STRUCTURAL PHASE TRANSITIONS IN JAHN-TELLER CRYSTAL PLATES

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Abstract. The cooperative Jahn-Teller effect is considered in the crystal samples of finite size. Peculiarities of the plate sample phonon spectra and their influence on the microscopic theory of the structural phase transitions are in the focus of attention. The mutual orientation of the crystal axes and the plate plane is discussed. As an example the Lamb wave role is analyzed in detail. It is shown that the ferrodistortive ordered phase is significantly inhomogeneous. This inhomogeneity is the consequence of the space coordinate dependence of the intersite electron-electron interaction. Some new thermodynamic and dynamic effects are considered as a result of the microscopic theory of structural phase transitions in plates.

1. Introduction

The cooperative Jahn-Teller effect (CJTE) is the most developed microscopic theory of the structural phase transitions in crystals. It is based on taking into account the electronic structure of the crystals and their real phonon spectrum. The interaction of the electrons with the crystal vibrations leads to a virtual phonon exchange between the electrons causing a crystal structural transformation at some required conditions – temperature, external magnetic or electric field, external pressure, and so on [1-4]. In general all crystal vibrations – acoustic and optical – producing the local distortions active in the (JTE) are participating in the microscopic mechanism of structural phase transition.

The Jahn-Teller crystals are characterized by a wide spectrum of anomalous properties that make this class of materials very perspective for numerous applications [5]. Naturally, in these applications the real finite size samples of different shape are used. At the same time nowadays the interest to the physics, chemistry, and biology of interfaces is quickly growing. It is related to the miniaturization of electronics, development of nanotechnology, and discovery of monoatomic monolayer, bilayer, and multilayer materials.
In this situation the role of the microscopic theory of structural phase transitions in finite size crystals becomes significant. Here a based on (CJTE) approach to plates problem is presented.

2. Phonon spectra of plates

For the beginning the crystal samples under discussion will be considered in the shape of plates, while, of course, other shape samples (rods, pipes, spheres, and cubes) should be later analyzed also. If in the crystal samples the plate thickness \(2h\) is much bigger than the wavelength \(\lambda\) of the vibrations acting in the virtual phonon exchange, the size of the crystals in all three directions is considered as infinitely big. In this case no modification of the (CJTE) theory is necessary. However if the wavelength \(\lambda\) is of order or bigger than \(2h\), some theory reconsideration is required. This necessity results from the significant changes in the phonon spectrum of crystal plates in comparison with the one of the infinite size crystal. It is well known that in infinite size crystals there are only transverse and longitudinal vibrations propagating independently in any high symmetry crystal direction. At the same time in crystal plates additionally there are four families of normal modes: symmetric horizontal (SH) and antisymmetric horizontal (AH) modes, and symmetric (LS) and antisymmetric (LA) Lamb waves [6, 7], propagating in the similar directions. In the horizontal (SH) and (AH) waves the wave displacement is parallel to the plate and is perpendicular to the propagation direction so that only one displacement component is not zero. The terms “symmetric” and “antisymmetric” represent the symmetry of the wave displacement distribution relatively the middle plane of the plate. In case of the Lamb family waves each vibration is characterized by two non-zero displacement components: one along the propagation direction, another one in the sagittal plane perpendicular to the plate. In general the Lamb waves are more complicated than (SH) and (AH) waves as each of them is a combination of two transverse and two longitudinal waves coupled on the surfaces of the plate due to boundary conditions. Symmetric and antisymmetric character of Lamb waves is again connected to the displacement vector symmetry relatively the middle plate plane. If we choose the plate to be parallel to the xy-plane and the waves are propagating in the x-direction (\(k_x\)), then for the four wave families the displacement vector components could be represented as follows (see for example [6])

\[\text{(SH):}\ U_x=0\]
\[U_y=(-\beta H+ikC)\cos(\beta z)\exp[i(kx-\omega t)]\]
\[U_z=0\]

\[\text{(AH):}\ U_x=0\]
\[U_y=(\beta G+ikD)\sin(\beta z)\exp[i(kx-\omega t)]\]
\[U_z=0\]

\[\text{(LS):}\ U_x=[\beta F\cos(\beta z)+ikA\cos(\alpha z)]\exp[i(kx-\omega t)]\]
\[U_y=0\]
\[U_z=-\alpha A\sin(\alpha z)-ikF\sin(\beta z)\exp[i(kx-\omega t)]\]

\[\text{(LA):}\ U_x=[-\beta E\sin(\beta z)+ikB\sin(\alpha z)]\exp[i(kx-\omega t)]\]
In the formulae (1-4) the eight unknown variables A, B, C, D, E, F, G, and H are related to eight homogeneous equations found from the boundary conditions at \( z=\pm h \). The parameters \( \alpha \) and \( \beta \) are connected to the velocities \( V_s \) and \( V_l \) of the transversal and longitudinal bare waves correspondingly in the plate crystal in the following way

\[
\alpha^2 + k^2 = \left( \frac{\omega}{V_s} \right)^2
\]

\[
\beta^2 + k^2 = \left( \frac{\omega}{V_l} \right)^2
\]

The dispersion equations for the first two wave families – horizontal symmetrical and antisymmetric waves – could be represented by one equation

\[
\frac{\omega h}{V_t} = \pm \sqrt{\left( kh \right)^2 + \left( \pi r \right)^2}
\]

where \( r=q=0, 1, 2, \ldots \) for SH-waves and \( r=(p-1)/2=1/2, 3/2, 5/2\ldots \) for AH-waves. For the Lamb waves the dispersion equations are slightly more complicated [7]

\[
\frac{tg(\beta h)}{tg(ah)} = \frac{4(kh)^2(\beta h)(ah)}{[(kh)^2-(\beta h)^2]^2}
\]

\[
\frac{tg(\beta h)}{tg(ah)} = \frac{[(kh)^2-(\beta h)^2]}{4(kh)^2(\beta h)(ah)}
\]

Equation (8) describes the dependence of frequency upon the wave number for the symmetric Lamb waves, and the equation (9) correspondingly relates to the antisymmetric Lamb waves. Sometimes these equations are called the Rayleigh-Lamb dispersion equations as they are containing the Rayleigh surface wave solution at \( h \to \infty \).
The fundamental property of the plate waves (horizontal SH and AH and Lamb S and A) is a finite number of propagating waves at the fixed thickness 2h and frequency ω. The bigger the dimensionless product $kth=\omega h/Vt$ is, the bigger is the number of these waves. At $kth \ll 1$ there is only one propagating horizontal wave (SH wave with phase velocity $V=Vt$ of a transverse wave in infinite size crystal) and two Lamb waves ($LS0$ with $Ux>>Uz$ and $LA0$ with $Uz>>Ux$). The phase velocities for $S0$ and $A0$ modes at $kth<<1$ could be represented by formulae.
LS\textsubscript{0}: \quad V_\text{S} = V_l (1 - 2\nu)^{1/2} (1 - \nu) = \left[ \frac{E}{\rho (1 - \nu^2)} \right]^{1/2} ; \quad (10)

LA\textsubscript{0}: \quad V_\Lambda = \left[ \frac{4h^2 E}{3\rho (1 - \nu^2)} \right]^{1/2} k, \quad (11)

Where \( E \) is the Young modulus of elasticity, \( \rho \) is the density of the plate, and the Poisson’s coefficient \( \nu \) is related to the velocities \( V_t \) and \( V_l \) by the equation

\[
\frac{V_t}{V_l} = \frac{1 - 2\nu}{2(1 - \nu)}. \quad (12)
\]

As it is seen from (10) and (11), at small \( k \) the symmetrical Lamb wave is propagating dispersionlessly and its velocity is not significantly different from the velocity of the longitudinal wave in the infinite size samples. However the situation is completely different in the case of the antisymmetric (sometimes called “flexural”) Lamb wave. In thin plates and at small frequencies the dispersion is significant. As a result of that the phase velocity is proportional to the wave number \( k \) (as in (11)), and the mode frequency can be written as \[8\]

\[
\omega = k^2 \left[ \frac{h^2 E}{3\rho (1 - \nu^2)} \right]^{1/2}. \quad (13)
\]

Therefore the frequency is not linear in the wave number \( k \) as it takes place for all acoustic waves in 3-dimensional infinite size crystals, but it is quadratic in \( k \). This result is very important for the description of the structural phase transitions in plates. Peculiarities related to this result in the phenomenological theory of structural phase transition were mentioned in [9-11]. In this article we are going to discuss possible consequences of it in the microscopic theory of structural phase transitions.

For a GaAs plate the examples of the calculated [12] Lamb wave spectra are shown in the Fig.2 and Fig.3.
Fig. 2. Spectrum of several symmetrical Lamb waves in GaAs plate with $2h=10^{-8}$m [12].

Fig. 3. Spectrum of several antisymmetric (flexural) Lamb waves in GaAs plate with $2h=10^{-8}$m [12].
3. Structural phase transitions in TmVO$_4$ crystal type plates

Switching to the microscopic model of a structural phase transition in a concrete crystal plate, it is important to remind that all crystal plate vibrations – acoustic and optical - are contributing to the virtual phonon exchange responsible for the phenomenon. However it is well known that in some crystals the main contribution is coming from the long wave acoustic modes and homogeneous strains. This is just the case with the TmVO$_4$ crystal [2, 4, 13, 14]. The 3-dimensional sample of it suffers a structural phase transition from the tetragonal D$_4$h phase to the orthorhombic D$_2$h phase when the lowering temperature is passing through the critical one $T_c=2.1K$. At this transition the crystal strain $\xi$ is changing from $\xi(B2g(D4h))$ to $\xi(A1g(D2h))$, while the local distortion is changing from U(D2d) to U(D2). In the 3-dimensional crystal of TmVO$_4$ the soft mode is the acoustic transverse mode propagating along the [100] direction with the polarization vector $\vec{e}$ parallel to the [010] direction. The soft modulus of elasticity is C$_{66}$(D$_4$h).

Taking into account all of the above information, it becomes clear that the detail of the structural transition mechanism is depending upon the type of the crystal cut. In other words it is important what is the orientation of the crystal plate relatively the crystal axes directions. In this article below it is accepted that the crystal plate is containing the [100] and [001] crystal axes. We will choose that the [100] direction is the plate’s x-direction, and [001] is y-direction. The perpendicular to the plate z-direction is parallel to the [010] crystal axis. In this case all horizontal SH and AH waves propagating along x-direction are not active in the virtual phonon exchange as they are not creating the shift $\xi_{zx} = \xi(B2g(D4h))$ strain. At the same time the Lamb waves – both families – do create $\xi_{zx}$ and are active in the CJTE. After finding the connections between the constants A and F and B and E for the Lamb LS and LA waves from (2) and (3) it is convenient to rewrite the displacement expressions in the following form [7]

\[
\text{LS: } U_{s_0} = -iA_0kS_0\left[\frac{\text{ch}(qS_0)/\text{sh}(qS_0) - 2kS_0^2\text{sh}(qS_0)/(kS_0^2+sS_0^2)\text{sh}(sS_0)}{kS_0^2+sS_0^2}\right]\exp(i(kS_0x-\omega t)),
\]

\[
U_{s_0} = 0
\]  \hspace{1cm} (14)

\[
U_{s_0} = -AqS_0\left[\frac{\text{sh}(qS_0)/\text{sh}(qS_0) - 2kS_0^2\text{sh}(sS_0)/(kS_0^2+sS_0^2)\text{sh}(sS_0)}{kS_0^2+sS_0^2}\right]\exp(i(kS_0x-\omega t))
\]

\[
\text{LA: } U_{A_0} = iBkA_0\left[\frac{\text{ch}(qA_0)/\text{ch}(qA_0) - 2kA_0^2\text{ch}(sA_0)/(kA_0^2+sA_0^2)\text{ch}(sA_0)}{kA_0^2+sA_0^2}\right]\exp(i(kA_0x-\omega t))
\]

\[
U_{A_0} = 0
\]  \hspace{1cm} (15)

\[
U_{A_0} = -BqA_0\left[\frac{\text{ch}(qA_0)/\text{ch}(qA_0) - 2kA_0^2\text{ch}(sA_0)/(kA_0^2+sA_0^2)\text{ch}(sA_0)}{kA_0^2+sA_0^2}\right]\exp(i(kA_0x-\omega t))
\]

\[
q_{S,A} = \alpha = (kS,A^2-kl^2)^{1/2}; \quad s_{S,A} = \beta = (kS,A^2-kL^2)^{1/2}
\]  \hspace{1cm} (16)

Using (14) and (15) it is easy to get the expressions for the shift strains $\xi_{zx}$ active in the (CJTE):

\[
\xi = 1/2(\partial U_0/\partial z + \partial U_0/\partial x)
\]  \hspace{1cm} (17)

\[
\xi_S = -(i/2)A_0kS_0\left[\frac{(\text{sh}(qS_0)/\text{sh}(qS_0) - 2sS_0^2\text{sh}(sS_0)/(kS_0^2+sS_0^2)\text{sh}(sS_0)\text{sh}(qS_0)/\text{sh}(qS_0))}{kS_0^2+sS_0^2}\right]\exp(i(kS_0x-\omega t))
\]

\[
-2kS_0^2\text{sh}(sS_0)/(kS_0^2+sS_0^2)\text{sh}(sS_0)\exp(i(kS_0x-\omega t))
\]  \hspace{1cm} (18)

\[
\xi_A = -(i/2)BkA_0\left[\frac{(\text{ch}(qA_0)/\text{ch}(qA_0) - 2sA_0^2\text{ch}(sA_0)/(kA_0^2+sA_0^2)\text{ch}(sA_0)\text{ch}(qA_0)/\text{ch}(qA_0))}{kA_0^2+sA_0^2}\right]\exp(i(kA_0x-\omega t))
\]

\[
-2kA_0^2\text{ch}(sA_0)/(kA_0^2+sA_0^2)\text{ch}(sA_0)\exp(i(kA_0x-\omega t))
\]  \hspace{1cm} (19)
Or

$$\xi_s = -iA_k S q S [\text{sh}(q_s z)/\text{sh}(q_S h) - \text{sh}(s_s z)/\text{sh}(s_S h)] \exp(i(k_s x - \omega t))$$  \hspace{1cm} (20)$$

$$\xi_A = -iB_k A q A [\text{ch}(q_A z)/\text{ch}(q_A h) - \text{ch}(s_A z)/\text{ch}(s_A h)] \exp(ik_A x - \omega t))$$  \hspace{1cm} (21)$$

After standard quantization of the Lamb waves (waves propagate along \(k=k_x||[100]\), the space axis \(z||[010]\), for each \(k_x\) there are \(n=1,2,3\ldots\) Lamb modes with \(n\) depending upon the plate thickness \(2h\) and wave frequency \(\omega\) as in Fig.3 and 4), the operator of the interaction of the Lamb waves with the electrons can be written as

$$H_{el-ph} = \sum_{m=1}^{L} V_{m k} F_n^L(z) \sigma_{m n} (b_{q n} + b_{q n}^*) ,$$  \hspace{1cm} (22)$$

where

$$V_{m k} = V \exp(i k m) ,$$  \hspace{1cm} (23)$$

$$F_n^{LS(A)}(z) = W_n^{LS(A)}(z) \sqrt{\frac{h}{2 \rho \omega_n (q_n)}}$$  \hspace{1cm} (24)$$

$$W_n^{LS} = -i A_k S q S [\text{sh}(q_s z)/\text{sh}(q_S h) - \text{sh}(s_s z)/\text{sh}(s_S h)]$$  \hspace{1cm} (25)$$

$$W_n^{LA} = -i B_k A q A [\text{ch}(q_A z)/\text{ch}(q_A h) - \text{ch}(s_A z)/\text{ch}(s_A h)]$$  \hspace{1cm} (26)$$

In the formulae (22)-(26) \(V\) is the electron-phonon interaction constant, \(q||\) is the wave vector parallel to the plate plane, \(\sigma_{m n}\) is the \(n\)-component of the electron operator for the \(m\) crystal site, \(b_{q n}\), \(b_{q n}^+\) are the phonon operators, \(L\) is the symbol of Lamb wave that is equal to LS (symmetric) or LA (antisymmetric) wave with the frequency \(\omega_n\), \(\rho\) is the crystal density. The \(F_n^L(z)\) functions describe the strain distribution in the plate waves along the space \(z\)-direction (do not to be confused with the \(z\)-axis of quantization for the electronic pseudospin operators \(\sigma\)) and are responsible for the orthonormality of the displacement functions in the L wave. The form of the Hel-ph operator reflects the accepted approximation according to which the acoustic waves are modified by the finite size of the crystal plate (\(2h \lesssim \lambda\)), but the electrons are not affected by the plate boundaries as the effective electron radius \(r_{eff}\) is much smaller than plate thickness \(h\) (\(r_{eff} \lesssim h\)). (Of course, on the contrary to the situation that is discussed in this article, when the crystal plate is formed by a single atomic layer or a few of them, the electronic states are influenced by the plate surfaces).

The crystal plate phonons are described as

$$H_{ph} = \sum_{m n} \hbar \omega_{m n} (b_{m n}^* b_{m n} + \frac{1}{2})$$  \hspace{1cm} (27)$$

(n numbers the acoustic symmetric and antisymmetric waves, and its maximum depends upon plate thickness and wave vector \(q||\)).
After the canonical shift transformation \([4]\) of the Hamiltonian \(H = H_{el-ph} + H_{ph}\)

\[
H = \exp(iR)H \exp(-iR),
\]

\[
R = i \sum_{mnL} (\hbar \omega_{mn})^{-1}[V_{mn}b_{mn} + V_{mnb}^{+} b_{mn}]F_{n}^{+}(z)\sigma_{zm}
\]

in the case of the plate shape samples the intersite electron-electron interaction operator in the molecular field approximation looks like that

\[
H_{el-el} = -A(z)\overline{\sigma_{z}}\sum_{m} \sigma_{zm},
\]

\[
A(z) = \sum_{mnL} (\hbar \omega_{mn})^{-1}[V_{mn}^{2} [F_{n}^{+}(z)]^{2}
\]

Then the order parameter equation is

\[
\overline{\sigma_{z}} = \sigma_{z}(z) = \hbar \frac{A(z)\overline{\sigma_{z}}(z)}{kT}
\]

As it follows from eqn. (32), the critical temperature of the structural phase transition depends upon the space coordinate \(z\) –

\[
kT_{c} = kT_{c}(z) = A(z)
\]

In other words each layer of the plate is ordered at some different critical temperature \(T_{c}\). Another consequence of the eqn. (34) is that spontaneous crystal strain \(U_{z}=U_{z}(D_{z})\) becomes inhomogeneous – \(U_{z}=U_{z}(z)\). That means that in the crystal plate of the TmVO4 compound that is cut as it is described at the beginning of this article (the crystal plane is perpendicular to the (110) crystal symmetry plane), the ferroelastic phase transition is non-homogeneous.

4. Inhomogeneity manifestations in thermodynamic and dynamic properties

There are many consequences of this inhomogeneity important for thermodynamic and dynamic properties of the crystal plates with the structural phase transitions. Of course it is impossible in one article to discuss all of them, so that we will mention a few.

1. As the electronic orbital filling is not homogeneous at the (CJTE) in plates, all properties of the sample are in general inhomogeneous. For example, even in the homogeneous external magnetic field the magnetic moment is not homogeneous over the sample as the electron-electron interaction operator (eq. (30)) is not.

2. For the same reason the elementary excitations of the crystal plate sample will be smeared out depending upon the magnitude of the crystal area from which the experimental information is collected. In part, the dispersion of the electronic excitations will be inhomogeneous.
3. One of the significant peculiarities of the dynamic electron-phonon interaction in the crystal Jahn-Teller plates is the significant interaction of the electronic mode with many different symmetric and antisymmetric (flexural) Lamb phonons. When the crystal temperature is decreasing from the high one to the critical temperature $T_c$, the interaction takes place at smaller wave numbers and smaller phonon frequencies. As the lowest in frequency Lamb antisymmetric wave is $LA_0$ and its frequency $\omega_A$ is proportional to the square of the wave number (see eq. (13), this phonon mode will be the soft one at the phase transition. At this softening some surface “goffering” could take place. So that this quite often experimentally observed fact can be explained as the condensation of the soft antisymmetric $A_0$ Lamb mode at the ferroelastic inhomogeneous structural phase transition. The dynamic interaction between the vibron (pseudospin) and phonon excitations can be described by the following equation

$$\hbar^2 \omega(k)(\omega^2(k) - \omega^2_0(k)) = 4\omega^2(k)\Delta S_z \sum_n \frac{K_{d,LA}(z,k)}{\omega^2_n(k) - \omega^2_{d,LA}(k)}$$

(34)

$$K(k) = \frac{2V^2(k)}{h\omega(k)}[K_{d,LA}(z)]^2$$

(35)

$$\hbar^2 \omega^2(k) = 4[(\lambda + 3\hbar^2 S_z^2 + \Delta_0 - S_z A(k))]$$

(36)

where the most significant peculiarity is related to the space $z$-coordinate dependence of the constant $K_{d,LA}(z,k)$.

4. In the fast developing field of phononics a striking similarity between the phonon Lamb spectra and the electronic spectra of graphene is found. The presence of Dirac points and possible different types of conical intersections in the Lamb wave spectra [15] and their connection with the field of Berry phase problems [16] opens a giant amount of interesting possibilities for analysis of fundamental physics questions about the (CJTE) mechanism of structural phase transitions in plates and numerous industrial applications.

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