

# Off-center $\text{Li}^+$ ions: solid state rotators described by Mathieu's nonlinear-oscillator equation

M. Georgiev<sup>1</sup>, M. Mladenova<sup>2</sup>, V. Krastev<sup>3</sup>, and A. Andreev<sup>4,a</sup>

<sup>1</sup> Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

<sup>2</sup> Department of Condensed Matter Physics, Physics Faculty, Sofia University, 5 James Bourchier Blvd., 1126 Sofia, Bulgaria

<sup>3</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Block 11, Acad. G. Bonchev Street, 1113 Sofia, Bulgaria

<sup>4</sup> Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, Block 109, Acad. G. Bonchev Street, 1113 Sofia, Bulgaria

Received 18 October 2001 / Received in final form 5 March 2002

Published online 2 October 2002 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2002

**Abstract.** Substitutional impurity ions in crystals are known to displace off-center and to perform hindered rotations around the ideal lattice positions. The vibronic theory to describe both the off-center displacements and the hindered rotations by a single angular equation incorporates terms up to 3rd order in the off-center displacement coordinates. When the rotation is confined to a single plane, the corresponding vibronic equation is equivalent to Mathieu's equation. Extending our earlier work, we derive here the dipole-dipole coupling to take into account cooperative phenomena. We also derive the optical absorption band arising from dipolar transitions across “Mexican Hat” surfaces, and we show that hindered rotations gives rise to magnetic moments quantized in rotational bands.

**PACS.** 61.72.-y Defects and impurities in crystals; microstructure – 71.38.-k Polarons and electron-phonon interactions – 76.30.Mi Color centers and other defects

## 1 Revisiting a topic of the late seventies

$\text{Li}^+$  substituted for the host cations in KCl is known to displace off-center and to rotate around the center of the former  $\text{K}^+$  [1]. This is also the case for a substitutional  $\text{Li}^+$  with a F center as nearest neighbor. The origin of the local symmetry breaking points to a strong mixing of nearly degenerate electronic states of the Li-lattice cluster by an odd-parity vibrational mode, that is to a *Pseudo-Jahn-Teller (PJT) effect* [2,3]. The roundabout rotation restores on the average the original site symmetry. The off-center species are hindered rigid rotors with energy spectra quantized in rotational bands [4]. When isolated, the  $\text{Li}^+$  ions occupy 8 off-center sites along the  $\langle 111 \rangle$  body diagonals [5], or 4 sites along the  $\langle 110 \rangle$  face diagonals in equatorial (001) plane if an F center sits in the apex [001] site to form the  $F_A$  center [6–8]. The central F – Li axis can be aligned optically along the [001] crystallographic axis whereby the Li hindered rotations will all be in the normal (001) planes. The adiabatic potential energy surface (APES) to control both the off-center displacements

and the in-plane rotations is a *Mexican Hat* with prominent off-center  $\rightarrow$  on-center top barrier and rotational barriers along the brim.

This paper extends our published work in the field [4,9,10]. We now focus on the electrostatic response, the dispersive oscillator coupling, and the optical spectra attributed to  $\text{Li}^+$  off-center ions. Magnetic moments associated with the brim currents are also considered in hope of stimulating an experiment.

## 2 Off-centering Hamiltonian

### 2.1 3D rotor in fcc crystal

$\text{Li}^+$  ions in KCl are driven off-center by the vibronic mixing of nearly-degenerate opposite-parity electronic states at the impurity by ungerade vibrations which render unstable the lattice site configuration. For a  $\text{Li}^+$  impurity ion, we choose  $|s\rangle = |a_{1g}\rangle$ ,  $|p_i\rangle = |t_{1ui}\rangle$  ( $i = x, y, z$ ) (triply degenerate) electronic basis states to be mixed by a  $T_{1u}$  vibrational mode, as explained elsewhere [2]. Solving for

<sup>a</sup> e-mail: allxrose@hotmail.com

the secular equation, two of its roots represent a doubly-branched APES [4]:

$$E_{AD\pm}(Q_l) = \frac{1}{2} \sum_i K_i Q_i^2 \pm \sqrt{\sum_i \left( b_i Q_i + \sum_{jk} d_{ijk} Q_i Q_j Q_k \right)^2 + (E_{sp}/2)^2}$$

where  $K_i = M_i \omega_i^2$ , while  $E_{sp} = |E_s - E_p|$  is the  $s \rightarrow p$  gap energy. APES controls the off-center instability by creating rotational sites (*cf. Devonshire potential*) [5].

Introducing  $E_{JT} = b^2/2K$ , the Jahn-Teller energy, the extremal properties of  $E_{AD\pm}(Q_l)$  depend on whether  $4E_{JT}/E_{sp} < 1$  (weak coupling) or  $4E_{JT}/E_{sp} > 1$  (strong coupling). In the former case, the upper and lower branches are both anharmonic rotational parabolooids which bottom at  $Q = 0$  and extend upwards. In the latter, the lower branch collapses to a radial-valley surface which tops at  $Q = 0$  and bends upwards at  $Q_0$ , the off-center radius. The rotational sites are disposed along the spherical valley of radius  $Q_0$ . We introduce the radial vibrational coordinate  $Q$  and minimize  $E_{AD-}(Q)$  in  $Q$  at  $d_{ijk} = 0$ , to obtain the valley radius [4]:  $Q_0 = \sqrt{(2E_{JT}/K)[1 - (E_{sp}/4E_{JT})^2]}$  for  $4E_{JT} \geq E_{sp}$ . We model the  $d$ -tensor:  $d_{ijj} = d_b$ ,  $d_{iii} = d_c$ ,  $d_{ijk} = 0$  otherwise and set  $d_b > d_c$ ,  $b_i = b$ ,  $K_i = K$  [2]. Neglecting terms 6th order in  $Q_i$  in  $E_{AD\pm}(Q_l)$  and since the  $d$ -dependent corrections are small, APES near  $Q = Q_0$  generates a Hamiltonian for hindered rotation upon the  $Q_0$ -radius sphere:

$$H_{vib}(Q_0)(3D) = -(\hbar^2/2I)\Delta_{\theta\varphi} \pm (M\omega^2/b)Q_0^4\{(d_c - d_b) \times [(\cos\varphi \sin\theta)^4 + (\sin\varphi \sin\theta)^4 + (\cos\theta)^4] + d_b\} + E_{JT}[(1 \pm 2) - (E_{sp}/4E_{JT})^2]$$

where  $Q_0$ ,  $\theta$ ,  $\varphi$  are spherical coordinates and  $I = MQ_0^2$  is the off-center inertial moment.

## 2.2 2D rotor in fcc crystal

We next freeze in the apical vibrational coordinate  $Q_Z = 0$  ( $\theta = \pi/2$ ). Now the rotation is confined to the equatorial plane converting the site symmetry from cubic  $O_h$  ( $T_{1u}$  symmetry-breaking mode), pertinent to an isolated impurity, to axial  $C_{4v}$  ( $E_u$  symmetry breaking mode), pertinent to an impurity confined to a plane. The  $O_h \rightarrow C_{4v}$  symmetry lowering results from the immobilization of a vibrating halogen pair along the  $Q_Z$  axis, as an  $F$  center sits in the neighboring  $\langle 001 \rangle$  site [10]. The basic states change alongside:  $|s\rangle \rightarrow |\alpha\rangle$ ,  $|p\rangle \rightarrow |\beta\rangle$ . The 2D rotation Hamiltonian is

$$H_{vib}(Q_0)(2D) = ((\hbar^2/2I)(d^2/d\varphi^2) \pm (I\omega^2/b) \{((d_b - d_c)[(1/4)(3 + \cos(4\varphi))] + d_b\} Q_0^2 + \frac{1}{2} [(1 \pm 2)(b^2/M\omega^2)(M\omega^2 E_{\alpha\beta}^2)/4b^2].$$

The extrema of  $E_{AD-}$  are at  $\varphi = n(\pi/4)$ , the minima and maxima on  $E_{AD+}$  are similar but dephased.  $E_{AD-}(\varphi)$  is a Mexican Hat [4]. The reorientational barrier  $E_{BII}$ , difference between a maximum and a minimum on  $E_{AD-}$  (or  $E_{AD+}$ ), is  $E_{BII} = I\omega_{renII}^2/8$ , while the energy gap, *i.e.* splitting between a minimum on  $E_{AD+}$  and a maximum on  $E_{AD-}$ , is  $E_{12} = 4\{E_{BII}[d_c/(d_b - d_c)] + E_{JT}\}$ .  $\omega_{renII} = \omega_{Q_0}\sqrt{(d_b - d_c)/4b}$  is the renormalized vibrational frequency [4].

## 3 The Mathieu equation

We rewrite the 2D Schrödinger equation in the form:

$$((\hbar^2/2I)(d^2Y(\varphi)/d\varphi^2) - 2B_{\pm} \cos(4\varphi)Y(\varphi) + (C_{\pm} - E)Y(\varphi) = 0$$

where  $B_{\pm} = \pm(1/2)E_{BII}$ ,  $C_{\pm} = \pm(1/2)E_{BII}[(3d_c + d_b)/(d_b - d_c)] + E_{JT}[(1 \pm 2) - (E_{\alpha\beta}/4E_{JT})^2]$ . This is Mathieu's equation, its solutions are Mathieu's functions [12,13]. We introduce  $z = 2\varphi$ ,  $a = (2I/\hbar^2)(E - C_{\pm})$ , and Mathieu's parameter

$$q = 2(B_{\pm}I/\hbar^2) = \pm(2E_B/\hbar\omega_{renII})^2.$$

### 3.1 Mathieu's eigenstates and eigenvalues

According to Floquet's theorem, the general solution to Mathieu's equation is

$$Y(z, q) = A_1 B_1(z) \exp(\mu z) + A_2 B_2(z) \exp(-\mu z),$$

where  $\mu = im$  is imaginary for a spatially undamped solution, while it is real or complex for a spatially damped solution [13]. Spatially undamped solutions exist in specific regions only defined by  $\mu = \mu(\alpha, q)$  and referred to as *allowed energy bands*. There are four types of periodic solutions, even  $z$ -parity  $ce_m(z, q)$  and odd  $z$ -parity  $se_m(z, q)$  in 2 classes, even integer at  $m = 2n$  and odd-integer at  $m = 2n + 1$ , with respective eigenvalues  $a_m(q)$  to  $ce_m(z, q)$  and  $b_m(q)$  to  $se_m(z, q)$ . The functions are normalized so as  $(1/\pi) \int_0^{2\pi} [Y_m(x)]^2 dx = 1$ . At small  $q \ll 1$ ,  $ce_0(z, q) \approx 1$ ,  $ce_m(z, q) \approx \cos(mz)$ ,  $se_m(z, q) \approx \sin(mz)$  and  $a_m \approx m^2$ ,  $b_m \approx m^2$ . Integer class periodic functions define the edges of allowed energy bands, as shown below. In the interior, the undamped functions  $ce_m(z, q)$  and  $se_m(z, q)$  are to be extended to noninteger  $m$ . Noninteger extensions below are based on a proportional segmenting of an allowed energy range by a LC of the respective edge functions. One defines undamped functions  $ce_m(z, q)$  and  $se_m(z, q)$  as well as their eigenvalues  $a_m(q)$  and  $b_m(q)$  at  $0 \leq m \leq 1$ . The allowed eigenenergies at  $m$  integer or fractional are  $E_{\{am, bm\}}(q) = (\hbar^2/2I)\{a_m(q), b_m(q)\} + C_{\{\pm\}}$ .

### 3.2 Rotational bands

Mathieu's eigenvalue equation defines allowed energy bands at  $q < 0$  (upper-sign branch) and at  $q > 0$  (lower sign branch), respectively [12,13]. As  $q$  is increased, the allowed bands get narrower turning to single levels at high barriers. The allowed band borders in the energy versus  $q$  plane are described by Mathieu's eigenvalues  $a_n(q)$  and  $b_n(q)$ , or, alternatively, by the corresponding periodic eigenfunctions  $ce_n(z, q)$  or  $se_n(z, q)$  at integral  $n$  ( $n = 1, 2, 3, 4, \dots$ ), while each energy in the interior is generated by pairs of Mathieu's functions  $ce_m(z, q)$  and  $se_m(z, q)$  at intermediate nonintegral  $m$ . Within an allowed band, Mathieu's eigenstates and eigenvalues are functions of the wavenumber  $k = m\pi$  where  $0 \leq m \leq 1$  for the 1st Brillouin zone [13]. At  $q < 0$ , the allowed bands are delineated as follows:  $(a_0, a_1)$ ,  $(b_1, b_2)$ ,  $(a_2, a_3)$ , etc., while at  $q > 0$  the border pairs are:  $(a_0, b_1)$ ,  $(a_1, b_2)$ , etc.

## 4 Electrostatics

### 4.1 Electrostatics of off-center dipoles

The adiabatic eigenstates of the two APES branches ( $E_{AD\pm}$ ) are:

$$|\mathbf{r}, \mathbf{Q}\rangle_{U,L} = \pm \frac{1}{\sqrt{2}} \frac{[\rho(Q_l) \pm E_{sp}]|s\rangle \pm \sum_{i=x,y,z} 2G_i Q_i |p_i\rangle}{\sqrt{\sum_{i=x,y,z} G_i^2 Q_i^2 + E_{sp}^2} [\rho(Q_l) \pm E_{sp}]},$$

where  $\rho(Q_l) = \sqrt{4 \sum_{i=x,y,z} G_i^2 Q_i^2 + E_{sp}^2}$ . Associated mixing electric dipole generates optical transitions between  $E_{AD\pm}$ :

$$\begin{aligned} p_{UL}(Q) &\equiv \langle \mathbf{r}; \mathbf{Q} | \mathbf{er} | \mathbf{r}; \mathbf{Q} \rangle_{UL} = \\ &\frac{1}{2\rho(Q_l)} \sum_{i=x,y,z} 2G_i Q_i \left[ \langle s | \mathbf{er} | p_i \rangle - \langle p_i | \mathbf{er} | s \rangle \right] \\ &- \frac{E_{sp}}{\rho(Q_l)} (\langle s | \mathbf{er} | p_i \rangle + \langle p_i | \mathbf{er} | s \rangle). \end{aligned}$$

Dipole averages in the adiabatic states control the system's electrostatic response [14]

$$\begin{aligned} p_{LL}(Q) &\equiv \langle \mathbf{r}, \mathbf{Q} | \mathbf{er} | \mathbf{r}, \mathbf{Q} \rangle_{LL} \\ &= \frac{\sum_{i=x,y,z} G_i Q_i [\langle s | \mathbf{er} | p_i \rangle + \langle p_i | \mathbf{er} | s \rangle]}{\sqrt{\sum_{i=x,y,z} 4G_i^2 Q_i^2 + E_{sp}^2}}, \\ p_{UU}(Q) &\equiv \langle \mathbf{r}, \mathbf{Q} | \mathbf{er} | \mathbf{r}, \mathbf{Q} \rangle_{UU} = -p_{LL}(Q). \end{aligned}$$

### 4.2 Dispersive coupling of off-center ions

If averaged over the reorientational sites, the inversion dipole  $p_{LL}$  should vanish since the rotation tends to restore the cubic site symmetry. Yet, nearby fluctuating dipoles couple as  $p_{LL1}(Q_0)p_{LL2}(Q_0)/\kappa R^3$  along their interconnecting line. As a result, the rotational bandwidths, *e.g.*  $\Delta E(q) = (\hbar^2/2I)/(a_1(q) - a_0(q))$ , broaden by the small coupling magnitude. The broadened bandwidth is derived by 1st order perturbation theory, as in harmonic-oscillator analyses [14]:

$$\begin{aligned} \Delta E_{12}(q) &= \sqrt{[\Delta E(q)]^2 + (p_{LL1}(Q_0)p_{LL2}(Q_0))/\kappa R^3]^2} \\ &\sim \Delta E(q) + \frac{1}{2} \Delta E(q) (\alpha_1 \alpha_2 / \kappa^2 R^6). \end{aligned}$$

$R$  is the intercenter separation,  $\alpha = p_{LL}(Q_0)^2/\Delta E(q)$  is the  *vibronic polarizability*. The quantity  $\hbar\Omega_{rot}(q) = (1/2)\Delta E(q)$  in 1D is the intersite rotational hopping energy.  $U_B = (1/2)\Delta E(q)(\alpha_1 \alpha_2 / \kappa^2 R^6)$  is the  *vibronic Van-der-Waals binding energy* of off-center dipoles. The middle-of-the-band energy,  *polaron binding energy*  $E_{polbind} = (\hbar^2/4I) \times (a_0 + a_1) + C_-$ , is not affected by the perturbation, as it is not in harmonic analyses [14].

### 4.3 Optical spectra

Optical absorption associated with transitions at off-center rotors is  $\propto |p_{UL}(Q_l)|^2$  mixing initial and final Mathieu states. We get for a rigid 2D off-center rotor along the brim at  $Q = Q_0$ :

$$\begin{aligned} p_{UL}(Q_0) &= (E_{sp}/4E_{JT}) \sqrt{1 - (E_{sp}/4E_{JT})^2} \\ &\times \sum_{i=x,y,z} (Q_{i0}/Q_0) \langle s | \mathbf{er} | p_i \rangle. \end{aligned}$$

Matrix elements of  $p_{UL}(Q_l)$  are calculated between initial and final states

$$\begin{aligned} ce_{0+m}(z, q) &= \frac{(1-m)ce_0(z, q) + mce_1(z, q)}{\sqrt{m^2 + (1-m)^2}} \\ (ce_{n-1}, se_n)_{+m}(z, q) &= \frac{(1-m)ce_{n-1}(z, q) + mse_n(z, q)}{\sqrt{m^2 + (1-m)^2}} \end{aligned}$$

with corresponding eigenvalues

$$\begin{aligned} a_{0+m}(q) &= \frac{(1-m)^2 a_0(q) + m^2 a_1(q)}{m^2 + (1-m)^2} \\ (a_{n-1}, b_n)_{+m}(q) &= \frac{(1-m)^2 a_{n-1}(q) + m^2 b_n(q)}{m^2 + (1-m)^2}. \end{aligned}$$

At low temperature, the absorption coefficient reads:

$$\begin{aligned} \kappa(\Omega) &= [(2\pi)^2 N/3c] \sum_{nm} \Omega \rho_{Lm}(T) \\ &\times |\langle ce_{0+m}(z, q) | p_{UL}(Q_i) | (ce_{n-1}, se_n)_{+m}(z, q) \rangle|^2 \\ &\times \delta(\epsilon_{U_{n+m}} - \epsilon_{L_{0+m}} - \hbar\Omega), \\ \epsilon_{U_{n+m}} &= (\hbar^2/2I)(a_{n-1}, b_n)_{+m}(q), \\ \epsilon_{L_{0+m}} &= (\hbar^2/2I)a_{0+m}(q) \end{aligned}$$

where  $N$  is the number of absorbing centers, L(U) is the lower (upper) APES branch, n,m number bands and intraband energy levels, respectively,  $\rho_{Lm}(T)$  is the initial state thermal occupation factor,  $p_{UL}$  is the optical transition dipole. Calculated optical spectra of off-center ions will be reported at length elsewhere.

## 5 Magnetostatics

### 5.1 Magnetic moments of quasifree in-plane rotators

We assume a statistical distribution in  $\{110\}$  plane of orbiting ions with magnetic moments  $-\mu_J$ , 0,  $+\mu_J$  arising from circular currents  $-J$ , 0,  $+J$ , respectively. For a more transparent physics, we use Ampere's theorem to derive a relation between  $J$  and  $\mu_J$  [15]:

$$\mu_J = (4\pi\mu/c)(\pi a^2)J = (4\pi e\mu/c)(\pi a^2)\Omega_{rot}$$

$a$  is the ring radius,  $\mu$  the magnetic permeability,  $\Omega_{rot}$  the rotational frequency.

The current-ring magnetic moment  $\mu_J$  will couple to an axial field  $H = B/\mu$ . There are 3 obvious eigenenergies:  $-\mu_J H$ , 0,  $+\mu_J H$  for a magnetic triplet. A microwave power of frequency  $\nu_{mw}$  will incite 2 resonant transitions, singlet and doublet, between the magnetic energy levels:

$$\begin{aligned} h\nu_{Jmw1} &= 2g_J\mu_J H \\ h\nu_{Jmw2,3} &= g_J\mu_J H. \end{aligned}$$

The gyromagnetic correction to  $\mu_J$  is [15]:

$$\Delta\mu_B = (e/2c)a^2\Omega_B$$

$\Omega_B = eB/mc$  is the gyration frequency. From Ampere's theorem,  $\Delta\mu_B = (4\pi\mu/c) \times (\pi a^2)J_B$ , so that  $\Delta\mu_B$  is the moment arising from a field-induced loop current  $J_B = (e^2/8\pi^2 mc)H$ .

### 5.2 Magnetic moments of hindered in-plane rotators

For a hindered rotator,  $\Omega_{rot} = \Omega_{rot(a,b)n}(q)$  being quantized in rotational bands  $E_{(a,b)n}(q)$ , so is the magnetic moment  $\mu_J = \mu_{J(a,b)n}$ . (The barrierless  $q = 0$  case is included in the category even though the disappearance of the barriers converts the bands into separate energy levels

quantized as  $m^2$ .) Now, the gyration frequency  $\Omega_B$  can assume only values equal to the rotational frequencies  $\Omega_{rot}$  in the allowed bands:

$$\Omega_B = \Omega_{rot(a,b)m}.$$

This requirement quantizes the magnetic field  $B$ . The rotational frequencies are proportional to the allowed bandwidths  $\Omega_{rot(a,b)n} = (1/4\hbar)W_{(a,b)n}$  where:

$$W_{(a,a)n} = (2\hbar^2/I)(a_{n+1} - a_n)(q < 0, n \text{ even})$$

$$W_{(b,b)n} = (2\hbar^2/I)(b_{n+1} - b_n)(q < 0, n \text{ odd})$$

$$W_{(b,a)n} = (2\hbar^2/I)(b_{n+1} - a_n)(q > 0, \text{all } n)$$

$a_m(q) = m^2 + c_{am}(q)$ ,  $b_m(q) = m^2 + c_{bm}(q)$ , while  $c_{(a,b)m}(q)$  are the tunneling corrections.

Combining, the quantized magnetic field is:

$$B = B_{(a,b)m} = \left(\frac{c}{e}\right) \cdot \frac{I_{(a,b)m}\Omega_{rot(a,b)m}}{Q_0^2}$$

while the quantized magnetic flux across the off-center ring of radius  $Q_0$  is:

$$\Phi = \Phi_{(a,b)m} \equiv \pi \left(\frac{c}{e}\right) I_{(a,b)m}\Omega_{rot(a,b)m},$$

where  $I_{(a,b)m}$  is the inertial moment of a particle rotating in a band. Other quantities are: the gyromagnetic moment quantized as

$$\Delta\mu_B = \Delta\mu_{B(a,b)m} \equiv \frac{e}{2c}\Omega_{rot(a,b)m}Q_0^2$$

and the field-induced loop current quantized as

$$J_B = J_{(a,b)m} = \frac{e}{8\pi^2\mu}\Omega_{rot(a,b)m}.$$

Finally, we compare  $\Delta\mu_B$  and  $\mu_J$  to get  $\mu_J/\Delta\mu_B = 8\pi^2\mu > 1$ . The gyration correction being always positive along  $B$ ,  $\Delta\mu_B$  splits the doublet transition at  $\Delta\mu_B \neq 0$ . Now, 3 eigenenergy levels of the full moment in an external field  $H$  give rise to 3 resonances:

$$h\nu_{Bmw1} = 2\mu_J H = 8\pi^2 I_{(a,b)m}(\Omega_{rot(a,b)m})^2$$

$$h\nu_{Bmw2} = g_{0+}\mu_J H = 4\pi^2 g_{0+} I_{(a,b)m}(\Omega_{rot(a,b)m})^2$$

$$h\nu_{Bmw3} = g_{0-}\mu_J H = 4\pi^2 g_{0-} I_{(a,b)m}(\Omega_{rot(a,b)m})^2$$

where  $g_{0\pm} = 1 \pm 1/(8\pi^2\mu)$ . Using the pertinent  $\text{Li}^+$  parameters [2, 4, 10], the numerical estimates show that  $\mu_{J(a,b)n}$  are accessible to present-day SQUID and possibly resonance measurements.

## References

1. R. Smoluchowski, *Colloque Ampere XV* (North Holland, Amsterdam, 1969), p. 120
2. M.D. Glinchuk in *The Dynamical Jahn-Teller Effect in Localized Systems*, edited by Yu.E. Perlin, M. Wagner (Elsevier, Amsterdam, 1984), p. 823, and literature cited therein
3. I.B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry* (Academic Press, New York, 1966)
4. P. Petrova, M. Ivanovich, M. Georgiev, M. Mladenova, G. Baldacchini, R.M. Montereali, U.M. Grassano, A. Scacco in: *Quantum Systems in Chemistry and Physics*, edited by R. McWeeny *et al.* (Kluwer, Dordrecht, 1997), p. 373
5. F. Bridges, *CRC Critical Revs. Solid State Phys.* **5**, 1 (1975)
6. F. Luty in: *Physics of Color Centers*, edited by W.B. Fowler (Academic, Press, New York, 1968), p. 182
7. M. Leblans, W. Joosen, E. Goovaerts, D. Schoemaker, *Phys. Rev. B* **35**, 2405 (1987)
8. F. Luty, *J. Phys. Colloq. France* **34**, C9-49 (1973)
9. A. Diaz-Gongora, C. Medrano P., J.L. Boldu O., R.J. Gleason, M. Georgiev, *Revista Mexicana de Fisica* **32**, 475 (1986)
10. G. Baldacchini, U.M. Grassano, A. Scacco, F. Somma, M. Staikova, M. Georgiev, *Nuovo Cimento D* **13**, 1399 (1991)
11. See: S.G. Christov, *Collision Theory and Statistical Theory of Chemical Reactions*, *Lect. Notes Chem.* **18** (Springer, Berlin-Heidelberg-NY, 1980)
12. *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, edited by M. Abramowitz, I.A. Stegun (NBS Math. Series, 1964)
13. L. Brillouin, M. Parodi, *Propagation des Ondes dans les Milieux Périodiques* (Dunod, Paris, 1956)
14. M. Georgiev, M. Borissov, *Phys. Rev. B* **39**, 11624 (1989)
15. J.D. Jackson, *Classical Electrodynamics* (Wiley, London-New York, 1966), p. 410