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TRAJECTORY TREATMENT OF THE $F_A^{(II)}$-CENTER IN KC1:Li.

DECAY TIME IN THE EXCITED STATE

R. Englman, A. Ranfagni, A. Agresti and D. Mugnai

Soreq Nuclear Research Center, Yavne, Israel
'Istituto di Ricerca sulle Onde Elettromagnetiche del CNR, Pirenze, Italy

Abstract - We simulate the temperature dependence of the decay time of an impurity in its excited state by obtaining the classical trajectories of the ions in the crystal. The $F_A^{(II)}$-center in KC1:Li is treated.

I - INTRODUCTION

Recent developments of monitoring techniques in the range of picoseconds have allowed measurements of configurational relaxation times $T_R$ in excited states of impurities in crystals. By recording the rise time of emission from the relaxed excited state, a decrease in $T_R$ from about 15 ps to 1-2 ps was observed for the $F_A^{(II)}$ center in KC1:Li upon raising the temperature to about 30 K/1/ and about the same decrease was found more recently for the $^1T_1^-$ state in KI:Ag /2/. The analyses of the data, which were able to account for only a small fraction of the energy dissipated in the configurational relaxation, employed a multiphonon relaxation formula (Eq. 3.36 in /3/) for the temperature dependence of $T_R$. This quantum mechanical expression gives the residence time $t_r$ in the initial state before transition to a neighboring level belonging to a different state. We have performed computation of the classical trajectories of the ions for the $F_A^{(II)}$ center following excitation. The model for the center is shown in Figure 1, where the horizontal axis represents neighbor-correlated jumps of the vacancy between equivalent 100 type positions. We use a crystal-mode representation (amplitude $Q_u$, mode index $a$, wave number $q$) for the ionic displacements, instead of the more common individual atom displacements. We solve about $10^4$ equations of motions for $Q_u$, and obtain the time of residence $t_r$ as well as decay ($\tau'$) and correlation ($\tau_{cor}$) for the decay of $Q_{vac}$.
The classical motions proceed along an adiabatic potential energy surface (APES-) that is stable (namely, harmonic) for all displacements except $Q_{vac}$. In Figure 2 we show the relationship of our classical model with the multiphonon-relaxation model in /1/. Their formalism implies tunneling from the initial non-adiatatic $V_2$ to the surfaces $V_1$ or $V_3$. 

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- Fig. 1 - Ionic configurations near the FA(II) center, potentials in the ground and excited states and the experimental scheme of (/1/) which monitored the emission rise-time.

Fig. 2 - Relation between multiphonon transition mechanism $V_2 \rightarrow V_3$ and classical trajectory on APES.
II - FORMALISM

The excited-state potential, having a saddle point at $Q_{qs}=0$ and a decrease along $Q_{vac}$ in the 110 ($=X'$) direction, is

$$V_{ex} = \frac{1}{2} \sum_{k} \left( Q_{k}, j(t) - Q_{vac} e_{k,j} (K/nk) \right)^{1/2 \Delta E \cos \left( \frac{2\pi}{a} Q_{vac}(t) \right)}$$

where

$$Q_{vac} = \frac{1}{\sqrt{N}} \sum_{k=1}^{K} \sum_{j=1}^{K} Q_{k,j} e_{k,j} (K/nk)^{1/2} \text{ and } q_{q,s} = \left| q \right| F(\omega q,s), F(\omega) = e^{-\omega / \omega_D},$$

$q_{q,s}$ and $F(\omega)$ give the mode selective in the composition of $Q_{vac}; \omega_D$ is the circular Debye frequency.

The initial conditions for the amplitudes at temperature $T$ are

$$Q_{q,s}(t=0) = \left( \frac{2k_B T q_{q,s}}{M_{q,s} \omega_D} \right)^{1/2} \cos q_{q,s} \text{ and } q_{q,s}(t=0) = \left( \frac{2k_B T q_{q,s}}{M_{q,s}} \right)^{1/2} \sin q_{q,s}$$

where

$$k_B T q_{q,s} = \frac{n_{q,s} + 1/2}{M_{q,s}} \omega_D q_{q,s} \text{ and } n_{q,s} = (\exp(\omega_D q_{q,s} / k_B T) - 1)^{-1}$$

$a$ are random angles.

III - RESULTS

The amplitude $Q_{vac}$ shows three characteristic behaviors, depending on the energy excess $\Delta E$ and the Debye frequency $v_D = 2\pi / \omega_D$. For aperiodic motion, in the lower portion, one associates the decay time with the time of stay $\tau_r$ or residence time near the $Q_{qs}=0, 100$ position.

Quantitatively, this appears as in Figure 4, where curves are shown for three values of the high-frequency cut-off parameter $A$ in $F(\omega)$ and for simulations with a number of modes $\sim \frac{1}{2} K^3 \sim 10^4 \text{ (K=30).}$

![Fig. 3 - "Phase diagram" for the motion of $Q_{vac}$ in $\Delta E-v_D$ parameter space, $\xi = \frac{2 \Delta E}{M_{q,s} \omega_D a^2}$](image-url)
Fig. 4 - The vacancy mode amplitude rises after a residence time of cca 2-5 Debye periods and performs a decajng oscillatory motion around the RES configuration.

Fig. 5 - Computed residence and correlation times as function of temperature.
Raising the temperature lowers the residence time $\tau$ (Fig. 5). The decay of the damped oscillation represented by $\tau_{\text{cor}}$ in Figure 3 is likewise accelerated by a temperature rise. Results are given in /4,5/.

REFERENCES