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Alternative mechanism in phonon-assisted tunneling

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The Hamiltonian of the phonon-assisted tunneling problem in crystals contains three fundamental constituents (lattice and tunneling parts and the coupling between them), for which different hierarchical assumptions are possible. In previous theoretical work (e.g., on paraelectric centers) it has always been assumed that the dominating phonon frequency ω_d is much larger than the bare tunneling parameter $\Delta/\hbar$. Although this seems reasonable, the predicted transition rate is by far too small. In this paper we have discussed the competing influence of low-frequency phonons, for which $\hbar\omega_d < \Delta$. Here an alternative mechanism takes over, in which the tunneling is effectively transferred to the phonon system. This is discussed. Moreover, a new optimization procedure is given for the multimode problem, which is not confined to the specific mechanism considered here. In our approach the artifice of a static external field is not required. The calculated temperature behavior of the relaxation time turns out to be qualitatively similar to that of the conventional mechanism, but the relevant physical parameters entering the results are quite different. A future unified treatment of high- and low-frequency phonons proves urgent.

I. INTRODUCTION

Phonon-assisted tunneling is of lasting interest in the investigation of paraelectric and paraelastic defects in solids, and has become of growing interest recently in the context of glass investigation. For a good survey of earlier work we refer to the paper of Narayanamurti and Pohl.[1] A more recent review is given in the article of Bridges.[2]

One of the best-known examples for tunneling centers is OH^- in KCl. Here the OH^- ion replaces Cl^{-1} and aligns along the $\langle 100 \rangle$ directions of the host lattice. Thus the proton has six equivalent positions and can move from one to the other by phonon-assisted tunneling. In an external static (electric or elastic) field one of the positions may be occupied preferentially. If one switches off the field, the system will relax to its equilibrium state where all sites are equally occupied. This relaxation process, which is mainly due to 90° transitions, has been experimentally investigated[3,4] by Kapphan and Lüty. They have measured the temperature dependance of the relaxation time τ and have found a T^{-1} law for low temperatures corresponding to one-phonon processes and a T^{-4} law for higher temperatures, when multiphonon processes become important.

In the theoretical description of tunneling centers the same specific mechanism has always been considered,[5-7] which is explained in a very transparent way in a paper of Dick.[7] It is based on the fundamental assumptions that the dominating phonon energy $\hbar\omega_d$ is very large with respect to the tunneling splitting Δ, and that external static fields establish a strong energy difference ϵ_0 between the equilibrium positions of the tunneling particle ($\epsilon_0 \gg \Delta$). These assumptions effectively lead to a phonon-induced screening of the tunneling parameter Δ by a kind of Debye-Waller factor. However, in these approaches the Debye-Waller exponent appears to be by far too large.[7]

On the other hand, it has been argued by Sander and Shore[6] that the assumption $\hbar\omega_D \gg \Delta$ seems reasonable on the grounds that Δ cannot be larger than $\hbar^2/2I$, which describes the splitting between rotational energy levels of the dipole in free space (~ 27 K for OH^-). Thus Δ should be much smaller than the Debye frequency ω_D. This argument may well be true, but one should note also that the low-frequency lattice modes may have an enhanced influence by means of their frequency being close to Δ. In the overlap region $\hbar\omega_d \approx \Delta$ there may even be something like Fano behavior, but we will not discuss this here.

The motivation for our work is the question of whether the influence of low-frequency phonons

can yield an effective diminution of the exceedingly large Debye-Waller exponent. Therefore, we consider a tunneling mechanism, for which the hierarchical assumptions are opposite to the conventional ones. Our principal interest concerns the question of what kind of relaxation behavior one obtains if one assumes the dominating phonon frequency ω_d to be smaller than $\Delta/\hbar$ and the phonon-tunneling interaction to be strong. However, we do not claim that this relaxation path is the dominating one. Rather, we assume that the conventional and the alternative tunneling mechanisms compete with each other. Before discussing this competition it seems worthwhile to investigate the alternative mechanism alone. In our approach, the theoretical description does not require the existence of a static field. In passing we mention that in a recent communication[8] we have shown how the artifice of a static field can be avoided also in the computation of the conventional mechanism. In Section II we present our model Hamiltonian. In Sec. III we describe a method of handling the fundamental multiphonon-mode problem by means of an optimization procedure. Performing a unitary exponential transformation in Sec. IV, we can profit from our hierarchical assumptions in a very effective way. The calculation of the relaxation behavior is given in Sec. V. We employ the Kubo formalism. The respective Green functions are calculated from their equations of motion in the transformed space. Up to Sec. V the tunneling system is treated in a two-state picture, which seems adequate to a fixed 90° transition. In Sec. VI the procedure is generalized to a six-state tunneling description.

II. MODEL HAMILTONIAN

A model Hamiltonian for KCl:OH^- has been derived in a recent paper of Kuhn and Wagner.[9] Considering a fixed 90° transition, we can confine ourselves to a two-state defect system; then the Hamiltonian reads

$$H = H_L + H_D + H_{DL} ,$$

where

$$H_L = \frac{1}{2}\sum_{\vec{k},\lambda}[P_{\vec{k}\lambda}P_{-\vec{k}\lambda} + \omega^2(\vec{k},\lambda)Q_{\vec{k}\lambda}Q_{-\vec{k}\lambda}] , \tag{1a}$$

$$H_D = \frac{\Delta}{2}(a_1^\dagger a_2 + a_2^\dagger a_1) , \tag{1b}$$

and

$$H_{DL} = \sum_{\vec{k},\lambda}\sum_{i=1}^{2} K_i(\vec{k},\lambda)Q_{\vec{k}\lambda}a_i^\dagger a_i . \tag{1c}$$

The first term H_L is the lattice Hamiltonian, H_D describes the defect (tunneling) system, and H_{DL} is the coupling between the phonon and the tunneling systems. The coupling constants $K_i(\vec{k},\lambda)$ given in the article of Kuhn and Wagner[9] include a nonadiabatic description of the tunneling proton. For the following calculations we need only the symmetry relations

$$K_i(-\vec{k},\lambda) = [K_i(\vec{k},\lambda)]^* \quad (i=1,2) . \tag{2}$$

Introducing spin operators

$$\sigma_x = \tfrac{1}{2}(a_1^\dagger a_2 + a_2^\dagger a_1) ,$$

$$\sigma_y = \frac{1}{2i}(a_1^\dagger a_2 - a_2^\dagger a_1) ,$$

$$\sigma_z = \tfrac{1}{2}(a_1^\dagger a_1 - a_2^\dagger a_2) ,$$

which satisfy the usual commutation rules, we can write the Hamiltonian in the form

$$H = H_L + \Delta\sigma_x + q\sigma_z + \sum_{\vec{k},\lambda} Q_{\vec{k}\lambda}\tfrac{1}{2}[K_1(\vec{k},\lambda) + K_2(\vec{k}_1,\lambda)] , \tag{3}$$

where

$$q = \sum_{\vec{k},\lambda} Q_{\vec{k}\lambda}[K_1(\vec{k},\lambda) - K_2(\vec{k},\lambda)] .$$

q is a special linear combination of the phonon coordinates $Q_{\vec{k}\lambda}$, by which the lattice couples to the defect system. The fundamental idea is, to interpret q as a kind of new representative coordinate. This will be discussed in more detail in the following section.

III. CANONICAL TRANSFORMATION OF THE PHONON COORDINATES

We now go from our original phonon coordinates $\{Q_{\vec{k}\lambda}, P_{\vec{k}\lambda}\}$ to new coordinates $\{\tilde{Q}_{\vec{k}\lambda}, \tilde{P}_{\vec{k}\lambda}\}$ in such a way that q represents a single "configurational" mode. This can be achieved by the linear unitary transformation

$$\tilde{Q}_{\vec{k}\lambda} = \sum_{\vec{k}',\lambda'} L_{\vec{k}\lambda;\vec{k}'\lambda'}Q_{\vec{k}'\lambda'} ,$$
$$\tilde{P}_{\vec{k}\lambda} = \sum_{\vec{k}',\lambda'} L_{\vec{k}\lambda;\vec{k}'\lambda'}P_{\vec{k}'\lambda'} . \tag{4}$$

Introducing the total coupling K by

$$K^2=\sum_{\vec{k},\lambda}|K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)|^2 ,$$

we can define

$$L_{01;\vec{k}'\lambda'}=\frac{K_1(\vec{k}',\lambda')-K_2(\vec{k}',\lambda')}{K} . \tag{5}$$

Then we have that $q=K\tilde{Q}_{01}$. Thus $\tilde{Q}_{01}$ is the configurational lattice coordinate. Taken as a legitimate phonon coordinate, it is the only one which couples to the tunneling system. It should be emphasized that by Eq. (5) only $\tilde{Q}_{01}$ and $\tilde{P}_{01}$ have been determined. For the remaining new coordinates multiple choices are still possible; however, there is a best way to choose them. We note that the new coordinates are no longer normal coordinates of the lattice. Thus H_L, expressed in terms of $\{\tilde{Q}_{\vec{k}\lambda},\tilde{P}_{\vec{k}\lambda}\}$, is not diagonal. This disadvantage can be minimized by a suitable choice of the new coordinates $\{\tilde{Q}_{\vec{k}\lambda},\tilde{P}_{\vec{k}\lambda}\}$ or of the transformation coefficients $L_{\vec{k}\lambda;\vec{k}'\lambda'}$, respectively. We now describe an optimization procedure to find the most suitable transformation matrix $\underline{L}=(L_{\vec{k}\lambda;\vec{k}'\lambda'})$.

Since $\underline{L}$ is assumed to be unitary ($\underline{L}^{-1}=\underline{L}^{\dagger}$), the inversion of Eq. (4) is given by

$$\begin{aligned} Q_{\vec{k}\lambda}&=\sum_{\vec{k}',\lambda'}L^{*}_{\vec{k}'\lambda';\vec{k}\lambda}\tilde{Q}_{\vec{k}'\lambda'},\\ P_{\vec{k}\lambda}&=\sum_{\vec{k}',\lambda'}L^{*}_{\vec{k}'\lambda';\vec{k}\lambda}\tilde{P}_{\vec{k}'\lambda'} . \end{aligned} \tag{6}$$

In addition to unitarity, we want the transformation coefficients to satisfy the condition

$$L_{-\vec{k}\lambda;-\vec{k}'\lambda'}=L^{*}_{\vec{k}\lambda;\vec{k}'\lambda'} . \tag{7}$$

Then the new phonon coordinates $\{\tilde{Q}_{\vec{k}\lambda},\tilde{P}_{\vec{k}\lambda}\}$ satisfy the same commutation relations as $\{Q_{\vec{k}\lambda},P_{\vec{k}\lambda}\}$:

$$\begin{aligned} &[\tilde{Q}_{\vec{k}\lambda},\tilde{Q}_{\vec{k}'\lambda'}]_-=[\tilde{P}_{\vec{k}\lambda},\tilde{P}_{\vec{k}'\lambda'}]_-=0,\\ &[\tilde{Q}_{\vec{k}\lambda},\tilde{P}_{\vec{k}'\lambda'}]_-=i\hbar\delta_{-\vec{k}\vec{k}'}\delta_{\lambda\lambda'} , \end{aligned} \tag{8}$$

$$\tilde{Q}^{\dagger}_{\vec{k}\lambda}=\tilde{Q}_{-\vec{k}\lambda},\quad \tilde{P}^{\dagger}_{\vec{k}\lambda}=\tilde{P}_{-\vec{k}\lambda} . \tag{9}$$

Using Eqs. (6) and (7) we can express the lattice Hamiltonian H_L in terms of $\{\tilde{Q}_{\vec{k}\lambda},\tilde{P}_{\vec{k}\lambda}\}$:

$$\begin{aligned} H_L=&\tfrac{1}{2}\tilde{P}^2_{01}+\tfrac{1}{2}\sum_{\vec{k},\lambda\neq(0,1)}\tilde{P}_{\vec{k}\lambda}\tilde{P}_{-\vec{k}\lambda}+\tfrac{1}{2}\tilde{\omega}_0^2\tilde{Q}^2_{01}+W\\ &+\tilde{Q}_{01}\sum_{\vec{k},\lambda\neq(0,1)}\tilde{Q}_{\vec{k}\lambda}\tfrac{1}{2}\sum_{\vec{k}',\lambda'}\omega^2(\vec{k}',\lambda')(L^{*}_{01;\vec{k}'\lambda'}L_{-\vec{k}\lambda;\vec{k}'\lambda'}+L^{*}_{\vec{k}\lambda;\vec{k}'\lambda'}L_{01;\vec{k}'\lambda'}) , \end{aligned} \tag{10}$$

where

$$W=\tfrac{1}{2}\sum_{\vec{k},\lambda'}\sum_{\substack{\vec{k}'',\lambda''\\ \neq(0,1)}}\tilde{Q}_{\vec{k}'\lambda'}\tilde{Q}_{\vec{k}''\lambda''}\sum_{\vec{k},\lambda}L^{*}_{\vec{k}'\lambda';\vec{k}\lambda}\omega^2(\vec{k},\lambda)L_{-\vec{k}''\lambda'';\vec{k}\lambda}$$

and where $\tilde{\omega}_0$ is the frequency which is attached to the configuration mode $\tilde{Q}_{01}$:

$$\tilde{\omega}_0^2=\sum_{\vec{k},\lambda}\omega^2(\vec{k},\lambda)\frac{|K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)|^2}{K^2} . \tag{11}$$

The potential energy in Eq. (10) has three different constituents, namely the configurational mode part $\frac{1}{2}\tilde{\omega}_0^2\tilde{Q}^2_{01}$, the interaction between $\tilde{Q}_{01}$ and the remaining phonon coordinates $\tilde{Q}_{\vec{k}\lambda}$, and the part which is denoted by W. We will determine the transformation coefficients $L_{\vec{k}\lambda;\vec{k}'\lambda'}$ by minimizing this last term W. The notation becomes more transparent, if we introduce the vectors $\vec{1}_{\vec{k}\lambda}$ and the matrices $\underline{D},\underline{E},\underline{P}$ in the following way:

$$\vec{1}_{\vec{k}\lambda}=\{L_{\vec{k}\lambda;\vec{k}'\lambda'}\}_{\vec{k}'\lambda'} \tag{12}$$

[especially $\vec{1}_{01}=\{K_1(\vec{k}',\lambda')-K_2(\vec{k}',\lambda')/K\}_{\vec{k}'\lambda'}$],

$$\underline{D}=(\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}\omega^2(\vec{k},\lambda))_{\vec{k}\lambda,\vec{k}'\lambda'} \tag{13}$$

(diagonal matrix),

$$\underline{E}=(\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'})_{\vec{k}\lambda,\vec{k}'\lambda'} \tag{14}$$

(unity matrix), and

$$\underline{P}=((\vec{l}_{01})_{\vec{k}\lambda}(\vec{l}_{01})^{*}_{\vec{k}'\lambda'})_{\vec{k}\lambda,\vec{k}'\lambda'}=\left[\frac{[K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)][K_1^{*}(\vec{k}',\lambda')-K_2^{*}(\vec{k}',\lambda')]}{K^2}\right]_{\vec{k}\lambda,\vec{k}'\lambda'}. \tag{15}$$

In this notation the unitarity condition for $\underline{L}$ reads

$$\langle \vec{l}_{\vec{k}\lambda} | \vec{l}_{\vec{k}'\lambda'}\rangle=\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}\ , \tag{16}$$

and W can be written in the form

$$W=\sum_{\substack{\vec{k}',\lambda'\\ \neq(0,1)}}\sum_{\vec{k}'',\lambda''}\tilde{Q}_{\vec{k}'\lambda'}\tilde{Q}_{\vec{k}''\lambda''}\tfrac{1}{2}\langle \vec{l}_{\vec{k}'\lambda'} | \underline{D} | \vec{l}_{-\vec{k}''\lambda''}\rangle\ . \tag{17}$$

Minimizing W, we will preferentially try to make the coefficients of the diagonal terms $\tilde{Q}_{\vec{k}'\lambda'}\tilde{Q}_{-\vec{k}'\lambda'}$ as small as possible under the conditions (16). That leads to the restricted variational problem

$$\delta\frac{\langle \vec{l}_{\vec{k}\lambda} | \underline{D} | \vec{l}_{\vec{k}\lambda}\rangle}{\langle \vec{l}_{\vec{k}\lambda} | \vec{l}_{\vec{k}\lambda}\rangle}=0\ , \tag{18}$$

where

$$\langle \delta\vec{l}_{\vec{k}\lambda} | \vec{l}_{01}\rangle=0\ ,\quad \langle \vec{l}_{\vec{k}\lambda} | \vec{l}_{01}\rangle=0\ . \tag{19}$$

By means of the projection matrix $\underline{P}$, we can go from $\vec{l}_{\vec{k}\lambda}$ to the vector $\vec{x}$:

$$\vec{l}_{\vec{k}\lambda}=\vec{x}-\vec{l}_{01}\langle \vec{l}_{01} | \vec{x}\rangle=(\underline{E}-\underline{P})\vec{x}\ . \tag{20}$$

Then Eq. (18), expressed in terms of $\vec{x}$, reads

$$\delta\langle \vec{x} | (\underline{E}-\underline{P})(\underline{D}-\mu^{(\vec{k},\lambda)}\underline{E})(\underline{E}-\underline{P}) | \vec{x}\rangle=0\ , \tag{21}$$

where we have used the abbreviation $\mu^{(\vec{k},\lambda)}=\langle \vec{l}_{\vec{k}\lambda} | \underline{D} | \vec{l}_{\vec{k}\lambda}\rangle\ /\langle \vec{l}_{\vec{k}\lambda} | \vec{l}_{\vec{k}\lambda}\rangle$. Contrary to $\vec{l}_{\vec{k}\lambda}$, $\vec{x}$ allows a free variation, so we finally end up with the eigenvalue problem

$$(\underline{E}-\underline{P})\underline{D}\,\vec{l}_{\vec{k}\lambda}=\mu^{(\vec{k},\lambda)}\vec{l}_{\vec{k}\lambda}\ . \tag{22}$$

In a component representation, Eq. (22) reads

$$\mu^{(\vec{k},\lambda)}(\vec{l}_{\vec{k}\lambda})_{\vec{k}'\lambda'}=\sum_{\vec{k}'',\lambda''}\left[\delta_{\vec{k}'\vec{k}''}\delta_{\lambda'\lambda''}-\frac{[K_1(\vec{k}',\lambda')-K_2(\vec{k}',\lambda')][K_1^{*}(\vec{k}'',\lambda'')-K_2^{*}(\vec{k}'',\lambda'')]}{K^2}\right]\omega^2(\vec{k}'',\lambda'')(\vec{l}_{\vec{k}\lambda})_{\vec{k}''\lambda''}$$

$$\text{for } (\vec{k},\lambda)\neq(0,1)\ . \tag{23}$$

Equation (23) represents a nondiagonal $3N$-dimensional problem, N being the total particle number of the crystal. So an exact solution of this problem seems to be very difficult. However, from the analytical form of Eq. (23) we can guess an approximate solution. If, for instance, we set $\mu^{(\vec{k},\lambda)}=\omega^2(\vec{k},\lambda)$, Eq. (23) can be satisfied up to terms of order $O(1/N)$ by

$$(\vec{l}_{\vec{k}\lambda})_{\vec{k}'\lambda'}=L_{\vec{k}\lambda;\vec{k}'\lambda'}\equiv\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}-\frac{[K_1^{*}(\vec{k},\lambda)-K_2^{*}(\vec{k},\lambda)][K_1(\vec{k}',\lambda')-K_2(\vec{k}',\lambda')]}{K^2}$$

$$\text{for } (\vec{k},\lambda),(\vec{k}',\lambda')\neq(0,1)\ . \tag{24}$$

To normalize our vectors $\vec{l}_{\vec{k}\lambda}$ [viz. Eq. (16)], we define

$$(\vec{l}_{\vec{k}\lambda})_{01}=L_{\vec{k}\lambda;01}=\frac{K_1^{*}(\vec{k},\lambda)-K_2^{*}(\vec{k},\lambda)}{K}\ . \tag{25}$$

By Eqs. (5), (24), and (25) the transformation coefficients $L_{\vec{k}\lambda;\vec{k}'\lambda'}$ are completely determined. Although we have confined ourselves to an approximative solution of Eq. (23), one can easily prove that the resulting transformation matrix $\underline{L}$ is exactly unitary and Hermitian ($\underline{L}^{-1}=\underline{L}^{\dagger}=\underline{L}$) and satisfies the conditions (7).

We can now express our total Hamiltonian H in terms of $\{\tilde{P}_{\vec{k}\lambda},\tilde{Q}_{\vec{k}\lambda}\}$. Inserting (6) in Eq. (3) and using definitions (5), (24), and (25), one obtains after some calculation:

$$H=H_1+H_2+H_3+H_4+H_5\ , \tag{26}$$

where

$$H_1=\tfrac{1}{2}(\tilde{P}_{01}^2+\tilde{\omega}_0^2\tilde{Q}_{01}^2)+\Delta\sigma_x+K\tilde{Q}_{01}\sigma_z,\quad H_2=\sum_{\vec{k}\neq 0,\lambda}\tilde{Q}_{\vec{k}\lambda}\tfrac{1}{2}[K_1(\vec{k},\lambda)+K_2(\vec{k},\lambda)]\ ,$$

$$H_3=\tfrac{1}{2}\sum_{\vec{k}\neq 0,\lambda}[\tilde{P}_{\vec{k}\lambda}\tilde{P}_{-\vec{k}\lambda}+\tilde{\omega}^2(\vec{k},\lambda)\tilde{Q}_{\vec{k}\lambda}\tilde{Q}_{-\vec{k}\lambda}],\quad H_4=\tilde{Q}_{01}\sum_{\vec{k}\neq 0,\lambda}\tilde{Q}_{\vec{k}\lambda}\frac{K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)}{K}[\omega^2(\vec{k},\lambda)-\tilde{\omega}_0^2]\ ,$$

$$H_5=\sum_{\substack{\vec{k}'\neq 0,\lambda'\\(\vec{k}',\lambda')\neq(-\vec{k}'',\lambda'')}}\sum_{\vec{k}''\neq 0,\lambda''}m(\vec{k}',\lambda',\vec{k}'',\lambda'')\tilde{Q}_{\vec{k}'\lambda'}\tilde{Q}_{\vec{k}''\lambda''}\ .$$

Here we have used the following abbreviations:

$$\tilde{\omega}^2(\vec{k},\lambda)=\omega^2(\vec{k}',\lambda)+\frac{|K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)|^2}{K^2}[\tilde{\omega}_0^2-2\omega^2(\vec{k},\lambda)]=\omega^2(\vec{k},\lambda)+O\left[\frac{1}{N}\right]\ , \tag{27}$$

$$m(\vec{k}',\lambda',\vec{k}'',\lambda'')=\frac{1}{2}\frac{[K_1(\vec{k}',\lambda')-K_2(\vec{k}',\lambda')][K_1(\vec{k}'',\lambda'')-K_2(\vec{k}'',\lambda'')]}{K^2}[\tilde{\omega}_0^2-\omega^2(\vec{k}',\lambda')-\omega^2(\vec{k}'',\lambda'')]\ . \tag{28}$$

It should be emphasized that Eq. (26) is still exact. The first term H_1 in (26) describes a two-state tunneling system coupled to a single representative phonon mode. H_3 is the Hamiltonian of the remaining phonons; their coupling to the representative mode is given by H_4. The nondiagonal expression H_5 describes the different mode coupling within the system of the remaining phonons. In the following considerations, we will neglect H_5. The mathematical reason is that we have chosen the new phonon coordinates in an optimal way; the physical argument is that we are not primarily interested in damping effects within the "phonon bath."

H_2 can be eliminated by a linear shift of the phonon coordinates $\{\tilde{P}_{\vec{k}\lambda},\tilde{Q}_{\vec{k}\lambda}\}_{\vec{k}\neq 0,\lambda}$:

$$\hat{Q}_{\vec{k}\lambda}=\tilde{Q}_{\vec{k}\lambda}+\frac{1}{2}\frac{K_1(-\vec{k},\lambda)+K_2(-\vec{k},\lambda)}{\tilde{\omega}^2(\vec{k},\lambda)},\qquad \hat{P}_{\vec{k}\lambda}=\tilde{P}_{\vec{k}\lambda}\ (\vec{k}\neq 0)\ . \tag{29}$$

We now introduce creation and annihilation operators $\{b^{\dagger}_{\vec{k}\lambda},b_{\vec{k}\lambda}\}_{\vec{k}\neq 0,\lambda}$:

$$b_{\vec{k}\lambda}=\left[\frac{\tilde{\omega}(\vec{k},\lambda)}{2\hbar}\right]^{1/2}\hat{Q}_{\vec{k}\lambda}+i\left[\frac{1}{2\hbar\tilde{\omega}(\vec{k},\lambda)}\right]^{1/2}\hat{P}_{\vec{k}\lambda}\ ,$$

$$b^{\dagger}_{\vec{k}\lambda}=\left[\frac{\tilde{\omega}(\vec{k},\lambda)}{2\hbar}\right]^{1/2}\hat{Q}_{-\vec{k}\lambda}-i\left[\frac{1}{2\hbar\tilde{\omega}(\vec{k},\lambda)}\right]^{1/2}\hat{P}_{-\vec{k}\lambda}\ . \tag{30}$$

Simply writing Q and P instead of $\tilde{Q}_{01}$, and $\tilde{P}_{01}$, we finally obtain our Hamiltonian in the form

$$H=H_1+\sum_{\vec{k}\neq 0,\lambda}\hbar\tilde{\omega}(\vec{k},\lambda)(b^{\dagger}_{\vec{k}\lambda}b_{\vec{k}\lambda}+\tfrac{1}{2})+KQ\sum_{\vec{k}\neq 0,\lambda}F(\vec{k},\lambda)(b_{\vec{k}\lambda}+b^{\dagger}_{-\vec{k}\lambda})\ , \tag{31}$$

where

$$F(\vec{k},\lambda)=\frac{K_1(\vec{k},\lambda)-K_2(\vec{k},\lambda)}{K^2}\left[\frac{\hbar}{2\tilde{\omega}(\vec{k},\lambda)}\right]^{1/2}\times[\omega^2(\vec{k},\lambda)-\tilde{\omega}_0^2] \text{ for } \vec{k}\neq 0 , \tag{32}$$

and

$$H_1=\tfrac{1}{2}(P^2+\tilde{\omega}_0^2Q^2)+\Delta\sigma_x+KQ\sigma_z .$$

IV. UNITARY EXPONENTIAL TRANSFORMATION

H_1 is the Hamiltonian of a problem, which has been discussed by one of us[10] for different hierarchies of the parameters K, $\tilde{\omega}_0$, and Δ. In the case of strong phonon-tunneling interactions and of low phonon frequency $\tilde{\omega}_0$, H_1 can be approximately diagonalized with respect to the tunneling system by the exponential transformation $U=e^{i\gamma(Q)\sigma_y}$,

$$\sin[\gamma(Q)]=\frac{\Delta}{[\Delta^2+(KQ)^2]^{1/2}} ,\qquad \cos[\gamma(Q)]=\frac{-KQ}{[\Delta^2+(KQ)^2]^{1/2}} . \tag{33}$$

The transformed operator H_1 then reads

$$U^{\dagger}H_1U=-\sigma_z[\Delta^2+(KQ)^2]^{1/2}+\tfrac{1}{2}[P^2+\tilde{\omega}_0^2Q^2]+\frac{\hbar^2}{8}\frac{(\Delta K)^2}{[\Delta^2+(KQ)^2]^2}+\hbar\Delta K\sigma_y\left[i\hbar\frac{K^2Q}{[\Delta^2+(KQ)^2]^2}+\frac{1}{\Delta^2+(KQ)^2}P\right] . \tag{34}$$

The last term in Eq. (34) is nondiagonal with respect to the tunneling system. We will further make the hierarchical assumption

$$K\left[\frac{\hbar}{\tilde{\omega}_0}\right]^{1/2}\gg\Delta\gg\hbar\tilde{\omega}_0 . \tag{35}$$

Then the nondiagonal term is small of order $O(\Delta/K(\hbar/\tilde{\omega}_0)^{1/2})$ and can be neglected. The remaining part of $U^{\dagger}H_1U$ in Eq. (34) is attached to two pure oscillatory problems (belonging to $\sigma_z=\pm\frac{1}{2}$), which both are extremely anharmonic. The respective potential sheets are shown in Fig. 1.

We will consider the low-temperature case, for

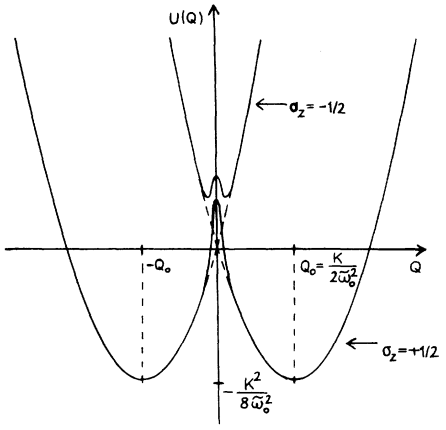

FIG. 1. Potential sheets for the "effective lattice mode" in the transformed space.

which only the sheet belonging to $\sigma_z=\frac{1}{2}$ is relevant. Wagner has shown[10] that the eigenstates of the problem are in a good approximation those of a double oscillator. Thus the lowest two eigenfunctions are

$$\varphi_e(Q)=\frac{1}{(2)^{1/2}}\frac{1}{(1+C)^{1/2}}\times[\chi_0(Q-Q_0)+\chi_0(Q+Q_0)] \tag{36}$$

(even),

$$\varphi_0(Q)=\frac{1}{(2)^{1/2}}\frac{1}{(1-C)^{1/2}}\times[\chi_0(Q-Q_0)-\chi_0(Q+Q_0)]$$

(odd), where

$$C=\exp[-\tfrac{1}{4}(K^2/\hbar\tilde{\omega}_0^3)] , \tag{37a}$$

$$Q_0=K/2\tilde{\omega}_0^2 , \tag{37b}$$

and where $\chi_0(Q)$ is the oscillatory ground-state wave function.

The energy splitting $\delta=E^{(0)}-E^{(e)}$ in first order is given as

$$\delta=\frac{1}{(\pi)^{1/2}}K\left[\frac{\hbar}{\tilde{\omega}_0}\right]^{1/2}C=\frac{\hbar\tilde{\omega}_0}{(\pi)^{1/2}}\frac{K\left[\frac{\hbar}{\omega_0}\right]^{1/2}}{\hbar\tilde{\omega}_0}\exp\left[-\frac{1}{4}\frac{K^2}{\hbar\tilde{\omega}_0^3}\right]\ll\hbar\omega_0 . \tag{38}$$

We introduce the abbreviations $|1\rangle=\varphi_e(Q)|a_1^\dagger\rangle$, $|2\rangle=\varphi_0(Q)|a_1^\dagger\rangle$. $\{|1\rangle,|2\rangle\}$ denote the lowest eigenstates of $U^\dagger H_1 U$; they can be taken as an orthonormal base in the transformed space (at least for low temperatures). The projection of $U^\dagger H_1 U$ on this base yields

$$U^\dagger H_1 U \simeq \sum_{i,j=1,2} |i\rangle\langle i|U^\dagger H_1 U|j\rangle\langle j| = -\tfrac{1}{2}\delta(|1\rangle\langle 1|-|2\rangle\langle 2|). \quad (39)$$

In a similar way, $U^\dagger Q U$ and $U^\dagger \sigma_z U$ can be projected onto $\{|1\rangle,|2\rangle\}$:

$$U^\dagger Q U=\sum_{i,j=1,2}|i\rangle\langle i|U^\dagger Q U|j\rangle\langle j| =\frac{K}{2\tilde{\omega}_0^2}(|1\rangle\langle 2|+|2\rangle\langle 1|), \quad (40)$$

$$U^\dagger \sigma_z U=\sum_{i,j=1,2}|i\rangle\langle i|U^\dagger \sigma_z U|j\rangle\langle j| =-\tfrac{1}{2}(|1\rangle\langle 2|+|2\rangle\langle 1|). \quad (41)$$

The two-state description $\{|1\rangle,|2\rangle\}$ is isomorphic to a spin-$\frac{1}{2}$ formulation, introducing the operators

$$S_x=\tfrac{1}{2}(|1\rangle\langle 2|+|2\rangle\langle 1|),$$
$$S_y=\frac{1}{2i}(|1\rangle\langle 2|-|2\rangle\langle 1|), \quad (42)$$
$$S_z=\tfrac{1}{2}(|1\rangle\langle 1|-|2\rangle\langle 2|).$$

S_x,S_y,S_z satisfy the well-known relations ($[S_x,S_y]$ cyclic):

$$[S_x,S_y]_-=iS_z, \qquad S_x^2=S_y^2=S_z^2=\tfrac{1}{4}. \quad (43)$$

Then the transformed operators $U^\dagger H_1 U, U^\dagger Q U, U^\dagger \sigma_z U$ read

$$U^\dagger H_1 U=-\delta S_z,\quad U^\dagger Q U=\frac{K}{\tilde{\omega}_0^2}S_x,\quad U^\dagger \sigma_z U=-S_x. \quad (44)$$

Let us now return to the end of Sec. III, where the total Hamiltonian H of our coupled tunneling-phonon problem is given in Eq. (31). If we apply the exponential unitary transformation U [viz., Eqs. (33)] to H (having in mind that the operators $\{b_{\vec{k}\lambda},b_{\vec{k}\lambda}^\dagger\}_{\vec{k}\neq 0,\lambda}$ remain unchanged) we obtain

$$H'\equiv U^\dagger H U=-\delta S_z+\sum_{\vec{k}\neq 0,\lambda}\hbar\tilde{\omega}(\vec{k},\lambda)(b_{\vec{k}\lambda}^\dagger b_{\vec{k}\lambda}+\tfrac{1}{2}) +\frac{K^2}{\tilde{\omega}_0^2}S_x\sum_{\vec{k}\neq 0,\lambda}F(\vec{k},\lambda)(b_{\vec{k}\lambda}+b_{-k\lambda}^\dagger). \quad (45)$$

V. RELAXATION BEHAVIOR

The relaxation behavior of the system can be investigated by the following device. A very small static external field is applied adiabatically to the crystal, causing a nonvanishing "dipole" moment $\langle\sigma_z\rangle$ for $t=0$. If now the field is switched off, the time evolution of $\langle\sigma_z\rangle(t)$ reveals how the system reaches its equilibrium state $\langle\sigma_z\rangle_T=0$. From the Kubo formalism we get

$$\langle\sigma_z\rangle(t)=\frac{i}{\hbar}(\vec{p}\cdot\vec{E})\int_{-\infty}^{t}\Theta(-t')\times e^{\epsilon t'}\langle[\sigma_z(t),\sigma_z(t')]_-\rangle_T dt', \quad (46)$$

Θ being the step function and $\vec{p}\cdot\vec{E}$ being the energy of the OH^- dipole $\vec{p}$ in the electric field $\vec{E}$.

We now define the advanced and retarded Zubarev[11] Green functions for any operators A and B as

$$\langle\langle A(t);B(t')\rangle\rangle_{a/r}=\pm i\Theta[\mp(t-t')]\times\langle[A(t),B(t')]_-\rangle_T. \quad (47)$$

Their Fourier transform is denoted by $\langle\langle A;B\rangle\rangle(E)$. Then Eq. (46) can be written in the form

$$\langle\sigma_z\rangle(t)=-\vec{p}\cdot\vec{E}\int_{-\infty}^{+\infty}\frac{\langle\langle\sigma_z;\sigma_z\rangle\rangle(\omega+i\epsilon)-\langle\langle\sigma_z;\sigma_z\rangle\rangle(\omega-i\epsilon)}{i\omega+\epsilon}e^{-i\omega t}d\omega, \quad (48)$$

whence the main problem left is the calculation of the Fourier-transformed Green function $\langle\langle\sigma_z;\sigma_z\rangle\rangle(E)$. By means of the identities

$$\langle\langle\sigma_z;\sigma_z\rangle\rangle^H(E)=\langle\langle U^\dagger\sigma_z U;U^\dagger\sigma_z U\rangle\rangle^{H'}(E) =\langle\langle S_x;S_x\rangle\rangle^{H'}(E), \quad (49)$$

we may transfer the calculation to the transformed Hamiltonian $H'=U^\dagger H U$ of Eq. (45) and the relevant Green function is then $\langle\langle S_x;S_x\rangle\rangle^{H'}(E)$. From its equations of motion (with respect to H') we get

$$\langle\langle S_x;S_x\rangle\rangle^{H'}(E)=\frac{1}{2\pi}\frac{1}{2}\tanh\left[\frac{\delta}{2k_BT}\right]\times\frac{\delta/\hbar}{E^2-\delta^2/\hbar^2-A(E)}\,, \quad (50)$$

where

$$A(E)=2\left[\frac{K^2}{\hbar\tilde{\omega}_0^2}\right]^2 E^2\sum_{\vec{k}\neq 0,\lambda}|F(\vec{k},\lambda)|^2(\bar{n}_{\vec{k}\lambda}+\tfrac{1}{2})\times\frac{1}{E^2-\omega^2(\vec{k},\lambda)}\,, \quad (51)$$

$$\bar{n}_{\vec{k}\lambda}=\{\exp[\hbar\tilde{\omega}(\vec{k},\lambda)/k_BT]-1\}^{-1}\,. \quad (52)$$

Replacing the sum by an integral with phonon state density $\rho(\omega)$ we get

$$A(E)=2\left[\frac{K^2}{\hbar\tilde{\omega}_0^2}\right]^2 E^2\int_{-\infty}^{+\infty}\rho(\omega)|F|^2(\omega)\times\frac{\bar{n}(\omega)+\frac{1}{2}}{E^2-\omega^2}d\omega\,, \quad (53)$$

where an isotropic Debye approximation has been used. Inserting Eqs. (50) and (53) in expression (48) we get the tunneling behavior of the system:

$$\langle\sigma_z\rangle(t)=\frac{\vec{p}\cdot\vec{E}}{\delta}\tanh\left[\frac{\delta}{2k_BT}\right]\frac{1}{2}\cos\left[\frac{\delta}{\hbar}t\right]e^{-G(T)t} \quad (t\geq 0)\,, \quad (54)$$

$$G(T)=\frac{\pi}{4}\left[\frac{K^2}{\hbar\tilde{\omega}_0^2}\right]^2(\rho|F|^2)\left[\frac{\delta}{\hbar}\right]\coth\left[\frac{\delta}{2k_BT}\right]. \quad (55)$$

The periodic tunneling term $\cos[(\delta/\hbar)t]$ is damped by an exponential factor $\exp(-Gt)$. The tunneling frequency $\delta/\hbar$ does not depend on temperature. (This is probably due to the fact that we have handled H_1 as two-state system in Sec. IV.) Much more interesting is the damping $G(T)$, which must be understood as the inverse of the relaxation time. $G(T)$ increases rapidly with temperature as can be seen in Fig. 2.

For $k_BT>\delta/2$ we have a linear increase of G with T. So the T^1 dependence of the damping as measured[3,4] by Kapphan and Lüty and verified in the conventional theory also results from our alternative approach. It should be remarked that our results are no longer valid for high temperatures, since in Sec. IV we have taken into account only the two lowest eigenstates of the transformed Hamiltonian $U^\dagger H_1 U$.

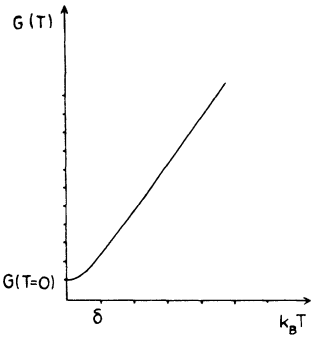

FIG. 2. Temperature dependence of the damping $G(T)$.

The most striking fact is that the relaxation behavior of the system now does not depend on the tunneling parameter Δ at all; the tunneling has been transferred from the original tunneling particle to an effective lattice mode. Naturally this is due to the fact that Δ has been taken to be much larger than $\hbar\tilde{\omega}_0$. Physically our relaxation mechanism is such that the low-frequency lattice motion displays the tunneling behavior, whereas the original tunneling particle itself, having a strong coupling to the phonons, is carried along adiabatically with the lattice motion.

VI. SIX-STATE TUNNELING DESCRIPTION

Considering a fixed 90° transition of the proton, we have so far treated the defect system as a two-state system. A two-state description has been given also in previous theoretical work.[5–7] It is possible, however, to generalize the theoretical description of our alternative relaxation mechanism to a six-state tunneling system, if 180° transitions are neglected. Of course, the calculations are much more complicated and we will not discuss these difficulties here in detail.

Instead of a single representative phonon coordinate Q (see Sec. III) we now have three degenerate representative modes Q_1,Q_2,Q_3. Let us recall our procedure in Sec. IV, where by means of the exponential transformation U we have transferred a phonon-assisted tunneling problem to anharmonic

pure phonon problems. In the six-state tunneling case, a generalization of U yields six anharmonic phonon problems, from which in the low-temperature case only the sheet with the lowest energy is relevant. The corresponding adiabatic potential is that of a double oscillator in the Q_1,Q_2,Q_3 space and has, aside from its two principal minima, four other minima of higher energy. The energy splitting δ_1 of the two lowest eigenstates is then

$$\delta_1=\frac{\hbar\tilde{\omega}_1}{\pi}\left[\frac{64\hbar\tilde{\omega}_1^3}{\bar{K}^2}\right]^2\exp\left[-\frac{13}{16}\frac{\bar{K}^2}{\hbar\tilde{\omega}_1^3}\right], \tag{56}$$

where

$$\bar{K}^2=\sum_{\vec{k},\lambda}[\mathrm{Re}K_1(\vec{k},\lambda)]^2, \tag{57}$$

$$\tilde{\omega}_1^2=\frac{1}{\bar{K}^2}\sum_{\vec{k},\lambda}[\mathrm{Re}K_1(\vec{k},\lambda)]^2\omega^2(\vec{k},\lambda). \tag{58}$$

As to the relaxation behavior in the six-state-defect case, we have an exponentially damped oscillation with tunneling frequency $\delta_1/\hbar$ and damping $G_1(T)$:

$$G_1(T)=\frac{\pi}{4}\left[\frac{2\bar{K}^2}{\hbar\tilde{\omega}_1^2}\right]^2(\rho F_1^2)\left[\frac{\delta_1}{\hbar}\right]\times\coth\left[\frac{\delta_1}{2k_BT}\right], \tag{59}$$

where

$$F_1^2(\vec{k},\lambda)\approx\frac{[\mathrm{Re}K_1(\vec{k},\lambda)]^2}{\bar{K}^4}[\omega^2(\vec{k},\lambda)-\tilde{\omega}_1^2]^2\times\frac{\hbar}{2\omega(\vec{k},\lambda)}. \tag{60}$$

The comparison between the results of Secs. V and VI displays no significant qualitative differences. So, in principle, the temperature dependence of the damping factor drawn in Fig. 2 is also valid for the six-state description. There are obviously quantitative differences. We especially stress the fact that in Eqs. (57), (58), and (60) only the real parts of the original coupling constants $K_i(\vec{k},\lambda)$ appear.

VII. SUMMARY

In this paper we have discussed an alternative mechanism for the relaxation of tunneling centers in crystals. This mechanism is based on the assumptions of a strong defect-lattice interaction and the dominance of low-frequency phonons. We have calculated the relaxation behavior of the system and we have demonstrated that the damping increases with the temperature. Within a certain temperature region the increase is proportional to T. We emphasize that the conventional approach (we especially refer to the paper of Dick[7]) also yields this T^1 law, which has been experimentally measured[3,4] by Kapphan and Lüty. Thus it is not possible to decide from the experimental results which of the relaxation paths is the dominating one. Probably both mechanisms compete with each other.

The main difference between our alternative approach and the conventional theory consists in the fact that the results depend on other parameters. In particular, the tunneling splitting Δ, the measurement of which is very difficult and controversial,[4] has no influence on the relaxation behavior in the case of our mechanism. The question, how large the reducing Debye-Waller factor for Δ should be, has led to many discussions during the past. As far as the alternative mechanism is concerned, this question does not arise for Δ itself, since the tunneling is conveyed to an effective phonon coordinate. In a future, more realistic calculation both mechanisms must be allowed to interplay with each other. Depending on the weight of our alternative mechanism in this interplay, the Debye-Waller reduction of Δ will be altered.

In our paper we have handled the lattice as an ideal KCl crystal. Such a treatment is also given in the previous theoretical work. However, the perturbation of the crystal around the defect modifies the lattice dynamics considerably. Probably in our alternative approach the effects of the disturbed lattice dynamics are more pronounced than in the conventional theory, since the tunneling is completely transferred to the phonon system. We leave this question to a future investigation.

From the fact that Δ does not enter the results in the case of the alternative mechanism, one cannot conclude that we consequently have no isotope effect. The change of Δ, if, e.g., the tunneling proton is replaced by D^+, is only one kind of isotope effect. In a recent paper,[9] Kuhn and Wagner have shown that there is a second kind of isotope effect due to the nonadiabatic treatment of the tunneling particle. Such a treatment is also possible for the alternative mechanism by a suitable choice of the coupling constants $K_i(\vec{k},\lambda)$. Finally the defect-induced perturbation of the lattice modes also leads to an isotope effect, which can be calculated only on

the basis of a disturbed-lattice theory.

We hope the new relaxation path that we have presented here contributes to a better description of tunneling centers in crystals. A realistic future theory should include a nonadiabatic treatment of the tunneling particle and the disturbed-lattice dynamics as well as the competition between the conventional and the alternative tunneling mechanisms. Moreover, we think that our mechanism is not confined to defects in crystals only, but may also be of importance in other physical areas, such as superionic conductors and amorphous materials.

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