Understanding the electron-phonon interaction in polar crystals: Perspective presented by the vibronic theory

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Abstract. We outline our novel results relating to the physics of the electron-TO-phonon (el-TO-ph) interaction in a polar crystal. We explained why the el-TO-ph interaction becomes effectively strong in a ferroelectric, and showed how the electron density redistribution establishes favorable conditions for soft-behavior of the long-wavelength branch of the active TO vibration. In the context of the vibronic theory it has been demonstrated that at the macroscopic level the interaction of electrons with the polar zone-centre TO phonons can be associated with the internal long-range dipole forces. Also we elucidated a methodological issue of how local field effects are incorporated within the vibronic theory. These result provided not only substantial support for the vibronic mechanism of ferroelectricity but also presented direct evidence of equivalence between vibronic and the other lattice dynamics models. The corresponding comparison allowed us to introduce the original parametrization for constants of the vibronic interaction in terms of key material constants. The applicability of the suggested formula has been tested for a wide class of polar materials.

1. Introduction

In a lattice dynamics model of a polar crystalline material the expression for the squared dipole-active vibration in the Γ point has an effective representation in terms of two contributions:

$$\Omega_{0j}^2 = \widetilde{\omega}_{0j}^2 + \Delta\omega_{0j}^2 \,. \tag{1}$$

The first one $\widetilde{\omega}_{0j}^2$ describes an overall positive contribution of the short range forces acting between ions. Since the second contribution $\Delta\omega_{0j}^2$ is negative, comparison of $\widetilde{\omega}_{0j}^2$ and $\Delta\omega_{0j}^2$ indicates that the lattice becomes dynamically unstable through the imaginary transverse mode. Microscopic understanding of $\Delta\omega_{0j}^2$, was given by the vibronic theory (e.g., [1, 2, 3, 4, 5, 6, 7]). According to the vibronic mechanism the interband mixing of valence electrons by the zone-center polar TO lattice vibrations is the leading driving force of displacive structural instability. Outstanding success has been established in an explanation of structural changes in the perovskite oxides for which the lattice instability was associated with the effect of dynamical hybridization. The hybridization involves the mixing the filled O 2p and the empty Ti d^0 electronic states by the IR-active TO F_{1u} soft vibrations and gives rise to an additional chemical interaction, known as dynamic covalency, that governs a structural distortion of a parent high-symmetry cubic configuration.

On the other hand, as it has been previously observed in a number of classic works on lattice dynamics [8, 9, 10, 11], just the presence of long-range forces predetermines the polar properties of crystals. Furthermore, in the context of Born and Huang theory of lattice dynamics [8], the specific contribution represented by the second term of (1) can be expressed via the regular part of the Coulomb contribution to the force matrix of the system[12, 13]:

$$\Delta\omega_{0j}^2 = -\frac{4\pi e^2}{v} \sum_{\alpha,\beta} \frac{\delta_{\alpha\beta}}{(\epsilon_\infty + 2)} \left(\sum_s Z_s^* \frac{w_\alpha(s,0j)}{\sqrt{M_s}} \right) \left(\sum_t Z_t^* \frac{w_\beta(t,0j)}{\sqrt{M_t}} \right), \tag{2}$$

where v is the volume of the unit cell, Z_s^* are the Born dynamical charges, and ϵ_∞ is the electronic (static-high-frequency) dielectric constant. Comparison of (1) and (2) allows to interpret the stability issue of a polar material as a delicate balance of the short-range and long-range internal forces.

The vibronic theory has been the subject of intense development over the past several decades. The results were reported in a number of books and review papers (e.g., [1, 2, 3, 4, 5, 6, 7] and references therein). One of its fundamental results is that the theory provided a faithfully microscopic insight into the origin of displacive structural transitions in crystalline solids. As it follows from the theory, the magnitude of vibronic interaction is particularly important to promote and trigger displacive structural instability. However, the problem of accurate characterizing the interaction of valence electrons with vibrations of the transverse optical branch received much less attention and had remained a challenge for a substantially long time. Furthermore, the

important part of the challenge has been the methodological difference positioned as the difference between the underlying mechanisms of the structural instability, one of which is based on the vibronic interaction and the other one relies upon the long-wavelength dynamics of force balances. Thus, the main purpose of the present paper was (i) to clarify why the e-TO-ph interaction is strong enough in polar materials, and (ii) to find a proper way according which the vibronic interaction and mechanism relating structure and forces could be entirely linked at the level of the specific contribution $\Delta\omega_{0j}^2$ to the dipole-active vibrational mode.

2. Results

We first present here the vibronic Hamiltonian in terms of the second-quantization formalism:

$$H_{el-ph} = N^{-1/2} \sum_{\sigma,\sigma'\,j} \sum_{\mathbf{k},\mathbf{q}} g_{\sigma\sigma'}(\mathbf{k},\mathbf{q}j)\, a_{\sigma\mathbf{k}}^{+} a_{\sigma'\mathbf{k}-\mathbf{q}}\, u_{\mathbf{q}j}\,, \tag{3}$$

where $g_{\sigma\sigma'}(\mathbf{k},\mathbf{q}j)$ are the matrix elements of the electron-TO-phonon interaction (the vibronic coupling) calculated on the Bloch wave functions $\psi_{\sigma\mathbf{k}}$. As usual, $\psi_{\sigma\mathbf{k}}$ labeled by the band index σ represent the basis of the one-particle electronic states with energies $E_\sigma(\mathbf{k})$ and Fermi occupation factors $f_\sigma(\mathbf{k})\equiv f(E_\sigma(\mathbf{k}))$. Note that the detailed evaluation of how the electron-TO-phonon interaction contributes into the total energy of the system has been performed in [14].

2.1. Why the e-TO-ph interaction is strong enough in polar materials

As we consider a model of the polar crystal at the atomistic level, it is important to emphasize that the microscopic expression for the quantities $g_{\sigma\sigma'}(\mathbf{k},\mathbf{q}j)$ involves the dipole polarization (dipole moment per unit volume) $\mathbf{P}(\mathbf{q}j)$ (defined in [8]) associated with the polar TO mode. Let us introduce in the long-wavelength limit $\mathbf{q} \to 0$ the amplitude of the interband el-TO-ph interaction $|g_{\sigma\sigma'}(\mathbf{k})| = (\lim_{\mathbf{q}\to 0} |g_{\sigma\sigma'}(\mathbf{k},\mathbf{q}j)|^2)^{1/2}$. Due to the dependence of $|g_{\sigma\sigma'}(\mathbf{k})|$ on the polarization $P(0j)$ one can represent the amplitude in terms of macroscopic quantities by using results of [8]. Details of calculations can be found in [14]. We demonstrate here the final expression:

$$|g_{\sigma\sigma'}(\mathbf{k})| \cong \sqrt{\frac{v}{4\pi}\,\epsilon_\infty\,(\Delta\Omega_{LT})^2}\, \left|< \sigma\mathbf{k}|\,\nabla\phi_e(\mathbf{r})\,|\sigma'\mathbf{k}>\right|\,. \tag{4}$$

The most important feature of equation (4) is that it displays the straightforward interplay of two macroscopic effects:
(i) it depends directly on the LO-TO splitting $\Delta\Omega_{LT} = (\Omega_{LO}^2 - \Omega_{TO}^2)^{1/2}$, the magnitude of which is determined by the difference between the longitudinal (Ω_{LO}) and the transverse (Ω_{TO}) vibrational modes, and
(ii) it is determined by the spatial distribution of gradients of the overall Coulomb

electrostatic potential $\phi_e(\mathbf{r})$

$$\phi_e(\mathbf{r}) = \sum_{\mathbf{l}} \frac{e}{|\mathbf{r} - \mathbf{l}|} . \tag{5}$$

represented as the sum over the lattice site $\mathbf{l}$. The potential is associated with an internal electric field which via macroscopic changes in valence electron charge densities $\delta\rho_e(\mathbf{r}) = e\sum_{\mathbf{l}}\delta(\mathbf{r} - \mathbf{l})$ is generated by the actual long-wavelength distortions [14].

Another feature of equation (4) is determined by the product of two macroscopic parameters: $\epsilon_\infty (\Delta\Omega_{LT})^2 \sim |Z^*|^2$. Thereby, equation (4) provides the necessary link connecting theoretical result (4) with the corresponding results of studies [16] on Born's dynamical effective charges in ferroelectrics. The comparison shows that the presence of $\epsilon_\infty (\Delta\Omega_{LT})^2$ guarantees the significantly large values of the el-TO-ph interaction in ferroelectrics [15]. We can thus conclude that the vibronic coupling of valence band electrons with dipole-active zone-centre TO phonons has a long-range character, is governed by the internal electric field, and is essentially sensitive to a key macroscopic parameter of a polar material – Born's dynamical effective charge.

2.2. Vibronic mechanism and long-range forces

In previous subsection we demonstrated a proof of the canonical view of the vibronic theory that in a polar crystalline material the dipole-active vibrational modes may strongly interact with valence band electrons. We now show how vibronic interaction channel (3) can be related to lattice dynamics models of a polar insulator considered in [8, 9, 10, 11]. The idea is to reconcile the microscopic results by mapping theirs to the macroscopic scale determined by equation (2) of the Born and Huang theory [8]. Thus, our task is to check whether calculations of the softening vibronic contribution to the TO vibrational mode can reveal a solution that corresponds exactly the formulation of equation (2). In a general RPA approach, such examination was performed in [14]. In order to draw comparisons with the previous theoretical studies we here report a special case of the zone-centre TO vibrational modes. At the Γ point, the vibronic renormalization of the TO phonon frequency is given by

$$
\begin{cases}
\Delta\omega_{0j}^2 = 4\pi v \sum_{\alpha,\beta} B_{\alpha\beta}(0)\, P_\alpha(0j)\, P_\beta(0j)\,, \\[2ex]
B_{\alpha\beta} = \dfrac{v}{4\pi e^2} \sum_{\mathbf{G},\mathbf{G}'\neq 0} \left[\, G_\alpha\, v_c(\mathbf{G})\, \chi_{el}(\mathbf{G},\mathbf{G}')v_c(\mathbf{G}')\, G_\beta'\,\right], \\[2ex]
v_c(\mathbf{G}) = \dfrac{4\pi e^2}{v\,|\mathbf{G}|^2}\,, \quad \hat{\chi}_{el} = \dfrac{\hat{\Pi}_0}{\hat{I} - \hat{v}_c\hat{\Pi}_0}\,, \\[2ex]
\Pi_0(\mathbf{G},\mathbf{G}') = -\dfrac{1}{N}\sum_{\sigma,\sigma'}\sum_{\mathbf{k}} \dfrac{f_\sigma(\mathbf{k}) - f_{\sigma'}(\mathbf{k})}{E_{\sigma'}(\mathbf{k}) - E_\sigma(\mathbf{k})} \\[2ex]
\times \int \psi_{\sigma\mathbf{k}}^* e^{i\mathbf{G}\,\mathbf{r}}\psi_{\sigma'\mathbf{k}-\mathbf{q}}\, d\tau \int \psi_{\sigma'\mathbf{k}-\mathbf{q}}^* e^{-i\mathbf{G}'\,\mathbf{r}'}\psi_{\sigma\mathbf{k}}\, d\tau'\,,
\end{cases}
\tag{6}
$$

where the microscopical dielectric susceptibility of the electron subsystem $\chi_{el}(\mathbf{G}, \mathbf{G}')$, written in the operator form, is expressed via the polarization operator $\hat{\Pi}_0$, the identity matrix $\hat{I}$, the bare Coulomb interaction $\hat{v}_c$. In the context of summation over the reciprocal lattice vectors $\mathbf{G}$ and $\mathbf{G}'$, it is important to emphasize that thanks to a fractional form of $\hat{\chi}_{el}$ the system of equations (6) accounts for the many-body polarization effects. As shown in [14], comparison with previously reported studies on the "macroscopic" counterpart of $\Delta\omega_{0j}^2$ [17] allowed one to obtain a result of summation over all $\mathbf{G}$, $\mathbf{G}'$ in the equation for the tensor $B_{\alpha\beta}(0)$. The final expression contains the local-field factor:

$$B_{\alpha\beta}(0) \, = \, \frac{v}{4\pi e^2} \sum_{\mathbf{G}, \mathbf{G}' \neq 0} G_\alpha v_c(\mathbf{G}) \, \chi_{el}(\mathbf{G}, \mathbf{G}') \, v_c(\mathbf{G}') \, G_\beta' = \, -\frac{\delta_{\alpha\beta}}{(\epsilon_\infty + 2)} \, . \quad (7)$$

The minus sign displayed on the right hand of (7) implies that the elements of $B_{\alpha\beta}(0)$ are allowed to take only negative values, and, correspondingly, $\Delta\omega_{0j}^2$ describes the destabilizing contribution. Result (7) leads to the following expression for $\Delta\omega_{0j}^2$ which is represented in terms of the local field factor and the dipole oscillator strengths $S_{\alpha\beta}(j)$:

$$\begin{cases} \Delta\omega_{0j}^2 \, = \, \sum_{\alpha,\beta} B_{\alpha\beta}(0) \, S_{\alpha\beta}(j) \, ; \\[2mm] S_{\alpha\beta}(j) \, = \, \frac{4\pi e^2}{v} \left(\sum_s Z_s^* \frac{w_\alpha(s, 0j)}{\sqrt{M_s}} \right) \left(\sum_t Z_t^* \frac{w_\beta(t, 0j)}{\sqrt{M_t}} \right) \, . \end{cases} \quad (8)$$

Comparison of equation (2) with its vibronic counterpart given at the macroscopic level by equation (8) recognizes the typical patterns corresponding to the contribution of the long-range dipole forces. It is clearly seen that both equations display a full identity. In this context, we can thus conclude that we achieved the link between two different descriptions of the dynamics of TO vibrations: with respect to final results the description based on the vibronic mechanism appears entirely identical with that [8, 12, 13] exploiting the mechanism based on the dipole-dipole interactions.

2.3. El-TO-ph coupling via macroscopic parameters

The results of previous subsection offer an interesting possibility to connect (conceptually) the microscopic nature of the interaction of the valence band electrons with the polar long-wavelength TO modes to the regular part of the long-range dipole-dipole interaction. A comparative analysis revealed that the quantities $S_{\alpha\beta}(j)$ that serve as a direct mediator of the long-range dipole forces can be used for the parametrization of the el-TO-ph interaction in terms of material parameters. As it was reported in [14, 15], for an insulator with the electron band gap E_g the square of the effective $\mathbf{k}$-independent vibronic interaction renormalized (due to screening) by the local field factor can be represented as follows

$$\bar{g}_j^2 \, = \, 3g_{0j}^2 / (\epsilon_\infty + 2) \, , \; g_{0j}^2 \, = \, \frac{1}{12} E_g \, M_j \, S(j) \, . \quad (9)$$

Here g_{0j}^2 are the squared el-TO-ph matrix elements averaged over the one-particle electronic states:

$$g_{0j}^2 = \sum_{\sigma' > \sigma} \frac{1}{2N} \sum_{\mathbf{k}} |g_{\sigma\sigma'}^j(\mathbf{k})|^2 \frac{E_g}{|E_{\sigma'}(\mathbf{k}) - E_\sigma(\mathbf{k})|} \;;$$

$S(j) = \sum_\alpha S_{\alpha\alpha}(j)$, and the dipole oscillator strengths $S_{\alpha\alpha}(j)$ are associated with the dipole-active vibrational modes of the branch j and of the reduced mass M_j; the band gap value E_g plays the role of a material parameter. In analyzing relation (9), we should note three significant points. First, with respect to direct dependence on Born's dynamic charges it is fully consistent with microscopic equation (4). Likewise, the presence of Born's dynamic charges represents here a key signature indicating that the el-TO-ph coupling is particularly strong in a ferroelectric system. Second, the useful prognostic potential of (9), i. e. it allows directly evaluate the el-TO-ph coupling constants from the experimental/computational data. Third, very important is the observation that the electron-phonon Fröhlich Hamiltonian can be employed as the model Hamiltonian of the vibronic theory under the following rigorous requirement: the model constants of el-TO-ph interaction should be taken renormalized by the local field effect.

2.4. Tailoring of macroscopic measure of ferroelectricity

Based on the results of our comparative analysis, one can demonstrate that the vibronic theory describes the lattice instability for a wide number of ferroelectric materials. We start our rationale from the following arguments. On a microscopic scale, the vibronic theory rationalizes the underlying physics of the ferroelectric instability in terms of the specific matching of structural and electronic parameters. On the other hand, on a macroscopic scale, the dipole oscillator strengths provide reliable information on the properties of dipole-active lattice vibrational modes. Taking into account that the dipole oscillator strengths contain information on the strength of vibronic interactions in the system, we can quantify the interplay of both scales by introducing parameter τ written in terms of material constants Ω_{0j}, $S(j)$, and ϵ_∞:

$$\tau_j = \frac{\widetilde{S}(j)}{\widetilde{S}(j) + \epsilon_\infty + 2}, \quad \text{where} \quad \widetilde{S}(j) = S(j)/\Omega_{0j}^2 \tag{10}$$

In ferroelectrics, $\widetilde{S}(j) >> \epsilon_\infty + 2$ for the soft-mode, so that $\tau_j \to 1$. Accordingly, the parameter τ_j represents a measure of the polarity. In fact, τ integrates the polar features of the system via the presence of the material constants in equation (10). In this sense one can say that (10) indicates how close the system under consideration resides to the point of ferroelectric instability.

The numerical investigation of (10) was performed in our recent work [18] for several representative polar compounds such as typical insulating perovskites, and the $A^{IV}B^{VI}$-type narrow-gap semiconductors. Estimates were made for the case of the most low-lying zone-center polar TO vibrational mode. Calculations demonstrated that in accordance

with out theoretical description the values of the parameter τ fall for all the materials considered within the range: 0.89 (SnTe) – 0.99 (BaTiO$_3$).

3. Conclusion

In conclusion, we showed the full correspondence between two different lattice dynamics models on description of displacive structural instabilities in polar crystals. The obtained result is of principal importance because it confirms that the vibronic theory a priori accounts for the effects of the local field. We suggested a representation of the vibronic coupling via a combination of dipole oscillator strengths of the zone-center TO vibrational mode, electronic forbidden gap, and the dielectric constant. This approach provided a novel relationship that by using infrared spectroscopy and electron structure data allows one to estimate the strength of the el-TO-ph interaction in any polar crystalline material.

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