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Journal of Alloys and Compounds 464 (2008) 18–22

Journal of ALLOYS AND COMPOUNDS

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Studies on the defect structures for two Rh^{2+} centers in LiD

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Received 17 June 2007; received in revised form 28 September 2007; accepted 1 October 2007
Available online 5 October 2007

Abstract

The defect structures for two Rh^{2+} centers {A} and {O} in LiD are theoretically studied by analyzing their experimental EPR parameters, based on the perturbation formulas of these parameters for a $4d^7$ ion with low spin ($S = 1/2$) in tetragonally compressed octahedra and orthorhombically elongated octahedra. Center {A} can be attributed to the substitutional Rh^{2+} at the Li^+ site, associated with the next nearest neighbouring (nnn) Li^+ vacancy V_{Li} along [0 0 1] (or C_4) axis as the compensator. In this center, the intervening ligand D^- in Rh^{2+} and the V_{Li} is found to shift towards Rh^{2+} by an amount $\Delta Z_A \approx 0.01$ Å due to the electrostatic repulsion of the V_{Li}. Center {O} is assigned to the elongation $\delta \approx 0.072$ Å of the ligand octahedron along [0 0 1] axis due to the Jahn–Teller effect, associated with one nnn V_{Li} along [1 0 0] (or X) axis. The intervening ligand may also suffer a displacement $\Delta X_O \approx 0.11$ Å towards Rh^{2+}. In the calculations of the hyperfine structure constants, the reduction factors H (≈0.49 and 0.93) due to the Rh^{2+} 4d–5s orbital admixture are obtained for centers {A} and {O}.

Keywords: Inorganic materials; Crystal and ligand fields; Point defects; Electron paramagnetic resonance

1. Introduction

LiD (or LiH) has attracted interest of researchers due to its useful optical [1–3], resonant Raman scattering properties [4,5] and unique state equation under high pressure [6,7]. In addition, it is also regarded as a promising material for high-temperature superconductors [8]. Usually, these properties depend mainly upon structure of this material, which can be probed by some transition-metal (e.g., $3d^n$) ions with the aid of electron paramagnetic resonance (EPR) technique [9–11]. Unfortunately, studies on the second group transition-metal ($4d^n$) ions in this less common compound are relatively scarce. For example, EPR spectra for Rh^{2+} ($4d^7$) in LiD single crystal have been observed after ultraviolet light illumination, and the EPR parameters anisotropic g factors and the hyperfine structure constants for one tetragonal center {A} and another orthorhombic center {O} were also measured at 210 K and 77 K, respectively [12].

Until now, however, no satisfactory interpretation to the above experimental results has been made, and information about defect structures for the two Rh^{2+} centers has not been obtained, either. In the previous work [12], the simple second-order perturbation formulas of the EPR parameters for a $3d^9$ ion in tetragonally elongated or compressed octahedra were adopted for center {A} or {O}. Secondly, the contributions from the low symmetrical distortions due to the charge compensation and the Jahn–Teller effect were not taken into account. Finally, the hyperfine structure constants were calculated by using the experimental g factors [12]. Further, the contributions from the reduction effect due to the Rh^{2+} 4d–5s orbital admixtures can be important [13]. However, these contributions were neglected as well, leading to the unreasonably small covalency factor 0.47 for center {A} [12]. In order to study the defect structures and the EPR parameters for LiD:Rh^{2+} to a better extent, in this work, the third-order perturbation formulas of the EPR parameters are established for a $4d^7$ ion with low spin ($S = 1/2$) under tetrag-

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doi:10.1016/j.jallcom.2007.10.002

onally compressed octahedra and orthorhombically elongated ones, and then applied to centers {A} and {O}.

2. Theory and formulas

LiD has NaCl type structure. Rh^{2+} doped into LiD may occupy the host Li^+ site. Since Rh^{2+} has an extra charge compared with the replaced Li^+, a next nearest neighbouring (nnn) V_{Li} may occur along [0 0 1] (or C_4) axis due to charge compensation. Because of the negative effective charge of V_{Li}, the ligand D^- intervening in the V_{Li} and Rh^{2+} is expected to shift towards Rh^{2+} by an amount ΔZ_A along the C_4 axis due to the electrostatic repulsion, forming a tetragonally compressed octahedron (center {A}). As for center {O}, it can be attributed to Rh^{2+} locating on an elongated octahedron (characterized by the relative elongation δ of the octahedron along [0 0 1] axis) due to the Jahn–Teller effect, associated with one nnn V_{Li} along [1 0 0] (or X) axis as the compensator. Similarly, the intervening ligand may suffer another displacement ΔX_O towards Rh^{2+} and thus form an orthorhombically elongated octahedron. Therefore, the defect structure around Rh^{2+} in LiD can be described as ΔZ_A (or δ and ΔX_O) for center {A} (or {O}), respectively. Note that the displacement direction towards Rh^{2+} is defined as positive here.

Belonging to the case of strong crystal-fields, Rh^{2+} ($4d^7$) ions in crystals have the orbital doublet ^2E_g ($t_{2g}^6e_g$) with low spin ($S = 1/2$) as the ground state, which can be described as an unpaired electron in e_g state [14–16]. As the ligand octahedron is compressed (or elongated), the ground ^2E_g state would be split into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$, with the former (or latter) lying lowest.

For the lowest $^2B_{1g}$ state of a $Rh^{2+}(4d^7)$ ion in tetragonally compressed octahedra, the third-order perturbation formulas of the EPR parameters can be derived from the perturbation procedure [11,15]. Here we include the contributions from the central ion spin–orbit coupling coefficient ζ_d, the tetragonal distortion (characterized by the tetragonal field parameters D_s and D_t) and the reduction effect (characterized by the reduction factor H) in the anisotropic parts of the hyperfine structure constants due to the metal 4d–5s orbital admixtures. Thus, one can obtain:

$$\begin{aligned} g_{||} &= g_s + 2k\frac{\zeta_d^2}{E_{1||}^2} + 4k\frac{\zeta_d}{E_{||}}, \\ g_{\perp} &= g_s + 2k\frac{\zeta_d^2}{E_{1\perp}^2} + k\frac{\zeta_d}{E_{\perp}}, \\ A_{||} &= P\left[-\kappa - \frac{4}{7}H + \frac{3}{7}(g_{\perp} - g_s) + (g_{||} - g_s)\right], \\ A_{\perp} &= P\left[-\kappa + \frac{2}{7}H + \frac{11}{14}(g_{\perp} - g_s)\right], \end{aligned} \tag{1}$$

where the denominators $E_{||}$ and $E_{\perp}$ can be written as:

$$\begin{aligned} E_{||} &= \frac{1}{E_{3||}} + \frac{1}{E_{4||}} + 0.38\left(\frac{1}{E_{3||}} - \frac{1}{E_{4||}}\right), \\ E_{\perp} &= \frac{1}{E_{3\perp}} + \frac{1}{E_{4\perp}} + 0.38\left(\frac{1}{E_{3\perp}} - \frac{1}{E_{4\perp}}\right). \end{aligned} \tag{2}$$

Here g_s ($\approx$2.0023) is the spin-only value. k is the orbital reduction factor, indication of the covalency of the studied system. P and κ are the dipolar hyperfine structure parameter and the core polarization constant, respectively. The energy denominators $E_{i\alpha}$ ($i = 1, 3, 4$; $\alpha = ||$ and $\perp$) denote the various tetragonal components of the separations between the excited $^4T_{1b}(t_2^5e^2)$, $^2T_{2a}(t_2^5e^2)$, and $^2T_{2b}(t_2^5e^2)$ and the ground $^2B_{1g}(t_2^6e)$ states [11,15,16]. They can be obtained from the energy matrices of the $4d^7$ ion under tetragonal symmetry in terms of the cubic field parameter D_q, the tetragonal field parameters D_s, D_t and the Racah parameters B and C [16,17].

Similarly, for the lowest $^2A_{1g}$ state of a $Rh^{2+}(4d^7)$ ion in orthorhombically elongated octahedra, the perturbation formulas of the EPR parameters can be established as follows:

$$\begin{aligned} g_x &= g_s + 2k\frac{\zeta_d^2}{E_{1x}^2} + 3k\frac{\zeta_d}{E_x} - k\zeta_d\left(\frac{1}{E_{2x}} - \frac{1}{E_{5x}}\right), \\ g_y &= g_s + 2k\frac{\zeta_d^2}{E_{1y}^2} + 3k\frac{\zeta_d}{E_y} - k\zeta_d\left(\frac{1}{E_{2y}} - \frac{1}{E_{5y}}\right), \\ g_z &= g_s + 2k\frac{\zeta_d^2}{E_{1z}^2} - 4k\zeta_d\left(\frac{1}{E_{2z}} - \frac{1}{E_{5z}}\right), \\ A_x &= P\left[-\kappa - \frac{2}{7}H + \frac{15}{14}(g_y - g_s)\right], \\ A_y &= P\left[-\kappa - \frac{2}{7}H + \frac{15}{14}(g_x - g_s)\right], \\ A_z &= P\left[-\kappa + \frac{4}{7}H - \frac{1}{14}(g_x + g_y - 2g_s)\right]. \end{aligned} \tag{3}$$

Here E_x and E_y are expressed as:

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

In the above formulas, the energy denominators $E_{i\alpha}$ ($i = 1$, 2, 3, 4, 5; $\alpha = x, y, z$) denote the separations between the excited $^4T_{1b}(t_2^5e^2)$, $^2T_{1a}(t_2^5e^2)$, $^2T_{2a}(t_2^5e^2)$, $^2T_{2b}(t_2^5e^2)$ and $^2T_{1b}(t_2^5e^2)$ and the ground $^2A_{1g}(t_2^6e)$ states. They can be determined from the energy matrices of a $4d^7$ ion under orthorhombic symmetry, in terms of the orthorhombic field parameters D_s, D_t, D_ξ and D_η.

3. Applications

From Eqs. (1) to (4), the EPR parameters can be connected with the local structures of the studied systems in terms of the tetragonal or orthorhombic field parameters, which depend upon the local structural parameter ΔZ_A (or δ and ΔX_O) for center {A} (or {O}), respectively.

3.1. Center {A}

For center {A}, the tetragonal field parameters can be determined from the superposition model [18] and the ligand