operator $\langle \mathbf{k}s|N|\mathbf{k}'s' \rangle \equiv \delta_{ss'} \delta \mathbf{k}\mathbf{k}' \delta(\epsilon_{\mathbf{k}} - E_F)$; here s and s' are spin indices, $\epsilon_{\mathbf{k}}$ the band energy, and E_F the Fermi level. This approach allows to clearly distinguish the contributions of the different orbitals and of the different interactions and thus makes the physical interpretation easier. The Stoner factor and the core shifts are obtained separately, i.e., from a self-consistent LSDA calculation with an external magnetic field, B_{ext} . The latter produces a core polarization $m(\mathbf{r})$; the core shift is the ratio B_{core}/B_{ext} between the (core) contact hyperfine field, $B_{core} = \mu_B(8\pi/3)m(0)$, and the external magnetic field. About 450 \mathbf{k} points in the irreducible Brillouin zone were needed in order to obtain well converged results. We tested several different LMTO set ups,³⁴ with consistent results. The different contributions of conduction electrons to the Knight shift are displayed in Table III.

The second approach is the one implemented in the LAPW WIEN2k package.³⁵ All the contributions to the Knight were obtained from the ratio between the hyperfine field B and the external magnetic field B_{ext} from which B originates. Clearly, all the Knight shifts calculated in this way are already Stoner renormalized. The Knight shifts were

TABLE III. Knight shift, K_α in %. The label $\alpha=x,y,z$ indicates the direction of the external magnetic field. The first panel presents the results obtained with the LMTO method in the scalar relativistic approximation; the Stoner enhancement factor $R=6.8$ is used for the renormalized values. The second and the third panels are the results obtained with LAPW without and with spin-orbit (SO) interaction; the Stoner factor is already included by construction. The last panel lists available experimental data. For O1 the shifts for the (1/2,0,0) site are presented.

	Dipole			Contact	Orbital	Core	Total (xyz) (renormalized)		
	x	y	z				x	y	z
Ru	0.007	0.007	-0.014	0.006	0	-0.727	-1.366	-1.366	-1.508
O1	0.020	-0.043	0.023	0.003	0	0.027	0.210	-0.218	0.231
O2	0.001	0.001	-0.002	0.004	0	0.002	0.038	0.038	0.018
Sr	0.000	0.000	-0.001	0.059	0	-0.007	0.390	0.390	0.382

	Dipole			Orbital	Contact + core	Total		
	x	y	z			x	y	z
Ru	0.238	0.238	-0.475	0	-1.437	-1.200	-1.200	-1.912
O1	0.216	-0.257	0.041	0	0.008	0.224	-0.249	0.048
O2	0.021	0.021	-0.042	0	0.015	0.036	0.036	-0.027
Sr	0.002	0.002	-0.003	0	0.113	0.114	0.114	0.110

	Dipole			Orbital			Contact + core	Total		
	x	y	z	x	y	z		x	y	z
Ru	0.232	0.232	-0.463	-1.146	-1.146	-1.078	-1.436	-2.350	-2.350	-2.977
O1	0.211	-0.254	0.043	-0.104	-0.067	-0.125	0.006	0.113	-0.315	-0.076
O2	0.022	0.022	-0.043	-0.088	-0.088	-0.117	0.014	-0.052	-0.052	-0.060
Sr	0.001	0.001	-0.003	-0.138	-0.138	-0.134	0.112	-0.024	-0.024	-0.025

	Expt. ^a			Expt. ^b			Expt. ^c		
	x	y	z	x	y	z	x	y	z
Ru	-2.75	-2.75	-3.44	-2.70	-2.70	-3.32			
O1	0.50	-0.15	0.30	0.48	0.18		0.40	-0.15	0.28
O2	0.08	0.08	0.04				0.04	0.04	0.03
Sr									

^aFor Ru, Ref. 29; for O1 ($T=4.2$ K) and O2, Ref. 44.

^bFor Ru, Refs. 6 and 30. For O1 Ref. 5 ($T=2$ K).

^cFor O1 and O2, Ref. 45 (4.2 K).

obtained from the highly accurate LAPW band structure, and the effects of spin-orbit could be accurately analyzed. The results are again displayed in Table III.

Let us examine first the results obtained for the Ru isotropic Knight shift, $K_{iso} \equiv (K_x + K_y + K_z)/3$. We found that the s -electron contribution from the conduction bands to K_{iso} is negligible; this is understandable because N_s , the Ru- s projected density of states (see Table IV) is negligible at the Fermi level ($N_s/N_{t_{2g}} \approx 2 \times 10^{-4}$). The main contribution is the core polarization (the dipole-dipole term is sizable, but purely anisotropic).

At this point, it is interesting to compare the core-polarization Knight shifts in LMTO and LAPW (no spin-orbit), Table III. As already explained, in both LMTO and LAPW the core-polarization shifts were obtained from self-consistent electronic structure calculations in an external magnetic field, and are therefore renormalized by the Stoner

factor. Still, the LMTO yields a core shift a factor 1/2 too small; this is consistent with our results on the Stoner enhancing factor R , which turned out to be a factor 2 smaller in LMTO than in LAPW. For this reason, in calculating the Stoner renormalized shifts for the LMTO (the rightmost column of Table III) we took into account this discrepancy and multiplied the core term by this missing factor 2. This is an important technical point and we would like to reiterate it: In LAPW calculations all calculated contributions are by construction already Stoner-renormalized. In LMTO, the core polarization is renormalized by a factor inherent to the ASA-LMTO calculation, which we found to be underestimated in ASA by 50%, compared to our full-potential result. Spherical approximations for the crystal potential commonly underestimate the tendency to magnetism compared to the full-potential calculations in materials near a quantum critical point (cf., e.g., Ref. 32). The other contributions calculated in

TABLE IV. Projected density of states (states/Ry/atom), obtained with the LMTO method (set up with three empty spheres³⁴) and a comparison with LAPW. In the last two columns $|\phi_s(0)|^2$ and $\langle 1/r^3 \rangle_l \equiv \int dr r^2 |\phi_l(r)| (1/r^3)$ (a.u.) are displayed, where $\phi_l(r)$ is the radial solution of the Schrödinger equation for the free atom and l its angular quantum number.

	N_d	N_{xy}	N_{xz}	N_{yz}	N_s	$ \phi_s(0) ^2$	$\langle 1/r^3 \rangle_l$
Ru (LMTO)	27.67	10.33	8.65	8.65	0.005	3.46	5.38 ($l=2$)
Ru (LAPW)	29.28	14.45	7.40	7.40	0.002		
	N_p	N_x	N_y	N_z	N_s	$ \phi_s(0) ^2$	$\langle 1/r^3 \rangle_l$
O _{1x} (LMTO)	5.54	0.02	2.44	3.06	0.010	8.00	5.15 ($l=1$)
O _{1x} (LAPW)	6.30	0.02	3.90	2.39	0.011		
O _{1y} (LMTO)	5.54	2.44	0.02	3.06	0.010	8.00	5.15 ($l=1$)
O _{1y} (LAPW)	6.30	3.90	0.02	2.39	0.011		
O _{2z} (LMTO)	0.88	0.36	0.36	0.16	0.015	8.00	5.15 ($l=1$)
O _{2z} (LAPW)	0.94	0.42	0.42	0.08	0.015		

LMTO are found via linear response formulas and do not include *any* renormalization. Therefore, the final result in the rightmost column of the Table III includes a renormalization by a factor of two for the LMTO core polarization, of 6.8 for all other LMTO contributions, and no renormalization for the LAPW results.

We notice that the LAPW and the Stoner renormalized LMTO results for K_{iso} (spin part) agree rather well; $K_{iso} \equiv RK_{iso}^0 = -1.41$ in LMTO and -1.44 in the nonrelativistic LAPW (spin-orbit hardly affects this term). The small discrepancies can be attributed to small differences in the band structure and in the calculation procedure.³⁵

The dipole contribution to K_{iso} is zero by symmetry. However, the orbital contribution is not, and it appears to be comparable to the contact term (as opposed to the magnetic susceptibility, where the orbital part is rather small). While nonrelativistic LMTO calculation cannot be used to evaluate this contribution, the WIEN2k code includes an option of relativistic calculations in an applied magnetic field. Importantly, we found that it was absolutely necessary to include not only spin-orbit interaction, but interaction of the orbital moment with the external field as well. We found that after including the orbital part, $K_{iso} = -2.56$. Regarding the oxygen Knight shift, we get $K_{iso} = -0.09$ and -0.05 for the in-plane and apical oxygen, respectively.

Experimentally, $K_{iso} \approx -2.98$ was reported in Ref. 29, and a slightly smaller value, $K_{iso} \approx -2.91$, in later papers by the same group.⁶ Our calculated number of -2.56 is 12% smaller than the later data, reminiscent of the 15% underestimation of the total susceptibility (Table II).³⁶ While the calculated K_{iso} for oxygens has the wrong sign, this does not seem disturbing, since both the experimental and the calculated numbers are very small and result from a substantial cancellation of various anisotropic terms, and the absolute magnitude of the error is rather small.

This agreement seems impressively good, but, just as with the magnetic susceptibility, this is probably deceptive. As mentioned, Sr_2RuO_4 is close to a magnetic quantum critical point, and therefore belongs to a growing class of materials where LDA overestimates the tendency to magnetism (see,

e.g., Ref. 37 and references therein). It is generally believed that magnetic fluctuations play an important part in linear response in such materials, suppressing the magnetic susceptibility compared to the essentially mean field LDA treatment.³⁸ Indirect evidence indicates that LDA does indeed overestimate the propensity to magnetism; for instance, in LDA Sr_2RuO_4 is unstable against the formation of a spin density wave at the nesting vector $(1/3, 1/3, 0)$.³⁹ It is hard to imagine that the same fluctuations that stabilize the paramagnetic state as opposed to the spin density wave ground state in LDA would not reduce χ, K (and also $1/T_1 T$). Also, calculations predict Sr_2RuO_4 to be ferromagnetic at the surface,⁴⁰ while experimentally it is not the case.⁴¹ We conclude that the good agreement of the calculated χ and K_{iso} is largely due to a cancellation of errors: we *overestimate* the spin susceptibility, but *underestimate* the orbital susceptibility, as also evidenced by our failure to reproduce the sign of the anisotropy in χ .⁴² Note that underestimation of the orbital polarization, due to correlation effects, is very typical for d shells in the transition metals.

Let us now analyze the anisotropy of the Knight shift. Experimentally, Ishida *et al.*²⁹ reported for Ru $K_{aniso} \equiv (K_z - K_x)/3 = -0.23\%$ and later -0.20% (Refs. 6 and 30). Within the spherical approximation for the potential, the LMTO calculations (Table III) give $K_{aniso} = -0.05$ (which is solely a dipole effect). On the other hand, a full potential approach (LAPW) results in $K_{aniso} = -0.23$ in the dipole part, which is reduced to -0.21 by the orbital effects. This excellent agreement reflects the fact that the largest share of the calculated anisotropy comes from the dipole part. Note that a possible overestimation of the contact interaction would not affect K_{aniso} .

It is instructive to analyze why LMTO underestimates the dipole contribution compared to the full-potential calculations, by as much as a factor of 4.5 (for Ru), despite the fact that it is very accurate for the contact term. To this end, let us recall that for the dipole interaction, the contributions from xy and yz/xz bands have opposite signs and tend to cancel each other. Keeping only the dominant diagonal terms, we find

TABLE V. $1/T_1T$ in $(\text{K sec})^{-1}$, results based on LMTO calculations. The Stoner factors $R^{1.7} \approx 26$ and $2^{1.7} \approx 3.25$ (core) are used for the renormalized values (see text). The fourth and fifth column display the total relaxation rate obtained after Stoner renormalization of, respectively, the spin terms and of both spin and orbital terms.

	Orbital	Dipole	Contact	Core	Total (Spin renormalized)	Total (all renormalized)	Expt. ^a	Expt. ^b
¹⁰¹ Ru	0.18692	0.02855	0.00004	0.53340	2.67	7.3	15	-
¹⁷ O1	0.03291	0.01392	0.00007	0.00541	0.41	1.23	0.8	1.1
¹⁷ O2	0.00085	0.00028	0.00011	0.00004	0.011	0.032	0.025	0.025
⁸⁷ Sr	0.00029	0.00009	0.00254	0.00003	0.069	0.076	-	-

^aFor ¹⁰¹Ru, Refs. 43 and 44 ($T=4.2$ K). For ¹⁷O (planar and apical) data are from Ref. 44 ($T=4.2$ K).

^bReference 45, sample with $T_c=1.5$ K ($T=4.2$ K).

$$K_{\text{aniso}}^{\text{dip}} \equiv \frac{K_z^{\text{dip}}}{2} \approx -\frac{\mu_B^2 \langle r^{-3} \rangle_2}{7} [2N_{xy} - (N_{yz} + N_{xz})]. \quad (5)$$

Here N_{xy} , N_{yz} , and N_{xz} are the orbital-projected density of states at the Fermi level (Table IV) per atom and $\langle r^{-3} \rangle_l \equiv \int dr |\phi_l(r)|^2 / r^3$, where $\phi_l(r)$ is the radial solution of the Schrödinger equation with angular momentum quantum number l . We found in ASA-LMTO (see Table IV) that $N_{xy} \approx N_{xz} = N_{yz}$, and therefore the dipole contributions nearly cancel each other. On the other hand, this cancellation is far less complete in LAPW (see Table IV): in LMTO the ratio $N_{xy}/N_{xz} \approx 1.2$, while in LAPW it is nearly 2. A similar discrepancy is observed in the $N_x/N_y/N_z$ ratios for oxygens. On the other hand, the total DOSs, N_d and N_p agree reasonably well. Although one can expect that the spherical approximation somewhat underestimates the DOS anisotropy, the observed discrepancies seem to be too large. A close inspection reveals the secret: LMTO underestimates the electrostatic crystal field splitting, that is, the shift between the on-site energies of the d_{xy} and d_{xz} orbitals, by approximately 4 mRy, which leads to a relative shift of the xy and xz/yz band by ± 4 mRy compared to the LAPW calculations. This seems like a small effect, and it is, but because the Fermi level is situated on a slope of the DOS, shifting these bands in the opposite direction leads to a serious redistribution of the DOS at E_F between them. The more accurate NMTO bands, with a better account for nonspherical effects, are closer to LAPW: we find $N_{xy} - N_{xz} = 4.9$ states/Ry/atom.

It is more complicated to analyze K_{aniso} for oxygen, because of bigger experimental uncertainty, strong temperature dependence (on the O1 site), and a somewhat larger orbital contribution in the calculations. The in-plane anisotropy on the oxygen bridging two Ru along x , defined as $K_{\text{aniso}}^{\parallel} \equiv (K_y - K_x)/2$, is -0.32% in the experiment, while in the calculation it is -0.21 , mostly dipole. The out-of-plane anisotropy, $K_{\text{aniso}}^{\perp} \equiv [K_z - (K_x + K_y)/2]/3$, is 0.04 in the experiment and 0.01 in the calculations. Again, one ought to keep in mind the overall small magnitude. Finally, for the apical oxygen K_{aniso} is essentially zero both in the experiment and theory. Note that in the case of oxygen, LMTO also underestimates the dipole contribution, by virtue of the same argument (for O, $K_z \approx -\frac{2}{5} \mu_B^2 [2N_z - (N_x + N_y)] \langle r^{-3} \rangle_1$).

Finally, strontium appears to be the only site where the Fermi contact term dominates. Unfortunately, to the best of our knowledge at present there are no experimental data available for Sr.

V. NMR RELAXATION RATES

Let us now analyze the relaxation rates. We calculated $1/T_1$ with the procedure described in Ref. 33 and based on the LMTO band structure. Within this approach, the relaxation rate is obtained from Fermi's golden rule and linear response theory; for a polycrystalline sample $1/T_1T$ can be expressed as

$$\frac{1}{T_1T} = 2\pi k_B \hbar \gamma_n^2 \left[\text{Tr} \frac{1}{3} |\mathbf{H}\mathbf{N}|^2 \right], \quad (6)$$

where \mathbf{H} is the hyperfine field operator previously introduced. Since the cross terms in Eq. (6) vanish exactly for a polycrystal,³³ the relaxation rate is, apart from the core polarization contribution, the sum of contact, a dipole-dipole, and an orbital term

$$\frac{1}{T_1T} = 2\pi k_B \hbar \gamma_n^2 \text{Tr} \frac{1}{3} [|\mathbf{H}^c \mathbf{N}|^2 + |\mathbf{H}^d \mathbf{N}|^2 + |\mathbf{H}^o \mathbf{N}|^2]. \quad (7)$$

We calculated these contributions using the LMTO basis set; the results are displayed in Table V. The core polarization term was obtained separately from the core Knight shift and the Korringa law.

The LAPW WIEN2k package currently available to us does not allow for calculations of the relaxation rate. However, we can make use of the understanding gained on the previous stage by comparing LMTO and LAPW results for the Knight shifts to evaluate the reliability of the LMTO calculations.

We obtained the bare relaxation rate (Table V) and calculated the Stoner enhancing factor separately. The computation of the Stoner enhancing factor for the relaxation rate, R_{1/T_1T} , requires knowledge of the \mathbf{q} dependence of the spin susceptibility, according to the following formula:⁴⁶

$$R_{1/T_1T} \approx \left\langle \frac{\text{Im } \chi_0(\mathbf{q})}{[1 - I(\mathbf{q})\text{Re } \chi_0(\mathbf{q})]^2} \right\rangle / \langle \text{Im } \chi_0(\mathbf{q}) \rangle. \quad (8)$$

Using the Lindhart susceptibility we showed earlier³³ that in three dimensional (3D), $R_{1/T_1T} \approx R^{5/3}$. However, Sr_2RuO_4 is rather two dimensional (2D), in which case the real part of the noninteracting susceptibility is constant, and, assuming a \mathbf{q} -independent I , we get simply $R_{1/T_1T} \approx R^2$, as first pointed out by Shastry and Abraham.⁴⁶ The actual dependence of I on q in Sr_2RuO_4 is discussed in Ref. 24, where it was estimated as $I(q) = I/[1 + b(q/G)^2]$, where $G = \pi/a$, and b is a numerical constant close to 0.08. Using this with Eq. (8) and taking into account the actual q dependence of $\text{Im } \chi_0(\mathbf{q})$ we find $R_{1/T_1T} \approx R^{1.7} = 26$. We use this enhancement factor R_{1/T_1T} to renormalize the contact and the dipole-dipole contributions to the relaxation rates. Similar to the Knight shift, as discussed in Sec. IV, the calculated core polarization contribution to the relaxation rate is Stoner-renormalized according to the LMTO Stoner factor, which by itself is smaller than the renormalization factor in LAPW. Thus, the core-polarization part was renormalized by a factor of $2^{1.7}$.

The renormalization of the orbital terms is more controversial. Even if we knew the renormalization factor for the spin shifts exactly, there is no guarantee that the renormalization for the orbital shifts is the same. Indeed, as discussed above in connection with the Knight shift, the orbital polarization is induced by both the direct interaction of the orbital currents with the external field, as well as, indirectly, via the spin-orbit interaction with the induced spin density. The former process is not a subject of Stoner renormalization, while the latter is. It is therefore likely that the renormalization of the total orbital term is not as large as the Stoner renormalization of the spin terms. In Table V we show the total relaxation rates obtained by renormalizing the spin shifts only, and those obtained renormalizing (with the same enhancing factor ≈ 26) the orbital shifts too. These numbers are the lower and upper limit for the LDA relaxation rates. Judging from the LAPW Knight shift (with spin-orbit) one may expect that the spin-orbit contribution to the relaxation rate is larger for Ru than for O; correspondingly, the renormalization of the orbital terms is expected to be larger for Ru than for O.

Since there are so many uncertainties in the renormalization of the orbital terms, first we discuss the relaxation rates obtained after the renormalization of the spin (contact, core, and dipole-dipole) terms only. The total calculated $1/T_1T \approx 2.67 \text{ (K sec)}^{-1}$, underestimating the low temperature $1/T_1T \approx 15 \text{ (K sec)}^{-1}$ by a factor 5. For O1 we find large orbital and dipole-dipole terms, and a sizable core-polarization contribution. We find $1/T_1T = 0.41 \text{ (K sec)}^{-1}$. Experimentally, $1/T_1T$ was found to be 0.8 (K sec)^{-1} at 4.2 K; now the calculated value is too small by a factor of 2. For O2 the value $1/T_1T = 0.023 \text{ (K sec)}^{-1}$ was measured.^{44,45} Our calculated value $1/T_1T = 0.011 \text{ (K sec)}^{-1}$, again too small of a factor of 2.

In order to understand better the source of this discrepancy we examine the case of Ru in more detail. The leading contribution to ^{101}Ru $1/T_1T$ is the core term; judging from the

Knight shift calculations, we do not expect the core polarization to be particularly poorly described by LMTO. The next largest term is the orbital contribution. It is given for Ru, for example, by the following expression:

$$\left(\frac{1}{T_1T} \right)_{orb} \approx \frac{4}{3} C (\mu_B^2 \langle r^{-3} \rangle_2)^2 [N_{xz}^2 + N_{yz}^2 + 4N_{xy}^2 + 2N_{xy}(N_{xz} + N_{yz})], \quad (9)$$

where $C \equiv (4\pi k_B/\hbar)(\gamma_n/\gamma_e)^2 \approx 0.404 \times 10^5 \text{ (K sec)}$ for Ru^{101} . Note that the orbital contribution to the relaxation rate does not *require* spin-orbit coupling (it appears already in the nonrelativistic approximation), but the spin-orbit coupling can and does contribute to the orbital polarization. Note that if the spin-orbit contribution to the relaxation rate would be of the same relative size as the corresponding contribution to the Knight shift (that is, of the order of the core contribution) we would expect an *additional* spin-orbit induced relaxation rate of about $\approx 1.75 \text{ (K sec)}^{-1}$. This would be the first contribution missing in Table V.

Furthermore, the orbital term is also partially underestimated because of the difference between the LMTO and LAPW DOSs, as already discussed in the previous section. Using LMTO partial DOSs in the approximate formula, Eq. (9), we find $(1/T_1T)_{orb} \approx 0.29 \text{ (K sec)}^{-1}$, in good agreement with the full calculations (Table V); using instead LAPW DOSs (the exact comparison of LAPW and LMTO is of course not possible because space is divided up differently in the two methods) we find $(1/T_1T)_{orb} \approx 0.4 \text{ (K sec)}^{-1}$, which indicates that the LMTO orbital term is underestimated by a factor ≈ 1.4 . Similar considerations apply to the dipole-dipole term, described by

$$\left(\frac{1}{T_1T} \right)_{dip} \approx \frac{2}{49} C (\mu_B^2 \langle r^{-3} \rangle_2)^2 [N_{xz}^2 + N_{yz}^2 + 4N_{xy}^2 + 3N_{xy}(N_{xz} + N_{yz})]. \quad (10)$$

This correction (for both terms) is about 0.4 (K sec)^{-1} .

Both these corrections together raise the estimate for the relaxation rate on Ru to $\sim 5 \text{ (K sec)}^{-1}$, still short of the experimental number of 7.3 (K sec)^{-1} . We take it to be yet another manifestation that the orbital effects on Ru are underestimated in LDA and that the leading relaxation mechanism is orbital.

One should expect that correlation effects on O are rather moderate and then, after correcting for the LAPW-LMTO DOS differences, we should get a reasonable agreement with the experiment (spin-orbit effects are also weak for O). Indeed, after this correction we obtain $(1/T_1T)_{O1} \approx 0.65 \text{ (K sec)}^{-1}$ and $(1/T_1T)_{O2} \approx 0.16 \text{ (K sec)}^{-1}$, reasonably close to the experiment.

Finally, we neglected the quadrupolar contribution to $1/T_1T$. For ^{101}Ru this term is small, but not negligible;⁴⁷ taking this term into account would therefore increase the agreement with experimental measurements. Interestingly, the quadrupolar term could partially contribute to smear out the Hebel-Slichter peak. The quadrupolar contribution is however negligible for O1 and ^{99}Ru ; measurements of the relaxation rate below T_c for these two ions could therefore

shed further light on our understanding of NMR data and clarify the absence of the Hebel-Slichter peak.

VI. SUPERCONDUCTIVITY

Finally, we want to make a few comments on a possible alternative interpretation of the invariance of the Knight shift across the superconducting transition. As we discussed in the Introduction (see also discussions in Refs. 3 and 12), the interpretation in terms of the order parameter, rotating in the field of 0.02 T, less than one percent of the superconducting gap, is very unlikely. The interpretation of the temperature independence of the Knight shift in the superconducting state of Sr_2RuO_4 in terms of a chiral p -state is not possible, at least not on the level of existing theory. Given that this is the *only* experiment uniquely identifying the superconductivity in Sr_2RuO_4 as chiral p -wave, this opens the door for other possibilities regarding the symmetry of the superconducting state, such as the chiral d -state proposed in Ref. 3, $\Delta \propto xz \pm iyz$, or a planar p -wave state, as suggested in Ref. 12.

Given the rather inexplicable absence of the Knight shift decay below T_c , it is tempting to bring up an analogy with such materials as V and Hg. Two explanations of the same phenomenon in these elemental metals have been proposed. The first one is the spin-flip scattering^{16,17} by the grain boundaries or point defects due to the spin-orbit coupling. Spin-orbit induced splitting of the conductivity bands is rather nonuniform over the Fermi surface, reaching 200 K at some places (Figs. 2 and 3). Anderson¹⁷ has derived a formula describing this effect: the ratio of the Knight shift at $T=0$ and at $T>T_c$ is $K_{\text{sup}}/K_{\text{norm}} \approx \gamma_{s-f}/6\Delta$, where γ_{s-f} is the rate of the spin-flip events, Δ is the superconducting order parameter, and $\gamma_{s-f} \geq \Delta$. If γ_{s-f} gets noticeably larger than Δ , the Knight shift changes rather little across T_c . In principle, there is nothing unimaginable in $\gamma_{s-f} > \Delta$, however, we should remember that nonmagnetic impurities in Sr_2RuO_4 are pair breakers, and samples with $T_c \approx 1.4$ K, and the experiments we strive to explain were performed on such samples, have to satisfy the pair breaking condition $\gamma_{tr} < \Delta$, where γ_{tr} is the transport relaxation rate. Even given the sizable spin-orbit interaction in Sr_2RuO_4 , it is totally unrealistic to assume spin-flip relaxation to be larger than momentum relaxation, that is, $\gamma_{s-f} \leq \gamma_{tr} < \Delta$ should hold.

Another mechanism that can emulate a temperature-independent Knight shift was described by MacLaughlin:¹⁹ if the Fermi contact and the core polarization contribution cancel each other, the remaining orbital part, being an entirely charge effect, will stay unsuppressed below T_c . This was supposed to be operative, for instance, in V. There are two objections against applying the same scenario to Sr_2RuO_4 . First, in Ru we find that the Fermi contact interaction is negligible, but the core polarization is responsible for about a half of the total Knight shift. Even though it is probably overestimated, we can guarantee it is not negligible. Moreover, for both O1 and Ru we find a sizable dipole term (in fact, for O1 it is the leading term). In Ref. 19 this term was neglected, but it also originates from the spins of electrons and should be sensitive to pairing. So, on this (probably

oversimplified, as discussed below) level neither of the two known explanations of the invariance of the Knight shift below T_c is applicable.

While this simplistic picture¹⁹ does not appear to work for Sr_2RuO_4 , it brings up an important point, that the standard theory of the Knight shift in the superconducting state, developed for Fermi-contact interaction in one-band superconductors has to be revised to be applicable to Sr_2RuO_4 . Indeed, while the orbital interaction does not dominate the Knight shift on Ru, it constitutes at least a half of the total K , and probably as much as 2/3, if we take into account that the core polarization is probably overestimated in LDA. This alone raises our expectation for $K(T=0)$ from zero to about 2/3 of its normal value. On top of that we have a sizable dipole term, which for the in-plane field is opposite in sign to the core polarization. Most interestingly, the temperature dependence below T_c should be highly nontrivial even for a singlet pairing: as discussed, this term comes about through near-cancellation of the contributions from the xy and $xz + yz$ bands. For several reasons, these bands are expected to react differently to magnetic field (and the actual measurements were performed in a sizable field): they have different Fermi velocities along the c -axis, and possibly rather different gap values. Therefore, the partial densities of states decay (in a singlet case) below T_c at different rates, with a possibility of the net dipole Knight shift to decrease, increase, or (accidentally) stay constant. The exact answer requires a quantitative analysis that goes beyond the framework of this paper, but we want to emphasize that *the fact that the dipole contribution is strong calls for an entirely new theory of the Knight shift below T_c* . A similar consideration applies to the Knight shift on O.

VII. CONCLUSIONS

We have calculated from first principles the magnetic susceptibility, the Knight shifts, and the relaxation rates in Sr_2RuO_4 . We adopted different LDA techniques (LMTO and LAPW) and performed calculations with and without explicit account for the spin-orbit interaction. The agreement with available experimental data is good, in some cases surprisingly good. The isotropic magnetic susceptibility, the isotropic and anisotropic Knight shift for Ru are all reproduced better than within 15%. However, there are notable discrepancies, of which most important is, probably, the incorrect anisotropy of magnetic susceptibility. We argue that this error is related to an enhancement of the orbital polarization due to correlation effects beyond LDA. Despite the good quantitative agreement with the experiment of the isotropic susceptibility and the isotropic Knight shift on Ru, we do think that we witness a cancellation of two errors: On one hand, we overestimate the spin susceptibility, which should be reduced by spin fluctuations missing in the LDA, and on the other hand we underestimate the orbital polarization in the Ru d shell. If this interpretation is correct, one has to conclude that orbital effects are extremely important and probably dominate both the Knight shift and the NMR relaxation on Ru.

We have considered the accepted mechanisms of the Knight shift invariance in elemental metals and conclude that

they cannot explain the same phenomenon in Sr_2RuO_4 . In particular, we can exclude the spin-flip scattering by defects in Sr_2RuO_4 . On the other hand, orbital polarization of electrons at the Fermi level, which was used earlier to explain a similar effect in vanadium, is also the leading contribution in Sr_2RuO_4 . Although it does not entirely dominate the Knight shift, as in V, it does substantially reduce the expected effect of singlet superconductivity on it. Finally, a sizable contribution of the dipole-dipole interactions together with the orbital-dependent order parameter essentially renders the existing theory of the Knight shift suppression by a singlet

pairing incomplete and calls for its revision. We hope that this conclusion will inspire further experimental and theoretical studies.

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- ³⁴The results presented were obtained for a setup with three empty spheres ($R_{\text{Sr}}=3.28$, $R_{\text{Ru}}=2.44$, $R_{\text{O1}}=1.8$, $R_{\text{O2}}=2.06$, $R_{\text{E1}}=1.92$, $R_{\text{E2}}=1.32$, $R_{\text{E3}}=1.26$).
- ³⁵In WIEN2k the Knight shifts are presently calculated retaining only the l -diagonal terms and only the contribution from the muffin-tin spheres. In the case of Sr_2RuO_4 , a detailed inspection of the LMTO NMR calculations, which take into account the off-diagonal terms, suggests that the latter are small.
- ³⁶The fact that both experimental and calculated susceptibilities and Knight shifts include several contributions of different physical origins complicates the comparison with the experiment. It is tempting to compare, for instance, our calculated spin susceptibility of 7.5×10^{-4} with the published number of $\chi_s \approx 7.6 \times 10^{-4}$ (Ref. 29) and claim an excellent agreement. However, as mentioned before, the standard procedure used in processing the experiment neglects the possible temperature dependence of the orbital susceptibility, which is questionable in the case of orbital contributions from electrons at the Fermi level. Besides, it makes use of free Ru^{4+} ion calculations of the orbital hyperfine field with a semiempirical reduction coefficient. On the other hand, we calculated the orbital contribution directly, but only from Ru $3d$ and O $2p$ electrons. Still, we believe that other

- contributions are small and a comparison of our calculations should be with the *total* experimental susceptibilities and Knight shifts.
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