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Investigations of the optical spectral bands, g factors and local structure for the tetragonal Cr^{5+} tetrahedral clusters in Cr-doped silica glasses

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A B S T R A C T

In this paper, the weaknesses and mistakes in the assignments of some optical absorption bands and the theoretical calculations of g factors ($g_{//} < g_{\perp}$) in the previous papers for the tetragonally-elongated $(CrO_4)^{3-}$ clusters in Cr-doped silica glasses prepared with sol–gel method are pointed out and corrected. On the basis of these, the g factors $g_{//}$ and $g_{\perp}$ for this Cr^{5+} cluster are calculated from the high-order perturbation formulas based on the two-mechanism model (where the contributions to g factors due to both the crystal field (CF) mechanism in the widely-used CF theory and the charge-transfer (CT) mechanism are included) for the tetragonally-elongated d^1 tetrahedral clusters with the ground state $|d_{x^2-y^2}\rangle$. From the calculated values and by considering the small admixture between the ground state $|d_{x^2-y^2}\rangle$ and the first excited state $|d_{z^2}\rangle$ owing to the vibrational motion of ligands (note: this dynamic effect leads the elongated $(CrO_4)^{3-}$ cluster to become the twinkling compressed one), the calculated $g_{//}$ and $g_{\perp}$ are in reasonable agreement with the experimental values. In the calculations, the needed CF energy levels (corresponding to the optical spectral bands) are obtained from CF theory in which the CF parameters are estimated from the superposition model. Thus, the optical band positions of $(CrO_4)^{3-}$ cluster in silica glassed are explained and the local structure of static $(CrO_4)^{3-}$ cluster is obtained. By considering the dynamic effect, the isotropic g factors ($g_{//} = g_{\perp}$) at room temperature for another $(CrO_4)^{3-}$ cluster in silica glasses and the anisotropic g factors ($g_{//} > g_{\perp}$) for the tetragonally-compressed $(CrO_4)^{3-}$ cluster in barium aluminophosphate glasses are also explained in a unified way. The results are discussed.

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1. Introduction

Silica glasses prepared by sol–gel method (i.e., sol–gel glasses) doped with transition-metal or rare-earth ions have been paid attention because they have the potential applications to luminescence (including upconversion), phosphor, solid state laser and magnetic materials [1–10]. So many spectroscopic studies for these doped glasses were made [1–10]. For example, Mukherjee et al. [10] measured the optical and electron paramagnetic resonance (EPR) spectra of chromium oxide doped sol–gel silica glasses calcined at 800 °C. In the EPR spectra, a narrow anisotropic EPR line (with $g_{//} \approx 1.955(5)$ and $g_{\perp} \approx 1.976(3)$) was detected and is assigned to isolated Cr^{5+} ion in a tetragonally-elongated oxygen tetrahedral cluster (i.e., $(CrO_4)^{3-}$). Three observed optical spectral bands at $6780\ cm^{-1}$, $7040\ cm^{-1}$ and $7250\ cm^{-1}$ were attributed, respectively, to the d–d transitions E_0 ($^2B_1|d_{x^2-y^2}\rangle \rightarrow {}^2A_1|d_{z^2}\rangle$), E_1 ($^2B_1|d_{x^2-y^2}\rangle \rightarrow {}^2B_2|d_{xy}\rangle$) and E_2 ($^2B_1|d_{x^2-y^2}\rangle \rightarrow {}^2E|d_{xz,yz}\rangle$) of this Cr^{5+} center [10]. In addition, another weaker sharp isotropic line ($g \approx 1.973(3)$) was also found at room temperature (RT) and disappears at liquid nitrogen temperature (LNT) [10]. They thought that the isotropic line probably arises from freely rotating individual $(CrO_4)^{3-}$ clusters at some other sites (called $Cr^{5+}(2)$ center) in silica glasses and its disappearance may be due to the rotation of $(CrO_4)^{3-}$ cluster ceases at LNT, giving rise to an anisotropic spectrum which merges with the above anisotropic narrow line spectrum already present at RT [10]. Recently, Wu et al. [11] calculated the anisotropic g factors and the optical band positions for this Cr^{5+} center in silica glasses. However, there are several mistakes and weaknesses in their calculations:

i. May be due to the difficulty in the calculations of the optical band positions assigned in Ref. [10] (in particular, for the band or transition E_0), they [11] assumed that the symmetry of $(CrO_4)^{3-}$ cluster in silica glasses is rhombic rather than tetragonal given in [10]. Thus, the doublet ^2E state is split

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into two singlets $^2B_3$ ($|d_{yz}\rangle$) and $^2B_4$ ($|d_{xz}\rangle$) and the three observed bands were assigned to $E'_1(^2B_1 \to {}^2B_2)$, $E'_2(^2B_1 \to {}^2B_3)$ and $E'_3(^2B_1 \to {}^2B_4)$. On the basis of these, the g factors g_j ($j = x, y, z$) were calculated from the high-order perturbation formulas based on the crystal-field (CF) mechanism for d^1 ion in rhombic tetrahedral clusters. However, the observed g factors unquestionably show that the $(CrO_4)^{3-}$ cluster is tetragonal [10] rather than rhombic. In fact, the $^2B_2$ and ^2E states are due to the splitting of $^2T_2(^2D)$ state by the tetragonal CF. This splitting ($\approx 7250 - 7040 \approx 210\ cm^{-1}$ [10]) is very small, suggesting that the tetragonal CF is weak. Thus, the transition E_0 ($^2B_1 \to {}^2A_1$) due to the splitting of ^2E (^2D) state by the same tetragonal CF should also be, as the splitting of $^2T_2$ (^2D), very small and on the order of $10^2\ cm^{-1}$. So, the peak (or band, which is not obvious in the observed spectrum [10]) at $6780\ cm^{-1}$ cannot be assigned to the transition E_0. It and the strong band at $5220\ cm^{-1}$ in Ref. [10] are not clear. So, we think that the $(CrO_4)^{3-}$ cluster in silica glasses is still tetragonal and the bands at $7040\ cm^{-1}$ and $7250\ cm^{-1}$ are still due to the transitions E_1 and E_2. The opinions in Ref. [10] are correct except the assignment of the band at $6780\ cm^{-1}$.

ii. The calculations of g factors in Ref. [11] considered only the contributions from the CF mechanism concerning the interactions of CF excited states with the ground state. However, for the high valence state d^n (e.g., Cr^{5+} studied) ions in crystals, the contributions due to charge-transfer (CT) mechanism concerning the interactions of CT excited states with the ground state are also considered and so a two (CF and CT)-mechanism model should be applied [12–14] because the CT energy levels of d^n ions in crystals lower with the increasing valence state of d^n ions [15].

iii. The isotropic g factor of another $(CrO_4)^{3-}$ cluster (Cr^{5+}(2) center) in silica glasses was not explained in Ref. [11].

iv. Importantly, by using the values of ζ', k' and E'_1 given in Ref. [11] to the dominant second-order perturbation term $-\frac{8k'\zeta'}{E'_1}$ in the formula of g_z in [11], one can obtain the second-order term is about 0.106 and so $g_z \approx 1.896$. Since each third- or fourth-order term in the formula of g_z in Ref. [11] is two or three orders in magnitude less than the second-order term, even these high-order terms are considered, the calculated g_z cannot be 1.949 given in Ref. [11]. So, the agreement of g factors between calculation and experiment in Ref. [11] is doubtful.

In fact, from the dominant second-order perturbation terms of g factor formulas in the CF mechanism, we have the ratio $\Delta g_{//}/\Delta g_{\perp} \approx 4$ (where $\Delta g_i = g_e - g_i, g_e \approx 2.0023$ is the g value of free electron and $i = //$ or $\perp$), which is much greater than the observed $\Delta g_{//}/\Delta g_{\perp}$ ($\approx$1.8 [10]) for the $(CrO_4)^{3-}$ cluster in silica glasses. The small ratio $\Delta g_{//}/\Delta g_{\perp}$ and hence small anisotropy of g factors suggest that there may be some admixture of the first excited state $|d_{z^2}\rangle$ with the ground state $|d_{x^2-y^2}\rangle$. However, the theoretical studies with molecular energy scheme [16,17] indicate that the static tetragonal CF cannot bring about the admixture. So, a dynamic effect owing to the vibrational motion of ligands may be considered to cause the admixture. In fact, similar admixtures owing to dynamic effect were found. For instance, in order to overcome the difficulties in the explanations of the observed $g_{//} > g_e$ for some tetragonally-compressed Cu^{2+} ($3d^9$ ion, the complementary ion of $3d^1$ ion) octahedral clusters in crystals [18–20] and the large deviation of $g_{//}$ from g_e for the tetragonally-compressed $(CrO_4)^{3-}$ clusters in YMO_4 (M = V, P) crystals [13] (note: according to the high-order perturbation formula in CF theory, in the two systems, $g_{//} \approx g_e - \frac{3\zeta^2(g_e-k)}{E_1^2}$ [12,18], so $g_{//}$ should be only slightly smaller than g_e), the dynamic effect due to vibrational motion of ligands (which leads the compressed octahedron (or tetrahedron) to become the twinkling elongated one) is introduced. This effect results in the admixture of the first excited state $|d_{x^2-y^2}\rangle$ with the ground state $|d_{z^2}\rangle$. Thus, the observed g_i are averaged in time for $g_i^{(comp.)}$ (corresponding to the pure $|d_{z^2}\rangle$ ground state) and $g_i^{(elong.)}$ (corresponding to the pure $|d_{x^2-y^2}\rangle$ ground state) and so the above difficulties are removed.

Similarly, we can apply the dynamic effect to explain the small ratio $\Delta g_{//}/\Delta g_{\perp}$ for the studied $(CrO_4)^{3-}$ cluster in silica glasses. This effect can lead a elongated $(CrO_4)^{3-}$ tetrahedron (where $\alpha < \alpha_0$, α is the angle between the metal–ligand bond and C_4 axis, see Fig. 1, and $\alpha_0 \approx 54.74°$ is the same angle in cubic symmetry) to become a twinkling compressed one ($\alpha > \alpha_0$) because of the vibrational motion of ligands. Thus, the ground state is the admixture between $|d_{x^2-y^2}\rangle$ and $|d_{z^2}\rangle$ states, namely [13,19,20]

$$|\varphi\rangle = \cos\theta|d_{x^2-y^2}\rangle + \sin\theta|d_{z^2}\rangle, \tag{1}$$

where θ is the mixing angle, an adjustable parameter. Eq. (1) means that the probabilities of $|d_{x^2-y^2}\rangle$ and $|d_{z^2}\rangle$ states in time are about $\cos^2\theta$ and $\sin^2\theta$, respectively.

Thus, averaged in time, the observed g factors g_i from Eq. (1) can be given by [13,19,20]

$$\begin{aligned} g_{//} &= \cos^2\theta g_{//}^{(elong.)} + \sin^2\theta g_{//}^{(comp.)}, \\ g_{\perp} &= \cos^2\theta g_{\perp}^{(elong.)} + \sin^2\theta g_{\perp}^{(comp.)}, \end{aligned} \tag{2}$$

in which the superscripts (*elong.*) and (*comp.*) denote the g_i values in the elongated and compressed $(CrO_4)^{3-}$ tetrahedra with the pure $|d_{x^2-y^2}\rangle$ and pure $|d_{z^2}\rangle$ ground states, respectively. Here, the $g_i^{(elong.)}$ of the elongated $(CrO_4)^{3-}$ cluster in silica glasses are calculated from the more reasonable and more exact high-order perturbation formulas based on the two-mechanism model with the pure $|d_{x^2-y^2}\rangle$ ground state. In the calculations, the needed CF energy levels are obtained from the CF theory [21] in which the CF parameters are estimated from the superposition model [22]. Thus, the optical band positions and the local structure of $(CrO_4)^{3-}$ cluster are estimated. The $g_i^{(comp.)}$ take [23]

$$g_{//} \approx 1.9936(5), \quad g_{\perp} \approx 1.9498(2), \tag{3}$$

the experimental values of compressed $(CrO_4)^{3-}$ cluster in Ca_2PO_4Cl crystal because they can be explained by using the high-order perturbation formulas based on the two-mechanism model with the pure $|d_{z^2}\rangle$ ground state [24]. Thus, from Eq. (2), the $g_{//}$ and $g_{\perp}$ of the $(CrO_4)^{3-}$ cluster (with the dominant tetragonal elongation) in silica glasses can be explained reasonably by adjusting the mixing

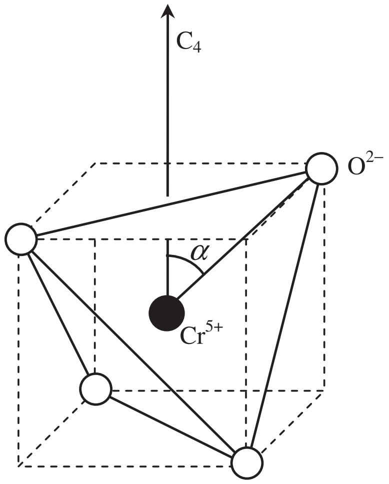

Fig. 1. The tetragonal distortion of $(CrO_4)^{3-}$ cluster in silica glasses.

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