Helvetica Physica Acta,
Vol. 56 (1983) 237-243

0018-0238/83/010237-07$1.50+0.20/0

JAHN-TELLER EFFECT IN ITINERANT ELECTRON SYSTEMS: THE JAHN-TELLER POLARON

K.-H. Höck, H. Nickisch and H. Thomas*
Institut für Festkörperphysik, Technische Hochschule Darmstadt, W. Germany
* Institut für Physik, Universität Basel, Switzerland

ABSTRACT

We study the formation of a Jahn-Teller polaron in a narrow-band conductor with strong Jahn-Teller coupling.

I. INTRODUCTION

In this paper we are concerned with electron-phonon coupling in crystals containing ions with orbitally degenerate ground-state, so-called Jahn-Teller (JT) ions. According to the JT-theorem /1/, the interactions of the degenerate orbital states with the vibrational modes of the crystal have a destabilizing effect on its lattice surrounding. It was found that this JT-instability provides a mechanism for structural phase transitions not only in insulating crystals (cooperative JT-effect /1,2/) but also in certain metallic compounds. Most prominent examples are the phase transitions in the A 15-compounds, e.g. Nb_3Sn and V_3Sn, which have been proposed to be driven by a so-called band JT-effect /3/. Here, the JT-interaction leads to a deformation-potential coupling of the degenerate conduction bands to the elastic deformations, which may destabilize the high-symmetry phase. This band-JT mechanism was also expected to be responsible for the structural phase transitions in the intermetallic compounds $LaAg_xIn_{1-x}$ and $La_{1-x}Yb_xAg_{1-y}In_y$ /4/. More recent experimental investigations, however, give strong evidence for a phase transition to an antiferro-distortive low-temperature structure /5/. Thus, the deformation-potential coupling is not applicable to these transitions. In addition, for systems where the JT-stabilization energy E_{JT} is comparable to or larger than the electron band-width, the conventional band-JT mechanism breaks down in any case. This raises the general question of the proper treatment of the JT-effect in narrow-band itinerant electron systems.

As a first step, we investigate the interplay between the JT-effect and the motion of a single electron through the crystal, the JT-polaron prob-

blem. We describe the system in terms of a molecular-crystal model with electronic orbital degeneracy in each cell, and intersite tunnelling. Apart from the difference in the underlying physics, the model is closely related to the small-polaron model first introduced by Holstein /6/ in order to discuss strong electron-phonon coupling in ionic crystals.

II. MODEL AND METHOD OF SOLUTION

We consider a crystal containing a molecular complex of tetragonal symmetry in each unit cell ℓ. The lowest electronic state of each complex is assumed to be a two-fold degenerate orbital state, $(\psi_{\ell 1}, \psi_{\ell 2})$, which transforms according to the two-dimensional E-representation of the tetragonal point group associated with each cell. According to the tight-binding approximation we assume the electron to move in a band, which is composed of the local doublets $(\psi_{\ell 1}, \psi_{\ell 2})$. In competition to the delocalization effect due to tunnelling of the electron from site ℓ to site ℓ', there is a tendency to localization due to electron-phonon coupling. If the electron occupies one of the orbitals $(\psi_{\ell 1}, \psi_{\ell 2})$ in an arbitrary cell ℓ, the system may gain energy due to a local JT-effect of type $E \times \beta$ which gives rise to a symmetry-breaking deformation of the molecular complex. The distortion of the complex is described in terms of a local normal coordinate Q_ℓ which transforms according to the one-dimensional irreducible β-representation of the tetragonal site group.

In the basis $(\psi_{\ell 1}, \psi_{\ell 2})$, the Hamiltonian we consider reads

$$H = H^{el} + H^{latt} + H^{JT} \tag{1}$$

with

$$H^{el} = \epsilon_0 \sum_\ell (c^+_{\ell 1} c_{\ell 1} + c^+_{\ell 2} c_{\ell 2}) - \frac{1}{2} \sum'_{\ell\ell',\gamma} t_\gamma(\ell\ell') c^+_{\ell\gamma} c_{\ell'\gamma} \quad , \tag{1a}$$

$$H^{latt} = \sum_\ell \left[P_\ell^2/2M + \frac{1}{2} M\Omega_S^2 Q_\ell^2 \right] - \frac{1}{2} \sum'_{\ell\ell'} v_{\ell\ell'} Q_\ell Q_{\ell'} \tag{1b}$$

and

$$H^{JT} = -A \sum_\ell Q_\ell (c^+_{\ell 1} c_{\ell 1} - c^+_{\ell 2} c_{\ell 2}) \quad , \tag{1c}$$

where the primes on the sums exclude the terms $\ell = \ell'$. $c^+_{\ell\gamma}$ $(c_{\ell\gamma})$ is the creation (destruction) operator for an electron in state $\gamma = 1$ or 2 at lattice site ℓ. ϵ_0 denotes the corresponding site energy and $t_\gamma(\ell\ell')$ is the tunnelling integral. Here, we consider tunnelling only between states with the same symmetry label γ. For nearest-neighbour tunnelling, off-diagonal terms are in any

case forbidden by symmetry. Further, Ω_s is the Einstein-frequency, M the effective mass of the local JT-active coordinate Q_ℓ; $V_{\ell\ell'}$ is the lattice-dynamical interaction, which gives rise to an optical phonon branch. The last term describes the JT-coupling which we have restricted to an interaction of the electron at lattice site ℓ with the local coordinate Q_ℓ at the same lattice site. The distinctive feature of the JT-coupling is the fact that the interaction occurs with a symmetry-breaking coordinate Q_ℓ, in contrast to ordinary electron-lattice coupling where the electron interacts with a fully-symmetric lattice distortion only. Typical coupling strengths of strong JT-ions yield JT-stabilization energies $E_{JT} = -A^2/2M\,\Omega_s^2$ of the order of several thousand cm^{-1}. This is two orders of magnitude more than the ordinary electron-lattice coupling strength in non-polar materials, and of the same order as in polar semiconductors. We are especially interested in the case of narrow-band conductors with band-widths ($\sim t$) of the same order of magnitude as E_{JT}. The JT-coupling gives rise to a local lattice distortion around the electron. For a given distortion pattern $\{Q_\ell\}$, the JT-term (1c) represents an effective potential for the electron, which has to be determined self-consistently. For sufficiently strong coupling, the electron may become trapped in this self-consistent potential and only the composite consisting of the electron and the surrounding lattice distortion - the JT-polaron - can move through the lattice as a whole. In contrast to an ordinary polaron consisting of an electron trapped in a fully-symmetric distortion pattern, the JT-polaron consists of an electron trapped in a distortion pattern of β-symmetry. The whole object may be characterized by the total crystal momentum $\underline{k}$ and - in the absence of off-diagonal tunnelling terms - by the symmetry label γ.

In order to evaluate the ground-state energy for given $\underline{k}$, we make a variational ansatz of the form

$$|\psi_{k\gamma}\rangle = C \sum_\ell e^{i\underline{k}\cdot\underline{R}_\ell} \prod_{\ell'} e^{\alpha_{\ell\ell'}^{(k\gamma)} (b_{\ell'}^\dagger - b_{\ell'})} \sum_{\ell''} a_{\ell\ell''}^{(k\gamma)} c_{\ell''\gamma}^\dagger |0\rangle \qquad (2)$$

with

$$Q_\ell = \sqrt{\frac{\hbar}{2M\,\Omega_s}}\,(b_\ell^\dagger + b_\ell) \quad \text{and} \quad P_\ell = i\sqrt{\frac{\hbar\,M\,\Omega_s}{2}}\,(b_\ell^\dagger - b_\ell)\,.$$

Here, the operator $\prod_\ell$, $\exp[\alpha_{\ell\ell'}^{(k\gamma)} (b_{\ell'}^\dagger - b_{\ell'})]$ generates a deformation of the molecular complexes at sites ℓ' around a given site ℓ. The shape of the deformation is determined by the variational parameters $\alpha_{\ell\ell'}^{(k\gamma)}$. The operator $\sum_{\ell''} a_{\ell\ell''}^{(k\gamma)} c_{\ell''\gamma}^\dagger$ creates an electron wave packet centred at site ℓ, with a form determined by the variational parameters $a_{\ell\ell''}^{(k\gamma)}$. The wave function (2) satis-

fies the Bloch condition

$$T_h \, |\psi_{k\gamma}\rangle = e^{-i\underline{k}\cdot\underline{R}h} \, |\psi_{k\gamma}\rangle \tag{3}$$

for arbitrary lattice translations T_h, if

$$\alpha^{(k\gamma)}_{\ell\ell'} = \alpha^{(k\gamma)}(\underline{R}_{\ell\ell'}) = \alpha^{(k\gamma)}_{\ell-\ell'} \quad ; \quad a^{(k\gamma)}_{\ell\ell'} = a^{(k\gamma)}(\underline{R}_{\ell\ell'}) = a^{(k\gamma)}_{\ell-\ell'}$$

with $\underline{R}_{\ell\ell'} = \underline{R}_\ell - R_{\ell'}$. Inversion or reflection symmetry requires

$$\alpha^{(k\gamma)}(\underline{R}_{\ell\ell'}) = \alpha^{(k\gamma)}(-\underline{R}_{\ell\ell'}) \quad ; \quad a^{(k\gamma)}(\underline{R}_{\ell\ell'}) = a^{(k\gamma)}(-\underline{R}_{\ell\ell'}).$$

With (2), the variational energy is obtained as

$$\langle\psi_{k\gamma}|H^{el}|\psi_{k\gamma}\rangle = \varepsilon_o \langle\psi_{k\gamma}|\psi_{k\gamma}\rangle - \hbar\Omega_s C^2 \sum_{\ell_1\ell_2} e^{i\underline{k}\cdot(\underline{R}_{\ell_2}-\underline{R}_{\ell_1})} \prod_{\ell''} e^{-\frac{1}{2}\left(\alpha^{(k\gamma)}_{\ell_1-\ell''} - \alpha^{(k\gamma)}_{\ell_2-\ell''}\right)^2} \sum_{\ell\ell'}{}' \hat{t}_\gamma(\ell\ell') \, a_{\ell_1-\ell} \, a_{\ell_2-\ell'} \tag{4a}$$

$$\langle\psi_{k\gamma}|H^{latt}|\psi_{k\gamma}\rangle = \tfrac{1}{2} N \hbar\Omega_s \langle\psi_{k\gamma}|\psi_{k\gamma}\rangle + \hbar\Omega_s C^2 \sum_{\ell_1\ell_2} e^{i\underline{k}\cdot(\underline{R}_{\ell_2}-\underline{R}_{\ell_1})} \prod_{\ell_o} e^{-\frac{1}{2}\left(\alpha^{(k\gamma)}_{\ell_1-\ell_o} - \alpha^{(k\gamma)}_{\ell_2-\ell_o}\right)^2} \sum_{\ell''} a^{(k\gamma)}_{\ell_1-\ell''} \, a^{(k\gamma)}_{\ell_2-\ell''} \cdot$$

$$\cdot \left[\sum_\ell \alpha^{(k\gamma)}_{\ell_1-\ell} \, \alpha^{(k\gamma)}_{\ell_2-\ell} - \tfrac{1}{2} \sum_{\ell\ell'}{}' \hat{V}_{\ell\ell'} \left(\alpha^{(k\gamma)}_{\ell_2-\ell} + \alpha^{(k\gamma)}_{\ell_1-\ell}\right)\left(\alpha^{(k\gamma)}_{\ell_2-\ell'} + \alpha^{(k\gamma)}_{\ell_1-\ell'}\right)\right] \tag{4b}$$

$$\langle\psi_{k\gamma}|H^{JT}|\psi_{k\gamma}\rangle = -\hbar\Omega_s C^2 \sigma_\gamma \hat{A} \sum_{\ell_1\ell_2} e^{i\underline{k}\cdot(\underline{R}_{\ell_2}-\underline{R}_{\ell_1})} \prod_{\ell'} e^{-\frac{1}{2}\left(\alpha^{(k\gamma)}_{\ell_1-\ell'} - \alpha^{(k\gamma)}_{\ell_2-\ell'}\right)^2} \sum_\ell \left(\alpha^{(k\gamma)}_{\ell_1-\ell} + \alpha^{(k\gamma)}_{\ell_2-\ell}\right) a_{\ell_1-\ell} \, a_{\ell_2-\ell} \tag{4c}$$

and the normalization constant C is given by

$$\langle\psi_{k\gamma}|\psi_{k\gamma}\rangle = 1 = C^2 \sum_{\ell_1\ell_2} e^{i\underline{k}\cdot(\underline{R}_{\ell_2}-\underline{R}_{\ell_1})} \prod_{\ell'} e^{-\frac{1}{2}\left(\alpha^{(k\gamma)}_{\ell_1-\ell'} - \alpha^{(k\gamma)}_{\ell_2-\ell'}\right)^2} \sum_{\ell''} a^{(k\gamma)}_{\ell_1-\ell''} \, a^{(k\gamma)}_{\ell_2-\ell''} \tag{4d}$$

Here $t_\gamma(\ell\ell') = t_\gamma(\ell\ell')/\hbar\Omega_S$, $\hbar\Omega_S \hat{V}_{\ell\ell'} = V_{\ell\ell'}/2M\Omega_S^2$, $\hat{A} = A(\hbar/2M\Omega_S)^{1/2}/\hbar\Omega_S$ with $\hat{A}^2 = E_{JT}/\hbar\Omega_S$, $\sigma_\gamma = 1$ for $\gamma = 1$ and $\sigma_\gamma = -1$ for $\gamma = 2$. In order to obtain the approximate ground-state energy, we first minimize $\langle\psi_{k\gamma}|H - E_\gamma(\underline{k}; \{\alpha^{(k\gamma)}_{\ell-\ell'}\}) \, \underline{1}|\psi_{k\gamma}\rangle$ with respect to the set $\{a^{(k\gamma)}_{\ell-\ell'}\}$. This leads to a secular equation which has to be solved for the ground-state energy $E^{(o)}_\gamma(\underline{k}; \alpha^{(k\gamma)}_{\ell-\ell'})$. The parameters $\{\alpha^{(k\gamma)}_{\ell-\ell'}\}$ are then chosen to minimize $E^{(o)}_\gamma(\underline{k})$.

If the wave packet $\sum_{\ell''} a^{(k\gamma)}_{\ell-\ell''} \, c_{\ell''\gamma}|0\rangle$ has small width, the wave function (2) is a superposition of terms describing an electron which is well localized near lattice site ℓ, in a deformation pattern given by the $\alpha^{(k\gamma)}_{\ell-\ell'}$. The

phase factors $e^{i\underline{k}\cdot\underline{R}_\ell}$ are chosen to yield a state with given total crystal momentum $\underline{k}$. This is the fully developed JT-polaron state which we expect in the limit $E_{JT} >> t, \hbar\Omega_S$.

In the limit of small displacements $\alpha_{\ell-\ell'}^{(k\gamma)}$, on the other hand, the state described by $|\psi_{k\gamma}$ depends on the value of the Fourier transform $a_k^{(k\gamma)}$ of $a_{\ell-\ell''}^{(k\gamma)}$: If $a_k^{(k\gamma)} \neq 0$, then $|\psi_{k\gamma}>$ represents an electron moving freely through the crystal with crystal momentum $\underline{k}$. If $a_{\ell-\ell''}^{(k\gamma)} = a = \text{const.}$, then $|\psi_{k\gamma}>$ represents an unbound pair consisting of an electron with zero crystal momentum and a phonon with crystal momentum $\underline{k}$. These are the ground states for given $\underline{k}$ in the limit of small JT-coupling, depending on whether $\varepsilon_{k\gamma} < \hbar\omega_k$ or $\varepsilon_{k\gamma} > \hbar\omega_k$, respectively, where $\varepsilon_{k\gamma}$ is the bare electronic energy and ω_k is the optical phonon frequency. Thus, the variational ansatz (2) is able to reproduce the true wave function in the limiting cases, and may therefore be expected to yield reasonable results also in the intermediate cases. In fact, in the case of a two JT-centre one-electron model, the wave function gives ground-state energies which differ less than 1% from exact numerical results.

III. RESULTS AND DISCUSSION FOR A LINEAR CHAIN

We apply the method described above to the case of a linear chain with nearest neighbour tunnelling

$$t(\ell\ell') = t(\delta_{\ell,\ell'+1} + \delta_{\ell,\ell'-1}) \tag{5}$$

i.e. band width 2t, and an Einstein model ($V_{\ell\ell'} = 0$) for the lattice vibrations. Here, we consider the case $E_{JT} \gtrsim t$ and restrict the number of variational parameters $a_{\ell-\ell'}^{(k\gamma)} = a_{\ell'-\ell}^{(k\gamma)}$ to ten: $\{a_0^{(k\gamma)} = a_0^{(k)}, \ldots, a_9^{(k\gamma)} = a_9^{(k)}\}$. The distortion parameters $\alpha_{\ell-\ell'}^{(k\gamma)} = \alpha_{\ell'-\ell}^{(k\gamma)}$ are restricted to $\alpha_0^{(k\gamma)}$, associated with the on-site electron amplitude $a_0^{(k)}$, and the nearest-neighbour values $\alpha_1^{(k\gamma)}$. Investigations, including a larger number of variational parameters will be presented in a forthcoming paper. Clearly, due to (5), the symmetry-related states $|\psi_{k\gamma}>$, $\gamma = 1, 2$ are still degenerate with $\alpha_0^{(k1)} = -\alpha_0^{(k2)}$ and $\alpha_1^{(k1)} = -\alpha_1^{(k2)}$.

By minimization we obtain an energy-momentum relation for the JT-polaron which is shown in fig. 1 for various values of the JT-stabilization energy $E_{JT} = -\hat{A}^2$ and fixed $\hat{t} = 4$. We use $\hbar\Omega_S = 1$ for the unit of energy. As can be seen from fig. 1, the ground-state energy $\hat{E}^{(o)}(\underline{k})$ varies quadratically for small values of the crystal momentum $\underline{k}$ and can be written in the usual

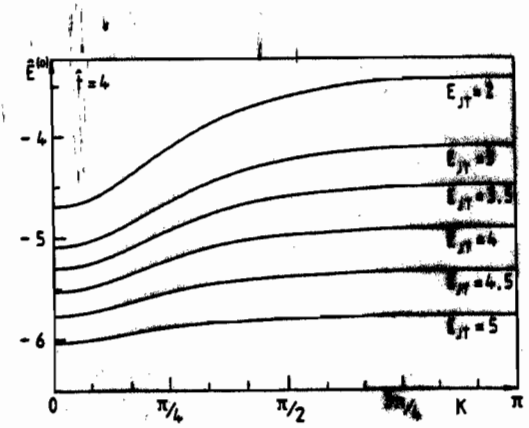

Fig. 1

JT-polaron ground-state energies $\hat{E}^{(o)}(k)$, vs. crystal momentum k for various values of the JT-stabilization energy E_{JT} (energies are given in units of $\hbar\,\Omega_S = 1$).

form

$$\hat{E}_k^{(o)} = \hat{E}_0^{(o)} + (\hbar^2/2\,m_{eff})\,K^2 \qquad (6)$$

For K = 0 we find values for the ground-state energy $\hat{E}_0^{(o)}$ and the on-site JT-distortion $\alpha_0^{(o)}$, which are displayed in fig. 2 as a function of E_{JT} for the case of $\hat{t} = 4$. The results show that for $E_{JT} << \hat{t}$ the JT-distortion is small, the electron travels through the lattice with a tunnelling constant slightly perturbed by the coupling. With increasing E_{JT}, the JT-distortion increases and for $E_{JT} >> \hat{t}$, the ground-state energy $\hat{E}_0^{(o)}$ and the JT-distortion $\alpha_0^{(o)}$ approach $\hat{E}_0^{(o)} \to -\hat{A}^2 = -\hat{A}^2/2M\,\Omega_S^2$ and $\alpha_0^{(o)} \to \hat{A} \sim A/M\,\Omega_S^2$, respectively, the values

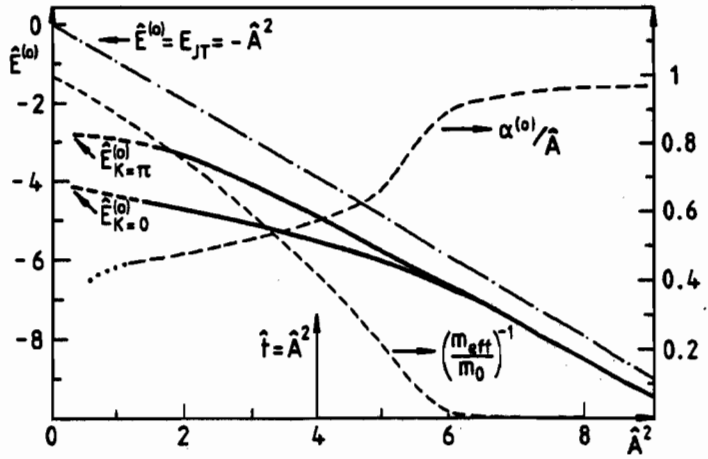

Fig. 2 Left scale: Ground-state energies $\hat{E}^{(o)}(K=0)$ and $\hat{E}^{(o)}(K=\pi)$ for fixed $\hat{t} = 4$ vs. $\hat{A}^2 = -E_{JT}$. The broken line indicates the limit value $E_{JT} = -A^2/2M\,\Omega_S^2$ of an isolated JT-complex. Right scale: Normalized on-site JT-distortion. $\alpha_0^{(o)}/\hat{A}$, and reciprocal effective mass, $(m_{eff}/m_0)^{-1}$ vs. $\hat{A}^2$. m_0 is the effective mass of the bare electron.

of an isolated JT-active molecular complex, i.e. one obtains a fully developed polaron.

With increasing localization we expect a quenching of the tunnelling due to the exponential factors in (4a). This competition between energy gain due to tunnelling and due to localization on the other hand, is clearly displayed by the values found for the effective mass m_{eff}, associated with the complex, which is defined by the form (6) of the ground-state energy for small k. Figure 2 shows that $(m_{eff}/m_o)^{-1}$ is diminished drastically in the region $E_{JT} \gtrsim \tilde{t}$, where localization occurs. The same effect is shown by the total band width, $\tilde{E}^{(o)}_{K=\pi} - \tilde{E}^{(o)}_{K=0}$, which can be read off from fig. 2.

In conclusion, we have shown that the competition between the delocalization effect of tunnelling and the localization effect of JT-coupling gives rise to a transition from an itinerant electron state to a JT-polaron state with very high effective mass.

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