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ON USING SAW IN STUDYING NEAR–SURFACE VIBRONIC DEFECTS[1),2)]

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The paper deals with peculiar features associated with SAW scattering on vibronic near-surface centres. The considerations are directed at indicating a potential inherent in using high frequency SAW for examining near surface defect-induced vibronic characteristics. Peculiar phenomena associated with that sort of scattering are highlighted.

I. INTRODUCTION

The continuing development of SAW devices technology pays an ever growing attention to the higher frequency region, well above 1 GHz. The tendency toward an increase of the working frequency is stimulated by the need to perform more sophisticated signal processing functions, usually requiring a large bandwidth (e.g., in a spread spectrum communication). This, in turn provides suitable (prospective) means for using SAW as a probe in investigating various physical characteristics of near-surface microscopic entities such as adsorbates, impurities and other defects including the very wide domain of tunnelling phenomena.

In the present paper some ingredients of this problem will be briefly highligted for the case of vibronic centres. This kind of centres is from many aspects very interesting. They are well-defined sources of paraelectric and paraelastic phenomena, being thus prospective as a means for inducing a controllable modification of mechanical and electrical material parameters of near-surface dielectric layers. Provided the layer is sufficiently thick, it can be regarded as an effective substrate for SAW (We have treated these problems elsewhere [1,2].).

Especially interesting is a specific mechanism of the acoustic scattering process in such defects. In many ways it is similar to that of tunnelling centres, but has also important peculiar features involving a fundamental role of symmetry.

In the near-surface region this peculiarity involves new important elements. First, there is a different (lower) symmetry than that in the bulk of the crystal, and secondly, the real structure in that region can hardly be considered ideal and the existing field are much less uniform.

Such a situation being responsible for an unequivalence of potential energy minima and thus, for a remarkable increase in their height, creates a condition conducing to the static $J-T$ regime at the cost of the dynamic one. In effect the corresponding critical temperature in which the first regime can exist should be essentially higher here.

For brevity, we confine our attention to the $E-B$ case, in which the doubly degenerate localized electrons of the E symetry are coupled (adiabatically) with the B_1 or B_2 mode of vibration of the cluster surrounding the centre.

II. VIBRONIC BEHAVIOUR IN THE PRESENCE OF SAW

To be concrete let us consider the cluster as composed of the nearest oxygen ions surrounding the near-surface normal centre located at the site of Ti ions of a $BaTiO_3$ type structure (see Fig. 1). The calculation will be performed for symetry-adapted combinations corresponding to the irreducible representations of that point symetry group irrespective of the location of the cluster with respect to the surface plane. Provided that the near-surface relaxation responsible for the decrease of the local symmetry ($O_h \rightarrow D_{4h}$) is taken into account, it makes the description to be, in some sense, uniform.

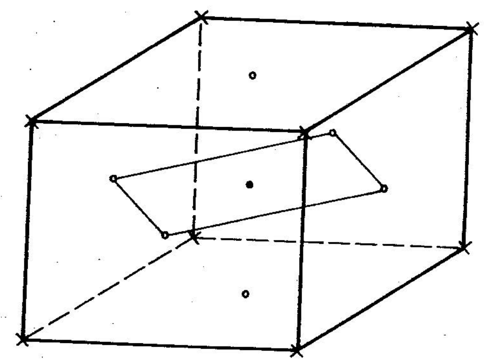

Fig. 1. The basic cluster in consideration: • Titanium ion; ∘ Oxygen ions; × Cadmium ions (projection).

The displacements of two oxygen ligands from the cluster which are situated at the centre's lattice plane have no B-symmetry component, so thay do not contribute to the vibronic coupling of interest and will be omitted in further considerations.

The distortion of the remaining (plane) part of the oxygen cluster under consideration is described by 12 components of displacements $u_\alpha(\mu)$ ($\mu = 1,2,3,4$).

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Calculating the characters for particular classes by means of the general formula

$$\varkappa(R) = n_R(1 + 2\cos\phi) \tag{1}$$

with n_R denoting the number of sites fixed upon the group rotation of the angle ϕ, one obtains by means of the relation

$$\varkappa(R) = \sum_{\Gamma} n_\Gamma \varkappa_\Gamma(R) \tag{2}$$

the distribution with respect to the symmetrized components of the $u_z(\mu)$ set. It results in:

$$G = 2A_1 + A_2 + 2B_1 + 2B_2 + 3E, \tag{3}$$

where the spectroscopic notation is used.

Because the cluster is a portion of the crystal, the above distribution comprises the representations describing its translations and rotations as a whole.

The symmetry-adapted combinations of displacements components can be determined from the relation:

$$Q_{\Gamma\gamma\gamma^k} = A\Sigma\Gamma^*_{\gamma'\gamma}(R)\hat{R} = \Sigma a(\Gamma^k\gamma^k; q)Q_q \tag{4}$$

with $\hat{R}$ - being the respective rotation matrix, A - the normalizing coefficient, the index k is to label various basis functions of the same representation (as generated from u^k vectors). Parameters in (4) have the meaning of the Van Vleck coefficients with Q_q denoting the respective normal mode.

When the cluster in consideration is situated at the surface plane, the propagating SAW has the following symmetry - adapted amplitudes:

$$\begin{aligned}
a(A_1^1, q) &= \mathrm{Re}\left\{ie_y(\hat{q})\sin\left(\frac{a}{2}q_y\right) + ie_x(\hat{q})\sin\left(\frac{a}{2}q_x\right)\right\}\\
a(A_1^2, q) &= \mathrm{Re}\left\{e_z(\hat{q})\left[\cos\left(\frac{a}{2}q_x\right) + \cos\left(\frac{a}{2}q_y\right)\right]\right\}\\
a(A_2^1, q) &= \mathrm{Re}\left\{ie_x(\hat{q})\sin\left(\frac{a}{2}q_y\right) - ie_y(\hat{q})\sin\left(\frac{a}{2}q_x\right)\right\}\\
a(B_1^1, q) &= \mathrm{Re}\left\{e_z(\hat{q})\left[\cos\left(\frac{a}{2}q_y\right) - \cos\left(\frac{a}{2}q_x\right)\right]\right\}\\
a(B_1^2, q) &= \mathrm{Re}\left\{-ie_x(\hat{q})\sin\left(\frac{a}{2}q_x\right) + ie_y(\hat{q})\sin\left(\frac{a}{2}q_y\right)\right\}\\
a(B_2^1, q) &= \mathrm{Re}\left\{ie_x(\hat{q})\sin\left(\frac{a}{2}q_y\right) + ie_y(\hat{q})\sin\left(\frac{a}{2}q_x\right)\right\}.
\end{aligned} \tag{5}$$

The linear vibronic part of the adiabatic potential is then given by

$$\sum_{\Gamma\gamma\gamma^k} \hat{V}_{\Gamma\gamma\gamma^k} Q_{\Gamma\gamma\gamma^k} = \varepsilon_{A_1}\vartheta + \varepsilon_{B_1}\sigma_z + \varepsilon_{B_2}\sigma_x, \tag{6}$$

where σ_i and ϑ are the Pauli and the unit second order matrices, respectively.

It results in the contribution to the energy respectively of the form

$$\delta E^{\pm} = \varepsilon_{A_1} \pm \sqrt{\varepsilon_{B_1}^2 + \varepsilon_{B_2}^2} \tag{7}$$

with

$$\begin{aligned}
\varepsilon_{A_1} &= W_{A_1^1}Q_{A_1^1} + W_{A_1^2}Q_{A_1^2}\\
\varepsilon_{B_1} &= W_{B_1^1}Q_{B_1^1} + W_{B_1^2}Q_{B_1^2}\\
\varepsilon_{B_2} &= W_{B_2^1}Q_{B_2^1},
\end{aligned} \tag{8}$$

where $W_{\Gamma^k\gamma^k}$ can be viewed as phenomenological coefficients describing the respective components of the vibronic coupling. As it is seen from Eq. (7) the linear dependence $\delta E(Q)$, for which the static Jahn-Teller regime takes place, is conditioned by either ε_{B_1} or ε_{B_2} vanishing. In the statical case it can be satisfied if the respective $W_{\Gamma^k\gamma^k}$ coefficients vanish.

The condition for the static J-T regime is less stringent, however, if the cluster vibrations are stimulated by a propagating elastic wave. Indeed, inserting (5) into (8), to linear terms in q_i, we obtain

$$\frac{q_y}{q_x} = \frac{e_x(\hat{q})}{e_y(\hat{q})} \quad \text{for} \quad \varepsilon_{B_1} = 0$$

and

$$\frac{q_y}{q_x} = \frac{e_y(\hat{q})}{e_x(\hat{q})} \quad \text{for} \quad \varepsilon_{B_2} = 0. \tag{9}$$

These conditions are of such a particularly simple form only for the $2D$ cluster under consideration. It can easily be seen that if the cluster is extended by including succesive coordination spheres, then the dependence of $W_{\Gamma^k\gamma^k}$ on the right-hand side of Eg. (9) will appear.

III. THE VIBRONIC – ORIGINATED SAW ATTENUATION

For vibronic centres the tunnelling between equivalent distorted configurations corresponds to the dynamic Jahn-Teller regime and can be measured by the value of the corresponding "inversion" or "tunnelling" splitting. This splitting concerns each of the sublevels resulting from the vibronic (Jahn-Teller) removing of the orbital degeneration. It provides a basic mechanisms for a resonance-type scattering of elastic waves on vibronic centres.

One, however, should have in mind that in typical cases of the dynamic Jahn-Teller regime the value of that splitting is considerably larger than the elastic phonon energy, thus the resonance absorption should be considered as concerning thermal phonons associated with the wave, with the emission being generally a combination of the Raman and the unradiative processes. A fundamental parameter is then the transition rate for the excitation which is inversely proportional to the transition probability times the number of thermal phonons with energies greater than that of the splitting. In such a case the maximum value of the attenuation occurs when the truncation rate is equal to the elastic phonon frequency [8]. As the transition rate is a monotone temperature function the attenuation maximum is associated with a specified temperature. By measuring that temperature for various acoustic modes differing in the propagation direction and polarization one can obtain a relatively large information of the vibronic coupling parameters and their symmetry properties. The peculiar potential of the SAW as an acoustic probe of the kind, stems from specific conditions for vibronic effects at the surface region. In view of a generally lower symmetry as compared to the bulk the number of equivalent potential minima is reduced and their relative positions are modified. Other important factors are random stresses existing in that region, the influence of surface charge (usually also randomly distirbuted) and external fields. A consequence of such a situation is that the potential distribution becomes eventually asymmetric and the barriers between various minima are, generally, enhanced. It, in turn, leads to a considerable reduction of the tunnelling splitting to the value for which direct resonance processes, especially for high frequency SAW, are possible, thus giving an additional contribution to the attenuation.

The attenuation rate can be calculated with the help of the system t-matrix according to the formula

$$\tau_{qj} = -\omega_q^{-1} cN \lim_{\epsilon \to 0+} \mathrm{Im} t(\omega_q + i\epsilon)_{qj,qj}. \tag{10}$$

In turn the linear terms in the adiabatic potential provide a contribution to the lattice self energy of the form

$$\sum_{qj,g'j'}{}^{(1)}(\omega, T) = -2\pi c(q' - q) \sum_{\Gamma\gamma,\Gamma'\gamma'} \frac{\vartheta^{j}_{\Gamma\gamma,\Gamma'\gamma'}(-q)\vartheta^{j'}_{\Gamma'\gamma',\Gamma\gamma}(q')}{\hbar\omega - \delta_{\Gamma'\Gamma}} \times (f_{\Gamma'}(T) - f_{\Gamma'}(T)) \tag{11}$$

[3], with f_Γ denoting the thermal occupation of the sublevel Γ,

$$c(q, n) = \frac{1}{N} \sum_{l} c(l, n) e^{iql} \tag{12}$$

being the $2D$ Fourier transform of the number describing the (l, n) cells occupation by the $J - T$ centre.

The $\vartheta_{\Gamma\gamma,\Gamma'\gamma'}$ are the symmetrized vibronic coupling coefficients, representing $v_{\Gamma\gamma}$ in a projection to symmetry-adapted phonon polarization vectors.

In the case considered they can be represented as

$$\vartheta_{B_{1(2)}}(q) = \eta_{B_{1(2)}} a(B_{1(2)}; q) \tag{13}$$

where the coefficient η_B is proportional to the coupling strength v_B. For uniform distributions of the centres it leads to the formula

$$\sum_{qj,q'j'} (\omega, \tau) = -2\pi c \frac{|\vartheta_{B_{1(2)}}(-q)|^2}{\hbar\omega - 2\Delta} \,\mathrm{th}\, \frac{\Delta}{kT} \tag{14}$$

with 2Δ denoting the tunnelling splitting.

The other important contributions to δK can be proveded as discussed in [1], by piezoelastic coupling, by the temperature dependent influence from other centres of the kind existing in the lattice [4] or by other mechanisms depending on the concrete physical situation.

Adding these contributions we obtain

$$\sum = \sum{}^{(j)} = ct(qj, q'j'), \tag{15}$$

where $t(qj, g'j')$ stands for the effective t - matrix for the system of uniformly distributed J-T centres. The formulas (10-15) indicate a way in which the attenuation rate can be calculated.

A more detailed treatment of the SAW attenuation should take into account a contribution from the surface corrugation which requires including to the description also normal derivatives of the wave functions of the tunnelling states [5]. The effect of this particularly essential for a higher frequency of the SAW and shoulf then be treated simultaneously with the contribution associated with other material nonhomogeneities, which are typical for the topmost layer.

IV. SOME RELATED PHENOMENA

Qualitatively similar properties are exhibited by some amorphous materials. It has been proved [5] that observed anomalies in acoustic phonons behaviour can be explained within a model with two equilibrium positions in an asymmetric double-well potential broadly distributed in their value. Transitions between the wells are then responsible for the resonance attenuation of the acoustic wave. In [5] this sort of attenuation for the case of SAW propagating beneath the amorphic thin film was investigated in detail. The treatment based on the deformation potential model of the perturbation due to SAW, resulted in a simple formula for the attenuation rate.

A specific case represents phonon anomalies in Cu halides, where equivalent secondary off-center minima in the cation potential energy occur. The off-center Cu^{2+} population is a function of both the temperature and the pressure via the highly anharmonic difference between the off-center and central well potential minima. The tunnelling corresponds here to transitions between particular off-centre positions [6].

That sort of phenomena is typical for paraelectric and paraelastic problems in solids. The characteristic example is the KC1 : Li^+ case, where the impurity Li^+ assumes one of several off centre equivalent positions between which a tunel move is possible [7].

It should be mentioned that the problem treated in Sect. III. has also a "statical" side. It is connected with tha fact that the presence of near-surface irregularities affects not only SAW propagation characteristics but at the same time contributes to conditions which determine the SAW itself. For instance, in the dipole-moment representation of defect forces the full elastic part of the Hamiltonian can be written

$$\varkappa_{el} = \frac{1}{2}\int d^3r \varepsilon_{\alpha\beta}(r) C_{\alpha\beta\gamma\delta}\varepsilon_{\gamma\delta}(r) + \int d^3r P_{\alpha\beta}(r)\varepsilon_{\alpha\beta}(r), \tag{16}$$

where $\hat{C}$ is the elastic tensor and $\hat{P}$ – the corresponding force tensor of the second degree. It leads to mechanical boundary conditions of the form

$$C_{\alpha z\gamma\delta}\varepsilon_{\gamma\delta} + P_{\alpha z} = 0 \tag{17}$$

with z being the direction normal to the surface plane, and consequently to the near-surface static deformation

$$\varepsilon^s_{\alpha\beta} = S_{\alpha\beta z\delta}P_{\delta z}, \tag{18}$$

where $\hat{S} = \hat{C}$ represents the stiffness tensor of the medium.

Note that when the effective-mass approximation is applicable, the role of the dipole tensor $P_{\alpha\beta}$ as applied to Jahn-Teller defects is played by the vibronic contribution to the stress tensor, which can be represented as

$$\sigma'_{\alpha\beta} = \sum_{nn'} D^{\alpha\beta}_{nn'}, \phi^*_n(r)\phi_{n'}(r) \tag{19}$$

with ϕ_n being the envelope wave function of the localized defect state n.

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О ПРИМЕНЕНИИ ПАВ В ИССЛЕДОВАНИИ ПРИПОВЕРХНОСТНЫХ ВИБРОННЫХ ДЕФЕКТОВ

Работа посвящена особым свойствам рассеяния ПАВ на приповерхностных вибронных центрах. Особое внимание направляется на возможность использования высокочастотного ПАВ при исследовании вибронных характеристик индуцированых на приповерхностных дефектах. Особое явление связаное с таким видом рассеяния поясняется.