Studies of the EPR g-Shift of [Cr(CN)\textsubscript{6}]\textsuperscript{3–} Clusters due to Crystal-Field and Charge-Transfer Mechanisms

Xiao-Xuan Wu\textsuperscript{a,c,d}, Wen-Ling Feng\textsuperscript{b,c}, Wang Fang\textsuperscript{e}, and Wen-Chen Zheng\textsuperscript{c,d}

\textsuperscript{a} Department of Physics, Civil Aviation Flying Institute of China, Guanghan 618307, P. R. China
\textsuperscript{b} Department of Applied Physics, Chongqing Institute of Technology, Chongqing 400050, P. R. China
\textsuperscript{c} Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
\textsuperscript{d} International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests to X.-X. W.; E-mail: wxxdd@163.com


The EPR g-shift \( \Delta g \approx g - g_e \) of the metal-cyanide cluster [Cr(CN)\textsubscript{6}]\textsuperscript{3–} is calculated by high-order perturbation formulas based on both the crystal-field (CF) and charge-transfer (CT) mechanisms (the latter is often neglected in the crystal-field theory). The result agrees with the experimental value. The sign of the g-shift \( \Delta g_{\text{CT}} \) due to the contribution of the CT mechanism is opposite to that of \( \Delta g_{\text{CF}} \) due to the contribution of the CF mechanism, and the absolute value of \( \Delta g_{\text{CT}} \) is about 34% of that of \( \Delta g_{\text{CF}} \). It appears that for transition metal ions in a strong covalent cluster, a reasonable theoretical explanation of the g-shift should take both the CF and CT mechanism into account.

1. Introduction

The EPR spectra of the metal-cyanide clusters [Cr(CN)\textsubscript{6}]\textsuperscript{3–} in crystals, such as alkali halides, have received interest [1 – 5]. It is found that within the cubic symmetry approximation, the g-factor of [Cr(CN)\textsubscript{6}]\textsuperscript{3–} clusters in various crystals is about 1.992(1) [1 – 5]. The small g-shift \( \Delta g \approx g - g_e \), where \( g_e \approx 2.0023 \) is the g-factor of the free electron, suggests that the covalence in [Cr(CN)\textsubscript{6}]\textsuperscript{3–} clusters is strong. In general, the contribution of covalence to the g-shift \( \Delta g \) comes from two effects: (i) The d electrons of the central 3d\textsuperscript{n} ion are mixed with the p electrons of ligands via the covalence effect, and so the spin-orbit (SO) coupling parameter of the ligand ion can contribute to the g-shift. In this case, a two-SO-parameter model (in which the contributions to the g-shift due to both the SO coupling parameter of the central 3d\textsuperscript{n} ion and that of ligands are included [6 – 8]) should be used. (ii) The strong covalence results in a lower charge-transfer (CT) energy level; thus the contribution to the g-shift \( \Delta g \) due to the mixture of the CT excited state with the ground state becomes larger, so that a reasonable explanation of the g-shift should take not only the crystal-field (CF) mechanism, but also the (CT) mechanism into account [9]. In [Cr(CN)\textsubscript{6}]\textsuperscript{3–} clusters, since the SO coupling parameter \( \zeta_0 \approx 49 \text{ cm}^{-1} \) [10] of the ligand ion C\textsubscript{4} is much smaller than that \( \zeta_0 \approx 273 \text{ cm}^{-1} \) [11] of the central ion Cr\textsuperscript{3+}, the second effect is more important. So, in this paper, we apply the complete high-order perturbation formula based on both mechanisms to calculate the g-shift \( \Delta g \) of [Cr(CN)\textsubscript{6}]\textsuperscript{3–} clusters in various crystals. The results (including the relative importance of the CT mechanism) are discussed.

2. Calculation

For an octahedral 3d\textsuperscript{n} MX\textsubscript{6} cluster, the one-electron basis functions based on the molecular orbital (MO) theory can be expressed as

\[
|\Psi\rangle = N^X_\gamma (|d_\gamma\rangle + \lambda^X_{\gamma} |p_\gamma\rangle),
\]

where \( |d_\gamma\rangle \) and \( |p_\gamma\rangle \) are the d orbitals of the central 3d\textsuperscript{n} ion and p orbitals of ligands, respectively. The superscript \( X = a \) or \( b \) stands for anti-bonding orbitals (related to CF-excited states) or bonding orbitals (related to CT-excited states). The subscript \( \gamma = t \) or \( e \) indicates the irreducible representation \( t_2g \) or \( e_g \) of the

0932-0784 / 07 / 0300-0218 $ 06.00 © 2007 Verlag der Zeitschrift für Naturforschung, Tübingen - http://znaturforsch.com
\( O_b \) group. \( \lambda^X_g \) and \( \lambda^X_e \) denote the normalization coefficients and the orbital mixing coefficients, respectively.

From the above functions, and by adding the SO coupling Hamiltonian \( H^S_{\text{SO}} \) and the Zeeman term \( H^S_{\text{Z}} \) based on the CT mechanism to the perturbation Hamiltonian in the CF mechanism, the complete high-order perturbation formula of the \( g \)-shift \( \Delta g \) including both the CF and CT mechanisms for the 3d\(^3\) ions in the cubic octahedral cluster, was derived as [9]

\[
\Delta g = \Delta g_{\text{CF}} + \Delta g_{\text{CT}},
\]

\[
\Delta g_{\text{CF}} = \frac{8k'_a a'_e}{3E_1} + \frac{4k'_a a'_e}{9E_1^2} + \frac{2k'_a a'_e}{9E_1^3} - \frac{4g_a a'_e}{9E_1^2} - \frac{4g_a a'_e}{9E_1^3} - \frac{4g_a a'_e}{9E_1^3} - \frac{4g_a a'_e}{9E_1^3},
\]

\[
\Delta g_{\text{CT}} = \frac{8k'_a a'_e}{3E_n},
\]

in which the zero-order energy denominators \( E_i \) related to the CF mechanism are

\[
E_1 = 10Dq, \quad E_2 = 15B + 5C,
\]

\[
E_3 = 9B + 3C + 10Dq,
\]

where \( Dq \) is the cubic field parameter and \( B \) and \( C \) are the Racah parameters. These parameters and the CT energy level \( E_n \) can be estimated from the optical spectra of the studied system. For \([\text{Cr(CN)}_6]^{3-}\) clusters, from the optical spectra including the \( d-d \) transitions and charge-transfer from ligand to metal (CTLM) transition [12, 13] (all these transitions are shown in Table 1 of [12]), we have

\[
B \approx 620 \text{ cm}^{-1}, \quad C \approx 2985 \text{ cm}^{-1},
\]

\[
Dq \approx 2700 \text{ cm}^{-1}, \quad E_n \approx 38600 \text{ cm}^{-1}.
\]

Since the one-electron basis functions include \( t_{2g} \) and \( e_g \) orbitals, the one-electron SO interaction involves two SO coupling parameters \( \zeta \) and \( \zeta' \). The parameter \( \zeta \) denotes the interaction only within \( t_{2g} \) orbitals, and \( \zeta' \) the interaction between \( t_{2g} \) and \( e_g \) orbitals. The differentiation between \( \zeta \) and \( \zeta' \) is related to the covalence of the studied cases. Similar cases can also occur in the orbital reduction factor. Thus,
the parameters in (5) and hence the $g$-shift $\Delta g$ can be calculated. We take $\lambda_4^\gamma = \lambda_4^\delta = \lambda_5^\delta$ for decreasing the number of adjustable parameters as the only adjustable parameter. By fitting the calculated $g$-shift $\Delta g$ of $[\text{Cr(CN)}_6]^{3-}$ to the experimental value, we obtain

$$\lambda_4^\gamma \approx -0.5038. \quad (8)$$

The other MO coefficients and the parameters in (5) are, respectively, shown in Tables 1 and 2. The comparison between the calculated and experimental $g$-shift $\Delta g$ is shown in Table 3.

### 3. Discussion

Table 2 shows that the parameter $\zeta$ and factor $k$ are indeed different from the corresponding parameter $\zeta'$ and factor $k'$, suggesting that the studied $[\text{Cr(CN)}_6]^{3-}$ clusters have strong covalence.

Table 3 shows that, if only the CF mechanism is considered, the calculated $g$-shift $\Delta g_{\text{CF}}$ of $[\text{Cr(CN)}_6]^{3-}$ clusters agrees poorly with the observed value, whereas, if the contribution $\Delta g_{\text{CT}}$ of the CT mechanism is added, the calculated $\Delta g_{\text{total}}$ is consistent with the observed value. The contribution $\Delta g_{\text{CT}}$ due to the CT mechanism is opposite in sign and about 34% in magnitude compared with the contribution $\Delta g_{\text{CF}}$ due to the CF mechanism. So, for $[\text{Cr(CN)}_6]^{3-}$ and other transition metal cyanide clusters $[\text{M(CN)}_6]^n-$, because of the strong covalence, a reasonable theoretical explanation of the $g$-shift (or other EPR parameters) should take both the CF and CT mechanism into account.

### Acknowledgements

This project was supported by the National Natural Science Foundation of China (Grant No. 10274054) and the CAAC Scientific Research Base of Civil Aviation Flight Technology and Safety.

---