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Theoretical studies of ^{63}Cu Knight shifts of the normal state of $YBa_2Cu_3O_7$

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The ^{63}Cu Knight shifts and g factors for the normal state of $YBa_2Cu_3O_7$ in tetragonal phase are theoretically studied in a uniform way from the high (fourth-) order perturbation formulas of these parameters for a $3d^9$ ion under tetragonally elongated octahedra. The calculations are quantitatively correlated with the local structure of the $Cu^{2+}(2)$ site in $YBa_2Cu_3O_7$. The theoretical results show good agreement with the observed values, and the improvements are achieved by adopting fewer adjustable parameters as compared to the previous works. It is found that the significant anisotropy of the Knight shifts is mainly attributed to the anisotropy of the g factors due to the orbital interactions.

Key words: *electron paramagnetic resonance, nuclear magnetic resonance, Knight Shift, ^{63}Cu, $YBa_2Cu_3O_7$*

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1. Introduction

$YBa_2Cu_3O_7$ has become an important topic in the microwave [1], magnetism [2, 3] as well as nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) [4, 5] researches. In particular, the Knight shifts as the results of NMR experiments can yield important information about the local environments and electronic distribution around the magnetic nuclei. For example, the Knight shifts $K_{\parallel}$ and $K_{\perp}$ as well as the anisotropic g factors $g_{\parallel}$ and $g_{\perp}$ were measured [6, 7] for the tetragonal $Cu^{2+}(2)$ site in $YBa_2Cu_3O_7$ of normal state at room temperature. However, the theoretical studies [6] on the Knight shifts seem unsatisfactory. Firstly, 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. Secondly, the analysis on the Knight shifts was not correlated to the local structure of the magnetic site, but was treated by introducing various adjustable parameters (e.g., the related energy separations). Finally, the g factors were not quantitatively treated in a uniform way. In order to study the Knight shifts and the g factors of $YBa_2Cu_3O_7$ to a better extent, the high (fourth-) order perturbation formulas of the Knight shifts and the g factors for a $3d^9$ ion located in tetragonally elongated octahedra are applied to the tetragonal $Cu^{2+}(2)$ site of $YBa_2Cu_3O_7$ in this work, and the local structure of this site is quantitatively involved in the calculations.

2. Calculation

The anisotropic Knight shifts and g factors may be ascribed to the tetragonal $Cu^{2+}(2)$ site in $YBa_2Cu_3O_7$, which is coordinated to five oxygen ions forming a tetragonally elongated octahedron (i.e., one of the apical ligands in the oxygen octahedron is moved to infinity) [8] As regards a $Cu^{2+}(3d^9)$ ion in tetragonally elongated octahedra, its original cubic ^2E_g ground state would be separated into two orbital singlets $^2B_{1g}$ (or $|x^2-y^2\rangle$) and $^2A_{1g}$ (or $|z^2\rangle$), and the former is

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the lowest level. Meanwhile, the original cubic ${}^2T_{2g}$ exited state may spilt into an orbital singlet ${}^2B_{2g}$ (or $|xy\rangle$) and a doublet ${}^2E_g$ (or $|yz\rangle$ and $|xz\rangle$) [9]. In order to make uniform investigations of the Knight shifts and the g factors as well as to overcome the shortcomings of the previous study [6] based on the simple second-order perturbation formulas, the high order perturbation g formulas [10] including the third- and fourth- order perturbation terms for a tetragonally elongated octahedral $3d^9$ cluster are adopted here. Applying the Macfarlane's perturbation loop method [11], the perturbation Hamiltonian for an orthorhombic $3d^9$ cluster under external magnetic field can be written as follows:

$$H' = H_{\mathrm{SO}}(\zeta) + H_{\mathrm{Ze}}(k) + H_{\mathrm{hf}}(P), \tag{1}$$

where H_{SO}, H_{Ze} and H_{hf} are, respectively, the spin-orbit coupling interactions, the Zeeman term and the hyperfine interactions, with the corresponding spin-orbit coupling coefficient ζ, the orbital reduction factor k and the dipolar hyperfine structure parameter P for a $3d^9$ ion in crystals. Utilizing the perturbation method [11], the perturbation formulas for an orthorhombically elongated $3d^9$ cluster can be derived as follows [10]:

$$\begin{aligned} g_{\parallel} &= g_{\mathrm{s}} + 8k\frac{\zeta}{E_1} + k\frac{\zeta^2}{E_2^2} + 4k\frac{\zeta^2}{E_1E_2} - g_{\mathrm{s}}\zeta^2\left(\frac{1}{E_1^2} - \frac{1}{2E_2^2}\right) \\ &+ k\zeta^3\left(\frac{4}{E_1} - \frac{1}{E_2}\right)\frac{1}{E_2^2} - 2k\zeta^3\left(\frac{2}{E_1^2E_2} - \frac{1}{E_1E_2^2}\right) + g_{\mathrm{s}}\zeta^3\left(\frac{1}{E_1E_2^2} - \frac{1}{2E_2^3}\right), \\ g_{\perp} &= g_{\mathrm{s}} + 2k\frac{\zeta}{E_2} - 4k\frac{\zeta^2}{E_1E_2} + k\zeta^2\left(\frac{2}{E_1} - \frac{1}{E_2}\right)\frac{1}{E_2} + 2g_{\mathrm{s}}\frac{\zeta^2}{E_1^2} \\ &+ k\zeta^3\left(\frac{2}{E_1} - \frac{1}{E_2}\right)\left(\frac{1}{E_2} + \frac{2}{E_1}\right)\frac{1}{2E_2} - g_{\mathrm{s}}\zeta^3\left(\frac{1}{2E_1^2E_2} - \frac{1}{2E_1E_2^2} + \frac{1}{2E_2^3}\right), \end{aligned} \tag{2}$$

here $g_{\mathrm{s}}(\approx 2.0023)$ is the pure spin value. k is the orbital reduction factor. 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 as $\zeta \approx k\zeta_0$. It is noted that when the third- and fourth -order perturbation terms are neglected, i.e., only the first and second terms in the right sides of equation (1) are reserved, the above formulas may be reduced to those of the previous work [6]. E_1 and E_2 are the energy separations between the excited ${}^2B_{2g}$ and ${}^2E_g$ and the ground ${}^2B_{1g}$ states [12]:

$$\begin{aligned} E_1 &= 10D_{\mathrm{q}}\,, \\ E_2 &= 10D_{\mathrm{q}} - 3D_{\mathrm{s}} + 5D_{\mathrm{t}}\,. \end{aligned} \tag{3}$$

Here D_{q} is the cubic field parameter, and D_{s} and D_{t} are the tetragonal field parameters. The local structure of the five-fold coordinated $Cu^{2+}(2)$ site in $YBa_2Cu_3O_7$ can be described as the parallel $Cu^{2+} - O^{2-}$ distance $R_{\parallel}$ (≈ 2.426 Å) along c axis and the four perpendicular distances $R_{\perp}(\approx 1.939$ Å) along a and b axes [8]. Thus, the tetragonal field parameters can be determined from the superposition model [12]:

$$D_{\mathrm{s}} = 2\overline{A}_2R_0\frac{1}{7}\left[\left(\frac{R_0}{R_{\parallel}}\right)^{t2} - 2\left(\frac{R_0}{R_{\perp}}\right)^{t2}\right], \qquad D_{\mathrm{t}} = 16\overline{A}_4R_0\frac{1}{21}\left[\left(\frac{R_0}{R_{\parallel}}\right)^{t4} - 2\left(\frac{R_0}{R_{\perp}}\right)^{t4}\right]. \tag{4}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [12]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters, with the reference bond length R_0 taken as the average $Cu^{2+} - O^{2-}$ distance, i.e., $R_0 = \overline{R} = (R_{\parallel} + 4R_{\perp})/5$. For octahedral $3d^n$ clusters, the relationships $\overline{A}_4(R_0) \approx (3/4)D_{\mathrm{q}}$ and $\overline{A}_2(R_0) \approx 10.8\overline{A}_4(R_0)$ [12] are proved valid for many systems and reasonably applied here.

According to the optical spectra for Cu^{2+} in oxides [13], the cubic field parameter $D_{\mathrm{q}} \approx 1260$ cm^{-1} and the orbital reduction factor $k \approx 0.76$ can be obtained for the studied system by fitting the observed d-d transitions. The spin-orbit coupling coefficient is determined using the free-ion value $\zeta_0(\approx 829$ cm^{-1} [14]) for Cu^{2+}. Substituting these values into equation (1), the theoretical g factors are calculated and shown in table 1.

Now we turn to the investigations of the Knight shifts. From the relationships between the g factors and the Knight shifts and the perturbation procedure similar to that in Ref. [6], the high order perturbation formulas (i.e., those containing the third- and fourth- order perturbation contributions) of the Knight shifts for the tetragonal Cu^{2+}(2) site in $YBa_2Cu_3O_7$ can be expressed as:

$$\begin{aligned}
K_{\parallel} &= 2\chi\Big[\frac{8k}{E_1}+\frac{k\zeta}{E_2^2}+4k\frac{\zeta}{E_1E_2}-g_{\mathrm{s}}\zeta\left(\frac{1}{E_1^2}-\frac{1}{2E_2^2}\right)+k\zeta^2\left(\frac{4}{E_1}-\frac{1}{E_2}\right)\frac{1}{E_2^2}\\
&- 2k\zeta^2\left(\frac{2}{E_1^2E_2}-\frac{1}{E_1E_2^2}\right)+g_{\mathrm{s}}\zeta^2\left(\frac{1}{E_1E_2^2}-\frac{1}{2E_2^3}\right)\Big],\\
K_{\perp} &= 2\chi\Big[\frac{2k}{E_2}-4k\frac{\zeta}{E_1E_2}+k\zeta\left(\frac{2}{E_1}-\frac{1}{E_2}\right)\frac{1}{E_2}+2g_{\mathrm{s}}\frac{\zeta}{E_1^2}\\
&+ k\zeta^2\left(\frac{2}{E_1}-\frac{1}{E_2}\right)\left(\frac{1}{E_2}+\frac{2}{E_1}\right)\frac{1}{2E_2}-g_{\mathrm{s}}\zeta^2\left(\frac{1}{2E_1^2E_2}-\frac{1}{2E_1E_2^2}+\frac{1}{2E_2^3}\right)\Big].
\end{aligned} \tag{5}$$

In the above expressions, $\chi = \langle r^{-3}\rangle_{3d} N_{\mathrm{A}}\mu_{\mathrm{B}}^2$. Here $\langle r^{-3}\rangle_{3d}(\approx 4.68$ a.u. [7]) is the expectation value of inverse cube of the $3d$ radial wave function of Cu^{2+} in the system studied. N_{A} is the Avogadro's number. μ_{B} is the Bohr magneton. Similarly, since the third- and fourth-order perturbation terms are neglected, i.e., only the first terms in the right sides of equation (5) are reserved, the above formulas are reduced to those of the previous work [6]. Substituting these values into equation (5), the Knight shifts are calculated and collected in table 1. For comparisons, the theoretical results of the previous work [6] based on the simple second-order g factors and various adjustable energy separations are listed in table 1.

Table 1. The Knight shifts and the g factors for the Cu^{2+}(2) site in $YBa_2Cu_3O_7$ of normal state.

	$g_{\parallel}$	$g_{\perp}$	$K_{\parallel}$	$K_{\perp}$
Cal.[a]	2.345	2.075	1.282	0.286
Cal.[b]	2.308	2.057	1.323	0.242
Expt.[6, 7]	2.37(10)	2.07(10)	1.320(5)	0.26(3)

a Calculations based on the simple second-order g factors and various adjustable energy separations in the previous work [6].

b Calculations based on the uniform high order perturbation formulas and the local structure of the tetragonal Cu^{2+}(2) site in $YBa_2Cu_3O_7$ in this work.

3. Discussion

From table 1, one can find that the theoretical Knight shifts and g factors of this work show reasonable agreement with the experimental data, and these parameters are also suitably explained in a uniform way.

In the present calculations, the relationships between the Knight shifts (and the g factors) and the local structure of the tetragonal Cu^{2+} site in $YBa_2Cu_3O_7$ are quantitatively established from the superposition model, and the shortcoming of the previous work [6] based on various adjustable energy separations is therefore overcome. Meanwhile, the high order perturbation formulas containing the third- and fourth-order perturbation contributions in this work are also superior to the simple second-order ones in the previous study. It is noted that a crude estimation of the contributions of the still higher (fifth) order perturbation terms yields $\sim \zeta^4/(E_1^3E_2)$, in the order of 10^{-6} and being safely negligible. In addition, the previous results (Cal.[a]) comparable with the observed values in view of the experimental uncertainties may be illustrated by the fact that the calculation errors happened to be canceled by the various adjustable energy separations [6].

The positive anisotropy $K_{\parallel} - K_{\perp}$ is consistent with the positive anisotropy $g_{\parallel} - g_{\perp}$. This can be ascribed to the approximate linear relationships between the g factors and the Knight shifts. Further, the above anisotropies may be attributable to the local tetragonal elongation of the $Cu^{2+}(2)$ site, i.e., the relatively longer parallel Cu-O bond as compared with the four perpendicular ones. Thus, the ground $^2B_{1g}$ state and hence the anisotropic orbital angular momentum and spin interaction between electron and nuclear can be understood. The calculated anisotropy $K_{\parallel} - K_{\perp}(\approx 1.081$ in Cal.$^b)$ of this work is somewhat larger than that (≈ 0.996 in Cal.^{a}) of the previous work [6]. This can be illustrated by the fact that the present anisotropy $g_{\parallel} - g_{\perp}(\approx 0.251$ in Cal.$^b)$ is smaller than the previous result (≈ 0.27 in Cal.^{a}) [6] and hence slightly worse as compared with the observed value (≈ 0.30 (20) [6, 7]). The above discrepancies are ascribed to the approximations of the theoretical model and formulas as well as to the calculation errors in this work. In view of the experimental uncertainties of the observed $K_{\parallel} - K_{\perp}$ and $g_{\parallel} - g_{\perp}$, the present calculations can still be regarded as suitable.

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Теоретичне вивчення зсувів Найта ^{63}Cu в основному стані $YBa_2Cu_3O_7$

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Зсуви Найта ^{63}Cu і g фактори в основному стані $YBa_2Cu_3O_7$ в тетрагональній фазі вивчаються теоретично в єдиному підході з формул теорії збурень високого (четвертого) порядку цих параметрів для $3d^9$ іона в тетрагонально видовженому октаедрі. Розрахунки кількісно корелюють з локальною структурою $Cu^{2+}(2)$ вузла в $YBa_2Cu_3O_7$. Теоретичні результати демонструють добре узгодження зі спостережуваними значеннями, і покращення досягається шляхом використання меншої кількості підгоночних параметрів ніж у попередніх роботах. Знайдено, що значна анізотропія зсувів Найта є в основному атрибутом анізотропії g факторів завдяки взаємодії.

Ключові слова: *електронний парамагнетичний резонанс, ядерний магнітний резонанс, зсув Найта, ^{63}Cu, $YBa_2Cu_3O_7$*