Relaxation and Acoustic Properties of Localized Electron Lowered Symmetry Centers

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JOURNAL DE PHYSIQUE IV
Colloque C8, supplément au Journal de Physique III, Volume 6, décembre 1996

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Abstract. Relaxation behavior of electron lowered symmetry centers is considered on the basis of numerical calculation of the Schrödinger equation. The relaxation behavior of these systems is either quantum-mechanical or classical, depending on the temperature. A "tunneling degree" parameter is introduced in order to describe the specific relaxation behavior of these systems in the framework of the both conventional tunneling model and classical Debye relaxation. A comparative analysis for electron lowered symmetry centers in α-quartz, such as E' defect centers, H^- ion at E_4' centers, and apex O(A) atoms in high-temperature superconducting cuprates is reported.

1. INTRODUCTION

In high-temperature superconducting cuprates (HTSC) and α-quartz there exist electron lowered symmetry centers (ELSC) [1,2]. They relax quantum-mechanically, by thermally activated tunneling and classically, depending on the temperature. Their relaxation behavior is similar to the conventional tunneling system (TS) at low temperature and to the classical Debye relaxation system (RS) at higher temperature. Thus, ELSC may be considered as tunneling-relaxation systems (TRS). *E*' centers and H^- ion at E_4' center in α-quartz, O(A) atoms in high-temperature superconducting cuprates (HTSC) are examples for TRS in non-amorphous solids [1,2,3].

The adiabatic electron transfer is characteristic of considered TRS [4]. By reason of this the configurational transitions dominate the electron ones. The relaxation absorption is a result of wave-TRS interaction. The relaxation rate calculation may be performed by the reaction rate method (RRM) [4]. The aim of this paper is to obtain the relaxation rates and related acoustic losses by calculating the eigenvalue problem of ELSC and using modified RRM scheme.

2. EIGENVALUE SPECTRUM OF DOUBLE-WELL POTENTIAL SYSTEMS

The one-dimensional uni-particle Schrödinger Equation (SE) for wave function $\chi(E,Q)$ (χ depends on energy E and configuration coordinate Q) is numerically solved using anharmonic double-well potential (DWP) $U(Q)$ in accordance with the pseudo Jahn-Teller effect (PJTE) description of ELSC, such as E' series centers in α-quartz and O(A) in HTSC [1,4]. The potential energy includes anharmonic term δq. Non-zero value of δq may cause drastic changes in the harmonic energy levels and the potential transforms into two deep separate wells. Then, one should expect linear-harmonic-oscillator(LHO)-like results (double degenerated LHO levels), but with modified condition for the energy quantisation: $2E/\hbar\omega=2n+1$, where ω is the renormalized phonon frequency. The numerical calculation of SE shows that in some investigated centers even the lowest energy levels are substantially different from the harmonic ones.

Using numerical calculation of SE, a thorough characterization of E' series centers, H^- ion at E_4' center, as well as O(A) centers is performed. As a result the eigenvalues E_n and eigenfunctions $\chi_n(Q)$ are obtained with PJT parameters taken from [3,4] (see for example Fig.1).

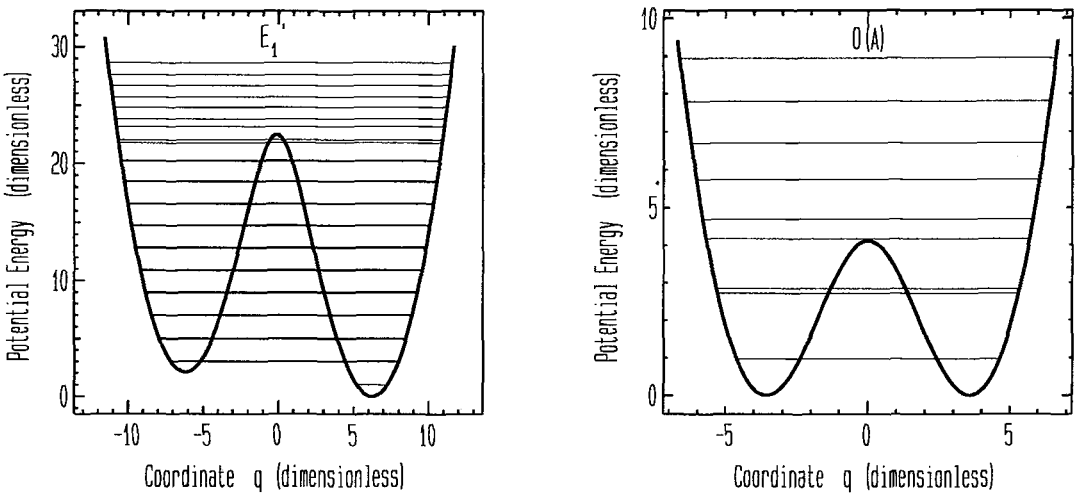

Figure 1. Double well potential energy U(q) with numerically calculated vibronic levels of E'$_1$ center in α-quartz and O(A) in $YBa_2Cu_3O_{7-\delta}$ (YBCO). The values of the lowest level tunneling splitting are listed in Table 1.

3. RELAXATION BEHAVIOR OF DOUBLE-WELL POTENTIAL SYSTEMS

DWPS are strongly relaxing systems. Interwell transfer rate can be calculated on the basis of numerically computed energy levels by the adapted for non-radiative transitions RRM. In accordance with this method, TRS relax via tunneling in ground state, thermally activated tunneling in remaining subbarrier states, and classical transitions in overbarrier states in temperature intervals $0 \div T_k$, $T_k \div 4T_k$, $4T_k \div \infty$ respectively, ($2T_k$ is the Christov's characteristic temperature). In the present calculations RRM is improved in order to calculate the temperature dependence of the relaxation rate of the lowest couple of tunnel splitted energy levels. This relaxation rate is obtained in accordance with the standard tunneling model (TM). The rest (sub- and overbarrier) energy levels' contribution is numerically computed using quasiclassical approximation.

The relaxation rate τ^{-1} is determined by the total transition probability W per unit time along the potential energy profile U. This transition probability is a sum over all the energy levels with thermal occupation factors A_n: $\tau^{-1} = W = \sum_{n=n_0}^{\infty} W_n$, $W_n = A_n T_n \nu_n$, where T_n is the transition probability. $A_n \nu_n$ is interpreted as a probability for closing to the barrier at energy in the interval $h\nu_n$, which includes the n^{th} level.

The first (lowest) couple of tunnel splitted energy levels (see Fig.1 and Table 1) with numbers n_0 and n_0+1 "forms" the classical TS. The normalized occupation probabilities of these levels are $\mu_{n_0} = 2A_{n_0}$ and $\mu_{n_0+1} = 2A_{n_0+1}$. The tunneling transition probability W^{TS} is defined in the framework of TM through the tunneling splitting of a "symmetric" PJT potential Δ_0, the mass density ρ, the wave velocity υ, the deformation potential $\mathcal{D}$ and "asymmetry energy" $\Delta = \sqrt{\Delta_E^2 - \Delta_0^2}$, where $\Delta_E = E_{n_0+1} - E_{n_0}$. In the case of the typical TS $\mu_{n_0} = \mu_{n_0+1} \approx 1$ the transition probability coincides with the formula for the "direct processes" in TM [5,6].

The transition probability W^{RS} for the remaining energy levels ($n > n_0+1$) is obtained using WKB-method. The temperature dependencies of W for E' centers, H^- ion at E_4' center in α-quartz, and O(A) atoms in HTSC are calculated [7]. The values of the input parameters and the most important derivative parameters are listed in Table 1. The frequencies ω_i are taken from experiments (see ref. [1,2]). ELSC relaxation depends on barrier height, interwell separation, asymmetry energy and the vibronic quant energy.

TS contribution dominates at lower temperature, while the RS contribution dominates at higher temperature. They are equal at some characteristic temperature T_c, which can be compared with T_k and with the position of the relaxation absorption peak T_0. The calculated temperature dependencies of the relaxation rates in the investigated systems show that these systems are mixed TRS at the vicinity of T_c. In order to calculate the relaxation losses in accordance with the both TM and Debye relaxation ratio, "tunneling degree" parameter λ is introduced. One can rewrite W as $W^{TS}+W^{RS}$ and λ is defined as: $\lambda=W^{TS}/(W^{TS}+W^{RS})$. For TS only the lowest tunnel splitted levels are occupied ($W_{n_0}=W_{n_0+1}\approx 0.5$ and $\lambda=1$). In the case of RS all levels have nearly the same occupation ($W^{RS} \gg W_{n_0}+W_{n_0+1}=W^{TS}$ and $\lambda\to 0$). $W^{TS}=W^{RS}$ ($\lambda=0.5$) at $T=T_c$.

Table 1. Input parameters and most important derivative parameters.

	Input parameters						Derivative parameters					
quantity	Δ, eV	$\mathfrak{D}$, eV	ρ, g/cm^3	v, m/s	$\omega_i/2\pi$, Hz	N, Å^{-3}	Δ_0, eV	ω, eV	$2T_k$, K	T_c, K	T_0, K	$\lambda(T_0)$
H^- at E'$_4$	0.063	1.0	2.65	3300	$5\times10^{+3}$	4.2×10^{-7}	2.74×10^{-3}	0.227	403	$>>T_0$	27	1.0
O(A)	1.8×10^{-5}	0.36	2.3	6400	1050	1×10^{-5}	1.76×10^{-6}	0.0535	173	27	30	0.177
E'$_1$	0.072	1.0	2.65	3300	$5\times10^{+6}$	4.2×10^{-7}	2.45×10^{-17}	0.0657	575	35	587	2.0×10^{-23}
E'$_{2,4}$	0.08	1.0	2.65	3300	$5\times10^{+6}$	8.4×10^{-7}	3.03×10^{-28}	0.0358	276	10	543	1.7×10^{-45}

The investigated TRS H^- at E'$_4$, O(A), E'$_1$ and E'$_{2,4}$ are ordered with the decreasing of the tunneling degree, which is calculated at $T=T_0$ (see Table 1) on Fig.2. The difference between the E' centers and O(A)/H^- ions is clearly seen. The E' center is a typical classical RS at $T\sim T_0$. TS absorption part is negligible small (the system is a clearly tunneling at $T<T_c$=35K for E'$_1$ and $T<T_c$=10 K for E'$_4$ center)because of the very high value of the barrier height (containing ~10 splitted levels) and asymmetry energy in order of 1-2 vibronic quanta. H^- ion at E'$_4$ is manifested as typical TS because of the lower barrier (containing 1 couple splitted levels) and the smaller asymmetry energy ($\lambda\sim1$ at $T\sim T_0$). O(A) proves as mixed TRS because the transition between the two limiting cases ($\lambda\sim0.5$, $T\sim T_c$) is near to T_0.

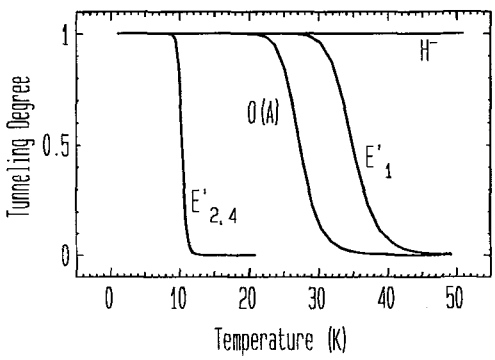

Figure 2. Temperature dependencies of the tunneling degree λ of E' centers, H^- ion at E'$_4$ center in α-quartz, and O(A) in HTSC.

4. ACOUSTIC LOSSES

The relaxation strength is $A\mathfrak{D}^2$ for classical RS ($A=N/4kT\rho v^2$, N is TRS concentration, $\mathfrak{D}$ - deformation potential) and $A\mathfrak{D}^2\mathrm{sech}^2(\Delta_E/2kT)$ in the case of TS. Acoustic losses are calculated constructing the relaxation strength as a sum of two terms $\zeta(T)\times A\mathfrak{D}^2\mathrm{sech}^2(\Delta_E/2kT)$ and $[1-\zeta(T)]\times NA\mathfrak{D}^2$ with weight coefficients ζ and $1-\zeta$ because of the treatment of ELSC as mixed TRS (Fig.3). The first term accounts for the "strongly separated TS" contribution to the wave energy losses, the second term accounts for the "classical RS"- and the "weekly separated TS" contribution. ζ is defined as $\zeta(T)=\lambda(T)\mu_{n_0+1}(T)$. The additional factor μ_{n_0+1} is the separation degree of the lowest couple tunneling levels against the remaining levels. This is necessary because the wave affects mainly these two levels, while the rest levels are almost unchanged.

The numerical calculations show that the tunneling degree λ contribution in ζ is essential at higher temperature ($T>T_c$, $\lambda\to0$, $\mu\to1$), while the tunneling levels separation degree μ_{n_0+1} - at lower temperature ($T<T_c$, $\mu\to0$, $\lambda\to1$). They are temperature dependent and form a temperature range, at which one can obtain the "tunneling formula" ($\zeta\approx1$, strongly separated TS). It should be noted that the classical formula ($\zeta\approx0$) is obtained in two cases: (i) at very high temperature, when the system is typical RS ($T>T_c$) and (ii) at very low temperature, when the system is weekly separated TS ($T\ll T_c$). The terms "weekly-" and "strongly-separated TS" illustrate the tunneling levels occupation - strongly separated TS possess nearly the same occupation of the levels, while the occupation of the lowest level is near 1 for weekly separated TS.

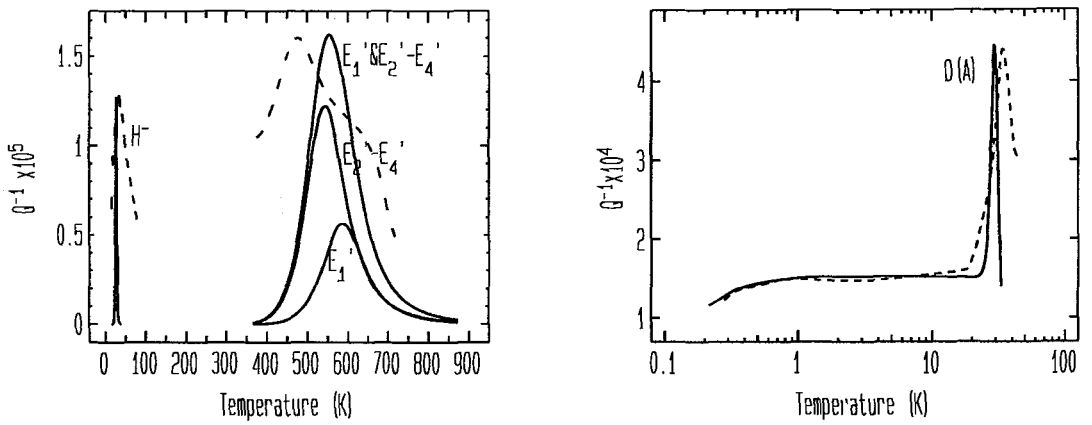

Figure 3. Temperature dependencies of the acoustic losses for E'$_1$, E'$_{2,4}$ centers, H^- ion at E'$_4$ center in α-quartz and O(A) in YBCO. The dashed lines represent experimental data [8] and [9]. Theoretical acoustic losses for the H^- ion are compared with experimental dielectric losses taken from [10] (the comparison is possible because of the parity between the acoustic and dielectric losses). The experimental peak in quartz near 500 K is broad because the specifics of the E' centers formation process (irradiation with fast neutrons).

5. CONCLUSION

Relaxation behavior of ELSC is considered on the basis of a numerical calculation of the eigenvalue spectrum and corresponding wave functions. This behavior is either quantum-mechanical or classical, depending on the temperature. The quantum-mechanical systems' behavior is very close to TS one. By reason of this an improvement of the relaxation rate method for the relaxation rates calculation is proposed. A "tunneling degree" parameter is introduced in order to connect the specific relaxation behavior of these systems in accordance with the both conventional tunneling model and the classical Debye relaxation. This parameter defines the system (at a given temperature) as a tunneling or a relaxation one. The proposed approach allows to obtain the relaxation times and the relaxation response of these systems under the action of external field. A comparative analysis of the relaxation behavior in α-quartz (E' defect centers, H^- ion at E_4' centers) and HTSC (O(A) atom in YBCO) is reported. The difference between the E' series centers and O(A)/H^- ion is clearly seen from the analysis of the temperature dependencies of the tunneling degree.

Acknowledgment

The authors are grateful to "Drouzhba" Ltd. - Plovdiv, "SID" Ltd. - Sofia, and to the Organizing Committee of ICIFUAS-11, for the financial support.

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