Anharmonic $T \otimes \varepsilon$ Jahn-Teller coupling in $LiCaAlF_6:Cr^{3+}$

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For an octahedral system, we analyzed the coupling between triple degenerate electronic states of a transition metal ion and the double degenerate vibration of the ligands of the host matrix. The vibrations of the ligands of the lattice are described by new anharmonic coherent states of the Morse potential. For the linear coupling between electronic states and anharmonic vibrations, we built the matrix elements of the interaction Hamiltonian and corresponding energy levels.

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In the last twenty years, considerable attention has been paid to the linear octahedral Jahn-Teller system $T \otimes (\varepsilon + \tau_2)$, in which an electronic state T of the transition metal ion is equally coupled to the vibrational modes of the ligands ε and τ_2 of the ligands, each of which corresponds to a common angular frequency [1–5].

The strong coupling limit has been explored by means of the Glauber state by Judd [6], and Judd and Vogel [7]. The studies of the Jahn-Teller effect using coherent states as well as some applications to particular systems are well known [8–11].

In all cases, the coupling of double and triple degenerate electronic states with harmonic vibrations described by harmonic coherent states was considered. For the laser crystals doped with transitional metal ions, the vibronic interactions are higher than another types of interactions and explain the experimental data concerning vibronic transitions. This is the case of $LiCaAlF_6:Cr^{3+}$.

In the cluster model [12], for the Cr^{3+} ion incorporated in $LiCaAlF_6$ in an octahedral site, the interaction of the triple degenerate electronic state $^4T_2$ of d^3 configuration of the chromium ion with the τ_{2g} (three-dimensional) vibrations of the ligands of the ligands was neglected since the ε_g (two-dimensional) mode of the octahedron of the ligands interacts more strongly with the same electronic states of the ion.

This is true because the ε_g mode of an octahedron which involves the radial motion of the ligand ions can couple to σ-bonding orbitals and should therefore couple more strongly than the τ_{2g} modes high only involves the tangential motion and couple only to π-orbitals. Thus, here is present the vibronic $T \otimes \varepsilon$ interaction.

In this paper, we studied the general case of an octahedral Jahn-Teller system of the $T \otimes \varepsilon$ type having triple degenerate electronic states coupled with the double degenerate anharmonic vibrational states, the latter described by the Morse potential.

For the Morse oscillator [13,14], there are different types of coherent states [15]. We used these states in order to extend the analytical treatment of the Jahn-Teller effect of the $E \otimes \varepsilon$ interaction in Jahn-Teller octahedral symmetries [16] presented in our old paper to the case of the $T \otimes \varepsilon$ coupling for the same symmetry.

1. Hamiltonian of the system

The Hamiltonian of the octahedral Jahn-Teller $T \otimes \varepsilon$ system is

$$H = H_e + H_v + H_{JT}, \tag{1}$$

where H_e represent the Hamiltonian of the electronic part of the system, H_v is the Hamiltonian of a double Morse oscillator, and H_{JT} is the Hamiltonian of the Jahn-Teller interaction between the triple degenerate electronic state T of the metal ion and the double degenerate vibrations of the ligands of a laser crystal.

The electronic Hamiltonian of the system is well known. We denote with $|\theta\rangle$ and $|\varepsilon\rangle$ the uncoupled electronic wave-functions which transform according to two-dimensional irreducible representation of the octahedral group. In order to obtain an analytic expression for the quantities of interest, such as the energy of the levels of the Ham factors, it is necessary to use the wave functions of the Hamiltonian $H_e + H_v$ from Eq. (1). Such wavefunctions are products between the electronic wave functions $|\theta\rangle$, $|\varepsilon\rangle$ and the wave functions which describe the vibrations of ligands.

For the vibrations of ligands, we suppose that the vibration Hamiltonian H_v is described by

$$H_v = H_{v1} + H_{v2} = \sum_{k=1}^{2} \left[\frac{p_k^2}{2m} + V_0 (e^{-2\alpha x_k} - e^{-\alpha x_k}) \right], \tag{2}$$

where $\alpha > 0$ is the anharmonicity constant of the oscillator, m is the mass of the oscillator, p_k is the momentum operator of the k oscillator, x_k is the displacement from the equilibrium position of the k oscillator, and V_0 is a positive constant.

We use the notation ν

$$\nu = \sqrt{\frac{8mV_0}{\alpha^2 \hbar^2}} \tag{3}$$

and introduce the variables y_k

$$y_k = \nu \exp(-\alpha x_k), \quad k = 1, 2. \tag{4}$$

The energy levels of the single Morse oscillator described by $H_{\upsilon k}$ are

$$E_0(n_k) = -\hbar\Omega\left(n_k - \frac{\nu-1}{2}\right)^2, \tag{5}$$

where $k = 1, 2$; $\hbar\Omega = V_0/\nu^2$; $n_i = 0, 1, 2, \ldots, N = \left[\frac{\nu-1}{2}\right]$, with $[\mu]$ representing the entire part of μ.

The eigenfunctions of the Hamiltonian H_{0k} (where $k = 1, 2$) are

$$\psi_{n_k}(y_k) = c_k y^{s_i} e^{-y_k/2} F(-n_k, 2s_k + 1, y_k), \tag{6}$$

where $2s_k + 1 = \nu - 2n_k$, $c_k = \frac{1}{\Gamma(\nu-2n_k)}\sqrt{\frac{\Gamma(\nu-n_k)}{n_k!}}$ is a normalization constant, and F represents the confluent hypergeometric function.

The vibrational states of the two-dimensional Morse oscillator are

$$|n_1 n_2\rangle = \psi_{n_1}(y_1)\psi_{n_2}(y_2). \tag{7}$$

These states have the orthonormalization properties as follows

$$\langle n_1 n_2 | n_1' n_2' \rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'}. \tag{8}$$

In the linear approximation, the Jahn-Teller Hamiltonian of interaction H_{JT} has the form

$$H_{JT} = \varkappa\hbar\Omega(\mu^+\mu)^{(E)}(x_1 + x_2), \tag{9}$$

where $\varkappa$ is the strength of the Jahn-Teller coupling μ^+ and μ represents the creation and annihilation operators of the triple degenerate electronic states of the vibronic system. The label (E) indicate that the operators acts on the electronic states of the system.

2. The algebra of the anharmonic oscillator

In our previous papers [15], we have established the creation operator B_+, the annihilation operator B_-, and the operator B_0 for the one-dimensional Morse oscillator. The relults of [15] will be extended to the two-dimensional isotropic Morse oscillator by introducing the creation operators B_{+k}, the annihilatons operators B_{-k}, and the operators B_{0k} ($k = 1, 2$), which have the analytical expressions

$$B_{\pm k} = (2s_k \mp 1)\frac{\partial}{\partial y_k} \pm \frac{s_k(2s_k \mp 1)}{y_k} \mp \frac{\nu}{2}, \tag{10}$$

$$B_{0k} = -y_k\frac{\partial^2}{\partial y_k^2} - \frac{\partial}{\partial y_k} + \frac{s_k^2}{y_k} + \frac{y_k}{2} - s_k + \frac{\nu}{2} - 1. \tag{11}$$

The operators obey the commutation relations

$$[B_{+k}, B_{-l}] = 2B_{0k}\delta_{kl}, \quad [B_{\pm k}, B_{0l}] = \pm B_{\pm k}\delta_{kl}, \tag{12}$$

where $k, l = 1, 2$.

Instead of the operators (10) and (11), which are s_k dependent, we introduce new operators independent on s_k. For this reason, the dynamic system can be expressed with the aid of auxiliary variables $\xi_k \in [0, 2\pi]$ (where $k = 1, 2$) of the extra-phase type. According to this method, the new operators are

$$a_{\pm k} = e^{\mp i\xi_k}\left\{\left[\frac{2}{i}\frac{\partial}{\partial \xi_k} \mp 1\right]\frac{\partial}{\partial y_k} \pm \frac{1}{y_k}\left[\frac{1}{i}\frac{\partial}{\partial \xi_k}\left(\frac{2}{i}\frac{\partial}{\partial \xi_k} \mp 1\right)\right] \mp \frac{\nu}{2}\right\}, \tag{13}$$

$$a_{0k} = \frac{1}{i}\frac{\partial}{\partial \xi_k}. \tag{14}$$

The commutators of the operators a_{0k} and $a_{\pm k}$ are

$$[a_{+k}, a_{-l}] = 2a_{0k}\delta_{kl}, \quad [a_{\pm k}, a_{0l}] = \pm a_{\pm k}\delta_{kl}, \tag{15}$$

and

$$[a_{0k}, e^{\pm i\xi_l}] = \pm e^{\pm i\xi_k}\delta_{kl}, \tag{16}$$

where $k, l = 1, 2$.

The new eigenfunctions of the Hamiltonian H_{υ_i} will be

$$\Phi_{n_k}(y_k, \xi_k) = e^{is_k\xi_k}\psi_{n_k}(y_k), \tag{17}$$

instead of $\psi_{n_i}(y_i)$ given by (6).

The action of the operators $a_{\pm k}$, a_{0k} on the eigenstates Φ_{n_k} is

$$a_{+l}\Phi_{n_k}(y_k, \xi_k) = \sqrt{(n_k+1)(\nu - n_k - 1)}\Phi_{n_k+1}(y_k, \xi_k)\delta_{kl},$$
$$a_{-l}\Phi_{n_k}(y_k, \xi_k) = -\sqrt{n_k(\nu - n_k)}\Phi_{n_k-1}(y_k, \xi_k)\delta_{kl},$$
$$a_{0l}\Phi_{n_k}(y_k, \xi_k) = s_k\Phi_{n_k}(y_k, \xi_k)\delta_{kl}, \tag{18}$$

where $k, l = 1, 2$.

The Hamiltonian H_υ can be expressed in terms of the operators a_{01} and a_{02}

$$H_\upsilon = -\hbar\Omega(a_{01}^2 + a_{02}^2). \tag{19}$$

3. The Jahn-Teller interaction

In order to express the Jahn-Teller interaction Hamiltonian H_{JT} in terms of the dynamic group operators $\{a_{\pm 1}, a_{\pm 2}, a_{01}, a_{02}\}$, we start with the relations [16]

$$\frac{\partial}{\partial y_k} = -\frac{1}{2}\sum_{n=0}^{\infty}(2a_{0k})^n \times \left[e^{i\xi_k}a_{+k} + \frac{\nu}{2} - (-1)^n\left(e^{-i\xi_k}a_{-k} - \frac{\nu}{2}\right)\right], \tag{20}$$

$$\frac{1}{y_k} = -\sum_{n=0}^{\infty}(2a_{0k})^{n-1} \times \left[e^{i\xi_k}a_{+k} + (-1)^n e^{-i\xi_k}a_{-k} + \frac{\nu}{2}[1 - (-1)^n]\right]. \tag{21}$$

The coordinate x_k from the Hamiltonian (9) can be written as

$$x_k = \frac{1}{\alpha}[\ln\nu - \ln y_k] = \frac{\ln\nu}{\alpha} - \frac{1}{\alpha}\sum_{n=1}^{\infty}\frac{1}{n}\left(1-\frac{1}{y_k}\right)^n$$
$$= \frac{1}{\alpha}\left\{\ln\nu - \sum_{n=1}^{\infty}\frac{1}{n}\left[1+\nu\sum_{m=0}^{\infty}(2a_{0k})^{2m}\right.\right.$$
$$\left.\left.+\sum_{m=0}^{\infty}(2a_{0k})^{m-1}(e^{i\xi_k}a_{+k}+(-1)^m e^{-i\xi_k}a_{-k})\right]^n\right\}. \quad (22)$$

The Hamiltonian H_{JT} in terms of $a_{\pm k}$ and a_{0k} operators has the final form

$$H_{JT} = \frac{1}{\alpha}\varkappa\hbar\Omega(\mu^+\mu)^{(E)}$$
$$\times\left\{2\ln\nu - \sum_{k=1}^{2}\sum_{n=0}^{\infty}\frac{1}{n}\left[1+\nu\sum_{m=0}^{\infty}(2a_{0k})^{2m}\right.\right.$$
$$\left.\left.-\sum_{m=0}^{\infty}(2a_{0k})^{m-1}[e^{i\xi_k}a_{+k}+(-1)^n e^{-i\xi_k}]\right]^n\right\}. \quad (23)$$

4. The coherent states

For the Morse oscillator, different kinds of coherent states [15,17] can be built. Form among the two types of coherent states are useful to the study of the Jahn-Teller interaction.

The first-type states are the displacement-operator coherent states defined as the states obtained by action of the displacement operator D on the vacuum state of the one-dimentional Morse oscillator

$$|\alpha\rangle = D(\alpha)|0\rangle = \exp[i(\alpha a_+ - \alpha^* a_-)]|0\rangle, \quad (24)$$

where $\alpha \in C$ is the complex valued parameter.

We extended these states to the case of the Morse double-oscillator as

$$|\alpha\rangle = D(\alpha_1)D(\alpha_2)|00\rangle$$
$$= \exp[i(\alpha_1 a_{+1} - \alpha_1^* a_{-1})]\exp[i(\alpha_2 a_{+2} - \alpha_2^* a_{-2})]|00\rangle,$$

where $\alpha_1, \alpha_2 \in C$ and $|n_1 n_2\rangle = |n_1\rangle|n_2\rangle$.

Another type of coherent states are the annihilation operator coherent states, designed by $|\lambda\rangle$ (where $\lambda \in C$). These are the states which have the following property

$$a_-|\lambda\rangle = \lambda|\lambda\rangle. \quad (25)$$

For the one-dimensional Morse oscillator, these states are

$$|\lambda\rangle = c_0\sum_{n=0}^{N}\frac{(-1)^n(\lambda a_+)^n}{n!(\nu-n)_n}|0\rangle, \quad (26)$$

where

$$c_0 = \left(\sum\frac{|\lambda|^{2n}}{n!(\nu-n)_n}\right)^{-1/2}$$

is the normalization constant.

The states (25) also can be extended to the Morse double-oscillator case. We denote these states $|\lambda\rangle = |\lambda_1\rangle|\lambda_2\rangle$, where $\lambda_1, \lambda_2 \in C$.

The general expression for these coherent states is

$$|\lambda\rangle = |\lambda_1\rangle|\lambda_2\rangle$$
$$= c_0^2\sum_{n,m=0}^{M}\frac{(-1)^n(\lambda_1 a_{+1})^n}{n!(\nu-n)_n}\,\frac{(-1)^m(\lambda_2 a_{+2})^n}{m!(\nu-m)_m}|00\rangle.$$

5. The generalized coherent states and the Jahn-Teller interaction

In order to establish the states which corresponds to non-vanishing average values of the H_{JT} energy, Judd [6] generalized the coherent states (24) introducing the wavefunctions of the electron-phonon system with vibronic interaction. For the case of an $E\otimes\varepsilon$ system Judd defined its coherent states as the overlap

$$|\beta nz\rangle = \int_0^{2\pi} d\varphi|\beta\rangle e^{iz\varphi}e^{i\varkappa b+}(b^+-\varkappa)^n|00\rangle, \quad (27)$$

where β refers to the lower branch ($\beta = l$) or to the upper branch ($\beta = u$).

Thus,

$$|l\rangle = \cos\frac{\varphi}{2}|\theta\rangle - \sin\frac{\varphi}{2}|\varepsilon\rangle, \quad (28)$$

$$|u\rangle = \sin\frac{\varphi}{2}|\theta\rangle + \cos\frac{\varphi}{2}|\varepsilon\rangle, \quad (29)$$

and the creation operator b^+ is defined by

$$b^+ = a_{+1}^{HO}\cos\varphi + a_{+2}^{HO}\sin\varphi. \quad (30)$$

The operators $a_{\pm k}^{HO}$ are the creation and annihilation operators for the double harmonic oscillarot, φ is an arbitrary angle, and the parameter z is (27) caracterized the type of coupling. For example, $z = 1/2$ corresponds to the states accesible be electric dipole radiation from the zero-phonon ground state.

Thus, the generalized coherent states (27) correspond to the case of Jahn-Teller interaction in the presence of harmonic vibrations. In their papers, Judd [6] and Chancey [8,9] studied the Jahn-Teller interaction for the systems with different symmetries in harmonic approximation.

Now we generalized the results of Judd and Chancey for the case of Morse anharmonic vibrations, considering instead of the creation and the annihilation operators for harmonic oscillator, the corresponding operators for Morse oscillator (13) and (14).

The first result was reported in [16], where we studied the case of $E\otimes\varepsilon$ for anharmonic vibrations.

For the anharmonic vibrations in (30), instead of the operators $a_{\pm k}^{HO}$ we use the corresponding operators $a_{\pm k}$, introduced in (13), corresponding to the Mose oscillators. Thus the operator b^+ became

$$b^+ = a_{+1} \cos\varphi + a_{+2} \sin\varphi, \quad (31)$$

where the operators $a_{\pm k}$ are given in (13).

We note that the operators (30) and (31) act on a state $|n\rangle$ of the double anharmonic oscillator defined by

$$|n\rangle = |n_1 + n_2\rangle = |n_1\rangle|n_2\rangle. \quad (32)$$

We will define a new set of generalized anharmonic coherent states as follows

$$|\beta nz\rangle = \int_0^{2\pi} d\varphi |\beta\rangle e^{i\varphi z}(b^+ - \varkappa)^n|\varkappa\rangle, \quad \text{with } \varkappa \in C, \quad (33)$$

where $|\beta\rangle$ are the electronic states of the system, and can be $\beta = (jmu)$, or $\beta = (jml)$, with $j = 1$ and $m = 0, \pm 1$. l refers to the lower branch and u to the upper branch of the electronic states. As in (27), z represents a coupling parameter.

In (33), $|\varkappa\rangle$ represents the annihilation operator coherent states

$$|\varkappa\rangle = c_0 \sum_{n=0}^{N} \frac{(-1)^n(\varkappa b_+)^n}{n!(\nu - n)_n}|0\rangle, \quad (34)$$

where the state $|0\rangle$ represents the state $|n\rangle$ from (32) for $n = 0$.

In the case $z = 0$, the states (33) correspond to the uncoupled case

$$|\beta nz\rangle_0 = |\beta\rangle(b - \varkappa)^n|\varkappa\rangle. \quad (35)$$

We can expand the states $|\beta nz\rangle$ in terms of uncoupled $|\beta nz\rangle_0$ states as follows

$$|\beta nz\rangle = c_0 \sum_{l=0}^{N}\sum_{j=0}^{n} \int_0^{2\pi} d\varphi e^{i\varphi\nu}|\beta\rangle,$$

$$C_n^j \frac{(-1)^{l+j}\varkappa^{l+j}(b^+)^{n+l-j}}{j!(\nu - j)_j}|0\rangle$$

$$= c_0 \sum_{l=0}^{N}\sum_{j=0}^{n} C_n^j \frac{(-1)^{l+j}\varkappa^{l+j}}{j!(\nu - j)_j}|\beta, n + l - j, z\rangle_0. \quad (36)$$

The states (36) give the possibility to calculate the average value of the Jahn-Teller interaction energy. We obtain

$$E_{JT} = c_0^2 \sum_{l=0}^{N}\sum_{j=0}^{n}\sum_{l'=0}^{N}\sum_{j'=0}^{n} C_n^j C_n^{j'} \frac{(-1)^{l+j}\varkappa^{l+j}}{j!(\nu - j)_j}\frac{(-1)^{l'+j'}\varkappa^{l'+j'}}{j!(\nu - j')_{j'}}$$

$$\times\, {}_0\langle\beta, n + l' - j', z|H_{JT}|\beta, n + l - j, z\rangle_0. \quad (37)$$

The final form of Eq. (37) is

$$E_{JT} = \frac{1}{\alpha}\varkappa\hbar\Omega c_0^2 \sum_{l=0}^{N}\sum_{j=0}^{n} \frac{|\varkappa|^{2(j+l)}(C_n^j)^2}{[j!(\nu - j)_j]^2}\, {}_0\langle\beta|(\mu^+\mu)^{(E)}|\beta\rangle$$

$$\times \left\{2\ln\nu - \sum_{k=1}^{2}\sum_{p=0}^{\infty}\frac{1}{p}\left[1 + \nu\sum_{m=0}^{\infty}(s_{n+l-j})^{2m}\right]\right\}. \quad (38)$$

Thus, we studied the vibronic coupling between triple degenerate electronic states of the transition metal ion, incorporated in a crystal laser, and double degenerate vibration states of the ligands of crystal for the octahedral symmetry.

We introduced a new type of coherent states by generalizing annihilation operator coherent states in order to describe the vibrations of ligands.

We used a new representation of the dynamic group of the system by introducing an auxiliary variable ξ_k of extra-phase type. In this representation, the eigenfunctions, the observables, and the Hamiltonian of anharmonic vibration were expressed. The eigenfunctions of the Hamiltonian of the system, in the absence of interaction, are built using the overlap of the electronic states and these new anharmonic coherent states.

The results show that the anharmonic effects on Jahn-Teller interaction can be expressed in a rigurous form which contain the dependence on the anharmonicity of the system.

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