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Theoretical studies of the defect structures for the two Cr^{3+} centers in KCl

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ABSTRACT

The spin Hamiltonian (SH) parameters (i.e. the zero-field splitting parameters (ZFSPs) and g factors) and local structures of the two Cr^{3+} centers I and II at room temperature in KCl single crystals are theoretically investigated from the perturbation calculations for a rhombically distorted octahedral $3d^3$ cluster. The impurity systems are attributed to the doped $Cr(CN)_6^{3-}$ groups into KCl replacing the host KCl_6^{5-} ones, associated with two nearest neighbor potassium vacancies V_K in [011] and [0$\bar{1}\bar{1}$] axes in center I and one nearest neighbor V_K along [0$\bar{1}$1] and another next-nearest neighbor V_K along [100] axis in center II, respectively. In center I, the four coplanar and two axial ligands CN^- undergo the shifts ΔR_1 (≈0.0044 nm) away from the V_K and $\Delta R_2'$ (≈0.0144 nm) away from the central ion along Z axis, respectively, because of the electrostatic interactions. In center II, the impurity Cr^{3+} is found to undergo the shift ΔR_C (≈0.0063 nm) towards the nearest neighbor V_K along [0$\bar{1}$1] axis, while the two ligands in [001] and [0$\bar{1}$0] axes closest to the V_K undergo the shifts ΔR_1 (≈0.0081 nm) away from the respective V_K, and the ligand intervening in the V_K and the central ion experiences the shift ΔR_2 (≈0.0238 nm) away from the V_K along [100] axis. The charge-transfer (CT) contributions to g-shifts are found to be opposite in sign and more than half (characterized by the ratios $|\Delta g_{CT}/\Delta g_{CF}| > 50\%$) in magnitude compared with the CF ones for both centers. The local structures and the microscopic mechanisms of the relevant impurity and ligand shifts are discussed for the two centers.

1. Introduction

In recent years, KCl has been widely used in e.g. electrochemistry [1], crystal growth [2] and to ensure good motility in preserved salmonid sperm samples [3]. There is great interest in the research on optical and magnetic character of functional materials, which can be considerably modified by transition-metal dopants with abundant energy levels and transitions as well as promising applications [4]. Hence, studies of alkali halides doped with transition-metal ions are especially attractive and important. The $Cr^{3+}(3d^3)$ ions are widely applied in the red persistent phosphorescent materials with high brightness, e.g. $Y_3Al_{5-x}Ga_xO_{12}$: Cr^{3+} [5]. Cr^{3+} ions play also an important role in the metabolism of fats, proteins, carbohydrates and nucleic acids by activating certain enzymes and stabilizing proteins and nucleic acids in the human body [6]. On the other hand, CN^- anions are extensively used in some industrial fields such as metallurgy [7] and plastics manufacturing [8]. Interestingly, $[Cr(CN)_6]^{3-}$ groups can provide wide applications in the molecule-based materials (e.g., $A_aB_b[D(CN)_6]_d \cdot mH_2O$, with A=alkali cations; B, D=transition-metal ions) [9]. The above features and applications may sensitively depend upon the defect structures and electronic properties of $Cr(CN)_6^{3-}$ groups in the hosts. The electron paramagnetic resonance (EPR) [10] is a powerful technique to reveal important information about defect structures of transition-metal impurities in crystals, which would be helpful to understand their structure and performance.

The EPR measurements were employed for KCl single crystals doped with $Cr(CN)_6^{3-}$ groups, and the spin Hamiltonian (SH) parameters, i.e. the zero-field splitting (ZFS) ones: D and E and g factors g_x, g_y and g_z [11,12], were obtained for the two rhombic Cr^{3+} centers I and II at 293 K showing slight differences [13]. Structurally equivalent to those in NaC1 [14], the centers I and II in KCl [13] were ascribed to the substitutional $Cr(CN)_6^{3-}$ groups replacing host KCl_6^{5-} groups with two potassium vacancies V_K as the compensators. This reduces the local symmetry from original cubic (O_h) of host K^+ site to approximately rhombic (D_{2h} or C_{2v}) in the impurity centers (see Fig. 1). For convenience, the ligands of XY plane closest to V_K or far from V_K are denoted as "1" or "1′", and the ligand(s) along Z axis intervening in V_K and the central impurity or far from V_K are denoted as "2" or "2′", respectively, in Fig. 1. In center I, the two nearest neighbor V_K along [011] and [0$\bar{1}\bar{1}$] axes can make the four coplanar ligands CN^- "1" take one shift ΔR_1 away from the V_K due to the electrostatic repulsion. Meanwhile, the two axial ligands "2′" may take another shift $\Delta R_2'$ away

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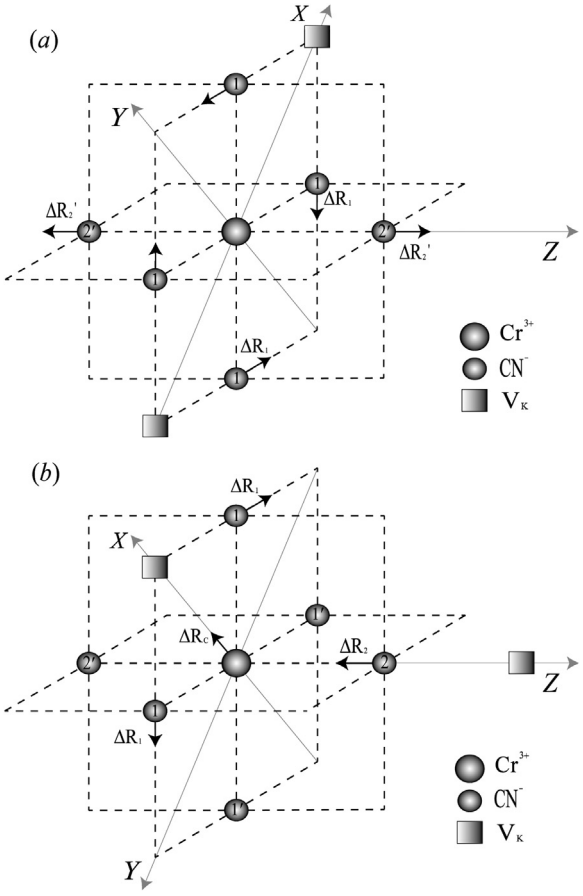

Fig. 1. Defect structures of centers I (a) and II (b) in KCl: $Cr(CN)_6^{3-}$. In center I, there are four ligands "1" in XY plane closest to V_K and two ligands "2′" along Z axis. In center II, there are two ligands "1" in XY plane closest to V_K, another two ligands "1′" in XY plane far from V_K, one ligand "2′" along –Z axis and one ligand "2" along Z axis intervening in V_K and the central impurity.

from the impurity ion along Z axis. In center II, one nearest neighbor V_K along $[0\bar{1}1]$ axis can make the central Cr^{3+} and the two ligands "1" take the shifts ΔR_C and ΔR_1 towards and away from the V_K, respectively. The other next-nearest neighbor V_K along [100] axis may force the ligand "2" to shift away from the V_K by another amount ΔR_2. Thus, the defect structures of both centers are denoted by the central ion (Cr^{3+}) shift ΔR_C and the ligand (CN^-) shifts ΔR_1, ΔR_2 and $\Delta R_2'$ (in Fig. 1).

2. Theoretical calculations

The energy levels of the ground spin state of transition metal ions doped in crystals can be described using a SH form including the Zeeman electronic (Ze) and ZFS terms [15,16]:

$$H = H_{ze} + H_{zfs} = \mu_B \mathbf{B}\cdot g\cdot \mathbf{s} + \sum B_k^q O_k^q = g_x\mu_B H_x \mathbf{S}_x + g_y\mu_B H_y \mathbf{S}_y + g_z\mu_B H_z \mathbf{S}_z + (DO_2^0 + 3EO_2^2)/3 + (b_4^0 O_4^0 + b_4^2 O_4^2 + b_4^2 O_4^2)/60. \quad (1)$$

To perform the theoretical calculations of the SH parameters (SHPs) for the Cr^{3+} centers in KCl, the perturbation formulas [17,18] for the SHPs suitable for a $3d^3$ ion in rhombically distorted octahedra obtained using the cluster approach [19,20] are employed here. The equations for ZFSPs and g_i-factors [17,18] involve both the contributions to g-shift from the charge-transfer (CT) mechanism (relevant to the CT excited states) and the crystal-field (CF) (relevant to the CF excited states) mechanism in view of significant covalency due to the high valence state of Cr^{3+} and strongly covalent cyanide ligands [21–23].

The ZFSPs (D, E) and g_i factors are expressed in terms of the quantities E_1, E_2 and E_3 representing the energy separations between the CF excited $^4T_{2g}[t_2^2(^3T_1)e]$, $^2T_{2a}(t_2^3)$ and $^2T_{2b}[t_2^2(^3T_1)e]$ states, respectively, and the ground $^4A_{2g}$. Applying the energy matrices of an octahedral $3d^3$ cluster [17], the above values can be determined from the cubic CF parameter Dq and the Racah parameters B and C [24,25] of the $3d^3$ ion in crystals:

$$E_1 \approx 10Dq,$$
$$E_2 \approx 15B + 5C,$$
$$E_3 \approx 9B + 3C + 10Dq. \quad (2)$$

E_n is the energy separation between the CT level $^4T_{2g}{}^n$ and the ground CF level $^4A_{2g}$, which can be determined in terms of the optical electronegativities χ(L) and χ(M) of ligand and central metal ions [21]:

$$E_n \approx 30000\ [\chi(L)-\chi(M)] + 14\ B\ (cm^{-1}). \quad (3)$$

The spin-orbit coupling coefficients (ζ_{CF}, ζ_{CF}' for the CF mechanism and ζ_{CT}' for the CT mechanism) and the orbital reduction factors (k_{CF}, k_{CF}' for the CF mechanism and k_{CT}' for the CT mechanism) can be expressed from the normalization factors (N_t^x and N_e^x) and the orbital admixture coefficients (λ_t^x, λ_e^x and λ_s^x) using the cluster approach [19,20]. The subscripts t and e denote the irreducible representations T_{2g} and E_g of cubic O_h group, and the superscripts x (=a and b) stand for the anti-bonding and bonding orbitals, respectively. These quantities can be obtained by applying the normalization conditions, the orthogonality relationships and the approximate relationships relevant to covalency factor N for the anti-bonding orbitals from the cluster approach [19,20].

The conventional rhombic CF parameters D_t, D_ξ and D_η [17,18,26,27], which can also be expressed in terms of the Wybourne notations Bkq [28–30], may be determined from the local geometries of the impurity centers.

2.1. Calculations of the SHPs for center I

For center I, the defect structure is characterized by the shifts ΔR_1 of the four coplanar ligands and $\Delta R_2'$ of the two axial ones (see Fig. 1), similar to the rhombic V_{Ag}-Cr^{3+}-V_{Ag} center in AgCl [17].

The conventional rhombic CF parameters D_t, D_ξ and D_η in Refs. [17,18,26,27] relevant to the Wybourne notations B_{kq} [28–30] are obtained from the defect structure of this center and the superposition model [10,16,31–34]:

$$D_t = -B_{40}/21 + Dq = -8\bar{A}_4[(1/14)(R/R_1)^{t4} + (2/21)(R/R_{2,})^{t4} - 1/6],$$
$$D_\xi = -2\sqrt{10}B_{42}/21 = (80/21)\bar{A}_4(R/R_1)^{t4}\cos 2\varphi_1,$$
$$D_\eta = \sqrt{630}B_{44}/63 - 5Dq = (20/3)\bar{A}_4[(R/R_1)^{t4}\cos 4\varphi_1 + 1], \quad (4)$$

with

$$R_1 = (R^2 + \Delta R_1^2)^{1/2}, \quad R_{2,} = R + \Delta R_2', \quad \varphi_1 = \pi/4 + \arctan(\Delta R_1/R). \quad (5)$$

In Eq. (4), the power-law exponents are usually taken as $t_2 \approx 3$ and $t_4 \approx 5$ [31]. $\bar{A}_u$ (u=2, 4) are the intrinsic parameters related to the reference distance R. For the octahedral $3d^n$ clusters, $\bar{A}_4 \approx 3Dq/4$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ [35–37] proved reliable in many crystals, are used in the present calculations.

Since the ionic radius r_i (≈0.0615 nm [38]) of impurity Cr^{3+} is much smaller than the radius r_h (≈0.138 nm [38]) of host K^+, the reference distance R can be dissimilar to the host cation-anion distance R_H (≈0.31466 nm [39]) in KCl. However, this effective distance can be determined from the empirical relationship $R \approx R_H + (r_i - r_h)/2$ [40], yielding 0.27641 nm. By using the Slater-type self-consistent field wave functions [41] and the distance R, the group overlap integrals are calculated for both centers: $S_{dpt} \approx 0.0052$, $S_{dpe} \approx 0.0206$, $S_s \approx 0.0117$ and