

Bound states with Jahn-Teller impurity centers

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It is shown that the dynamic Jahn-Teller effect with weak electron-phonon interaction leads to the appearance of local or pseudolocal (dielectric) modes in a model in which there are no excited electronic states.

Kogan and Suris^[1] have predicted a new type of local oscillations (dielectric modes), which occur when the phonon frequencies are at resonance with the frequency of an electronic transition in an impurity center. The general theory of such bound states in the case of weak coupling ($\alpha \ll 1$) is developed in the review of Levinson and Rashba.^[2] In^[1,3], effects connected with the degeneracy of the electronic levels are not considered, and the number of bound states turns out to be equal to the number of electronic excited states of the center. In the presence of degenerate levels, the impurity-center electrons interact with the nonfully-symmetrical oscillations that are active in the Jahn-Teller effect. We shall show below that this interaction produces dielectric modes in a model in which there are no excited electronic states.

Assuming the electronic level to be degenerate, we introduce the matrix Hamiltonian

$$H = (H_e + H_p)1 + V, \quad V = \hbar \omega_{\Gamma} \sum_{i,\gamma} \alpha_i 0_{\Gamma\gamma} q_i \Gamma_{\gamma} \quad (1)$$

H_e and H_p are the electron and phonon Hamiltonians, respectively; 1 is a unit matrix on the basis of the electronic functions of the degenerate term. The band of the Jahn-Teller modes numbered by the index i is assumed, just as in^[2], to be infinitesimally narrow with frequency ω_{Γ} , the symbols $q_{i\Gamma\gamma}$ denote the normal coordinates (Γ is the representation and γ is the row), $0_{\Gamma\gamma}$ are the interaction matrixes, and α_i are the dimensionless coupling constants. Carrying out a rotation in the space of the vibrational coordinates $q_{i\Gamma\gamma}$, we can eliminate the interaction with all the modes with the exception of a single one, $q_{\Gamma\gamma} = (1/\alpha) \sum_i \alpha_i q_{i\Gamma\gamma}$, where $\alpha^2 = \sum_i \alpha_i^2$. The electron-vibrational interaction operator then takes the form

$$V = \hbar \omega_{\Gamma} \alpha \sum_{\gamma} 0_{\Gamma\gamma} q_{\Gamma\gamma} \quad (2)$$

For the orbital doublet E of cubic and trigonal centers we have

$$V = \hbar \omega_E \alpha (q_u \vec{\sigma}_x + q_v \vec{\sigma}_y), \quad (3)$$

where u and v are the row indices of the E mode that is active in the Jahn-Teller excited, and $\vec{\sigma}_x$ and $\vec{\sigma}_y$ are Pauli matrices in the basis u_{\pm} .^[4] Subjecting the Hamiltonian (1) to a unitary transformation that excludes the terms linear in α , we obtain accurate to terms α^2 :

$$V^{(2)} = -\alpha^2 \hbar \omega_E [1 + (1/2) \vec{\sigma}_z (q_u p_u - q_v p_v)], \quad (4)$$

where $p_{u(v)}$ are the momenta. The transformation

$$\begin{aligned} Q_1 &= (1/\sqrt{2})(p_u + q_v), & Q_2 &= (1/\sqrt{2})(p_v + q_u), \\ P_1 &= (1/\sqrt{2})(p_u - q_v), & P_2 &= (1/\sqrt{2})(p_v - q_u) \end{aligned} \quad (5)$$

reduces (1) to the form

$$H = (H_e + H_p')1 + (\hbar \omega_E / 2) [(1 - \alpha^2 \vec{\sigma}_z)(Q_1^2 + P_1^2) + (1 + \alpha^2 \vec{\sigma}_z) \times (Q_2^2 + P_2^2)], \quad (6)$$

where H_p' is the free-phonon Hamiltonian, in which there is no "interacting" mode. The Hamiltonian (6) is diagonal. The operator H_p' gives the initial vibration band. From the term (6) in the square brackets we see directly that the Jahn-Teller interaction detaches from the top and from the bottom of the band two doubly-degenerate dielectric modes with frequencies $\omega_{\pm} = \omega_E (1 \pm \alpha^2)$.

It is of interest to trace the variation of the spectrum when the symmetry of the crystal is lowered (e.g., under conditions of uniaxial deformation). The electronic term and the doubly-degenerate phonon band are then split, and at certain values of the external field one of the detached vibrational bands goes into resonance with the energy of the electronic excitation. The dielectric modes that are produced in this case in first order in α were obtained by Kogan and Suris.^[1] In second order in α , however, there are produced also nonresonant bound states,^[2] owing to the interaction of the split electronic states with the other (nonresonant) phonon band.

The effective mode $q_{\Gamma\gamma}$ that interacts with the impurity-center electrons, can be separated in the absence of dispersion at any value of the coupling constant α . The Hamiltonian obtained in this case, with interaction (3), was investigated both analytically in the limiting cases of weak and strong coupling,^[4,5] as well as numerically at arbitrary values of α .^[6] The energy spectrum is a nonequidistant set of vibronic levels, which should be identified with the bound states of the impurity center with the phonons.

When the width of the vibrational dispersion band is not small, the effective mode $q_{\Gamma\gamma}$ cannot be separated by a rotation in the space of the normal coordinates $q_{\vec{k}}(\vec{k})$ is the wave vector). The interaction Hamiltonian takes, accurate to terms $\sim \alpha^2$, the form

$$\begin{aligned} V^{(2)} &= -\alpha^2 \{ 1 \sum_{\vec{k}} \alpha_{\vec{k}}^2 (E, \gamma) \hbar \omega_{\vec{k}} + (1/2) \vec{\sigma}_z \sum_{\vec{k}, \vec{k}'} \hbar \omega_{\vec{k}} p_{\vec{k}} q_{\vec{k}'} \\ &\times [a_{\vec{k}}(Eu) a_{\vec{k}'}(Ev) - a_{\vec{k}}(Ev) a_{\vec{k}'}(Eu)] \}, \end{aligned} \quad (7)$$

where $\alpha_{\vec{k}}(E, \gamma)$ are the coefficients of the expansion of

the symmetrized displacements of the nuclei of E -type in terms of the normal modes $q_{\vec{k}}$ of the crystal. The retarded Green's function $A_{\vec{k}\vec{k}'}(t) = \langle\langle p_{\vec{k}}(t) | p_{\vec{k}'}(0) \rangle\rangle$ with the interaction Hamiltonian (7) can be obtained exactly. The local and pseudolocal states are determined from the extrema of a spectral density $g(\omega) = (1/\pi) \text{Im Tr } A(\omega)$. The corresponding equation is

$$4\omega^2(\alpha^2/\hbar^2)\{[\text{Re } f(\omega)]^2 - [\text{Im } f(\omega)]^2\} = 1, \quad (8)$$

where

$$f(\omega) = \sum_{\vec{k}} \frac{a_{\vec{k}}^2(E\gamma)\omega_{\vec{k}}}{\omega_{\vec{k}}^2 - \omega^2 - i\epsilon} \quad \epsilon \rightarrow +0 \quad (9)$$

If the roots of Eq. (8) fall in the allowed band of the phonon frequencies, then pseudolocal states of the impurity center and of the phonon can appear.

An analysis similar to that carried out by Kogan and Suris^[1] leads to the following criterion for the appearance of local oscillations:

$$[2\omega_L \text{Re } f(\omega_L)]^{-1} < \alpha^2, \quad (10)$$

where ω_L is the end-point frequency of the vibration band. In particular, at a Debye dispersion law of the acoustic vibrations, there always appears a local mode with frequency

$$\tilde{\omega}_L = \omega_L + (1/2)\omega_L \exp(-Q^2/\alpha^2), \quad (11)$$

where the constant Q is expressed in terms of the elastic moduli of the crystal.

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