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Vibrational Raman scattering induced by Jahn-Teller systems in polar crystals

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The first-order vibrational Raman spectra due to Jahn-Teller impurities in a cubic-symmetry site are studied, and the contribution of the phonon densities of states to the Raman cross section in different polarization geometries is given. The case of a Γ_3^+ electronic doublet at a cubic crystal site is treated in detail.

I. INTRODUCTION

Recently particular attention has been paid to the Raman scattering induced by transitions between vibronic levels of Jahn-Teller (JT) impurities in polar crystals.[1,2] Such levels, generated by the interaction between the JT impurity electron in its degenerate ground state and the crystal vibrations,[3-5] have been seen as giving structures at low frequency in the Stokes region of the impurity-induced Raman spectra in CaO : Cu^{2+},[1] Al_2O_3 : Ni^{3+},[2] and BaF_2 : Eu^{2+}.[6] In the same Raman spectra, besides the structure due to the vibronic levels, it is possible to observe the vibrational structure[7] due to the first-order contribution of the phonon densities of states transforming according to the irreducible representations of the point group of the impurity-site symmetry in the rigid lattice. The vibronic contribution to the total Raman spectra falls in the low-frequency region and can be separated at low temperature from the contribution due to the phonon densities, when in the same region the phonon densities involved are flat and low in intensity (such as the alkaline-earth oxides and fluorides).

The two kinds of structures come from two independent Raman processes, which involve a different excitation, either a vibron or a phonon, when the lowest-order approximation is considered (linear electron-phonon interaction, harmonic lattice dynamics, few excitations involved).

The vibronic levels are determined by the JT-active linear electron-phonon (EP) interaction in the degenerate space of the ground electronic state of the impurity. They are due to a "rotational motion" inside this space, associated with the angular components of the JT-active symmetry modes, when the polar-coordinate representation is adopted.[3,4] Such a motion has been studied[5] with an effective Hamiltonian where the EP interaction is integrated over all the lattice vibration frequencies, and the energy spectrum is found to be discrete. The vibron is an excitation of this "rotational motion."

The vibrational energy spectrum is related to the details of the local perturbed lattice dynamics through the phonon densities of states.

The identification of the processes giving rise to the vibrational spectra in the Raman scattering and of the physical quantities supporting such processes for JT impurities is the aim of the present paper. Here we deduce the vibrational first-order contribution to the Raman cross section and present the results for the phonon-density symmetries and the selection rules involved in polarized spectra. We refer instead to Ref. 1 for the corresponding discussion about the vibronic spectra.

In Sec. II the electron-phonon interactions which create the phonons involved in the first-order spectra are identified and the assumptions made are discussed.

In Sec. III the first-order Raman cross section is reported. In Sec. IV symmetry arguments are applied to determine which phonon densities are present in the first-order Raman spectra, and in Sec. V the relations between the Raman intensities for different polarization are obtained. In Sec. VI the case of a JT impurity whose electronic ground state transforms according to the Γ_3^+ irreducible representation of the O_h point group is considered in detail.

A main result of the present work is that the symmetries of the phonons involved in a given polarized scattering geometry are found to obey new relations[8] with respect to the case of an impurity with a nondegenerate ground state.[9,10]

To our knowledge, such selection rules have been studied only for systems whose electronic ground state has been assumed to be a singlet state. They have been deduced for molecules and perfect crystals[9] as well as for impurities in crystals,[10] and are widely used. One consequence of the assumption that the ground state is a singlet state is that for impurities in solids the selection rules are found to depend only on the symmetry of the impurity site, and not on the detailed electronic structure of the impurity. Here we extend the theory to examine impurities with a degenerate ground state, such as the JT impurities. We show that one cannot identify the symmetry of the phonon density of states involved in the spectra in the usual way. In particular, the selection rules now depend on both the site symmetry and the electronic structure of the impurity. These results are important for a variety of systems, and are subject to straightforward experimental verification. We refer the reader to Engleman[4] for a discussion of the JT ion properties in general; to Abragam and Bleaney[11] for the properties of the JT rare-earth and transition-metal ions.

Unfortunately, the phonon contribution to the scattering has not been fully analyzed experimentally in the spectra reported in Refs. 1, 2, and 6. For this reason we cannot check the theory we present here with those experimental results.

The theory presented in Secs. II–VI can be applied to impurities whose ground state is degenerate, without actually discriminating the simple orbital degeneracy either from the total momentum degeneracy or from the simple spin degeneracy without orbital degneracy. Of course the last case is not that of a JT impurity, but it could concern impurities, such as *F* center in some alkali halides, which shows interesting and unusual behavior with respect to the Raman scattering[12,13] as do the JT impurities.

II. VIBRATIONAL RAMAN SCATTERING

In the problem we are considering the JT impurity is initially in its degenerate relaxed ground state at the thermal equilibrium with the lattice. This means that the linear EP interaction relative to the pure electronic degenerate ground state (i.e., the JT interaction[3-5]) has already been considered in defining the relaxed ground state and no residual linear interaction is left. In other words all the forces acting on the ions in the lattice are in equilibrium. The forces on each ion surrounding the JT impuritiy are essentially of two types: the direct forces between each ion and the electron of the JT impurity, and the forces between ions, supported directly by the ion-ion interaction and indirectly by the ion-core electrons interaction. At $T=0$ °K, the ground state has the symmetry and the degeneracy of the pure electronic ground state and neither phonons or vibrons are present.

In the off-resonance Raman scattering the electron (optical electron) of the impurity undergoes a virtual transition from a relaxed ground state to the excited states. At the same time, due to the transition, the ground state remains without the electron. All these states considered are in the equilibrium lattice configuration of the relaxed ground state (initial configuration). We describe this situation with a model in which the optical electron is in one of the excited states and there is a missing electron, i.e., a hole, in the ground state, both interacting with the ions. In fact, the direct interaction between the lattice and the electron is changed with respect to the initial situation of the JT impurity. The transition thus induces net forces on the ions around the impurity. These forces define the electron-lattice and hole-lattice interactions, that in the vibrational Raman scattering induce creation or annihilation of phonons. In particular, the first-order Raman processes can be divided in two classes.

(i) The processes arising from the *intrastate EP interaction* in which a phonon, emitted or absorbed, can induce mixing between the levels inside the degeneracy of the excited state, if degenerate, and of the hole, without any mixing between different states. This interaction is actually the difference between the EP interaction evaluated on the excited states and the hole-lattice interaction in the ground state.

(ii) The processes arising from the *interstate EP interaction*, in which a phonon is able to induce a transition among different electron states of the same parity. This EP interaction which mix together the excited states is, in the following, assumed not to involve the hole. Since in nonresonant conditions the interstate and the intrastate interactions can give comparable contributions to the Raman cross section,[14] both processes (i) and (ii) will be considered in the present paper.

III. VIBRATIONAL RAMAN CROSS SECTION: FIRST-ORDER SPECTRA

In order to deduce the vibrational Raman cross section from a JT impurity, we use the perturbation theory introduced in the nondegenerate case,[9,10] taking into account the modifications which arise from the fact that the ground state is in its degenerate relaxed state. We can still use the expressions deduced by Loudon,[9] provided one keeps in mind that the total EP interaction is zero when the electron is in its degenerate ground relaxed state. Then the EP interactions entering the problem are only the EP interactions for the electron in the excited states and for the hole in the ground state, and the EP interactions which mix the different electronic states. Otherwise the perturbative theory used by Loudon is no longer valid. Then the only difference between the JT case and the nondegenerate case lies in the fact that by following the response theory for degenerate states the trace (indicated by $\mathrm{Tr}|\cdots|$) over the initial degenerate ground state must be performed in obtaining the Raman cross section.

We indicate as usual by $d^2\sigma/d\Omega\, d\omega$ the differential cross section per solid angle Ω, and frequency shifted by ω from the incident light frequency ω_L. The first-order contribution to $d^2\sigma/d\Omega\, d\omega$ is related to $\vec{\mathcal{P}}'(\Gamma\gamma)$,[15] i.e., to the first derivative of the polarizability $\vec{\mathcal{P}}[\{u\}]$ with respect to the symmetrized ionic displacement $u(\Gamma\gamma)$, evaluated in the equilibrium position of the ions when the electron is in the relaxed ground state. The $u(\Gamma\gamma)$ are the combinations of the defect neighbor displacements transforming according to the irreducible representation Γ (partner γ) of the symmetry point group of the impurity site.[16] One obtains

$$\left(\frac{d^2\sigma}{d\omega d\Omega}\right)_V \sim \sum_{\Gamma\gamma} \mathrm{Tr}\,|\vec{n}^L\cdot\vec{\mathcal{P}}'(\Gamma\gamma)\cdot\vec{n}^R|^2\rho(\Gamma,\omega^2)\,. \qquad (1)$$

Here $(\cdots)_V$ means that only the vibrational contribution to the differential Raman cross section has been considered. $\vec{n}^L$ and $\vec{n}^R$ are the polarization vectors of the incident and scattered linearly polarized light, respectively. $\rho(\Gamma,\omega^2)$ is the density of one-phonon states[16] transforming according to the Γ irreducible representation.

In order to define $\vec{\mathcal{P}}'(\Gamma\gamma)$ [whose components we call $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$, $\alpha,\beta=x,y,z$] we use the perturbative approach used in Eq. (14) of Ref. 9. There the sum over the α and β states[17] in Eq. (14) is performed only on the virtual excited electronic states of the system considered: then in no case α and β[17] can be the initial and the final states of the systems, i.e., the ground relaxed state and the ground relaxed state plus one phonon. Moreover, for simplicity, we do not consider in the following any contribution coming from the phonon-induced mixing between the ground state and the excited states. This assumption does not change the results presented here because the contributions deleted in this way [i.e., the contributions coming from the first two and the last two terms in Eq. (14) of Ref. 9] give only negligible contribution in the example considered in detail in Sec. VI. In Appendix A we give the complete expression of the derivative of the polarizability taking into account those terms.

The derivation of $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$ is performed in the one-effective-particle approximation, with the assumptions stated in the previous sections. Furthermore, we do not take into account the interaction between the hole left in the ground state and the electron in one of the excited states. $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$ is given as follows:

$$\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)=\sum_{mm'}[\mathfrak{M}^0_\alpha(gm)\mathfrak{F}^e_{\Gamma\gamma}(mm')(\delta_{mm'}-1)\mathfrak{M}^0_\beta(m'\beta)-\mathfrak{M}^0_\alpha(gm)\mathfrak{F}^e_{\Gamma\gamma}(mm)\mathfrak{M}^0_\beta(mg)+\mathfrak{M}^0_\alpha(gm)\mathfrak{M}^0_\beta(mg)\mathfrak{F}^h_{\Gamma\gamma}(gg)]$$

$$\times\left(\frac{1}{(\omega_{m'g}-\omega_L)(\omega_{mg}-\omega_L)}+\frac{1}{(\omega_{m'g}+\omega_L)(\omega_{mg}+\omega_L)}\right)\,. \qquad (2)$$

We indicate by $|g\rangle$ the degenerate relaxed electronic state (degeneracy n_g and energy E_g); by $|m\rangle$ and $|m'\rangle$ the excited electronic states (degeneracy n_m and $n_{m'}$ and energies E_m and $E_{m'}$ respectively).

$\mathfrak{M}^0_\alpha(gm)$ are the radiation dipole moments of the virtual transition between the electronic ground state $|g\rangle$ and the electronic excited state $|m\rangle$. The usual definition of the dipole moments can be adopted with no change to degenerate initial-state case[18] provided it is understood that the symbols $|g\rangle$, $|m\rangle$, etc., in the following mean a set of ordered levels inside the manifold spaces of the ground and excited states, respectively. $\mathfrak{M}^0_\alpha(gm)$, given by

$$\mathfrak{M}^0_\alpha(gm)=e\langle g|\alpha|m\rangle \quad (\alpha=x,y,z)\,, \qquad (3)$$

are the $n_g\times n_m$ matrices. Here e is the electronic charge. In Appendix B, we report the matrices $\mathfrak{M}^0_\alpha(gm)$ and their elements for the case considered in detail in Sec. VI.

$\mathfrak{F}^e_{\Gamma\gamma}(mm')$ are the *interstate* EP interaction forces, transforming according to the Γ irreducible representation (partner γ) of the point symmetry group considered, which mixes the state $|m\rangle$ with the state $|m'\rangle$. As for the dipole moments, we adopt the matrix notation to represent such forces. They are $n_m\times n_{m'}$ matrices given by

$$\sum_{\Gamma\gamma}\mathfrak{F}^e_{\Gamma\gamma}(mm')u(\Gamma\gamma)=\langle m|\mathcal{H}_{\mathrm{EP}}|m'\rangle\;, \qquad (4)$$

where $\mathcal{H}_{\text{EP}}$ is the linear contributions to the interaction Hamiltonian between the electron and the lattice.

$\mathcal{F}^{e}_{\Gamma\gamma}(mm)$ are the *intrastate* EP interaction forces on the states $|m\rangle$ in the lattice configuration of the relaxed ground state. They are $n_m \times n_m$ matrices given by

$$\sum_{\Gamma\gamma} \mathcal{F}^{e}_{\Gamma\gamma}(mm)u(\Gamma\gamma) = \langle m\,|\mathcal{H}_{\text{EP}}\,|m\rangle \ . \tag{5}$$

$\mathcal{F}^{h}_{\gamma}(gg)$ are the *intrastate* EP interaction forces between the lattice and the hole left in the ground state in the initial lattice configuration. They are $n_g \times n_g$ matrices, given by

$$\sum_{\Gamma\gamma} \mathcal{F}^{h}_{\Gamma\gamma}(gg)u(\Gamma\gamma) = \langle g\,|\mathcal{H}_{\text{EP}}\,|g\rangle \ . \tag{6}$$

We give in Appendix B as an example, the matrices $\mathcal{F}^{e}_{\Gamma\gamma}(mm)$, $\mathcal{F}^{e}_{\Gamma\gamma}(mm')$, $\mathcal{F}^{h}_{\Gamma\gamma}(gg)$, and their matrix elements for the case considered in Sec. VI.

ω_{mg} and $\omega_{m'g}$ are the energies ($\hbar = 1$) of the excited states E_m with respect to the energy of the ground state E_g. From Eq. (2) it follows that $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$ is a matrix $n_g \times n_g$.

By using the quantities introduced before, we obtain for the first-order differential Raman cross section the following expression:

$$\left(\frac{d^2\sigma}{d\omega\, d\Omega}\right)_V \sim \sum_{\Gamma\gamma} \mathrm{Tr}\left| \sum_{\alpha\beta} \sum_{mm'} \{ n^L_\alpha [\mathfrak{M}^0_\alpha(gm)\mathcal{F}^{e}_{\Gamma\gamma}(mm')(\delta_{mm'} - 1)\mathfrak{M}^0_\beta(m'g) - \mathfrak{M}^0_\alpha(gm)\mathcal{F}^{e}_{\Gamma\gamma}(mm)\mathfrak{M}^0_\beta(mg) + \mathfrak{M}^0_\alpha(gm)\mathfrak{M}^0_\beta(mg)\mathcal{F}^{h}_{\Gamma\gamma}(gg)] n^R_\beta \} \left(\frac{1}{(\omega_{m'g} - \omega_L)(\alpha_{mg} - \omega_L)} + \frac{1}{(\omega_{m'g} + \omega_L)(\omega_{mg} + \omega_L)} \right) \right|^2 \rho(\Gamma, \omega^2) \ . \tag{7}$$

IV. SYMMETRY CONSIDERATIONS

By using symmetry considerations, we derive now from Eq. (2) which irreducible representation Γ of the densities of phonon states is involved in the first-order Raman scattering, given in Eqs. (1) and (7).

We call Γ_d, Γ_g, and Γ_m the irreducible representations according to which the dipole moment, the ground-state wave function, and the excited-state wave function, respectively, transform. Group theory states that the matrices which appear in Eq. (10), i.e., $\mathfrak{M}^0_\alpha(gm)$ and $\mathfrak{M}^0_\beta(m'g)$ [given in Eq. (3)] and $\mathcal{F}_{\Gamma\gamma}(mm')$ [given in Eqs. (4) and (5)] are different from zero only if the following relations hold:

$$\Gamma_g \times \Gamma_d \in \Gamma_m \text{ or } \Gamma_{m'} \ , \tag{8a}$$

$$\Gamma^2_m \in \Gamma \text{ or } \Gamma_m \times \Gamma_{m'} \in \Gamma \ . \tag{8b}$$

We may combine these two conditions into

$$(\Gamma^2_d \times \Gamma^2_g)_S \in \Gamma \ , \tag{9}$$

the irreducible representation Γ appearing in Eq. (9) must be contained in the symmetrized direct product $(\Gamma^2_d \times \Gamma^2_g)_S$.[19] This result includes also the condition on the irreducible representation for hole-lattice interaction forces $\mathcal{F}^{h}_{\Gamma\gamma}(gg)$ of Eq. (6), as one can see from Eq. (2). Note that the symmetry of the excited states is ineffective in determining the symmetry Γ of Eq. (9).

Let us consider Eq. (9) for impurities at a site of O_h symmetry, because there a high electronic degeneracy can occur. We recall that Γ_d transforms according to Γ^-_4 and

$$\Gamma^2_d = \Gamma^+_1 + \Gamma^+_3 + \Gamma^+_4 + \Gamma^+_5 \ , \tag{10}$$

where Γ^+_1, Γ^+_3, and Γ^+_5 represent the symmetric part of the direct product.

If the ground state is a singlet state $\Gamma^2_g = \Gamma^+_1$, so that from Eqs. (9) and (10) one gets that $\tilde{\mathcal{P}}'(\Gamma\gamma)$ must transform according to Γ, where

$$\Gamma = \Gamma^+_1, \Gamma^+_3, \Gamma^+_5 \ . \tag{11}$$

This is a well-known result that can also be obtained by symmetry arguments alone about the defect neighbors dynamics.[10] However, because the same symmetry arguments must work when the ground electronic state is degenerate, the irreducible representations involved in the JT case must be those of Eq. (11). This result too comes from Eqs. (9) and (10), since on one hand Γ^2_g always contains the identity representation Γ^+_1, so that the symmetric representation in Eq. (10) must be involved and, on the other hand, Γ^2_g does not introduce other irreducible representations into the symmetrized direct product of Eq. (9) but those of Eq. (11).

Therefore, the first-order Raman spectra induced by JT impurities are weighted superpositions of the same phonon densities $\rho(\Gamma, \omega^2)$ which are involved in the nondegenerate case. However, *the superposition is different in the two cases.* This is an important consequence of Eq. (9), as will be shown in Sec. V.

V. POLARIZATION SELECTION RULES

We present now the polarization selection rules for a O_h point group. We analyze first which irreducible components of Γ_g^2 are involved in a given scattering geometry and by using linearly polarized light. We write the irreducible representations in Eq. (10) as matrices in the real space x, y, z by noting that their representation is the same as that in the linear vector space spanned by the eigenfunctions of the threefold degenerate Γ_4^- state (given for instance in Ref. 4, pp.59–60). The scalar product $\vec{n}^L \cdot \Gamma_1^+ \cdot \vec{n}^R$, etc., for all the components of Γ_g^2 given in Eq. (10), can be evaluated and it is easily recognized that the Γ_1^+ and Γ_3^+ components contribute to the $\vec{n}^L[100]$ and $\vec{n}^R[100]$ polarization geometry (hereafter indicated by $[100]\rightarrow[100]$); the Γ_3^+ and Γ_4^+ components to the $[110]\rightarrow[1\bar{1}0]$ geometry; the Γ_4^+ and Γ_5^+ components to the $[100]\rightarrow[010]$ geometry. Thus

$$\vec{n}^L \cdot \Gamma_g^2 \cdot \vec{n}^R \in \begin{cases} \Gamma_1^+ + \Gamma_3^+ & \text{when } \vec{n}^L \,\|\, [100],\ \vec{n}^R \,\|\, [100] \\ \Gamma_3^+ + \Gamma_4^+ & \text{when } \vec{n}^L \,\|\, [110],\ \vec{n}^R \,\|\, [1\bar{1}0] \\ \Gamma_4^+ + \Gamma_5^+ & \text{when } \vec{n}^L \,\|\, [100],\ \vec{n}^R \,\|\, [010]. \end{cases} \tag{12}$$

Finally, we put the results of Eq. (12) in Eq. (9). One gets that a Γ-type phonon density $\rho(\Gamma, \omega^2)$ is involved in the Raman scattering for a given polarization geometry, only if it is contained in the symmetrized direct product, as follows:

$$\begin{aligned} &\Gamma \in [\Gamma_g^2 \times (\Gamma_1^+ + \Gamma_3^+)]_S \quad \text{when } \vec{n}^L \,\|\, [100],\ \vec{n}^R \,\|\, [100] \\ &\Gamma \in [\Gamma_g^2 \times (\Gamma_3^+ + \Gamma_4^+)]_S \quad \text{when } \vec{n}^L \,\|\, [110],\ \vec{n}^R \,\|\, [1\bar{1}0] \\ &\Gamma \in [\Gamma_g^2 \times (\Gamma_4^+ + \Gamma_5^+)]_S \quad \text{when } \vec{n}^L \,\|\, [100],\ \vec{n}^R \,\|\, [010]. \end{aligned} \tag{13}$$

Equation (13) holds also for non-JT impurities. In this case the ground state is not degenerate and $\Gamma_g^2 = \Gamma_1^+$. Therefore, from Eq. (13) the $\rho(\Gamma, \omega^2)$ contributing to the first-order Raman spectra are $\rho(\Gamma_1^+, \omega^2)$ and $\rho(\Gamma_3^+, \omega^2)$ in the $[100]\rightarrow[100]$ polarization geometry; $\rho(\Gamma_3^+, \omega^2)$ in the $[110]\rightarrow[1\bar{1}0]$ geometry; and $\rho(\Gamma_5^+, \omega^2)$ in the $[100]\rightarrow[010]$ geometry.

The selection rules reported above are also valid *mutatis mutandis* when the local site symmetry of the impurity center is T_d.

VI. JT IMPURITY WITH A Γ_3^+ ELECTRONIC GROUND STATE

We examine in particular the Raman cross section for different scattering geometries induced by an impurity in the local-site symmetry group O_h, whose electronic ground state transforms according to Γ_3^+. Such is the case of the impurities whose experimental Raman scattering spectra are reported in Refs. 1 and 2. This case is particularly interesting because the vibronic levels are determined by the ground-state EP interaction transforming according to Γ_3^+ which is JT active ($\Gamma_3^+ \times \Gamma_3^+$ case).[4] Then the Raman spectra show structure corresponding to the vibronic levels when the polarization geometry is either of the $[100]\rightarrow[100]$ or of $[110]\rightarrow[\bar{1}10]$ type.[1,2]

For what concerns the vibrational Raman scattering, the *polarization selection rules* of Eq. (13) of the Sec. V can be applied to this case, taking into account that $\Gamma_g = \Gamma_3^+$ and $\Gamma_3^+ \times \Gamma_3^+ = \Gamma_1^+ + \Gamma_3^+ + \Gamma_2^+$.[20] Then in the $[100]\rightarrow[100]$ polarization geometry, the densities of phonon states which determine the Raman spectra must transform according to $\Gamma_1^+ + \Gamma_3^+$. In the $[110]\rightarrow[1\bar{1}0]$ geometry they must transform according to $\Gamma_1^+ + \Gamma_3^+ + \Gamma_5^+$. In the $[100]\rightarrow[010]$ geometry, they must transform according to Γ_5^+.

We now evaluate the *intensities* of such process for the above-considered polarization geometries by using Eq. (7). First of all, we have to determine what excited states are connected to the ground state by dipole-allowed transitions and the relative dipole moments $\mathfrak{M}_\alpha^0(gm)$; then evaluate the terms corresponding to the (intrastate and interstate) EP interactions and analyze them in irreducible components; finally, once we have deduced $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$, we write the Raman differential cross section given in Eq. (7) for the different polarizations geometries.

Since the dipole moment transforms according to Γ_4^-, the excited states connected to a Γ_3^+ ground state must transform according to the threefold-degenerate irreducible representations Γ_4^- and Γ_5^- because $\Gamma_3^+ \times \Gamma_4^- = \Gamma_4^- + \Gamma_5^-$. In principle we consider several excited states of both the symmetries. The α component of the dipole moment $\mathfrak{M}_\alpha^0(gm)$ given in Eq. (3) corresponding to an allowed transition between the Γ_3^+-symmetry ground state and either a Γ_4^--symmetry or a Γ_5^--symmetry excited state, is therefore a 2×3 matrix (see Appendix B). The forces $\mathfrak{F}^e_{\Gamma\gamma}(mm)$ and $\mathfrak{F}^h_{\Gamma\gamma}(gg)$, appearing in the intrastate EP interaction Hamiltonian, are 3×3 and 2×2 matrices, respectively. $\mathfrak{F}^e_{\Gamma\gamma}(mm)$ transforms according to Γ_1^+, Γ_3^+, or Γ_5^+, and $\mathfrak{F}^h_{\Gamma\gamma}(gg)$ according to Γ_1^+ or Γ_3^+. The forces $\mathfrak{F}^e_{\Gamma\gamma}(mm')$ with $m \neq m'$, appearing in the interstate interaction Hamiltonian, are 3×3 matrices, transforming according to Γ_3^+ and Γ_5^+, but not according to Γ_1^+. In fact $u(\Gamma_1^+)$, i.e., the Γ_1^+-symmetrized displacement, has the total point symmetry of the defect and therefore cannot induce transitions between Γ_4^-- or Γ_5^--symmetry states (see Appendix B). We refer to Appendix A for the comments on the contributions coming from the terms neglected in the above analysis. We give in the present section the results for the differential cross sections in the different polarization geometries in the following cases: (i) all the considered excited states transform according to Γ_4^-; (ii) all the considered excited states transform according to Γ_5^-. In the Appendix C we give the general result by considering all the excited states transforming according to either Γ_4^- or Γ_5^-. Since the results for (i) and (ii) differ only by a sign, we report them in an unique expression,

$$\left(\frac{d^2\sigma}{d\omega d\Omega}\right)_V \sim \begin{cases} \frac{8}{3}\{(a'-a)^2\rho(\Gamma_1^+,\omega^2)+2[b^2+2(b'-b'')^2\pm 2b(b'-b'')]\rho(\Gamma_3^+,\omega^2)\} \text{ when } \vec{n}^L \parallel [100] \text{ and } \vec{n}^R \parallel [100] & \text{(14a)} \\ (a'-a)^2\rho(\Gamma_1^+,\omega^2)+2[b^2+3(b'-b'')^2\pm 2b(b'-b'')]\rho(\Gamma_3^+,\omega^2)+(c'-c'')^2\rho(\Gamma_5^+,\omega^2) & \\ \qquad\qquad \text{when } \vec{n}^L \parallel [110] \text{ and } \vec{n}^R \parallel [1\bar{1}0] & \text{(14b)} \\ \frac{8}{3}(c'-c'')^2\rho(\Gamma_5^+,\omega^2) \text{ when } \vec{n}^L \parallel [100] \text{ and } \vec{n}^R \parallel [010]. & \text{(14c)} \end{cases}$$

In Eqs. (14a) and (14b) the (±) sign is such that (+) refers to the case (i) and (−) refers to case (ii). The coefficients a, a', b, b', b'', c', c'' involve the oscillator strength of the virtual transitions, the transition frequency, and the EP coupling coefficients (see Appendix C). In particular a is related to the Γ_1^+ hole-lattice coupling coefficients, in the ground degenerate state Γ_3^+; a' is related to all the contributions of the Γ_1^+ coupling coefficients in the excited states Γ_4^- [or Γ_5^- for the case (ii)]; b and b' have the same meaning for the Γ_3^+ intrastate coupling coefficients; c' is related to the Γ_5^+ intrastate coupling coefficients relative to the excited states; b'' and c'' are related to the Γ_3^+ and the Γ_5^+ coupling coefficients, respectively, of the interstate EP interactions relative to all the Γ_4^- [or all the Γ_5^- for the case (ii)] excited state.[21]

The terms proportional to the densities $\rho(\Gamma_1^+,\omega^2)$ and $\rho(\Gamma_5^+,\omega^2)$ in Eq. (14b) owe their presence entirely to the degenerate character of the ground state. In fact, when the ground state is a singlet one, the density of phonon states appearing in the $[110]\to[1\bar{1}0]$ scattering is only that transforming according to Γ_3^+.[10]

Let us consider some cases that we think worth discussion.

(i) c' and c'' or $(c'-c'')$ are negligible: in the $[100]\to[010]$ geometry no first-order Raman spectra can be seen. Furthermore, scatterings $[100]\to[100]$ and $[110]\to[1\bar{1}0]$ become nearly equal in shape, apart from the intensity ratio 8/3. In fact, the relative weight of $\rho(\Gamma_1^+,\omega^2)$ with respect to $\rho(\Gamma_3^+,\omega^2)$ is practically the same in the two polarized spectra given in Eqs. (14a) and (14b).

(ii) Either a' and a or $(a'-a)$ are negligible. The three polarized spectra given in Eqs. (14) are all different. More specifically, the polarized spectrum $[100]\to[010]$ is determined only by $\rho(\Gamma_5^+,\omega^2)$ the polarized spectrum $[100]\to[100]$ only by $\rho(\Gamma_3^+,\omega^2)$, while the polarized spectrum $[110]\to[1\bar{1}0]$ is the sum of these two spectra, reduced by the factor 3/8.

(iii) Under the joint assumptions (i) and (ii), the two polarized spectra in Eqs. (14a) and (14b) are determined only by $\rho(\Gamma_3^+,\omega^2)$ and have an intensity ratio equal to 8/3.

Let us compare these results with those valid for non-JT impurities (singlet ground state). For non-JT impurities the first-order polarized spectra $[100]\to[100]$ and $[110]\to[1\bar{1}0]$ become equal in shape [actually the shape of $\rho(\Gamma_3^+,\omega^2)$ density of phonon states] only when the Γ_1^+-symmetry EP interaction coefficient is negligible, and their intensity ratio is then 4/3. This last result is only apparently similar to that considered in (iii), because the intensity ratio of the two spectra $[100]\to[100]$ and $[110]\to[1\bar{1}0]$ in the singlet case is one-half than that of the JT doublet case.

VII. CONCLUSIONS

We have given in Sec. III the theoretical expression for the first-order differential Raman cross section, in Sec. V the polarization selection rules for the first-order Raman processes, and in Sec. VI the differential Raman cross section for a JT impurity with a Γ_3^+ electronic ground state. Moreover in Sec. V the coefficients weighting the different densities of phonon states in the Raman spectra have been deduced in the assumption that the excited states are either of the Γ_4^- type or of the Γ_5^- type.

We try now to compare the theory presented here with the experimental results given by Guha and Chase[1] and concerning Cu^{2+} in CaO.[22] For this purpose we need very detailed information about the excited states of the JT impurity Cu^{2+} (energies, symmetries, and oscillator strengths for the allowed transitions from the Γ_3^+ ground state) which, unfortunately, to our knowledge do not exist in the literature. Because their evaluation is outside of the aim of the present paper, we assume first that either the oscillator strength for the Γ_4^--type states is stronger than that for Γ_5^--type states, or vice versa. The results of Sec. VI can then be used for a comparison with the experimental results. In Ref. 1 the authors report that no impurity-induced scattering has been detected in the [100] → [010] geometry. This means that assumption (i) of Sec. VI holds: c' and c'' or $(c'-c'')$ are negligible[23] and the experimental vibrational Raman spectra in the two polarization geometries [100] → [100] and [110] → [1$\bar{1}$0] should approximately have the same shape. This seems to be in agreement with the experimental results.[1,24] For these spectra the contributions of the Γ_3^+ density of phonon states cannot be separated from that of the Γ_1^+ density of phonon states because they appear together in both the spectra. Only in the case that the coefficient $(a'-a)$ is equal to zero [case (iii) of Sec. VI] the two spectra have the shape determined by the Γ_3^+ density of phonon states alone. Unfortunately the authors in Ref. 1 do not report the intensity ratio between the [100] → [100] and [110] → [1$\bar{1}$0] polarized spectra, which should be 8/3 in the present case and 4/3 in the non-JT case. If, on the contrary, all the oscillator strengths for the transitions $\Gamma_3^+ \to \Gamma_4^-$ and $\Gamma_3^+ \to \Gamma_5^-$ are equal in intensity, the theoretical results given in Eq. (C1) must be considered for a comparison with the experimental results. This is a difficult task because of too many coefficients appearing there. However, since there is no experimental scattering for (100) → (010) geometry,[1] this implies again that all the Γ_5^+ EP coupling coefficients c_{ij} $(i,j=\mu,\nu)$ are negligible. Then we can conclude as before and in agreement with the polarization selection rules (Sec. V) that the [100] → [100] and [110] → [1$\bar{1}$0] polarized spectra are a superposition of $\rho(\Gamma_1^+,\omega^2)$ and $\rho(\Gamma_3^+,\omega^2)$. *Only* when *all* the Γ_1^+-symmetry EP interaction coefficients a_{ij} are negligible, is the result again apparently similar to that obtained for non-JT impurities. But in the non-JT case the ratio of the intensities [100] → [100] and [110] → [1$\bar{1}$0] is rigorously equal to 4/3, while in the JT case the same ratio does not give this result at all [Eq. (C1)].

We conclude by emphasizing that a careful measurement of the Raman spectra intensities and of their intensity ratios should not only allow discrimination between JT and non-JT impurities, but also should give very interesting information about the composition of the spectra in terms of $\rho(\Gamma,\omega^2)$.

APPENDIX A

We give the complete expression of $[\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)]_{tot}$, following the Loudon theory of Ref. (9) Eq. (14). $\alpha,\beta=x,y,z$ in our notation. Here we take into account also the terms coming from the EP interactions which mix the ground state with the excited electronic states. These are the first two and the last two terms in Eq. (14) Ref. 9, we neglected in the text. In addition to the excited states $|m\rangle$ and $|m'\rangle$ in Eq. (2), we introduce the states $|q\rangle$ which are the excited states connected to the ground state through the interstate EP interaction.

$$\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)_{tot}=\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)-\sum_{qm}\left(\frac{\mathfrak{M}^0_\alpha(gm)\mathfrak{M}^0_\beta(mq)\mathfrak{F}^e_{\Gamma\gamma}(qg)+\mathfrak{F}^e_{\Gamma\gamma}(gq)\mathfrak{M}^0_\alpha(qm)\mathfrak{M}^0_\beta(mg)}{\omega_{qm}(\omega_{mg}+\omega_L)}\right.$$
$$\left.+\frac{\mathfrak{F}^e_{\Gamma\gamma}(gq)\mathfrak{M}^0_\beta(qm)\mathfrak{M}^0_\alpha(mg)+\mathfrak{M}^0_\beta(gm)\mathfrak{M}^0_\alpha(mq)\mathfrak{F}^e_{\Gamma\gamma}(qg)}{\omega_{qg}(\omega_{mg}-\omega_L)}\right), \qquad \text{(A1)}$$

where $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$ is the expression given in Eq. (2) of the text.

The excited states $|q\rangle$ are connected to the ground state $|g\rangle$ through the dipole moments $\mathfrak{M}^0_\alpha(gm)$. In O_h symmetry the excited states $|q\rangle$ must then have the same parity of the ground state $|g\rangle$ and different parity from the $|m\rangle$ state's parity. In O and T_d symmetry site, where the inversion symmetry does not exist any more, the previous restriction on the excited states $|q\rangle$ and $|m\rangle$ does not exist any longer and the two indices q and m can be interchanged in the sum in Eq. (A1).

In particular, in O_h site symmetry where $\Gamma=\Gamma_1^+$, Γ_3^+, Γ_5^+ and for a Γ_3^+ ground state (Sec. V of the text), the $|q\rangle$ states must transform as the irreducible representation of even symmetry, where

$$\Gamma_q \in \Gamma_3^+ \otimes \Gamma \quad (\Gamma=\Gamma_1^+, \Gamma_3^+, \Gamma_5^+)\,. \tag{A2}$$

In the example considered in Sec. VI ($\mathrm{CaO{:}Cu^{2+}}$), the lowest excited electronic state of even symmetry is of Γ_5^+ symmetry. Then according to Eq. (A2), $\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)_{\mathrm{tot}}-\mathcal{P}'_{\alpha\beta}(\Gamma\gamma)$ in Eq. (A1) is different from zero only for the components $\Gamma=\Gamma_5^+$. In the case considered in Sec. VI, the contribution of $\rho(\Gamma_5^+,\omega^2)$ weighted by the Γ_5^+ coupling coefficients appears in the spectra of the polarized scatterings $[110]\rightarrow[1\bar{1}0]$ and $[100]\rightarrow[010]$. [See Eqs. (14) of the text.] In particular, in Eq. (14c) $\rho(\Gamma_5^+,\omega^2)$ is the only one responsible of the shape of the first-order vibrational spectrum. Since from the experimental results there considered it turns out that the scattering is negligible for this geometry, it follows that all the Γ_5^+ coupling coefficients are negligible, as we say in Sec. VII. This also implies that the Γ_5^+ coupling coefficients, related to the EP interstate interaction forces considered in the present appendix, are negligible.

APPENDIX B

We determine the expressions for the dipole moments $\mathfrak{M}^0_\alpha(gm)$ and the interstate and intrastate EP interaction forces $\mathfrak{F}_\Gamma(mm)$ and $\mathfrak{F}_\Gamma(mm')$ introduced in Sec. IV and used in Sec. VI for the Γ_3^+ electronic ground state.

First of all we give the symmetry properties of the electronic wave functions. We use as a basis for the double ground state Γ_3^+ (E_g in German notation) the real wave functions $\psi_1=\psi_\theta$ and $\psi_2=\psi_\epsilon$ which are taken to transform, respectively, as $2z^2-x^2-y^2$ and $\sqrt{3}\,(x^2-y^2)$; for the triplet excited states we use the real functions ψ_1, ψ_2, ψ_3 which are taken to transform, respectively, for $\Gamma_4^-(T_{1u})$ as x, y, z and for $\Gamma_5^-(T_{2u})$ as $x(y^2-z^2)$, $y(z^2-x^2)$, $z(x^2-y^2)$.

We indicate with g the electronic Γ_3^+ state, with m the electronic Γ_4^- states, and with n the electronic Γ_5^- states.

By using these wave functions the dipole moment matrices are

$$\mathfrak{M}^0_x(gm)=e\langle g|x|m\rangle=M_{gm}\begin{vmatrix}-1 & 0 & 0\\ \sqrt{3} & 0 & 0\end{vmatrix}, \tag{B1}$$

$$\mathfrak{M}^0_y(gm)=e\langle g|y|m\rangle=M_{gm}\begin{vmatrix}0 & -1 & 0\\ 0 & -\sqrt{3} & 0\end{vmatrix},$$

$$\mathfrak{M}^0_z(gm)=e\langle g|z|m\rangle=M_{gm}\begin{vmatrix}0 & 0 & 2\\ 0 & 0 & 0\end{vmatrix},$$

and

$$\mathfrak{M}^0_x(gn)=e\langle g|x|n\rangle=M_{gn}\begin{vmatrix}\sqrt{3} & 0 & 0\\ 1 & 0 & 0\end{vmatrix}, \tag{B2}$$

$$\mathfrak{M}^0_y(gn)=e\langle g|y|n\rangle=M_{gn}\begin{vmatrix}0 & -\sqrt{3} & 0\\ 0 & 1 & 0\end{vmatrix},$$

$$\mathfrak{M}^0_z(gn)=e\langle g|z|n\rangle=M_{gn}\begin{vmatrix}0 & 0 & 0\\ 0 & 0 & -2\end{vmatrix}.$$

Note that for symmetry properties the coefficients M_{gm} in Eqs. (B1) are equal for x, y, z polarized transitions. The same properties is valid for M_{gn} in Eqs. (B2).

The dipole moments are related to the oscillator strength f_{gm} of the transition by the following expression:

$$f_{gm}=\frac{2m^*}{3\hbar^2e^2}\sum_\alpha \mathrm{Tr}\,[\mathfrak{M}^0_\alpha(gm)]^2\,\omega_{mg}\,, \tag{B3}$$

where ω_{mg} is given in the text and m^* is the effective mass of the optical electron.

In order to determine the intrastate and interstate forces, we give first the symmetry properties of symmetrized displacements $u(\Gamma\gamma)$ for $\Gamma=\Gamma_3^+(E_g)$ and $\Gamma=\Gamma_5^+(T_{2g})$. They are chosen in order to transform for Γ_3^+ as $(2z^2-x^2-y^2)$ and $\sqrt{3}(x^2-y^2)$ and for Γ_5^+ as yz, zx, xy. Then the matrices transforming as Γ_3^+ in the electronic wave-function spaces, have the following forms: in the $g\times g$ space

$$e_\theta=\begin{vmatrix}-1 & 0\\ 0 & 1\end{vmatrix}, \quad e_\epsilon=\begin{vmatrix}0 & 1\\ 1 & 0\end{vmatrix}; \tag{B4}$$

in the $m\times m$, $m\times m'$, $n\times n$, $n\times n'$ spaces

$$\mathcal{E}_\theta=\begin{vmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{vmatrix}, \quad \mathcal{E}_\epsilon=\begin{vmatrix}\sqrt{3} & 0 & 0\\ 0 & -\sqrt{3} & 0\\ 0 & 0 & 0\end{vmatrix}; \tag{B5}$$

in the $m\times n$ space

$$\mathcal{E}'_\theta=\mathcal{E}_\epsilon\,, \quad \mathcal{E}'_\epsilon=-\mathcal{E}_\theta\,; \tag{B6}$$

in the $m\times m$, $m\times m'$, $n\times n$, $n\times n'$ spaces

$$\mathcal{T}_{2x}=\begin{vmatrix}0 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{vmatrix}, \tag{B7}$$

with obvious changes, for $\mathcal{T}_{2y}$ and $\mathcal{T}_{2z}$; in the $m\times n$ space

$$\mathcal{T}'_{2x} = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{vmatrix} ,$$

$$\mathcal{T}'_{2y} = \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{vmatrix} , \tag{B8}$$

$$\mathcal{T}'_{2z} = \begin{vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} .$$

By using the matrices given in Eqs. (B4)–(B8) and by indicating by $\mathcal{I}$ the unit matrix, the interstate and intrastate forces transforming as Γ_1^+, Γ_3^+, and Γ_5^+ have the following expressions:

$$\mathfrak{F}^{h+}_{\Gamma_1}(gg) = F^h(\Gamma_1^+, gg)\mathcal{I}, \quad \mathfrak{F}^{e+}_{\Gamma_1}(mm) = F^e(\Gamma_1^+, mm)\mathcal{I},$$

$$\mathfrak{F}^{e+}_{\Gamma_1}(nn) = F^e(\Gamma_1^+, nn)\mathcal{I}, \tag{B9}$$

$$\mathfrak{F}^{h}_{\Gamma^+_{3,1}}(gg) = F^h(\Gamma_3^+, gg)e_\theta ,$$

$$\mathfrak{F}^{h+}_{\Gamma_{3,2}}(gg) = F^h(\Gamma_3^+, gg)e_\epsilon , \tag{B10}$$

$$\mathfrak{F}^{e}_{\Gamma^+_{3,1}}(mm) = F^e(\Gamma_3^+, mm)\mathcal{E}_\theta ,$$

$$\mathfrak{F}^{e}_{\Gamma^+_{3,2}}(mm) = F^e(\Gamma_3^+, mm)\mathcal{E}_\epsilon , \tag{B11}$$

$$\mathfrak{F}^{e}_{\Gamma^+_{3,1}}(mn) = F^e(\Gamma_3^+, mn)\mathcal{E}'_\theta ,$$

$$\mathfrak{F}^{e}_{\Gamma^+_{3,2}}(mn) = F^e(\Gamma_3^+, mn)\mathcal{E}'_\epsilon , \tag{B12}$$

$$\mathfrak{F}^{e}_{\Gamma^+_{5,1}}(mm) = F^e(\Gamma_5^+, mm)\mathcal{T}'_{2x} , \tag{B13}$$

with obvious changes for $\mathfrak{F}^{e}_{\Gamma^+_{5,2}}(mm)$ and $\mathfrak{F}^{e}_{\Gamma^+_{5,3}}(mm)$,

$$\mathfrak{F}^{e+}_{\Gamma_{5,1}}(mn) = F^e(\Gamma_5^+, mn)\mathcal{T}'_{2x} , \tag{B14}$$

with obvious changes for $\mathfrak{F}^{e+}_{\Gamma_{5,2}}(m,m)$ and $\mathfrak{F}^{e+}_{\Gamma_{5,3}}(mm)$.

$F^h(\Gamma, gg)$, $F^e(\Gamma, mm)$, $F^e(\Gamma, mn)$ in Eqs. (B9)–(B14) are scalar coupling coefficients evaluated in the electronic states as indicated. The EP intrastate forces $\mathfrak{F}^e_\Gamma(nn)$, the EP interstate forces $\mathfrak{F}^e_\Gamma(nn')$ $\mathfrak{F}^e_\Gamma(mm')$ have the same matrix representations given in Eqs. (B11) and (B13), only the coupling coefficients $F^e(\Gamma, nn)$, $F^e(\Gamma, mm')$, and $F^e(\Gamma, nn')$ being different.

APPENDIX C

We give the general result for the differential Raman cross section by considering all the excited states transforming according to $\Gamma_m = \Gamma_4^-$ and Γ_5^-, for different incident and scattered light polarizations:

$$\left(\frac{d^2\sigma}{d\omega d\Omega}\right)_V \sim \begin{cases} \frac{8}{3}[(a_{\mu\mu} - a_\mu)^2 + (a_{\nu\nu} - a_\nu)^2]\rho(\Gamma_1^+, \omega^2) + \frac{16}{3}[2(b_{\mu\mu}, - b_{\mu\mu}) + 2(b_{\nu\nu'} - b_{\nu\nu})^2 + 4b^2_{\mu\nu} + b^2_\mu \\ \qquad + b^2_\nu - 2(b_{\mu\mu'} - b_{\mu\mu})b_\mu + 2(b_{\nu\nu'} - b_{\nu\nu})b_\nu \\ \qquad + 2b_{\mu\nu}(b_\nu + b_\mu)]\rho(\Gamma_3^+, \omega^2) \text{ when } \vec{n}^L \| [100], \vec{n}^R \| [100]; \\ [(a_{\mu\mu} - a_\mu) - (a_{\nu\nu} - a_\nu)]^2 \rho(\Gamma_1^+, \omega^2) + 2\{3[(b_{\mu\mu'} - b_{\mu\mu})^2 + (b_{\nu\nu'} - b_{\nu\nu})^2 + 2b^2_{\mu\nu}] + (b_\mu - b_\nu)^2 \\ \qquad + 2(b_{\mu\mu'} - b_{\mu\mu} + b_{\nu\nu'} - b_{\nu\nu})(b_\nu - b_\mu) + 2(b_{\mu\mu'} - b_{\mu\mu} - b_{\nu\nu'} + b_{\nu\nu})b_{\mu\nu} \\ \qquad + 2(b_{\mu\mu'} - b_{\mu\mu})(b_{\nu\nu'} - b_{\nu\nu}) - 2b^2_{\mu\nu}\}\rho(\Gamma_3^+, \omega^2) \\ \qquad + [(c_{\nu\nu'} - c_{\nu\nu})^2 - (c_{\mu\mu'} - c_{\mu\mu})^2 + 2/\sqrt{3}\, c^2_{\mu\nu}] \\ \qquad \times \rho(\Gamma_5^+, \omega^2) \text{ when } \vec{n}^L \| 110|, \vec{n}^R \| [1\bar{1}0], \\ \frac{8}{3}[(c_{\mu\mu'} - c_{\mu\mu})^2 + (c_{\nu\nu'} - c_{\nu\nu})^2 + 2c^2_{\mu\nu}]\rho(\Gamma_5^+, \omega^2) \\ \text{when } \vec{n}^L \| [100], \quad \vec{n}^R \| [010], \end{cases} \tag{C1}$$

In what follows, as in Appendix B, we indicate with g the Γ_3^+-type electronic ground state, with m the Γ_4^--type electronic excited states and with n the Γ_5^--type electronic excited states. The coefficients appearing in Eq. (C1) are given by the following expressions:

$$\begin{aligned}
a_{\mu\mu} &= \sum_m M_{gm}^2 F^e(\Gamma_1^+, mm)\Omega_{\mathrm{mm}}^{-1}, \\
a_{\nu\nu} &= \sum_n M_{gn}^2 F^e(\Gamma_1^+, nn)\Omega_{nn}^{-1}, \\
a_{\mu} &= \sum_m M_{gm}^2 F^h(\Gamma_1^+, gg)\Omega_{\mathrm{mm}}^{-1}, \\
a_{\nu} &= \sum_n M_{gn}^2 F^h(\Gamma_1^+, gg)\Omega_{nn}^{-1};
\end{aligned} \tag{C2}$$

$$\begin{aligned}
b_{\mu\mu} &= \sum_m M_{gm}^2 F^e(\Gamma_3^+, mm)\,\Omega_{\mathrm{mm}}^{-1}, \\
b_{\mu\mu'} &= \sum_{\mathrm{m}}\sum_{\mathrm{m}'} M_{g\mathrm{m}} M_{\mathrm{m}'g}\,\Omega_{\mathrm{mm}'}^{-1}\, F^e(\Gamma_3^+, mm'), \\
b_{\mu\nu} &= \sum_m \sum_n M_{gm} M_{ng} F^e(\Gamma_3^+, mn)\,\Omega_{mn}^{-1} = b_{\nu\mu}, \\
b_{\nu\nu} &= \sum_n M_{gn}^2 F^e(\Gamma_3^+, nn)\,\Omega_{nn}^{-1}, \\
b_{\nu\nu'} &= \sum_n \sum_{n'} M_{gn} M_{n'g} F^e(\Gamma_3^+, nn')\,\Omega_{nn'}^{-1}, \\
b_{\mu} &= \sum_m M_{gm}^2 F^h(\Gamma_3^+, gg)\,\Omega_{\mathrm{mm}}^{-1}, \\
b_{\nu} &= \sum_n M_{gn}^2 F^h(\Gamma_3^+, gg)\,\Omega_{nn}^{-1};
\end{aligned} \tag{C3}$$

$$\begin{aligned}
c_{\mu\mu} &= \sum_m M_{gm}^2 F^e(\Gamma_5^+, mm)\,\Omega_{\mathrm{mm}}^{-1}, \\
c_{\mu\mu'} &= \sum_m \sum_{m'} M_{gm} M_{m'g} F^e(\Gamma_5^+, mm')\,\Omega_{\mathrm{mm}'}^{-1}, \\
c_{\mu\nu} &= \sum_m \sum_n M_{gm} M_{ng} F^e(\Gamma_5^+, mn)\,\Omega_{mn}^{-1} = c_{\nu\mu}, \\
c_{\nu\nu} &= \sum_n M_{gn}^2 F^e(\Gamma_5^+, nn)\,\Omega_{nn}^{-1}, \\
c_{\nu\nu'} &= \sum_n \sum_{n'} M_{gn} M_{n'g} F^e(\Gamma_5^+, nn')\,\Omega_{nn'}^{-1},
\end{aligned} \tag{C4}$$

where

$$\Omega_{mn}^{-1} = \left(\frac{1}{(\omega_{mg} - \omega_L)(\omega_{ng} - \omega_L)} + \frac{1}{(\omega_{mg} + \omega_L)(\omega_{ng} + \omega_L)}\right). \tag{C5}$$

All the other quantities in Eqs. (C2) and (C3) have been already defined in Appendix B.

In the case where only the Γ_4^- excited states are considered it turns out that

$$\begin{aligned}
&a_{\mu\mu} = a', \quad a_\mu = a \quad b_{\mu\mu} = b', \quad b_{\mu\mu'} = b'', \\
&a_{\nu\nu} = 0, \quad a_\nu = 0, \quad b_{\nu\nu} = 0, \quad b_{\nu\nu'} = 0, \\
&b_\mu = b, \quad c_{\mu\mu} = c', \quad c_{\mu\mu'} = c'', \quad b_{\mu\nu} = 0, \\
&b_\nu = 0, \quad c_{\nu\nu} = 0, \quad c_{\nu\nu'} = 0, \quad c_{\mu\nu} = 0.
\end{aligned} \tag{C6}$$

The opposite ($a_{\mu\mu} = 0$, $a_{\nu\nu} = a'$, etc.) holds when only the Γ_5^- excited states are considered. These two choices have been considered in the text, Eqs. (14a)–(14c).

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[14] G. Benedek and N. Terzi, Phys. Rev. B 10, 3552 (1974). In this paper the authors called diagonal and nondiagonal, respectively, the intrastate and interstate EP interactions.

[15] Here and in the following we use a script character in order to indicate a physical quantity which is a matrix in the manifold degenerate space relative to the ground or to excited electronic states. Moreover, we use the conventional notation to indicate tensors and vectors in three-dimensional real space. The polarizability $\overleftrightarrow{\mathcal{P}}(\{u\})$ for instance, is both a 3×3 matrix in the real space, whose components are $\mathcal{P}_{\alpha\beta}(\{u\})$ $(\alpha, \beta = x, y, z)$, and a $n_g \times n_g$ matrix in the linear vector space of the n_g wave functions of the degenerate ground state.

[16] It is worth noting that all the considerations in the fol-

lowing are independent both of the strength and of the range of $\overleftrightarrow{\mathcal{P}}'(\Gamma\gamma)$ in Eq. (1) and therefore of how many shells of neighbors of the impurity ("impurity space") are involved. The relation between the displacements of the ions of the impurity space, their symmetrized combinations $u(\Gamma\gamma)$, and the related densities of one-phonon states $\rho(\Gamma, \omega^2)$ can be found in M. V. Klein, Phys. Rev. 131, 1500 (1963), when the first-nearest-neighbor ion displacements are considered. See also W. Ludwig, Ergb. Exacten Naturwiss. 35, 1 (1964). When the impurity space includes also second neighbors, the even irreducible representations Γ are contained more than once in the reduction of ion displacements in terms of $u(\Gamma\gamma)$. As a consequence, $\rho(\Gamma, \omega^2)$ is actually a matrix. For a recent reference on this subject see, for instance, Dennis Robbins and John B. Page, Jr., Phys. Rev. B 13, 3604 (1976).

[17] Note that in the Loudon's notation, which we refer to only in these two sentences, α and β indicate the excited states of the system. α and β in our paper indicate the Cartesian components.

[18] See, for instance, Ref. 11., p. 800.

[19] The symmetrized direct product must be used in view of the symmetry of $\mathcal{P}_{\alpha\beta}(\{u\})$ in α and β and in the basis indices of the ground state, in the off-resonance case.

[20] The irreducible representations Γ_1^+ and Γ_3^+ are the symmetric part of the direct product $\Gamma_3^+ \times \Gamma_3^+$, while the irreducible representation Γ_2^+ is the antisymmetric part.

[21] In Ref. 8 the authors deduced in the *example 1* the Raman cross sections for the $\Gamma_3^+ \times \Gamma_3^+$ case, on the assumption that the hole-lattice interaction was negligible, i.e., $a = b = 0$, in Eqs. (14) of the present paper. By comparing Eqs. (14a) and (14b) it follows that when $b = 0$ the contribution of $\rho(\Gamma_3^+, \omega^2)$ to the cross section in the (100) → (100) scattering is practically twice the contribution of the same symmetry in the (110) → $(1\bar{1}0)$ scattering, as deduced in Ref. 8.

[22] We think that $CaO:Cu^{2+}$ is a good example for the theory presented in Sec. VI, where only the spatial degeneracy of the electronic ground state is considered. Actually the ground electronic state of $CaO:Cu^{2+}$ has also a doublet spin degeneracy. This last degeneracy does not play any role in determining the differential Raman cross section because, otherwise, in disagreement with the experimental data (Ref. 1), the (100) → (010) polarized spectra should show structure due to all three $\rho(\Gamma_1^+, \omega^2)$, $\rho(\Gamma_3^+, \omega^2)$, and $\rho(\Gamma_5^+, \omega^2)$ as in the other polarized spectra. (See example 3 in Ref. 8.)

[23] See the comments in Appendix A.

[24] In Ref. 1 this result is presented, following the notation for non-JT impurity, as "the $A_{1g} + E_g$ spectrum is identical to E_g spectrum within the experimental accuracy."