

# Spectra of bound phonons in crystals containing electron centers

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Modification of the phonon spectrum by an excess electron is studied for an  $F$  center in a crystal. The local phonon frequencies are calculated for the ground and first excited self-consistent states of an  $F$  center in KCl. It is found that local modes of frequencies higher than the optical phonon frequency exist for such centers.

One of the important problems in crystal lattice dynamics is the calculation of lattice vibrational spectra for lattices containing various defects and impurities. The existence of an excess electron interacting with lattice vibrations in a crystal can be regarded (from the point of view of lattice dynamics) as a special type of defect. If the electron interaction with the lattice is weak so that perturbation theory is applicable, such an interaction leads only to re-normalization of phonon frequencies and does not cause qualitative changes in the spectrum.<sup>1</sup> Phonon frequencies in the case of strong interaction were first calculated for an ionic crystal in the adiabatic limit in Ref. 2. According to Ref. 2, in this limiting case the phonon spectrum changes qualitatively and a discrete set of local vibrations is created. In practice, it is particularly interesting to calculate the phonon spectrum when an excess electron is localized near a lattice defect. For example, in the case of  $F$  centers in ionic crystals, the tight-binding approximation can be applied to the electron-phonon interaction with  $\alpha \geq 0.5$  (see Ref. 3), i.e., for most crystals. The lattice spectrum then changes not only because of the interaction of lattice vibrations with an electron localized at a defect, but also due to the effect of the defect itself. A self-consistent calculation of both these effects is at present rather difficult. Both effects usually contribute to different regions of the spectrum and can be identified experimentally. We shall consider the effect of the electron-phonon interaction on the lattice dynamics under tight-binding conditions. Our results for the lattice spectrum of a crystal containing electron centers can be very important in a study of infrared absorption and of Raman and neutron scattering in ionic crystals.

## 1. EQUATIONS OF THE ADIABATIC THEORY

Most general calculations of the phonon spectrum, irrespective of the type of defect, as based on the self-consistent solution of the equations of the adiabatic theory.<sup>4</sup> It follows from Ref. 4 that the solution of equations for the electron and phonon subsystems reduces to the solution of the following chain of equations:

$$(H_0^{(0)} - W^{(0)}) \varphi^{(0)} = 0 \quad (1)$$

$$(H_0^{(1)} - W^{(1)}) \varphi^{(1)} = -H_0^{(1)} \varphi^{(0)} \quad (2)$$

$$(H_0^{(2)} - W^{(2)}) \varphi^{(2)} = -H_0^{(2)} \varphi^{(1)} - (H_0^{(2)} - W^{(2)}) \varphi^{(0)} \quad (3)$$

$$(H_1^{(2)} + W^{(2)} - E^{(2)}) \varphi^{(2)} = 0 \quad (4)$$

where  $H^{(i)}$  and  $H_0^{(i)}$  are the nuclear kinetic energy and the Hamiltonian of the electron subsystem;  $E^{(i)}$  and  $W^{(i)}$  are the total and electron energies of the system;  $\varphi^{(i)}$  and  $\phi^{(i)}$  are the electron and phonon wave functions which appear in the expansions in terms of a small parameter

$$F = \sum_{i=0}^{\infty} \epsilon^i F^{(i)}, \quad (5)$$

$$F = (\varphi, \Phi, W, E, H). \quad (6)$$

It follows from Eqs (1)-(3) that

$$W^{(2)} = H_0^{(2)} + (\varphi^{(0)}, H_0^{(1)} \varphi^{(1)}), \quad (7)$$

$$(\varphi, \varphi) = \int \varphi(r) \varphi(r) d^3r. \quad (8)$$

We note that  $W^{(2)}$  is a quadratic form

$$W^{(2)} = \sum_{k,l} M_{kl} u_k u_l, \quad (9)$$

where  $\epsilon u_k = Q_k^{(0)} - Q_k$  are phonon coordinates characterizing the deviations from the equilibrium position  $Q_k^{(0)}$  which can be obtained from the requirement that the form

$$(\varphi^{(0)}, H_0^{(1)} \varphi^{(0)}) = 0. \quad (10)$$

linear in the displacements, vanishes.

The matrix  $M_{kl}$  is Hermitian and has the following properties:

$$\sum_k M_{kl} \Lambda_{sk} = \omega_s^2 \delta_{sl}, \quad (11)$$

$$M_{kl} = M_{lk}^* = M_{-k-l}, \quad (12)$$

$$\Lambda_{sk}^* = \Lambda_{-sk}. \quad (13)$$

Here,  $\Lambda_{sk}$  and  $\omega_s^2$  denote the orthonormalized eigenvectors and eigenvalues of  $M_{kl}$ . Their actual values will be obtained for an electron at an  $F$  center later.

## 2. ADIABATIC APPROXIMATION FOR AN F CENTER

The total Hamiltonian of an  $F$  center has the form

$$H = -\nabla^2 + \sum_k \left[ \frac{1}{2} (P_k P_{-k} - 1 + Q_k Q_{-k}) + C_k Q_k e^{ikr} \right] - \frac{\nu}{r}, \quad (14)$$

where  $r$  is the electron coordinate;  $\nu = ze^2/\epsilon$  is the effective defect charge;  $\{Q_k, P_k\}$  are complex lattice coordinates;  $C_k = \sqrt{8\pi\alpha/\Omega}$ . We set  $\hbar = 1$ ,  $\omega_0 = \text{const} = 1$ , and  $2m^* = 1$  in Eq. (14), where  $m^*$  is the effective electron mass and  $\omega_0$  is the optical phonon frequency. Following the adiabatic approximation treatment described earlier, we obtain

$$H_0^{(0)} = -\nabla^2 + \sum_k \left( \frac{1}{2} Q_k^{(0)} Q_{-k}^{(0)} + C_k Q_k^{(0)} e^{ikr} \right) - \frac{\nu}{r}, \quad (15)$$

$$H_0^{(1)} = \sum_k (C_k e^{ikr} + Q_k^{(0)}) u_k = \sum_k \hbar_k u_k, \quad (16)$$

$$H_0^{(2)} = \sum_k \frac{1}{2} u_k u_{-k}, \quad (17)$$

$$H_i^{(1)} = \frac{1}{2} \sum_k (P_k P_{-k} - 1). \quad (18)$$

Equation (1) for the electron wave function  $\phi^{(0)}$  then assumes the form

$$\left[ -\nabla^2 - \frac{\nu}{r} + \sum_k \left( \frac{1}{2} Q_k^{(0)} Q_{-k}^{(0)} + C_k Q_k^{(0)} e^{ikr} \right) - |V^{(0)}| \right] \varphi^{(0)} = 0. \quad (19)$$

Using Eq. (10), we obtain for  $Q_k^{(0)}$

$$Q_k^{(0)} = -C_k (\varphi^{(0)}, e^{-ikr} \varphi^{(0)}). \quad (20)$$

Equation (4) yields the following equation for the wave function of nuclei:

$$1/2 \left( \sum_k P_k P_{-k} - 1 \right) + |V^{(2)} - E^{(2)}| \phi^{(0)} = 0. \quad (21)$$

Introducing normal coordinates

$$\xi_s = \sum_k \Lambda_{sk} u_k, \quad \tau_s = -i (\partial / \partial \xi_s), \quad (22)$$

and using the properties (11)-(13) of the quadratic form  $W^{(2)}$ , we obtain from Eq. (22)

$$\left[ 1/2 \sum_s (\tau_s^2 - 1 + \omega_s^2 \xi_s^2) - E^{(2)} \right] \phi^{(0)} = 0. \quad (23)$$

To evaluate the frequencies of normal vibrations  $\omega_s$ , we shall make use of an equation for  $\phi^{(1)}$ . Setting

$$\varphi^{(1)}(r, \xi) = \sum_s \xi_s X_s(r), \quad (24)$$

and using Eq. (2), we obtain the following equation:

$$\left[ -\nabla^2 - \frac{\nu}{r} + \sum_k C_k Q_k^{(0)} e^{ikr} - \bar{W} \right] X_s(r) = -\varphi^{(0)} \sum_k h_k \Lambda_{sk}. \quad (25)$$

where

$$\bar{W} = W^{(0)} - 1/2 \sum_k Q_k^{(0)} Q_{-k}^{(0)}. \quad (26)$$

Using the properties (11)-(13) and the definition (26), we then obtain from Eq. (7)

$$\frac{1}{2} \sum_s \omega_s^2 \xi_s = \frac{1}{2} \sum_{s,t} \left[ \left( X_s, \sum_k h_k \Lambda_{tk} \varphi^{(0)} \right) + \left( X_t, \sum_k h_k \Lambda_{sk} \varphi^{(0)} \right) + \delta_{st} \right] \xi_s \xi_t. \quad (27)$$

The condition that the off-diagonal elements of the quadratic form in  $\xi_s$  on the right-hand side of Eq. (27) should vanish yields the following restriction on the eigenvectors  $\Lambda_{sk}$ :

$$(1 - \omega_s^2) \Lambda_{sk} = -2 (X_s, C_k e^{ikr} \varphi^{(0)}). \quad (28)$$

The system of equations (26) and (28) determines the frequencies of normal vibrations. We solved this system numerically.

### 3. RESULTS OF NUMERICAL CALCULATIONS

The equations of the zeroth approximation (19) and (20) yield the following system of equations:

$$\nabla^2 \varphi(r) + 2\alpha II(r) \varphi(r) + (\nu/r) \varphi(r) + \bar{W} \varphi(r) = 0, \quad (29)$$

$$\nabla^2 \Pi(r) + 4\pi \rho^s(r) = 0, \quad (30)$$

where the function  $2\alpha II(r)$  can be interpreted as the potential due to the polarization induced by an electron localized in the vicinity of a defect and  $\phi(r)$  is the zeroth-order electron wave function. According

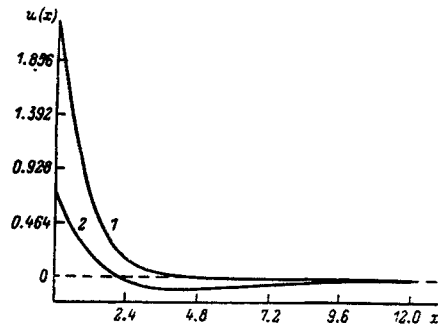


FIG. 1. Electron wave functions of an F center in KCl.

to the results of Ref. 5, the system (29) and (30) has a discrete set of spherically symmetric solutions each of which can be characterized by a quantum number  $n = n_{\Pi} + 1$ , where  $n_{\Pi}$  is the number of nodes of the wave function. The wave function with  $n = 1$  corresponds to the lowest energy level and describes the ground state, whereas all the other wave functions correspond to excited self-consistent states. Figure 1 shows the wave functions  $u(x) = u(\alpha r) = \sqrt{4\pi/\alpha^3} \phi(r)$  for the ground (1) and first excited (2) states of an F center in KCl obtained in Refs. 5 and 6. We would like to emphasize that our theory can be applied to all the self-consistent excited states determined from Eq. (29) and (30).

To determine the first-order electron wave function, we transform the system of equations (26) and (28) to

$$\left[ \nabla^2 + 2\alpha II(r) + \frac{\nu}{r} + \bar{W} \right] X_s(r) = \frac{4\pi}{1 - \omega_s^2} \left[ \int K(r, r') X_s(r') d^3r' - \varphi(r) \delta_s \right] \quad (31)$$

where

$$K(r, r') = \varphi(r) \varphi(r') / |r - r'|, \quad (32)$$

$$D = \int \int K(r, r') X(r') \varphi(r) d^3r d^3r'. \quad (33)$$

Here,  $\Pi(r)$  and  $\phi(r)$  can be determined from the zeroth-order equations (29) and (30). The linear integrodifferential equation (31) with a symmetric kernel defined by Eq. (32) determines a real set of eigenvalues  $\omega_s^2$  for the squares of the frequency; the ground state was investigated numerically in Ref. 7 in the case  $\nu = 0$  (free polaron). The results of numerical calculations for an F center in KCl ( $\nu = 0.84$ ) are listed in Table I; here,  $\omega_{n\ell}$  are the normal frequencies characterized by a principal quantum number  $n$  and an orbital quantum number  $\ell$ . The frequencies  $\omega_{n\ell}$  correspond to a discrete set of local vibrations which accumulate rapidly near the vibration frequency of an unperturbed lattice as  $s$  increases. We shall determine the spatial damping of such states. Equation (23) yields the following expression for the lattice displacements:

$$u_s(r) = \sum_k e^{-ikr} \Lambda_{sk} \xi_s = \frac{\Omega}{(2\pi)^3} \int e^{-ikr} \Lambda_{sk} \xi_s d^3k. \quad (34)$$

Using the expression (28) for  $\Lambda_{sk}$ , we obtain from Eq. (34)

$$u_s(r) \sim \frac{\alpha}{1 - \omega_s^2} \int \frac{\varphi(r') X(r')}{|r - r'|^2} d^3r'. \quad (35)$$

In the limit  $r \rightarrow \infty$ , we obtain for  $\ell > 0$  the dependence  $u_s(r) \propto r^{-\ell-2}$ . For  $\ell = 0$ , we can use the orthogonality condition  $(\phi, X_s) = 0$  and obtain  $u_s(r) \propto r^{-6}$  from Eq. (35). It thus follows that the

TABLE I. Phonon Frequencies  $\omega_{nl}$  of Ground and First Excited Self-Consistent States of F Center in KCl

l	Ground state			First self-consistent state			
	2	3	4	n			
				2	3	4	5
0	0.876	0.985	0.996	1.05	0.855	0.986	0.996
1	0.857	0.982	0.994	2.25	0.945	0.985	0.992
2		0.975	0.994		0.802	0.979	0.995
2			0.992			0.949	0.989
4							0.979

phonon wave functions satisfying Eq. (2) decay rapidly with increasing  $r$  and describe fairly localized states.

#### 4. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENTS

In contrast to local phonons, which appear due to lattice distortions caused by defects, the spectrum of bound phonons obtained earlier is due to the electron-phonon interaction (dielectric modes<sup>8-11</sup>). It appears that such modes were observed in experiments on GaP (Ref. 9) doped with donor impurities. A wide Raman scattering peak at an F center in KCl was observed in Ref. 12 near  $\omega_{\text{exp}} \approx 0.89\omega_0$  and was attributed to the scattering from bound electron-phonon modes. This value of  $\omega_{\text{exp}}$  is close to the calculated value listed in Table I,  $\omega = 0.876\omega_0$ . Observation of local phonon frequencies higher than the limiting frequency ( $\omega = 2.25\omega_0$  according to Table I) is of interest for the excited self-consistent states. It follows from the results of Refs. 2 and 11 that anomalously high ratios of intensities of the infrared and Raman scattering with participation of local phonons calculated per single electron center could be expected for the excited self-consistent states.

A numerical analysis of Eqs. (31)-(33) for an excited self-consistent state of an F center indicates that if  $\nu < \nu_{\text{cr}}$  ( $\nu_{\text{cr}} = 0.21$ ) the spectrum of bound phonons includes negative squares of the normal vibration frequencies. Such complex frequencies in the spectrum of F centers indicate the possibility of a phonon (pseudo-Jahn-Teller) instability of excited self-consistent states with a characteristic decay time  $\sim |\omega_0|^{-1}$ . Centers with  $\nu = \nu_{\text{cr}}$  occur for

LiCl, LiBr, and many fluorides of rare-earth metals. Clearly, this may be the cause of the absence of luminescence of such crystals observed in experiments on photoexcitation of color centers.<sup>3</sup>

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