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Journal of Alloys and Compounds 424 (2006) 55–59

Journal of ALLOYS AND COMPOUNDS

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Theoretical investigations on the local structures and the g factors of three Ni^{3+} centers in $LaSrAl_{1-x}Ni_xO_4$

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Received 24 November 2005; accepted 20 December 2005
Available online 2 February 2006

Abstract

The local structures and the EPR g factors of three Ni^{3+} centers (1)–(3) in $LaSrAl_{1-x}Ni_xO_4$ (LSAN) are theoretically investigated from the perturbation formulas of the g factors for a $3d^7$ ion of low spin ($S = 1/2$) in tetragonally and orthorhombically distorted octahedra. In these formulas, the contributions to the g factors from the low symmetrical parts of the crystal-fields, characterized by the crystal-field parameters D_s, D_t, D_ξ and D_η are taken into account. Based on the studies, it is found that the ligand octahedra are elongated along [0 0 1] axis by about 0.9, 0.7 and 1.0% for centers (1)–(3). The above distortions have a Jahn–Teller nature instead of ordinary lattice deformation, leading to the ligand octahedra less elongated than that (≈1.3%) in the host. Apart from the axial elongation, center (3) suffers additional orthorhombic distortion due to inequivalent variation by about ±0.3% of the planar bonding lengths along [1 0 0] and [0 1 0] axes, respectively. The calculated g factors show good agreement with the observed values.

Keywords: Defect structures; Electron paramagnetic resonance; Crystal-fields and spin Hamiltonians; Ni^{3+}; $LaSrAl_{1-x}Ni_xO_4$ (LSAN)

1. Introduction

$LaSrAlO_4$ belongs to the family of $AA'BO_4$ compounds (where A = La, Y; A′ = Sr, Ca and B = Al, Ga or some transition-metal element) and usually crystallizes in perovskite-like tetragonal La_2CuO_4-type structure ($I4/mmm$ space group) [1,2]. This material has attracted extensive interest due to its unique elastic and elasto-optic properties and applications as the promising substrates for high-T_c superconducting thin films [3–5]. In addition, electron paramagnetic resonance (EPR) investigations were carried out on this material doped with transition-metal ions (e.g., Cr^{3+}) [6,7], which may be helpful to the model studies of the energy states of the paramagnetic ions as well as local symmetry, strength and dispersion of the crystal-fields around them. Recently, magnetic structures and dynamics for Jahn–Teller (JT) ion Ni^{3+} (as well as Cu^{2+}) were investigated in $LaSrAl_{1-x}Ni_xO_4$ (LSAN) with $0 < x \leq 0.15$, and the EPR g factors $g_{//}$ and $g_\perp$ for two tetragonal Ni^{3+} centers (1) and (2), and g_x, g_y and g_z for one orthorhombic center (3) were also measured [8]. The above data ($g_{//} < g_\perp$ in centers (1) and (2) and $g_z < g_x$, g_y in center (3)) revealed the $3d_{z^2}$ ground state of the substitutional Ni^{3+} on Al^{3+} site, associated with the elongated $[NiO_6]^{9-}$ octahedra. However, up to now, these experimental results have not been theoretically interpreted, and the local structures for these Ni^{3+} centers in LSAN have not been quantitatively determined either. Considering that (i) the studies on the JT properties of Ni^{3+} are relatively fewer, compared with those of Cu^{2+} and (ii) EPR analyses on the LSAN:Ni^{3+} would be useful to understand the impurity structures and behaviours in this material, in this work, the g factors for these Ni^{3+} centers are investigated from the perturbation formulas of the g factors for a $3d^7$ ion of low spin ($S = 1/2$) in tetragonal and orthorhombic symmetries. In these formulas, the contributions from the low symmetrical (tetragonal and orthorhombic) distortions, characterized by the crystal-field parameters D_s, D_t, D_ξ and D_η describing the local structures of the impurity centers, are taken into account.

2. Calculations

In $LaSrAlO_4$, the host Al^{3+} site is surrounded by a tetragonally elongated oxygen octahedron with two longer bonding

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doi:10.1016/j.jallcom.2005.12.076

lengths $R_{//}$ (≈1.97 Å) parallel with the [0 0 1] (or C_4) axis, and four shorter bonding lengths $R_\perp$ (≈1.898 Å) perpendicular to the axis [8]. This point can be illustrated by the relative elongation parameters $\Delta T = (\bar{R}/R_\perp) - 1 = (1 - \bar{R}/R_{//})/2$, with the average distance $\bar{R} = (2R_\perp + R_{//})/3 \approx 1.922$ Å . Thus, we have $\Delta T_H \approx 1.3\%$ for the host Al^{3+} site, corresponding to the tetragonal distortion angle $\alpha_H = \tan^{-1}(R_\perp/R_{//}) \approx 43.93^\circ$, smaller than that (=45°) of cubic case. When the impurity Ni^{3+} ion enters the lattice of LSAN, it may occupy the Al^{3+} site because they have the same charge, and no charge compensation is needed. For a $Ni^{3+}(3d^7)$ ion in strong crystal-fields, it can be described as an unpaired E_g electron, associated with the ground state of the orbital doublet $^2E_g(t_{2g}{}^6e_g)$ having low spin ($S = 1/2$) [9,10]. As the octahedron is tetragonally elongated, the ground ^2E_g state would be split into two orbital singlets ε ($|x^2 - y^2\rangle$) and θ ($|z^2\rangle$), with the latter lying lowest [10].

For the anisotropic g factors $g_{//}$ and $g_\perp$ of the lowest θ state of the $3d^7$ ion in elongated octahedra, the perturbation formulas have been established by considering the contributions from the excited states via spin–orbit coupling and the cubic crystal-field interactions [10]:

$$g_{//} = g_s + \frac{2\zeta^2}{E_1^2},$$
$$g_\perp = g_s + \frac{2\zeta^2}{E_1^2} + \frac{3\zeta}{E}, \tag{1}$$

with

$$\frac{1}{E} = \frac{1}{E_3} + \frac{1}{E_4} + 0.38\left(\frac{1}{E_3} - \frac{1}{E_4}\right), \tag{2}$$

where g_s (=2.0023) is the spin only value. ζ is the spin–orbit coupling coefficient of the $3d^7$ ion in crystal. E_i (i = 1–3) are the energy separations between the excited $^4T_{1b}$, $^2T_{2a}$ and $^2T_{2b}$ and the ground ^2E_g states in cubic case [10,11]. However, the contributions from the low symmetrical crystal-fields and the orbital reduction factor due to the covalent reduction of the orbital angular momentum interaction were not taken into account.

In order to investigate the Ni^{3+} centers in LSAN, the above formulas can be improved by including the contributions from the low symmetrical (tetragonal or orthorhombic) crystal-fields and the orbital reduction factor k. In view that the orthorhombic formulas have not been established, one can derive the formulas of the g factors for the $3d^7$ ion in orthorhombic symmetry by using the method in Ref. [10]. Thus, we have

$$g_z = g_s + \frac{2k\zeta^2}{E_{1z}^2},$$
$$g_x = g_s + \frac{2k\zeta^2}{E_{1x}^2} + \frac{3k\zeta}{E_x}, \tag{3}$$
$$g_y = g_s + \frac{2k\zeta^2}{E_{1y}^2} + \frac{3k\zeta}{E_y},$$

with

$$\frac{1}{E_x} = \frac{1}{E_{3x}} + \frac{1}{E_{4x}} + 0.38\left(\frac{1}{E_{3x}} - \frac{1}{E_{4x}}\right),$$
$$\frac{1}{E_y} = \frac{1}{E_{3y}} + \frac{1}{E_{4y}} + 0.38\left(\frac{1}{E_{3y}} - \frac{1}{E_{4y}}\right). \tag{4}$$

Here $E_{i\alpha}$ (or E_α with $\alpha = x, y$ and z) denote the various components of the related energy differences due to the orthorhombic (or tetragonal) splittings. They can be obtained from the energy matrices of the $3d^7$ ion in orthorhombic symmetry:

$$\begin{aligned}
E_{1z} &= 10Dq - 4B - 4C,\\
E_{1x} &= 10Dq - 4B - 4C - 3D_s + 5D_t - 3D_\xi + 4D_\eta,\\
E_{1y} &= 10Dq - 4B - 4C - 3D_s + 5D_t + 3D_\xi - 4D_\eta,\\
E_{3x} &= 10Dq + 6B - C - 3D_s + 5D_t - 3D_\xi + 4D_\eta,\\
E_{3y} &= 10Dq + 6B - C - 3D_s + 5D_t + 3D_\xi - 4D_\eta,\\
E_{4x} &= 10Dq + 14B + C - 3D_s + 5D_t - 3D_\xi + 4D_\eta,\\
E_{4y} &= 10Dq + 14B + C - 3D_s + 5D_t + 3D_\xi - 4D_\eta,
\end{aligned} \tag{5}$$

where B and C are the Racah parameters of the $3d^7$ ion in crystals. Dq is the cubic field parameter, and D_s, D_t, D_ξ and D_η are the orthorhombic ones. Obviously, when neglecting the low symmetrical contributions in the above formulas, they are reduced to the original expressions in Ref. [10]. On the other hand, if we reserve only the tetragonal field parameters D_s and D_t (i.e., assuming $D_\xi = 0$ and $D_\eta = 0$), Eqs. (3)–(5) become those for the tetragonal symmetry. In the following, these formulas are applied to the investigations of the defect structures and the g factors of the tetragonal and orthorhombic Ni^{3+} centers in LSAN.

2.1. Studies on the tetragonal centers (1) and (2)

Judging from the difference in the experimental g factors, the centers (1) and (2) can be attributed to distinct tetragonal distortions due to Jahn–Teller effect [8]. The tetragonal distortions are therefore described by the elongation parameters $\Delta T^{(i)}$ (i = 1–3 stand for various centers), corresponding to the different parallel and perpendicular bonding lengths $R_{//}^{(i)} \approx \bar{R}(1 + 2\Delta T^{(i)})$ and $R_\perp^{(i)} \approx \bar{R}(1 - \Delta T^{(i)})$. By using the superposition model [12] and the local geometrical relationship of the tetragonal centers, the tetragonal field parameters for centers (1) and (2) can be determined as follows:

$$D_s \approx \left(\frac{4}{7}\right)\bar{A}_2(R_0)[(1 - \Delta T^{(i)})^{-t_2} - (1 + 2\Delta T^{(i)})^{-t_2}],$$
$$D_t \approx \left(\frac{16}{21}\right)\bar{A}_4(R_0)[(1 - \Delta T^{(i)})^{-t_4} - (1 + 2\Delta T^{(i)})^{-t_4}], \tag{6}$$

where $\bar{A}_2(R_0)$and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference bonding length R_0 taken as the average distance $\bar{R}$. For $3d^n$ ions in octahedra, $\bar{A}_4(R_0) \approx (3/4)Dq$ and $\bar{A}_2(R_0) \approx 10.8\bar{A}_4(R_0)$ are valid in many crystals [13–15]. t_2 (≈3) and t_4 (≈5) are the power–law exponents [12]. Therefore, the EPR g factors are connected with the low symmetrical (tetragonal or