Low Temperature Physics/Fizika Nizkikh Temperatur, 2014, v. 40, No. 8, pp. 869–872

Theoretical studies of $^{63}Cu^{2+}$ orbital Knight shifts of $HgBa_2Ca_2Cu_3O_{8+\delta}$

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Received February 17, 2014, revised March 13, 2014, published online June 23, 2014

The orbital Knight shifts and g factors for the tetragonal $^{63}Cu^{2+}$ site in $HgBa_2Ca_2Cu_3O_{8+\delta}$ at 133 and 115 K are theoretically investigated based on the high-order perturbation formulae of these quantities for a $3d^9$ ion situated into tetragonally elongated octahedra. The theoretical results reveal good agreement with the observed values. The significant anisotropies of the Knight shifts are illustrated as the considerable local tetragonal elongation distortions of the five-coordinated Cu^{2+} sites. The results at different temperatures are also discussed in view of the local structure of the Cu^{2+} sites.

PACS: 74.25.N– Response to electromagnetic fields;
75.10.Dg Crystal-field theory and spin Hamiltonians;
76.30.Fc Iron group (3*d*) ions and impurities (Ti–Cu).

Keywords: g factors, Knight shifts, $HgBa_2Ca_2Cu_3O_{8+\delta}$.

1. Introduction

The Hg-based multilayered cuprate superconductors have become an important subject due to the unique Josephson and magnetically couplings [1–3], magnetic [4] and resistivity and magnetization properties [5,6]. Usually, the Knight shifts of nuclear magnetic resonance (NMR) can demonstrate substantial information about the local structure and electronic properties of the copper-oxygen planes, which are helpful to the understandings of superconductivity and other physical properties of this material. For instance, the Knight shifts were measured for the tetragonal $^{63}Cu^{2+}$ sites in $HgBa_2Ca_2Cu_3O_{8+\delta}$ with the transition temperatures (T_c) (≈ 133 [7] and 115 [8] K, respectively), and the orbital Knight shifts $K_{||}$ and $K_{\perp}$ were obtained by extrapolation to zero temperature. However, these experimental results have not been theoretically explained until now. On the other hand, the simple second-order perturbation formulae were normally utilized in the previous studies [9,10] on the Knight shifts of Cu^{2+} sites in some high-T_c superconductors, while the higher (third- and fourth-) order perturbation contributions were not taken into account. Moreover, the previous calculations of Knight shifts did not connect with local structures of the magnetic sites but induced various adjusted energy separations.

In order to overcome the above shortcomings in the previous researches and to study the Knight shifts of $HgBa_2Ca_2Cu_3O_{8+\delta}$ to a better extent, the high-order perturbation formulae of Knight shifts for a tetragonally elongated $3d^9$ center are applied in this work. The theoretical calculations are carried out by correlating with the local structure of the tetragonal Cu^{2+} site using the superposition model.

2. Theory and calculations

The Knight shifts measured at low temperatures [7,8] can be ascribed to the tetragonal $^{63}Cu^{2+}$ site in $HgBa_2Ca_2Cu_3O_{8+\delta}$. This site is coordinated to five oxygen ions forming a tetragonally elongated octahedron (i.e., one of the apical ligands of the octahedron is moved to infinity) [11]. For a $Cu^{2+}(3d^9)$ ion in a tetragonally elongated octahedron, the original cubic ^2E_g ground state may split into two orbital singles $^2B_{1g}$ (or $|\varepsilon>$) and $^2A_{1g}$ (or $|\theta>$). The former is the lowest level, corresponding to the observed Knight shifts ($K_{||} > K_{\perp}$ [7,8]). Meanwhile, the original cubic $^2T_{2g}$ exited state can be separated into an orbital singlet $^2B_{2g}$ (or $|\zeta>$) and a doublet ^2E_g (or $|\xi>$ and $|\eta>$) [12,13]. As for the previous studies on Knight shifts [9,10], the orbital contributions from the susceptibility were normally insufficiently involved, and the third- and fourth-order perturbation contributions were not considered. Furthermore, the previous treatments failed to establish quantitative relationships between g factors and Knight shifts.

To remove the shortcoming of the previous simple second-order perturbation calculations, the high (third- and

fourth-) order perturbation formulae [14] are adopted here for a tetragonally elongated $3d^9$ center. Despite absence of experimental g factors, the unified studies of Knight shifts and g factors are performed in this work, since g factors are also closely relevant to the local structure of the system. In view of the related investigations [7–10] on Knight shifts and g factors, one can obtain the proportionality relationships between Knight shifts K_i and g shifts ($g_i - g_s$, with $i = \parallel$ and $\perp$). Thus, the perturbation formulae of these quantities can be expressed as follows:

$$g_{\parallel} = g_s + \frac{8k\zeta}{E_1} + \frac{k\zeta^2}{E_2^2} + \frac{4k\zeta^2}{E_1E_2} - g_s\zeta^2\left(\frac{1}{E_1^2} - \frac{1}{2E_2^2}\right) + \frac{k\zeta^3}{E_2^2}\left(\frac{4}{E_1} - \frac{1}{E_2}\right) - 2k\zeta^3\left(\frac{2}{E_1^2E_2} - \frac{1}{E_1E_2^2}\right) + g_s\zeta^3\left(\frac{1}{E_1E_2^2} - \frac{1}{2E_2^3}\right),$$

$$g_{\perp} = g_s + \frac{2k\zeta}{E_2} - \frac{4k\zeta^2}{E_1E_2} + \frac{k\zeta^2}{E_2}\left(\frac{2}{E_1} - \frac{1}{E_2}\right) + \frac{2g_s\zeta^2}{E_2^1} + \frac{k\zeta^3}{2E_2}\left(\frac{2}{E_1} - \frac{1}{E_2}\right)\left(\frac{1}{E_2} - \frac{2}{E_1}\right) - g_s\zeta^3\left(\frac{1}{2E_1^2E_2} - \frac{1}{2E_1E_2^2} + \frac{1}{2E_2^3}\right),$$

$$K_{\parallel} = 2N_A\mu_B^2 < r^{-3} >_{3d}\left\{\frac{8k}{E_1} + \frac{k\zeta}{E_2^2} + \frac{4k\zeta}{E_1E_2} - g_s\zeta\left(\frac{1}{E_1^2} - \frac{1}{2E_2^2}\right) + \frac{k\zeta^2}{E_2^2}\left(\frac{4}{E_1} - \frac{1}{E_2}\right) - \right.$$

$$\left. - 2k\zeta^2\left(\frac{2}{E_1^2E_2} - \frac{1}{E_1E_2^2}\right) + g_s\zeta^2\left(\frac{1}{E_1E_2^2} - \frac{1}{2E_2^3}\right)\right\},$$

$$K_{\perp} = 2N_A\mu_B^2 < r^{-3} >_{3d}\left\{\frac{2k}{E_2} - \frac{4k\zeta}{E_1E_2} + \frac{k\zeta}{E_2}\left(\frac{2}{E_1} - \frac{1}{E_2}\right) + \frac{k\zeta^2}{2E_2}\left(\frac{2}{E_1} - \frac{1}{E_2}\right)\left(\frac{1}{E_2} + \frac{2}{E_1}\right) + \right.$$

$$\left. + \frac{2g_s\zeta}{E_1^2} - g_s\zeta^2\left[\frac{1}{2E_1^2E_2} - \frac{1}{2E_1E_2^2} + \frac{1}{2E_2^3}\right]\right\}. \qquad (1)$$

In the above expressions, g_s (≈ 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 is usually expressed in terms of the corresponding free-ion value ζ_0 as $\zeta \approx k\zeta_0$; N_A is the Avogadro's number, and μ_B is the Bohr magneton. $< r^{-3} >_{3d}$ is the expectation value of inverse cube of the Cu^{2+} $3d$ radial wave function.

The denominators E_1 and E_2 in the above expressions are the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states, respectively. They can be written in terms of the cubic field parameter D_q and the tetragonal field parameters D_s and D_t using the energy matrices for a tetragonal $3d^9$ center [15]:

$$E_1 \approx 10D_q, \; E_2 \approx 10D_q - 3D_s + 5D_t, \qquad (2)$$

The structure of the Cu^{2+} site in $HgBa_2Ca_2Cu_3O_{8+\delta}$ is characterized by one bond length $R_{\parallel}$ along horizontal **c** axis and four bond lengths $R_{\perp}$ along vertical **a** and **b** axes [16]: $R_{\parallel}$ ≈ 2.741 and 2.786 Å and $R_{\perp}$ ≈ 1.9239 and 1.9273 Å for the Hg-1223 systems with T_c (≈ 135 and 107 K, close to 133 and 115 K, respectively, for those under study). Then the tetragonal field parameters are deduced from the superposition model using the local geometry of the system [17]:

$$D_s = 2\bar{A}_2\left[\left(\frac{R}{R_{\parallel}}\right)^{t2} - 2\left(\frac{R}{R_{\perp}}\right)^{t2}\right]/7,$$

$$D_t = 16\bar{A}_4\left[\left(\frac{R}{R_{\parallel}}\right)^{t4} - 2\left(\frac{R}{R_{\perp}}\right)^{t4}\right]/21. \qquad (3)$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [17], $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters, with the reference distance of the average Cu^{2+}–O^{2-} bond length: $R = \bar{R} = (R_{\parallel} + 4R_{\perp})/5$. For octahedral $3d^n$ ions in compounds, the relationships $\bar{A}_4 \approx (3/4)D_q$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ [17–20] have been proved suitable for many systems and are reasonably adopted here.

From the optical spectral data for Cu^{2+} in some oxides [13], the cubic field parameter D_q (≈ 1300 cm^{-1}) and the orbital reduction factor k (≈ 0.63) can be obtained for the Cu^{2+} site in $HgBa_2Ca_2Cu_3O_{8+\delta}$. The free-ion value of the spin-orbit coupling coefficient is $\zeta_0 \approx 829$ cm^{-1} [15] for Cu^{2+}. Substituting these values into Eq. (1), the g factors and Knight shifts are calculated and given in Table 1.

Table 1. The g factors and Knight shifts (in %) for the tetragonal $^{63}Cu^{2+}$ sites in $HgBa_2Ca_2Cu_3O_{8+\delta}$

T, K	Ref.	$g_{\|}$	$g_{\perp}$	$K_{\|}$	$K_{\perp}$
≤ 133	Calc.	2.21	2.04	1.22	0.24
	Exp. [7]	–	–	1.22(2)	0.22(2)
≤ 115	Calc.	2.20	2.04	1.14	0.22
	Exp. [8]	–	–	1.16	0.19

3. Discussions

From Table 1, one can find that the g factors and Knight shifts based on the high-order perturbation formulae in this work exhibit reasonable agreement with the experimental data, and these observed values are also suitably explained in a uniform way.

1. In the present calculations, the theoretical relationships between Knight shifts (and g factors) and the local structure of the tetragonal $^{63}Cu^{2+}$ site in $HgBa_2Ca_2Cu_3O_{8+\delta}$ are established from the superposition model. So the imperfection of the previous treatments [9,10] based on the simple second-order perturbation formulae using various adjustable energy separations is thus overcome. Notably, the positive anisotropy $(K_{\|} - K_{\perp} > 0)$ of Knight shifts is consistent with that $(g_{\|} - g_{\perp} > 0)$ of g factors, with the ratio $(K_{\|} - K_{\perp})/(g_{\|} - g_{\perp}) \approx 6\%$ due to the linear relationships between g-shifts and Knight shifts. Moreover, the anisotropies of g factors and Knight shifts can be illustrated as the local tetragonal elongation of the $^{63}Cu^{2+}$ site, characterized by one longer parallel Cu–O bond than the four perpendicular ones. In fact, the local tetragonal elongation of this site can be described as the relative elongation ratios $(R_{\|} - \bar{R})/\bar{R} \approx 31$ and 33% for the studies systems with T_c of 133 and 115 K, respectively. The highest T_c of the optimally doped Hg-1223 systems among multilayer cuprate superconductors is attributable to the intense hybridization of the $Cu(3d_{x^2-y^2})$–$O(2p_{\sigma})$–$Cu(4s)$ electron clouds arising from the long copper-apical oxygen bond lengths $R_{\|}$ and flat CuO_2 planes and remarkable antiferromagnetic spin fluctuations in the pairing mechanism [7,8]. In addition, the theoretical g factors in this work remain to be verified with further experimental measurements.

2. The g factors and orbital Knight shifts investigated here correspond to the temperatures slightly lower than T_c (≈ 133 and 115 K). The quantities used in the calculations (e.g., the energy denominators E_1 and E_2, the spin-orbit coupling coefficient ζ, the cubic field parameters D_q and the orbital reduction factors k (≈ N)) reflect the local ligand fields around copper sites and the Cu^{2+}–O^{2-} orbital admixtures (covalency) of the $[CuO_5]^{8-}$ clusters formed by the localized $Cu^{2+}(3d^9)$ and the nearest neighbour oxygen ligands with specific local structural data (e.g., the distinct bond lengths) at the relevant temperatures. So, the above parameters actually contain implicitly the respective contributions at the corresponding temperatures, and thus temperature T does not appear explicitly in the detailed calculations.

3. The errors of the present calculations may be discussed as follows. First, the approximations of the theoretical model and formulae would bring forward some errors. Second, the errors also arise from the approximation of the relationship $\bar{A}_2 \approx 10.8\bar{A}_4$, which may affect the tetragonal field parameters and the final results. The errors for the resultant Knight shifts are estimated to be not more than 3% when the ratio $\bar{A}_2/\bar{A}_4$ varies by 10%. Third, the calculations of this work are performed on the basis of the conventional crystal-field model where the ligand orbital and spin-orbit coupling contributions are ignored. In view that the studied Cu^{2+}–O^{2-} combination has much smaller ligand spin-orbit coupling coefficient (≈ 151 cm^{-1} [21]) as compared to that (≈ 829 cm^{-1} [15]) of Cu^{2+}, the above ligand contributions can be regarded as very small and negligible.

4. Conclusion

The g factors and orbital Knight shifts are theoretically calculated for the tetragonal Cu^{2+} sites in the Hg-1223 systems for temperatures slightly lower than T_c (≈ 133 and 115 K). The significant anisotropies of the Knight shifts are illustrated as the considerable tetragonal elongations of the five-coordinated Cu^{2+} sites. The higher T_c of the optimally doped Hg-1223 than other multilayer cuprate superconductors may be attributed to the stronger hybridization of the $Cu(3d_{x^2-y^2})$–$O(2p_{\sigma})$–$Cu(4s)$ electron clouds arising from the longer copper–apical oxygen bond lengths and flatter CuO_2 planes and more significant antiferromagnetic spin fluctuations in the pairing mechanism of cuprates. It appears that the present ^{63}Cu Knight shift analysis can be helpful to the further understandings of the electronic states and superconductivity of Hg-1223 systems.

Acknowledgment

This work was financially supported by the Sichuan Province Academic and Technical Leaders Support Fund and the Fundamental Research Funds for the Central Universities under granted No. ZYGX2012YB018.

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