

Investigations on the Anisotropic g Factors of the Ni^{3+} Site in $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$

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The anisotropic g factors g_{\parallel} and g_{\perp} of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ are theoretically investigated using the perturbation formulae of the g factors for a low spin ($S = 1/2$) $3d^7$ ion in tetragonally elongated octahedra. The studied $\text{Ni}^{3+}(3d^7)$ center arises from the original Ni^{2+} capturing one hole by Li^+ doping. The positive anisotropy $\Delta g (= g_{\perp} - g_{\parallel})$ can be ascribed to the lowest ${}^2A_{1g}$ state due to the obvious (about 0.14 Å) tetragonal elongation of the oxygen octahedron around the Ni^{3+} site via the Jahn–Teller effect, and the effective magnetic moment is also interpreted in a uniform way. The calculated results show good agreement with the experimental data, and the imperfection of the previous studies based on various adjusted tetragonal energy splittings without correlating to the local structure of the magnetic center is thus overcome in this work.

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1. Introduction

Belonging to La_2NiF_4 type-structure closely relevant to the high- T_c superconductors, La_2NiO_4 also exhibits interesting electrochemical and conductive [1–4], magnetic [5], and catalytic [6, 7] properties. Especially, Li doping can yield $\text{La}_2\text{Ni}_{1-x}\text{Li}_x\text{O}_4$ (i.e., Ni^{3+} arising from the original Ni^{2+} by capturing one hole during Li doping) compound which stabilizes the $\text{Ni}^{3+}(3d^7){}^2A_{1g}$ lowest configuration via the Jahn–Teller distortion of the oxygen octahedra [8]. This system shows unique electronic and structure properties due to the paramagnetic Ni^{3+} , which can be conveniently studied with the aid of electron paramagnetic resonance (EPR) spectra. For instance, EPR measurements were performed for $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$, and the anisotropic g factors were also obtained [8]. Although the above EPR experimental results were tentatively analyzed on the basis of the simple second-order g formulae for a $3d^7(\text{Ni}^{3+})$ ion in tetragonally elongated octahedra [8], the local structure around Ni^{3+} was not quantitatively involved in the calculations. Instead, various adjustable parameters (e.g., the related energy separations due to the tetragonal elongation of the Jahn–Teller nature) were induced to describe the low symmetrical distortion, and information about the local structure of Ni^{3+} has not been acquired yet.

Normally, information of local structure for Ni^{3+} in $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ would be helpful to understand the superconductive properties of the related materials, and the microscopic mechanisms of the EPR behaviours can also enhance the field of magnetic resonance spectroscopy. Therefore, further investigations on the g factors and the local structure for this system are of specific significance.

In this work, the g factors and the local structure of Ni^{3+} in $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ are theoretically studied from the high order perturbation formulae of the g factors for a $3d^7$ ion of low spin ($S = 1/2$) in a tetragonally elongated octahedron. In the calculations, the influence of the local tetragonal elongation due to the Jahn–Teller effect is quantitatively described in terms of the tetragonal field parameters D_s and D_t from the superposition model.

2. Calculations

In $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$, the Ni^{3+} site is coordinated to six oxygen ions, forming an almost regular octahedron with the average $\text{Ni}^{3+}-\text{O}^{2-}$ distance of about 2.0 Å [8]. $\text{Ni}^{3+}(3d^7)$ ions in strong crystal-fields (e.g., oxygen octahedra) have the orbital doublet ${}^2E_g(t_{2g}^6 e_g)$ with low spin ($S = 1/2$) as the ground state, which may be described as an unpaired electron in e_g state [9, 10]. The Jahn–Teller ion Ni^{3+} may undergo the Jahn–Teller effect via stretching the parallel $\text{Ni}^{3+}-\text{O}^{2-}$ bonds along the C_4 axis, characterized by the elongation ΔZ . Then the local symmetry becomes tetragonal (D_{4h}) around Ni^{3+} during the process of Li doping. Similar tetragonal elongation due to the Jahn–Teller effect is also found for Ni^{3+} on the Al^{3+} site in LaSrAlO_4 [11].

When the ligand octahedron is tetragonally elongated, the original ground 2E_g state would be split into two orbital singlets $\varepsilon (|x^2 - y^2\rangle)$ and $\theta (|z^2\rangle)$, with the latter lying lowest [10]. In view of the covalency and ligand contributions, the high order perturbation formulae of the g factors for a $3d^7$ ion in an elongated octahedron can be established on the basis of the cluster approach by considering the contributions from the ligand orbital and spin–orbit coupling interactions and the tetragonal distortion. Thus, we have [12]:

$$g_{\parallel} = g_s + 2k'\zeta'^2/E_{1\parallel}^2,$$

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$$g_{\perp} = g_s + 2k'\zeta'^2/E_{1\perp}^2 + 3k\zeta/E_{\perp}, \quad (1)$$

where

$$1/E_{\perp} = 1/E_{3\perp} + 1/E_{4\perp} + 0.38(1/E_{3\perp} - 1/E_{4\perp}). \quad (2)$$

Here g_s ($=2.0023$) is the spin-only value. The energy denominators $E_{i\alpha}$ ($i = 1, 3, 4$ denote the separations between the excited ${}^4T_{1b}(t_2^3e^2)$, ${}^2T_{2a}(t_2^5e^2)$, ${}^2T_{2b}(t_2^5e^2)$ and the ground ${}^2E_g(t_2^6e)$ states [9, 13], with $\alpha = \parallel$ and \perp standing for the two components of the corresponding tetragonal energy splittings) can be determined from the energy matrices for a $3d^7$ ion in tetragonal symmetry [12]:

$$\begin{aligned} E_{1\parallel} &= 10D_q - 4B - 4C, \\ E_{1\perp} &= 10D_q - 4B - 4C - 3D_s + 5D_t, \\ E_{3\perp} &= 10D_q + 6B - C - 3D_s + 5D_t, \\ E_{4\perp} &= 10D_q + 14B + C - 3D_s + 5D_t, \end{aligned} \quad (3)$$

where B and C are the Racah parameters for the $3d^7$ ion in crystals. D_q is the cubic field parameter, and D_s and D_t are the tetragonal ones. From the cluster approach containing both the ligand p - and s -orbital contributions, the normalization factors N_{γ} and the orbital admixture coefficients λ_{γ} (here $\gamma = e$ and t stand for the irreducible representations E_g and T_{2g} of the O_h group) can be determined from the approximation relationships [13]:

$$\begin{aligned} N^2 &= N_t^2(1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}), \\ N^2 &= N_e^2(1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}) \end{aligned} \quad (4)$$

and the normalization conditions [13]:

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (5)$$

Here $S_{d\gamma}$ (and S_{ds}) are the group overlap integrals. N is the average covalency factor characterizing the reduction of the Racah parameters of the central ion in a crystal. In general, orbital admixture and overlap between the central ion and ligands have consistent dependence on bond length, and one can approximately adopt the proportional relationship $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ between the orbital admixture coefficients and the related group overlap integrals. The spin-orbit coupling coefficients ζ (and ζ') and the orbital reduction factors k (and k'), which denote the diagonal (and off-diagonal) matrix elements of the spin-orbit coupling and the orbital angular momentum operators for the T_{2g} and E_g states can be expressed using the cluster approach [13]:

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \\ \zeta' &= (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2]. \end{aligned} \quad (6)$$

Here ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $3d^7$ and ligand ions, respectively. A denotes the integral $R\langle ns|\partial/\partial y|np_y\rangle$, with the reference or average $Ni^{3+}-O^{2-}$ distance R .

The tetragonal field parameters in Eq. (3) can be determined from the superposition model [14] and the geometrical relationship (i.e., the tetragonal elongation due to the Jahn-Teller effect) of the $[NiO_6]^{9-}$ cluster

$$\begin{aligned} D_s &= (4/7)\bar{A}_2(R)[(R/R_{\perp})^{t_2} - (R/R_{\parallel})^{t_2}], \\ D_t &= (16/21)\bar{A}_4(R)[(R/R_{\perp})^{t_4} - (R/R_{\parallel})^{t_4}]. \end{aligned} \quad (7)$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [14]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters, with the reference or average distance R . For octahedral $3d^n$ clusters, the relationships $\bar{A}_4(R) \approx (3/4)D_q$ and $\bar{A}_2(R) \approx 12\bar{A}_4(R)$ [15] are proved valid in many crystals and reasonably adopted here. R_{\parallel} and R_{\perp} are, respectively, the bond lengths parallel and perpendicular to the C_4 axis of the system due to the Jahn-Teller effect. So, the above bond lengths are expressed in terms of the tetragonal elongation ΔZ as $R_{\parallel} \approx R + 2\Delta Z$ and $R_{\perp} \approx R - \Delta Z$. Thus, the g factors, especially the anisotropy Δg ($= g_{\perp} - g_{\parallel}$) is connected with the tetragonal field parameters and hence with the local structure (i.e., the tetragonal elongation ΔZ of the studied system).

The spectral parameters $D_q \approx 1800 \text{ cm}^{-1}$ and $N \approx 0.74$ of the similar $[NiO_6]^{9-}$ cluster in $SrTiO_3:Ni^{3+}$ [16] can be suitably adopted for the studied $La_2Ni_{0.5}Li_{0.5}O_4$ here. From the distance R and the Slater-type self-consistent field (SCF) functions [17], the group overlap integrals $S_{dpt} \approx 0.0326$, $S_{dpe} \approx 0.0934$, $S_{ds} \approx 0.0737$ and the integral $A \approx 1.3286$ are calculated. Then the molecular orbital coefficients $N_t \approx 0.752$, $N_e \approx 0.797$, $\lambda_t \approx 0.608$, $\lambda_e \approx 0.500$ and $\lambda_s \approx 0.395$ are obtained from Eqs. (4) and (5). Utilizing the free-ion values $\zeta_d^0 \approx 816 \text{ cm}^{-1}$ [18] for Ni^{3+} and $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ [19] for O^{2-} , the spin-orbit coupling coefficients and the orbital reduction factors are determined from Eq. (6), i.e., $\zeta \approx 635 \text{ cm}^{-1}$, $\zeta' \approx 614 \text{ cm}^{-1}$, $k \approx 0.891$ and $k' \approx 0.533$. The Racah parameters B and C can be obtained from the relationships $B \approx N^2 B_0$ and $C \approx N^2 C_0$ [20] and the free-ion values $B_0 \approx 1115 \text{ cm}^{-1}$ and $C_0 \approx 5450 \text{ cm}^{-1}$ [9] for Ni^{3+} .

TABLE

The g factors and the effective magnetic moment (in μ_B) for the Ni^{3+} site in $La_2Ni_{0.5}Li_{0.5}O_4$.

	g_{\parallel}	g_{\perp}	Δg	μ_{eff}
Cal.	2.020	2.251	0.231	1.88
Exp. [8]	2.015 (1)	2.253 (1)	0.238 (2)	1.73

Thus only the tetragonal elongation ΔZ is unknown in the formulae of the g factors. Substituting the above data into Eq. (1) and fitting the calculated g factors to the observed values, one can obtain

$$\Delta Z \approx 0.14 \quad (8)$$

for the studied $La_2Ni_{0.5}Li_{0.5}O_4$. The corresponding theoretical g factors and the anisotropy are collected in Table. Then the effective magnetic moment can be calculated using the relationship $\mu_{\text{eff}} \approx g\sqrt{J(J+1)}$, where g is the average of the theoretical g factors and J ($= 1/2$) is the effective spin. The result is also shown in Table.

3. Discussion

Table reveals that the calculated g factors and the anisotropy for the Ni^{3+} site in $La_2Ni_{0.5}Li_{0.5}O_4$ based

on the perturbation formulae Eq. (1) and the tetragonal elongation ΔZ in Eq. (8) are in reasonable agreement with the observed values. Therefore, the experimental EPR results [8] are suitably interpreted for this system in this work, and the information about local structure around Ni^{3+} is also obtained.

1) The large elongation ΔZ ($\approx 0.14 \text{ \AA}$) obtained by analyzing the experimental g factors indicates significant tetragonal elongation distortion of the $[\text{NiO}_6]^{9-}$ cluster due to the Jahn–Teller effect by stretching the axial $\text{Ni}^{3+}-\text{O}^{2-}$ bonds via vibration interaction. The above elongation yields the lowest θ ($|z^2\rangle$) state, corresponding to the obvious positive anisotropy Δg (≈ 0.24 [8]). Similar tetragonal elongation of the oxygen octahedra was also found for Ni^{3+} in LaSrAlO_4 [11]. It is understandable that a low spin $3d^7$ (Ni^{3+}) ion situated in oxygen octahedra prefers to experience tetragonal elongations and exhibit positive anisotropies.

2) In view of the high valence state of Ni^{3+} , the system may exhibit significant covalency even in the oxygen environments, characterized by the low covalency factor N (≈ 0.74) and the moderate orbital admixture coefficients ($\approx 0.4-0.6$). When the contributions from the ligand orbital and spin–orbit coupling interactions are neglected, the theoretical results ($g_{\parallel} \approx 2.034$, $g_{\perp} \approx 2.238$, $\Delta g \approx 0.204$ and $\mu_{\text{eff}} \approx 1.88 \mu_{\text{B}}$) are not as good as those based on inclusion of the ligand contributions. Moreover, the above discrepancies can hardly be removed by adjusting ΔZ . In fact, the significant (about 67%) anisotropy (or relative difference) between k and k' for the orbital angular momentum operator is found from the present cluster approach calculations. So the contributions to the g factors from the anisotropic orbital admixtures (covalency effect) should be taken into account.

3) At low temperatures, the more anisotropic g factors were observed, e.g., $g_{\parallel} \approx 2.006$ (2) and $g_{\perp} \approx 2.261$ (2) at 5 K [8]. The slight deviation (i.e., increase in Δg) of the results can be attributed to the stronger Jahn–Teller elongation distortions at low temperatures, characterized by the larger c/a lattice constant ratios [8]. Based on the above calculation formulae, larger tetragonal elongations are expected at low temperatures, e.g., $\Delta Z \approx 0.149 \text{ \AA}$ at 5 K by fitting the experimental g factors. In addition, the reduction of μ_{eff} at low temperatures can be ascribed to the antiferromagnetic interactions between the occupancy disordering Ni^{3+} ions in $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ [8].

4. Summary

The EPR g factors and the effective magnetic moment of $\text{La}_2\text{Ni}_{0.5}\text{Li}_{0.5}\text{O}_4$ are theoretically investigated from the perturbation formulae for a low spin ($S = 1/2$) $3d^7$ ion under tetragonally elongated octahedra based on the cluster approach. The positive anisotropy Δg is attributed to the tetragonal elongation of about 0.14 \AA for the oxygen octahedron arising from the Jahn–Teller ef-

fect. In view of the high valence state of Ni^{3+} , the contributions to the g factors from the anisotropic orbital admixtures (covalency effect) should be taken into account.

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