Theoretical Investigations of the Knight Shifts and the Hyperfine Structure Constants for the Tetragonal Cu^{2+} Sites in the Bismuth- and Thallium-Based High-T_c Superconductors

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The Knight shifts and hyperfine structure constants for the tetragonal Cu^{2+} sites in bismuth- and thallium-based high-T_c superconductors ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$, $TlSr_2CaCu_2O_{7-y}$, and $Tl_2Ba_2CuO_y$) are theoretically investigated from the high-order perturbation formulas of these parameters for a $3d^9$ ion under tetragonally elongated octahedra in a unified way. The calculation results show good agreement with the observed values. The significant anisotropies of the Knight shifts are attributed to the local tetragonal elongation distortions of the five-(or six-)coordinated Cu^{2+} sites in these systems. The present studies would be beneficial to establish a complete physical scheme for unified understandings of electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectral behaviours of Cu^{2+} (or other similar $3d^9$ ions) in the high-T_c superconductors.

Key words: Knight Shifts; Hyperfine Structure Constants; $^{63}Cu^{2+}$; $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$; $TlSr_2CaCu_2O_{7-y}$; $Tl_2Ba_2CuO_y$.

1. Introduction

The bismuth- and thallium-based high-T_c superconductors have attracted extensive interest of researchers due to unique metal [1] and heat transportation [2, 3], ferromagnetism [4], temperature-dependent resistivity [5], quantum resistive behaviours [6], and the quantum oscillation effect [7, 8]. Meanwhile, the Knight shifts of $^{63}Cu^{2+}$ of nuclear magnetic resonance (NMR) experiments in heavily strontium- or barium-doped bismuth- and thallium-based high-T_c superconductors can yield important information about the local environments and electronic distribution in the copper–oxygen planes. Such information may be helpful to understand superconductive and other physical properties of these systems. For example, the Knight shifts $K_{//}$ and $K_{\perp}$ and the anisotropic hyperfine structure constants $A_{//}$ and $A_{\perp}$ were measured for the tetragonal $^{63}Cu^{2+}$ sites in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ [9], $TlSr_2CaCu_2O_{7-y}$ [10], and $Tl_2Ba_2CuO_y$ [11].

Until now, however, no satisfactory theoretical explanations to the above experimental results have been made. Usually, the previous calculations of the Knight shifts were generally based on the simple second-order perturbation formulas, while the contributions from the higher-(third- and fourth-)order perturbation terms were not taken into account. Moreover, the analysis on the Knight shifts was not correlated to the local structure of the magnetic sites but treated by introducing various adjustable parameters (e. g., the related energy separations). Finally, the hyperfine structure constants were not quantitatively analyzed in a uniform way. In order to study the Knight shifts and hyperfine structure constants of these systems more exactly, the high-order perturbation formulas of these quantities for a tetragonally elongated $3d^9$ cluster are adopted in the calculations. The local structures of the tetragonal $^{63}Cu^{2+}$ sites are quantitatively involved from the superposition model. The results are discussed.

2. Calculations

The observed anisotropic Knight shifts and hyperfine structure constants can be ascribed to the

tetragonal Cu^{2+} sites in the systems, i. e., the five-coordinated $^{63}Cu^{2+}$ sites in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$ and the six-coordinated $^{63}Cu^{2+}$ site in $Tl_2Ba_2CuO_y$, respectively. And the experimental anisotropies $K_{//} > K_{\perp}$ and $|A_{//}| > |A_{\perp}|$ [9–11] reveal the lowest $^2B_{1g}$ states for a $Cu^{2+}(3d^9)$ ion under tetragonally elongated octahedra [12–14]. For a $Cu^{2+}(3d^9)$ ion in tetragonally elongated octahedra, its original cubic ^2E_g ground state would be separated into two orbital singles $^2B_{1g}$ (or $|\varepsilon\rangle$) and $^2A_{1g}$ (or $|\theta\rangle$), with the former lying lowest. Meanwhile, the original cubic $^2T_{2g}$ exited state may split into an orbital singlet $^2B_{2g}$ (or $|\zeta\rangle$) and a doublet ^2E_g (or $|\xi\rangle$ and $|\eta\rangle$) [13, 14].

In the present studies, the high-(third- and fourth-) order perturbation formals for a tetragonally elongated octahedral $3d^9$ cluster are applied so that (i) unified investigations of Knight shifts and hyperfine structure constants can be made and (ii) the weakness of the simple second-order perturbation formulas using various adjustable parameters can be removed. In view of gyromagnetic factors closely relevant to hyperfine structure constants and local structures of the systems, the g factors are also treated here for the sake of completeness. Thus, we have [15]:

$$\begin{aligned}
g_{//} &= g_s + 8k\zeta/E_1 + k\zeta^2/E_2^2 + 4k\zeta^2/(E_1E_2) - g_s\zeta^2 \\
&\quad \cdot \left[1/E_1^2 - 1/(2E_2^2)\right] + k\zeta^3(4/E_1 - 1/E_2)/E_2^2 \\
&\quad - 2k\zeta^3\left[2/(E_1^2E_2) - 1/(E_1E_2^2)\right] + g_s\zeta^3[1/(E_1E_2^2) \\
&\quad - 1/(2E_2^3)]\,, \\
g_{\perp} &= g_s + 2k\zeta/E_2 - 4k\zeta^2/(E_1E_2) + k\zeta^2(2/E_1 \\
&\quad - 1/E_2)/E_2 + 2g_s\zeta^2/E_1^2 + k\zeta^3(2/E_1 - 1/E_2) \\
&\quad (1/E_2 + 2/E_1)/(2E_2) - g_s\zeta^3[1/(2E_1^2E_2) \\
&\quad - 1/(2E_1E_2^2) + 1/(2E_2^3)]\,, \\
A_{//} &= P\left(-\kappa - 4H/7 + (g_{//} - g_s) + 3(g_{\perp} - g_s)/7\right)\,, \\
A_{\perp} &= P\left(-\kappa + 2H/7 + 11(g_{\perp} - g_s)/14\right)\,.
\end{aligned} \tag{1}$$

Here g_s (≈ 2.0023) is the spin-only value; k is the orbital reduction factor (which is equivalent to covalency factor N), characteristic of covalency of the systems; ζ is the spin–orbit coupling coefficient for the $3d^9$ ion in crystals, which can be expressed in terms of the corresponding free-ion value ζ_0 and covalency factor N as $\zeta \approx N\zeta_0$. P is the dipolar hyperfine structure parameter of the $3d^9$ ion; κ is the core polarization constant, characteristic of the isotropic Fermi contact interactions; H is the reduction factor denoting Cu^{2+} 3d–3s (and –4s) orbital admixture due to tetragonal distortion [16]. E_1 and E_2 are the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states, respectively. They are usually written as the linear combinations of cubic field parameter D_q and tetragonal field parameters D_s and D_t from the energy matrices for a $3d^9$ ion under tetragonal symmetry [17]:

$$E_1 \approx 10D_q\,,\quad E_2 \approx 10D_q - 3D_s + 5D_t\,. \tag{2}$$

In the previous studies of Knight shifts [18, 19], the orbital contributions from the susceptibility were normally insufficiently treated, and the high-(third- and fourth-)order perturbation terms were neglected as well. Importantly, the previous authors failed to construct explicit quantitative relationships between g factors and Knight shifts. From the related studies [9, 10, 18, 19], the relationships between Knight shifts K_i and g shifts ($g_i - g_s$, with $i = //$ and $\perp$) can be determined as

$$K_i = -2N_A\mu_B^2\langle r^{-3}\rangle_{3d}(g_i - g_s)/\zeta\,. \tag{3}$$

Here N_A is the Avogadro number, and μ_B is the Bohr magneton; $\langle r^{-3}\rangle_{3d}$ is the expectation value of inverse cube of the 3d radial wave function of Cu^{2+} in the studied systems. Utilizing the perturbation method similar to that in [9, 10], the high-order perturbation formulas of the Knight shifts are derived for a $3d^9$ ion in tetragonally elongated octahedra:

$$\begin{aligned}
K_{//} &= 2N_A\mu_B^2\langle r^{-3}\rangle_{3d}\Big\{8k/E_1 + k\zeta/E_2^2 + 4k\zeta/(E_1E_2) \\
&\quad - g_s\zeta\left[1/E_1^2 - 1/(2E_2^2)\right] + k\zeta^2(4/E_1 - 1/E_2) \\
&\quad /E_2^2 - 2k\zeta^2\left[2/(E_1^2E_2) - 1/(E_1E_2^2)\right] \\
&\quad + g_s\zeta^2\left[1/(E_1E_2^2) - 1/(2E_2^3)\right]\Big\}\,, \\
K_{\perp} &= 2N_A\mu_B^2\langle r^{-3}\rangle_{3d}\Big\{2k/E_2 - 4k\zeta/(E_1E_2) \\
&\quad + k\zeta(2/E_1 - 1/E_2)/E_2 + k\zeta^2(2/E_1 - 1/E_2) \\
&\quad (1/E_2 + 2/E_1)/(2E_2) + 2g_s\zeta/E_1^2 \\
&\quad - g_s\zeta^2\left[1/(2E_1^2E_2) - 1/(2E_1E_2^2) + 1/(2E_2^3)\right]\Big\}\,.
\end{aligned} \tag{4}$$

In the following, the above formulas are applied to the five-coordinated ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$) and six-coordinated ($Tl_2Ba_2CuO_y$)

Cu^{2+} sites in the high-T_c superconductors, where Cu^{2+} is situated into tetragonally elongated oxygen octahedra.

2.1. Five-Coordinated Systems

There are one parallel Cu^{2+}–O^{2-} bond $R_{||}$ along the c-axis and four perpendicular bonds $R_{\perp}$ along a- and b-axes for the five-coordinated Cu^{2+} sites in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$ [20, 21]. These data are listed in Table 1. Thus, the tetragonal field parameters can be determined from the superposition model [22]:

$$\begin{aligned} D_s &= 2\bar{A}_2(R)\left[(R/R_{||})^{t2} - 2(R/R_{\perp})^{t2}\right]/7\,, \\ D_t &= 16\bar{A}_4(R)\left[(R/R_{||})^{t4} - 2(R/R_{\perp})^{t4}\right]/21\,. \end{aligned} \tag{5}$$

Here $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters, with the reference distance taken as the average Cu^{2+}–O^{2-} bond length: $R = R = (R_{||} + 4R_{\perp})/5$. For octahedral $3d^n$ ions in compounds, the relationships $\bar{A}_4(R) \approx (3/4)D_q$ and $\bar{A}_2(R) \approx 9\bar{A}_4(R)$ [22–25] have been proved valid for many systems and are reasonably adopted here.

From the optical spectral data for Cu^{2+} in some oxides [14], the cubic field parameters D_q and the covalency factors N are obtained and listed for the studied systems in Table 1. The free-ion value of the spin–orbit coupling coefficient is $\zeta_0 \approx 829\,cm^{-1}$ [17] for Cu^{2+}. The dipolar hyperfine structure parameter P is about $388 \cdot 10^{-4}\,cm^{-1}$ [26] for $^{63}Cu^{2+}$. The core polarization constant is taken as $\kappa \approx 0.230$ and 0.245 for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$ here, which is close to that (≈ 0.26 [27]) for Cu^{2+} in tutton salts and can be regarded as reasonable. The reduction factors $H \approx 0.72$ and 0.60 are adopted here for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$, respectively, in view of the Cu^{2+} 3d–3s (–4s) orbital admixtures due to tetragonal elongation distortion, i. e., nearly 30% and 40% lower than the ideal value of unit based on omission of the low symmetrical distortion.

Substituting these values into (1) and (4), the g factors, hyperfine structure constants, and Knight shifts are calculated for the five-coordinated Cu^{2+} sites in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ and $TlSr_2CaCu_2O_{7-y}$ and shown in Table 2.

2.2. Six-Coordinated Systems

For the six-coordinated Cu^{2+} site in $Tl_2Ba_2CuO_y$, the structural data (i. e., the two parallel Cu^{2+}–O^{2-} bond lengths $R_{//}$ along c-axis and the four perpendicular bond lengths $R_{\perp}$ along a- and b-axes [28, 29]) are also given in Table 1. Similarly, the tetragonal field parameters are expressed from the superposition model [22]:

$$\begin{aligned} D_s &= 4\bar{A}_2(R)\left[(R/R_{\perp})^{t2} - (R/R_{||})^{t2}\right]/7\,, \\ D_t &= 16\bar{A}_4(R)\left[(R/R_{\perp})^{t4} - (R/R_{||})^{t4}\right]/21\,. \end{aligned} \tag{6}$$

Here the superposition model parameters have the same definitions as those in (4). In view of the longer reference distance for this six-coordinated system, the cubic field parameter D_q should be lower than those for the five-coordinated systems, while the covalency factor would be slightly higher than the five-coordinated ones. These spectral parameters are given in Table 1. Considering the larger tetragonal elongation distortion for this six-coordinated Cu^{2+} site, higher core polarization constant κ and lower reduction factor H can be expected, and these values are shown in Table 1. Substituting the related quantities into (1) and (4), the theoretical results are calculated for this six-coordinated system and collected in Table 2.

3. Discussion

Table 2 reveals that the theoretical hyperfine structure constants and Knight shifts based on the high-order perturbation formulas adopted in this work show good agreement with the experimental data for both the five- and six-coordinated Cu^{2+} sites

Table 1. Local parallel and perpendicular Cu^{2+}–O^{2-} bond lengths (in Å), cubic field parameter D_q (in cm^{-1}) and covalency factor N, core polarization constant κ and reduction factor H for the tetragonal Cu^{2+} sites in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$, $TlSr_2CaCu_2O_{7-y}$, and $Tl_2Ba_2CuO_y$.

	$R_{//}$	$R_{\perp}$	D_q	N	κ	H
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$	2.36	1.925	1540	0.64	0.230	0.72
$TlSr_2CaCu_2O_{7-y}$	2.392	1.9003	1540	0.64	0.245	0.60
$Tl_2Ba_2CuO_y$	2.72	1.93	1260	0.65	0.253	0.53

Table 2. g factors, hyperfine structure constants (in 10^{-4} cm^{-1}), and Knight shifts (in %) for the bismuth-based and thallium-based high-T_c superconductors.

		$g_{//}$	$g_{\perp}$	$A_{//}$	$A_{\perp}$	$K_{//}$	$K_{\perp}$
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$	Calc.	2.18	2.04	−174.23	−1.33	1.03	0.20
	Expt. [9]	–	–	−179.72(150)	−1.50(150)	1.02(2)	0.18(2)
$TlSr_2CaCu_2O_{7-y}$	Calc.	2.20	2.04	−124.13	−27.96	1.13	0.22
	Expt. [10]	–	–	−127.83	−27.82	1.13	0.20
$Tl_2Ba_2CuO_y$	Calc.	2.22	2.04	−124.73	−27.70	1.26	0.22
	Expt. [11]	–	–	−127.83	−27.82	1.26	0.25

in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$, $TlSr_2CaCu_2O_{7-y}$, and $Tl_2Ba_2CuO_y$. There are several points that may be discussed here.

i) The relationships between the Knight shifts and the g factors are established in this work, and the studies of these parameters are also correlated with the local structures of the tetragonal Cu^{2+} sites in these systems. Thus, the shortcoming of the previous work [16] based on various adjustable energy separations is overcome. Moreover, the high-order perturbation formulas in the present studies are superior to the simple second-order perturbation formulas in the previous treatments. The positive anisotropy $K_{//} - K_{\perp}$ is consistent with the positive anisotropy $g_{//} - g_{\perp}$, with the ratios $(K_{//} - K_{\perp})/(g_{//} - g_{\perp}) \approx 6\%$ for all the systems. This can be ascribed to the approximately linear relationships between g shifts and Knight shifts (see (3)). Physically, the above anisotropies are attributable to the local tetragonal elongation distortions of the Cu^{2+} sites, i. e., the one (or two) relatively longer parallel Cu–O bond(s) than the four perpendicular ones. Therefore, the ground $^2B_{1g}$ state and the anisotropic behaviours of the orbital angular momentum and spin interactions between electron and nuclear can be understood. To our knowledge, observed g factors were not reported for these systems (or other similar bismuth- and thallium-based high-T_c superconductors), and the theoretical g factors obtained in this work remain to be further checked with experimental measurements.

ii) The local structures of the Cu^{2+} sites in the bismuth- and thallium-based superconductors show significant tetragonal elongation distortions, characterized by the relative elongation ratio $(R_{//} - \bar{R})/\bar{R} \approx$ 17%, 20%, and 24% for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$, $TlSr_2CaCu_2O_{7-y}$, and $Tl_2Ba_2CuO_y$, respectively. Thus, the declining reduction factor H in Table 1 is consistent with the increase of the relative elongation ratio and can be regarded as reasonable. Similarly, the core polarization constant exhibits an increase from $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ to $Tl_2Ba_2CuO_y$, which may be ascribed to the increase of the isotropic Fermi contact interactions of the Cu^{2+} $^2B_{1g}$ ($3d_{x2-y2}$) ground state due to the increasing tetragonal elongation distortion.

iii) The errors of the present calculations can be analyzed as follows. Firstly, the approximations of the theoretical model and formulas would induce some errors. Secondly, the errors arise from the approximation of the relationship $\bar{A}_2(R) \approx 9\bar{A}_4(R)$ for the superposition model intrinsic parameters, which may affect the tetragonal field parameters and the final results. The errors for the resultant Knight shifts and A factors are estimated to be no more than 3% as the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ varies by 10%. Thirdly, the errors are brought forward for the hyperfine structure constants due to the core polarization constants κ and the reduction factors H. The values of κ adopted in this work are close to that ($\approx 0.2-0.26$ [27]) for Cu^{2+} in tutton salts. Meanwhile, H (≈ 0.72) for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10}$ is also comparable with that (≈ 0.78 [30]) for similar elongated Cu^{2+} center in TiO_2 with near Cu^{2+}–O^{2-} distance. Thus, the above quantities and the calculated hyperfine structure constants can be regarded as reasonable. Finally, the calculations of this work are carried out from the conventional crystal-field model in the absence of the ligand orbital and spin–orbit coupling contributions. Since the studied systems have much smaller ligand spin–orbit coupling coefficient ($\approx 151\,cm^{-1}$ [31]) than that ($\approx 829\,cm^{-1}$ [17]) of Cu^{2+}, the above contributions are actually very small and negligible.

4. Summay

The Knight shifts and hyperfine structure constants are theoretically studied for the tetragonal Cu^{2+} sites in the bismuth- and thallium-based high-T_c superconductors, using the unified high-order perturbation formulas of these parameters. The significant anisotropies

of the Knight shifts are ascribed to the local tetragonal elongation distortions of the five-(or six-)coordinated Cu^{2+} sites. The present treatments can be beneficial to establish a complete physical scheme to understand the EPR and NMR behaviours of Cu^{2+} (or other similar $3d^9$ ions) in the high-T_c superconductors.

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