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Effects of in-band defect-induced phonon resonant modes on phonon-assisted defect tunneling*

B. G. Dick†
Max-Planck-Institut für Festkörperforschung, 7000-Stuttgart-80, Büsnauerstrasse 171, West Germany
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Transition rates for off-center or molecular-defect reorientations show polaron-like effects with one- or few-phonon assisted tunneling at low temperatures becoming Arrhenius-like processes at higher temperatures. Perturbation of the phonons by heavy and/or loosely coupled defects can produce in-band resonant modes. A simple model is used to show that such resonant modes can have significant effects on transition rates and, in particular, can extend the range of Arrhenius behavior to temperatures substantially lower than those predicted by models which use Debye phonons unaltered by the presence of the defect.

I. INTRODUCTION

Phonon-assisted tunneling of atoms and molecules in solids is a process which plays an important role in the dynamics of paraelectric and paraelastic defects[1] and in ultrasonic attenuation in glasses.[2] It has been suggested as the fundamental mechanism for hydrogen diffusion in transition metals.[3,4] In addition the theory of this process occurs in other, and apparently different, contexts: for example, in small-polaron theory[5,6] (where the basic theory originated in the work of Holstein[5] and Yamashita and Kurosawa[7]) and in the theory of optical-absorption-spectra line shapes.[8] A particularly interesting feature of these theories is the occurrence at sufficiently high temperatures, of Arrhenius-like rate processes in which the activation energy has a well-defined quantum-mechanical significance.

In a recent investigation of the phonon-assisted tunneling of off-center and molecular impurities in alkali-halide crystals, Shore and Sander[1] have pointed out that the perturbation of lattice phonons by the defect might have significant effects which are omitted from customary treatments of this problem. It is the purpose of this paper to develop a simplified theory of these effects for the case of in-band defect-induced phonon resonant modes. We conclude that such effects can reasonably be expected to produce significant alterations in defect-reorientation rates especially at low temperatures.

In order to fix the terminology, we will study the application of the theory to the calculation of transition rates of off-center or molecular defects in the presence of a degeneracy-lifting applied electric or stress field. In Sec. II, a model Hamiltonian is presented, and in Sec. III, a derivation of the required transition rate is outlined. High- and low-temperature limiting forms of this transition rate as well as numerical calculations for intermediate temperatures are discussed in Sec. IV. Section V contains a discussion of a generalization of the model which contains features expected to arise from the presence of an in-band resonant mode.

II. MODEL HAMILTONIAN

The model we use has been discussed by a number of workers.[9-13] We present only enough detail to establish notation and terminology.

A representation is used in which the defect is described by directed or pocket states $|i\rangle$. For a $\langle 100\rangle$ system, for example, there are six such states for which $i = x, \bar{x}, y, \bar{y}, z, \bar{z}$ corresponding to the six off-center positions or dipolar orientations. The lattice is described by phonon creation and annihilation operators, $a_\sigma^\dagger$ and a_σ, where σ is an abbreviation for wave-number vector and branch index.

The model Hamiltonian is

$$H = H_D + H_L + H_{DL(1)} + H_{DL(2)} + H_E + H_S . \tag{1}$$

H_D describes the kinetic and potential energy of the defect in a rigid lattice through tunneling matrix elements, Δ_{ij},

$$H_D = \sum_{i,j} \Delta_{ij} |i\rangle\langle j| . \tag{2}$$

Higher excited libration or vibration states are omitted. Without loss of generality the energy zero can be chosen so that $\Delta_{ii} = 0$. By symmetry, $\Delta_{ij} = \Delta_{ji}$. The form of the Δ matrix has been tabulated for $\langle 100\rangle$, $\langle 111\rangle$, and $\langle 110\rangle$ defects by Gomez *et al.*[14] Eigenstates of H_D, called tunneling states, are linear combinations of the directed states $|i\rangle$ and have been tabulated by Gomez *et al.*[14] and Bridges.[15]

H_L is the perfect-lattice Hamiltonian

$$H_L = \sum_\sigma \hbar\omega_\sigma a_\sigma^\dagger a_\sigma . \tag{3}$$

$H_{DL(1)}$ is that defect-lattice interaction which is linear in lattice displacements

$$H_{DL(1)} = \sum_{i,\sigma} D_i(\sigma)(a_\sigma - a_\sigma^\dagger)|i\rangle\langle i| . \tag{4}$$

Phonon eigenvector conventions used here are described in Ref. 12. A frequently used additional assumption treats only the coupling of the defect to lattice strains in which case $D_i(\sigma)$ is proportional to $(\omega_\sigma)^{1/2}$. Although this assumption is known to be a crude one[1,12] it does lead to a relatively simple expression for transition rates and will be used in this paper where our aims are primarily qualitative. This additional assumption is valid only for long-wavelength acoustical phonons and will be referred to as the long-wave limit (LWL) of $H_{DL(1)}$. In this LWL the $D_i(\sigma)$ coefficients are for ⟨100⟩ defects

$$D_{100}(\sigma) = D_{-100} = \tfrac{1}{6} i\alpha_1(\hbar/2M_c\omega_\sigma)^{1/2} \times [2e_x(\sigma)q_x - e_y(\sigma)q_y - e_z(\sigma)q_z], \tag{5}$$

for ⟨110⟩ defects

$$D_{1\pm1\,0}(\sigma) = D_{-1\mp1\,0}(\sigma) = i(\hbar/2M_c\omega_\sigma)^{1/2} \times \{\tfrac{1}{3}\alpha_1[e_x(\sigma)q_x + e_y(\sigma)q_y - 2e_z(\sigma)q_z] \pm \tfrac{3}{2}\alpha_2 e_x(\sigma)q_y\}, \tag{6}$$

and for ⟨111⟩ defects by

$$D_{1\pm1\pm1}(\sigma) = D_{-1\mp1\mp1}(\sigma) = i(\tfrac{3}{4}\alpha_2(\hbar/2M_c\omega_\sigma)^{1/2} \times \{[e_x(\sigma)q_y + e_y(\sigma)q_x] \pm [e_x(\sigma)q_z + e_z(\sigma)q_x] \pm [e_y(\sigma)q_z + e_z(\sigma)q_y]\}. \tag{7}$$

Other $D_i(\sigma)$ coefficients can be found by cyclic permutations. M_c is the mass of the crystal, $e_i(\sigma)$ the ith component of the σ phonon eigenvector, and the strain coupling coefficients α are given in the notation of Bridges.[15] The omission of off-diagonal $|i\rangle\langle j|$ terms in $H_{DL(1)}$ is often called the Condon approximation and asserts, in effect, that the Δ_{ij} are phonon independent.[16] There is some experimental evidence supporting this approximation in some cases.[17]

$H_{DL(2)}$ is a defect-lattice coupling due to defect-introduced mass and force-constant changes. It is thus quadratic in lattice displacements and momenta and is chosen diagonal in the directed representation as $H_{DL(1)}$ was. $H_{DL(1)}$ produces a static relaxation for a given defect orientation (new equilibrium positions of lattice atoms) but no phonon frequency or eigenvector changes. $H_{DL(2)}$ perturbs the phonons. Until Sec. V, $H_{DL(2)}$ will be assumed to be zero.

H_E and H_S are external strain and electric field interactions with the defect which has the form

$$H_E = -\sum_i \vec{p}_i \cdot \vec{\vec{E}}\, |i\rangle\langle i|, \tag{8}$$

$$H_S = \sum_i S_i |i\rangle\langle i|, \tag{9}$$

where p_i and S_i are tabulated by Bridges.[15] These bias terms will, in general, split the degeneracies of the tunneling eigenstates of H_D.

III. TRANSITION RATES

A quantity useful in the explanation of defect-lattice behavior is the transition rate w_{ij} for the defect reorientation process $i \to j$ occurring at a given temperature and energy difference $E_i - E_j$. One way to calculate this rate is to take $H_L + H_E + H_S$ as the unperturbed Hamiltonian and $H_D + H_{DL(1)} + H_{DL(2)}$ as the transition-producing perturbation. This was done in early work with[12] and without[10,11,18] including $H_{DL(2)}$. $H_{DL(1)}$, however, turns out not to be small and this perturbation approach is invalid. Perturbation theory can be in great measure avoided by eliminating $H_{DL(1)}$ from H by a unitary transformation the effect of which is to introduce static lattice relaxations about each of the directed states.[13,19] The required unitary operator is $\exp(A)$, where

$$A = \sum_{i,\sigma} [D_i(\sigma)/\hbar\omega\sigma](a_\sigma + a_\sigma^\dagger)|i\rangle\langle i| \tag{10}$$

and the transformed Hamiltonian (with $H_{DL(2)} = 0$) is

$$\tilde{H} = e^{-A} H e^{A} = \tilde{H}_D + H_L + H_S + H_E + H_r, \tag{11}$$

where

$$\tilde{H}_D = \sum_{i,j} \Delta_{ij} |i\rangle\langle j| \exp\left(\sum_\sigma |F_{ij}(\sigma)|^2 (a_\sigma + a_\sigma^\dagger)\right), \tag{12}$$

and

$$H_r = -E_r \sum_i |i\rangle\langle i|. \tag{13}$$

Here

$$F_{ij}(\sigma) = [D_i(\sigma) - D_j(\sigma)]/\hbar\omega\sigma, \tag{14}$$

and

$$E_r = \sum_\sigma |D_i(\sigma)|^2/\hbar\omega\sigma. \tag{15}$$

E_r is the self-trapping energy associated with lattice relaxation about a defect in a directed state. By symmetry it is independent of i. H_r can be eliminated by redefinition of energy zero.

Suppose that H_S is zero and an external field is applied so that defect orientational degeneracy is completely lifted and

$$H_E |i\rangle = E_i |i\rangle \tag{16}$$

with all E_i different and the $|i\rangle$ directed states. We investigate transitions between eigenstates of $H_E + H_L$ produced by $\tilde{H}_D$. These eigenstates are $|i\rangle \Pi_\sigma |n_\sigma\rangle$, where $\Pi_\sigma |n_\sigma\rangle$ are eigenstates of H_L.

Calculating the transition probability for a transition $i \to j$ to first order in $\tilde{H}_D$ (only a single tunneling but phonon processes to all orders), thermally averaging over initial phonon states, summing over final phonon states and converting to a transition rate one finds[3,13]

$$w_{ij} = \frac{\tilde{\Delta}_{ij}^2}{\hbar^2} \int_{-\infty}^{\infty} ds\, e^{i\omega_{ij}s} \exp\left(\sum_{\sigma} g_{\sigma}(s) |F_{ij}(\sigma)|^2 \right) , \quad (17)$$

where

$$\omega_{ij} = (E_i - E_j)/\hbar , \quad (18)$$

$$g_{\sigma}(s) = (n_{\sigma}+1)e^{-i\omega_{\sigma}s} + n_{\sigma} e^{i\omega_{\sigma}s} , \quad (19)$$

$$n_{\sigma} = [\exp(\hbar\omega_{\sigma}/kT) - 1]^{-1} , \quad (20)$$

and $\tilde{\Delta}_{ij}$ is the dressed tunneling matrix element,

$$\tilde{\Delta}_{ij} = \Delta_{ij} \exp(-R_{ij}) , \quad (21)$$

with dressing exponent

$$R_{ij} = \sum_{\sigma} |F_{ij}(\sigma)|^2 (n_{\sigma} + \tfrac{1}{2}) . \quad (22)$$

The temperature-dependent reduction of the bare Δ_{ij} to the dressed $\tilde{\Delta}_{ij}$ is the analog in the present context of the increase of carrier effective mass in polar crystals due to the polaron effect.

We now consider a special case of Eq. (17), that of a 90° reorientation transition for a ⟨100⟩ defect with two approximations: (i) The LWL form, Eq. (5), for $D_i(\sigma)$ and (ii) the phonons treated in the acoustical Debye approximation. This will be called the LWL-Debye approximation. Equation (17) then becomes

$$w = (\Delta/\hbar)^2 e^{-2R} \int_{-\infty}^{\infty} ds\, e^{i\bar{w}s} [e^{f(s)} - 1] , \quad (23)$$

where Δ is the bare 90° tunneling-matrix element, $\bar{w}$ is the bias splitting,

$$f(s) = A \int_0^{\Omega} d\omega\, \omega [(n_{\omega}+1)e^{-i\omega s} + n_{\omega} e^{i\omega s}] , \quad (24)$$

$$R = A \int_0^{\Omega} d\omega\, \omega (n_{\omega} + \tfrac{1}{2}) , \quad (25)$$

and Ω is the Debye frequency. The -1 occurring in Eq. (23) has been inserted, following Holstein,[5] to eliminate so-called diagonal transitions and suppress a nonphysical divergence of the integral in Eq. (23) for $\bar{\omega} = 0$. For simplicity we will henceforth suppose $\bar{\omega} > 0$, i.e., transitions in which the defect must give energy to the lattice. The zero T value of the dressing exponent is

$$R_0 = \frac{A\Omega^2}{4} = \frac{3\alpha_1^2\Omega^2}{32\pi^2 p\hbar} \frac{1}{5} \left(\frac{2}{c_l^5} + \frac{3}{c_t^5} \right) , \quad (26)$$

where ρ is the crystal density and c_l, c_t are longitudinal and transverse sound velocities used in the Debye model of the host crystal.

Expression (23) contains four parameters Δ, A, Ω, and $\bar{\omega}$ characterizing H_D, $H_{DL(1)}$, H_L, and H_E, respectively. The crudeness of the LWL-Debye approximation becomes evident if R_0 is evaluated using observed values of the quantities appearing in Eq. (26). One typically finds such R_0 to be unphysically large. For instance, for KCl:OH^- such an estimate of R_0 gives a value of 84. The observed[15] $\tilde{\Delta}/2\pi\hbar c$ is 18 cm^{-1}. Equation (21) would then imply an absurdly large value for the bare tunneling matrix element. This inconsistency of the theory arises, at least in part, from the use of the LWL-Debye approximation. The calculation of R_0 from observed quantities is also quite sensitive to how local electric and stress problems are treated.[1]

IV. LOW- AND HIGH-TEMPERATURE TRANSITION RATES

The dependence of w, Eq. (17), on temperature has been studied primarily in two temperature ranges. Gosar and Pirc[20] have shown that for T much less than the Debye temperature Θ the following series represents the w of Eq. (24):

$$w_{GP} \equiv \frac{\Delta^2}{\hbar k} e^{-2R} \frac{6T_b}{\pi T_0^2} \left[1 - \exp\left(\frac{-T_b}{T} \right) \right]^{-1} S , \quad (27)$$

where R is given by Eq. (25), $T_b = \hbar\bar{\omega}/k$,

$$S = 1 + \sum_{n=1}^{\infty} \left(\frac{(2\sqrt{3}/T_0)^{2n}(n!)^2}{(n+1)!\,(2n+1)!} \right) \prod_{m=1}^{n} \left[T^2 + \left(\frac{T_b}{2\pi m} \right)^2 \right] , \quad (28)$$

and

$$T_0 = (\Theta/2\pi)(3/R_0)^{1/2} . \quad (29)$$

This Gosar-Pirc series is convergent for all T and lends itself readily to calculation, but is a good approximation to w only for $T \ll \Theta$. As we will see below, T must in fact be less than T_0.

For $T < T_0$, $S \simeq 1$ and $R \simeq R_0$ in Eq. (27). The resulting form of Eq. (27) is the same as the w one gets by expanding $\exp[f(s)] - 1 \simeq f(s)$ in (23) and neglecting the temperature variation of R. The transition process described in this case is one-phonon-assisted tunneling. Subsequent terms coming from the expansion of $\exp[f(s)]$ or in the Gosar-Pirc series describe two-, three-, and more-phonon-assisted tunneling processes. T_0 is the temperature above which multiphonon-assisted tunneling begins to be important. If we require $T_b < T < T_0$ then

$$w_{GP} \simeq w_1 \equiv (\Delta^2/\hbar k) \exp(-2R_0)(8\pi R_0/\Theta^2)T , \quad (30)$$

showing the characteristic linear in T dependence of one-phonon processes. Within some, perhaps

narrow, temperature range w_1 is nearly the same as w_{GP}. This fact alone does not assure that either w_1 or w_{GP} will, in this temperature range, be a good approximation to w. Furthermore, expanding $\exp[f(s)]$ to get w_1 is not obviously an approximation which is expected to be valid at low T since $f(s)$ does not vanish as T approaches zero.

The other temperature range in which there is a useful approximation for Eq. (23) is $T>\Theta$. In this case the steepest descents argument of Holstein[5] applies. $f(s)$ becomes a rapidly vanishing function of s for increasing $|s|$ and can be replaced in the integral by its Taylor expansion to second order in s. The integral is then a Gaussian and one finds

$$w \simeq w_A \equiv \frac{\Delta^2}{\hbar k}\left(\frac{\pi}{4ET}\right)^{1/2} \exp\left[-\frac{E}{T}\left(1-\frac{T_b}{4E}\right)^2\right] \quad (31)$$

with the activation energy, in temperature units, given by

$$E = \tfrac{1}{3} R_0 \Theta . \quad (32)$$

Typically $T_b \ll E$, so the bias dependence of w_A is weak. Equation (31) is the well-known Arrhenius or hopping limit of phonon-assisted tunneling. Note that the bare tunneling matrix element occurs whereas the dressed form $\tilde{\Delta}$ occurs in w_{GP} and w_1. It is to be emphasized that E given by (32) is determined entirely by R_0 and Θ, i.e., $H_{DL(1)}$ and H_L. It has nothing whatever to do with Δ or the rigid-lattice potential barriers which determine Δ. Interpretations of the activation energy E have been offered by Stoneham[4] and by Norgett and Stoneham.[21] It is difficult to interpret the prefactor in (31) as an "attempt frequency." It is interesting to note that for $T>2E\,[1-(T_b/4E)]^2$, w_A decreases with increasing T although for such temperatures the neglect of higher libration or vibration states becomes increasingly questionable.

One expects w_{GP} and w_A to be good approximations to w so long as $T \ll \Theta$ and $T>\Theta$, respectively. It is not clear from their derivations how high T may be for w_{GP} or how low T may be for w_A to be good approximations. Norgett and Stoneham,[21] using a slightly different form of defect-lattice coupling such that the $D_i(\sigma)$ are proportional to $(\omega_\sigma)^{3/2}$ instead of the $(\omega_\sigma)^{1/2}$ characteristic of the LWL, have shown by numerical calculation that w_A can be a good approximation to w for T as low as about $(\frac{1}{2})\Theta$, but did not investigate lower temperatures.

To investigate these questions further, we have calculated the integral in Eq. (23) numerically for two strengths of defect-lattice coupling and for temperatures from $\frac{1}{20}\Theta$ to $\frac{5}{4}\Theta$. For the purposes of this calculation rather than use Eq. (23) it is more convenient to deform[5] the real axis s contour downward in the complex s plane so as to run parallel to the real axis, but through $-i\hbar/2kT$. This path goes directly over the integrand's saddle point, makes $f(s)$ real, and reduces the oscillatory character of the integrand. This transformed integral is

$$w = (\Delta^2/\hbar k)\exp[-2R + (T_b/2T)] \times \int_0^\infty \cos T_b y\,[e^{g(y)} - 1]\,dy , \quad (33)$$

where

$$g(y) = A\int_0^\theta dx\, x\, \mathrm{csch}(x/2T)\cos xy . \quad (34)$$

$g(y)$ was calculated by Simpson's rule for small y and by Filon's method for larger y. R and the integral over y in (33) were calculated by Romberg integration.

Figure 1 shows a plot of w from Eq. (33) along with w_{GP}, w_1, and w_A. We have chosen $\Theta = 200$ K and $T_b = 5$ K which are characteristic of typical host crystals and bias fields. Two different $H_{DL(1)}$ strengths represented by $R_0 = 3$ and 5 are shown. Numerical integration of Eq. (33) becomes impractical for R_0 much larger than 5, due to near cancellations of large positive and negative contributions.

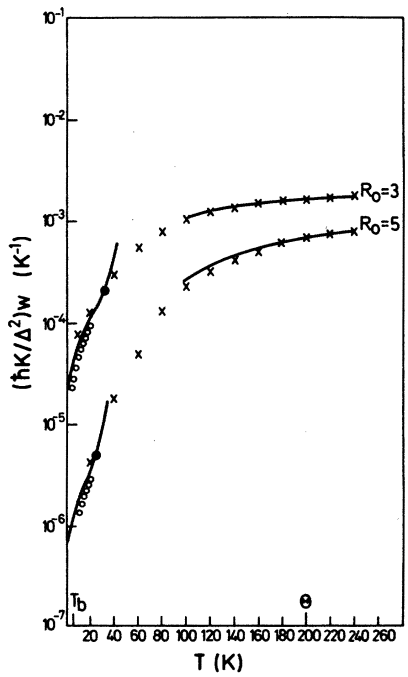

FIG. 1. Various approximations for the transition rate w vs T. Solid curves below $T = 60$ K are w_{GP}, Eq. (27). Solid curves above $T = 100$ K are w_A, Eq. (31). The points indicated by small circles are w_1, Eq. (30). Crosses mark numerically calculated w, Eq. (33). The points • indicate T_0, Eq. (29). The calculations were done for $T_B = 5$ K, $\Theta = 200$ K, and $R_0 = 3, 5$.

to the integral. For the parameters used, an upper limit of $y = 0.06$ in Eq. (33) is more than sufficient so long as $T > 10$ K. Figure 2, upper two curves, shows the same calculated values of w plotted against $1/T$.

We can reach the following conclusions, at least for the case considered.

(i) The Gosar-Pirc series, w_{GP}, is a good approximation to w only for $T < T_0$ even though the series converges for all T and might be expected to be a good approximation for $T > T_0$ so long as $T_0 \ll \Theta$.

(ii) In its range of validity, $T_b < T < T_0$, w_1 is a reasonably good approximation to w so that the expansion of $\exp[f(s)]$ is an acceptable approximation in this temperature range.

(iii) The Arrhenius approximation w_A is excellent for $T > \Theta$ and quite good down to $T \sim 0.3\Theta$ for $R_0 = 3$ and $T \sim 0.4\Theta$ for $R_0 = 5$. Stoneham's[22] calculations which found w_A good down to at least $T \sim 0.5\Theta$ correspond to $R_0 = 5$ and $R_0 = 18.75$.

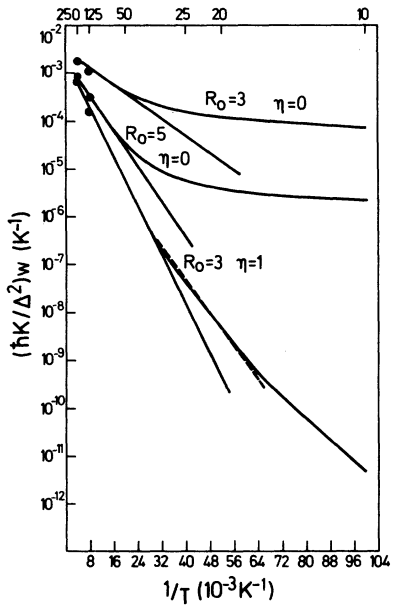

FIG. 2. Transition rates vs reciprocal temperature. The upper two curves show w calculated from Eq. (33) as in Fig. 1. The points • near these curves are calculated from Eq. (31). The lower curve is w' calculated from Eq. (33) with resonance mode modification (37) for $R_0 = 3$, $\eta = 1$, $\omega_R/2\pi c = 21$ cm^{-1}, $\delta/2\pi c = 5$ cm^{-1}, $\Theta = 200$ K. The points • near this curve are calculated from Eq. (31) with E', Eq. (42) replacing E. Solid straight lines are extrapolations of high-temperature Arrhenius behavior. The dashed line shows a range of near Arrhenius behavior near $T = 20$ K with an activation energy of 300 K in contrast to the high-temperature activation energy of 400 K.

From Fig. 1 it is evident that knowledge of the curves w_{GP} or w_1 for $T < T_0$ and w_A for $T > \frac{1}{2}\Theta$ can be sufficient to allow a good approximate w vs T at intermediate temperatures to be simply drawn in.

It is interesting to note in connection with the LWL-Debye approximation that for the cases of 60° and 90° reorientation transitions of ⟨110⟩ defects the zero-temperature dressing exponents are given by

$$R_0(60°) = \frac{\Omega}{240\rho\hbar\pi^2}\left[\frac{9}{2}\alpha_2^2\left(\frac{3}{c_t^5}+\frac{4}{c_l^5}\right)+2\alpha_1^2\left(\frac{3}{c_t^5}+\frac{2}{c_l^5}\right)\right] \tag{35}$$

and

$$R_0(90°) = \frac{\Omega}{240\rho\hbar\pi^2}\left[9\alpha_2^2\left(\frac{3}{c_t^5}+\frac{4}{c_l^5}\right)\right]. \tag{36}$$

Typically, for such systems, $\alpha_1 \gg \alpha_2$ so that even in the LWL-Debye approximation it is evident that 60° tunneling will be more strongly reduced by dressing effects than will 90° tunneling so that, somewhat surprisingly, 90° tunneling is a faster process than 60° tunneling at low temperatures. This feature of ⟨110⟩ systems was first pointed out by Kapphan and Lüty[22] and has been further studied experimentally by Jimenez and Lüty[23] and theoretically by Shore and Sander.[1] The fact that $R_0(60°) > R_0(90°)$ along with Eq. (32) for the activation energy E can explain the observation[22] that $E_{60°} > E_{90°}$ for the ⟨110⟩ off-center system RbBr:Ag$^+$. As Bridges[15] has pointed out this result is paradoxical in terms of a static potential model without dressing effects.

V. EFFECTS ON AN IN-BAND RESONANT PHONON MODE ON TRANSITION RATES

The rate given by Eq. (23) is based on the LWL-Debye approximation in which the defect-phonon coupling rises smoothly with phonon frequency as $(\omega_\sigma)^{1/2}$. If an off-center defect is heavy compared with the ion it replaces and/or the harmonic coupling between the defect and the lattice is weakened, $H_{DL(2)}$ can have the effect of producing in-band resonant phonon modes in the acoustical bands.[24] This is known to occur, for instance, in the case of the off-center system RbCl:Ag$^+$ in which the infrared-active resonances have been observed[25] and studied theoretically.[26,27] Characteristic of an in-band resonant mode is an enhancement of the amplitude of relative motion of the defect and its near neighbors.[28] Such an enhancement will lead to a peak in the frequency-dependent $H_{DL(1)}$ coupling coefficients $D_i(\sigma)$ in the vicinity of the resonant mode. In this section, we investigate

the effects on transition rates to be expected from the associated modification of the LWL-Debye approximation.

A motivation for this investigation is provided by the observation[22,23,29] that in RbCl:Ag^+ under strain 90° reorientation process are proportional to a low power of T for $T<3$ K and become Arrhenius-like functions of T with an activation energy of about 50 K for $T>3$ K. Although it would be attractive to think of this as an example of phonon-assisted tunneling and the change in T dependence as a transition from a low T, Eq. (27), to a high T, Eq. (31) form of w, this would appear to be ruled out since that transition occurs near $\frac{1}{2}\Theta$ which is about 85 K for RbCl. The high-T limit of phonon-assisted tunneling is, of course, not the only process exhibiting Arrhenius behavior. Classical thermal activation over a static barrier or thermal excitation to a state in which rapid reorientation motion can take place also produces such temperature dependence. However, before the phonon-assisted tunneling mechanism is abandoned it needs to be properly investigated with the inclusion of perturbed phonon effects. Equations (27) and (31) are based on the LWL- Debye approximation which, as we have just argued, we expect to be a poor one for RbCl:Ag^+ because of the resonant modes of this system.

In order to estimate the effect of resonant modes on w we replace $A\omega$, which in our model is the form taken by the $|F_{ij}(\sigma)|^2$ of Eq. (17) times the density of phonon states, where it appears in Eqs. (23)–(25) by the resonant-mode modified form

$$A\omega[1+KS(\omega)]\,, \tag{37}$$

where

$$S(\omega)=1\,,\quad \omega_R-\tfrac{1}{2}\delta<\omega<\omega_R+\tfrac{1}{2}\delta\,, \tag{38}$$

$$S(\omega)=0 \quad \text{elsewhere}\,.$$

The center of the resonant mode is ω_R and δ is its width. This step-function form of the resonant-mode peak is convenient for calculation and the infinite slopes associated with it do not produce spurious features. Calculations with a suitable Gaussian form for $S(\omega)$ give essentially the same results as the step-function form. The transition rate defined by substituting expression (37) for $A\omega$ in Eqs. (23)–(25) will be called w'.

The value of K in expression (35) can only be derived by detailed consideration of the interaction of the defect with phonons in the resonant mode region. K will be determined by projected densities of states for perturbed phonons. K can be quite large. The factor $A\omega$ arises from the product of a density of states factor $B\omega^2$ and a coupling factor $|F_{ij}(\sigma)|^2$ which in the LWL is of the form C/ω. If the fraction of the states in the resonant-mode region is f and if the resonant enhancement of amplitude of relative motion of the defect and its nearest neighbors is g then the resonant-mode alteration of A will be

$$A\omega=B\omega^2(C/\omega)\to B\omega^2[1+fS(\omega)](C/\omega)[1+g^2S(\omega)] \tag{39}$$

or

$$A\omega\to A\omega[1+(f+g^2+fg^2)S(\omega)]\,. \tag{40}$$

From Fig. 2 of Ref. 28 it can be seen that g can be of order 10 so that $K=f+(1+f)g^2$ can be of order 100. D. Tonks and I have examined[30] the appropriate projected densities of states for RbCl:Ag^+ where the perturbed-phonon Lifschitz Green's functions are known from infrared-absorption observations[25,26] and found that $K\sim 300$ for this case. Details of this calculation are outside the scope of this paper.

Consider how the approximations and results of Sec. IV are altered if expression (37) is used where $A\omega$ occurs in Eqs. (24) and (25). The Gosar-Pirc series, Eq. (27), is derived by special tricks which do not appear to generalize to this resonant-mode model, but analogs of Eqs. (30), w_1, and Eq. (31), w_A, are readily found. We shall see, however, that the expansion $\exp[f(s)]\sim 1+f(s)$ on which w_1 was based is no longer a good approximation so that the resonant mode analog of w_1 is no longer a good approximation to the rate w'. A resonant-mode enhancement of the linear defect-lattice coupling will clearly lead to an increase in R_0 and E and a reduction of rates. One finds that, so long as the resonance is narrow ($\delta\ll w_R$),

$$R_0'=R_0(1+2\eta\Omega/3\omega_R)\,, \tag{41}$$

and

$$E'=E(1+\eta)=\tfrac{1}{3}R_0\Theta(1+\eta)\,, \tag{42}$$

where

$$\eta=3K\omega_R^2\delta/\Omega^3\,, \tag{43}$$

are the new resonant-mode-altered values of the dressing exponent (26) and the Arrhenius activation energy (32). For $K=300$, $\hbar\Omega/k=\Theta=165$ K, $\omega_R/2\pi c=21$ cm^{-1}, and $\delta/2\pi c\sim 5$ cm^{-1} corresponding to features of the A_1 resonance in RbCl:Ag^+, η turns out to be about unity. Note that one resonant-mode effect is that of increasing the activation energy E' to a value higher than would be predicted on the basis of $H_{DL(1)}$ alone, i.e., on the basis of strain coupling parameters through Eqs. (26) and (32). Note also that in the case considered $\Omega/\omega_R\sim 5$ so that the resonance enhancement of R_0 is a larger effect than the enhancement of E. This suggests

that an effect of the resonance will be to reduce low-temperature rates, which depend sensitively on R_0, much more than high-temperature rates and could tend to straighten out the upper curves of Fig. 2 and extend the Arrhenius region to lower temperatures. This is indeed the case.

The lowest curve in Fig. 2 shows transition rates calculated numerically from Eq. (33), using the generalization (37), $\eta = 1$, $\Theta = 200$ K, and w_R and δ from the last paragraph. Note that this resonant-mode-altered w' remains Arrhenius-like down to 40 K, which is only $\frac{1}{5}\Theta$. Another region of near-Arrhenius behavior with an activation energy of 300 K occurs near $T = 20$ K. At high T w' is well given by Eq. (31) with E' from Eq. (42) substituted for E. This is shown by the two high-T points on the lowest curve of Fig. 2.

The low-T rates w' are not, however, given by Eq. (30) with R_0' from Eq. (41) substituted for R_0. Figure 3 shows $T = 20$ K rates w' as a function of increasing η for various values of R_0. For η not too small these rates are proportional to $\exp(-a\eta)$, where a is an R_0-dependent constant. If the expansion of $\exp[f(s)]$ were valid for the resonance case, arguments analogous to those leading to Eq. (30) show that w_1' would be given by Eq. (30) with R_0', Eq. (41), replacing R_0. If this were valid a would be given by $4\Omega R_0/3w_R$ which is 8.9 R_0 in the case considered here. In Fig. 3, it can be seen that calculated values of a are smaller than this and although a does increase with R_0 it is not proportional to R_0.

Call T_A the temperature above which w' is Arrhenius-like in its temperature dependence. One can get a rough idea of how T_A depends on the interplay of $H_{DL(1)}$ and $H_{DL(2)}$, that is on R_0 and η, in our model. Suppose T_A is 20 K. This requires, for a given R_0, that the resonance-modified Arrhenius rate [Eq. (31) with E replaced by E' Eq. (42)] evaluated at $T = 20$ K be equal to the low-temperature rate given by the curve for the same R_0 in Fig. 3, extrapolated to higher η if necessary. η must be adjusted to accomplish this. One finds that as R_0 is increased from 1 to 5, the required value of η increases from about 1 to about 100. If we take the case of RbCl:Ag$^+$, for which $\eta \sim 1$, as representative of physically reasonable values of η we see that a resonant-mode reduction of T_A to a temperature as low as 20 K is plausible only for values of R_0 not much greater than unity. Shore and Sander[1] found R_0 to be about 5 for the 90°-reorientation process in RbCl:Ag$^+$. It is therefore questionable whether the observed Arrhenius behavior of this process above $T = 3$ K could be an example of resonant-mode extension of the temperature range of phonon-assisted tunneling Arrhenius behavior. A more detailed investigation of this system is in progress and will be reported elsewhere.[30]

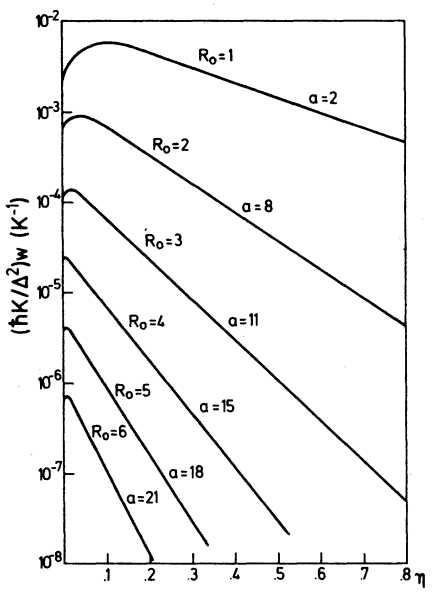

FIG. 3. Transition rate w' as a function of η for various values of R_0. For η not too small w' is proportional to $\exp(-a\eta)$. The a values are indicated for each curve.

It is interesting to note that in the off-center systems Cu$^+$ in KCl, KBr, KI low-temperature rates are so slow as to have been unobserved till now while Arrhenius behavior is observed at higher temperatures.[15] Cu$^+$ is a heavy substitutional impurity in potassium halides and so is a possible candidate for producing a resonant mode which, as we have just argued, could have as its consequence a marked suppression of low-temperature rates so that only Arrhenius rates would be observed and the Cu$^+$–potassium-halide systems would appear to be "classical," i.e., no obvious quantum-mechanical tunneling would be observed.[15]

We conclude that the effects of a resonant phonon mode on phonon-assisted tunneling rates of a defect can include an extension of Arrhenius behavior of transition rates to temperatures well below $\frac{1}{2}\Theta$. Nearly Arrhenius behavior with a lower activation energy can occur at even lower temperatures. These effects arise because of enhancement of the effect of linear defect-lattice coupling for phonons in the resonant-mode frequency region. This leads to reductions of both high- and low-temperature rates in comparison with rates calculated in the absence of a resonance. The low-temperature reduction is much greater than that of the high-temperature rate.

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†Permanent address: Dept. of Physics, University of Utah, Salt Lake City, Utah 84112.

[1]A recent paper with a bibliography of earlier work is H. B. Shore and L. M. Sander, Phys. Rev. B 12, 1546 (1975).

[2]J. Jäckle, Z. Phys. 257, 212 (1972).

[3]C. P. Flynn and A. M. Stoneham, Phys. Rev. B 1, 3966 (1970).

[4]A. M. Stoneham, Ber. Bunsenges. Phys. Chem. 76, 816 (1972).

[5]T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959); 8, 343 (1959).

[6]I. G. Lang and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. 43, 1843 (1962) [Sov. Phys.-JETP 16, 1301 (1963)].

[7]J. Yamashita and T. Kurosawa, J. Phys. Chem. Solids 5, 34 (1958).

[8]See, for example, J. J. Markham, Rev. Mod. Phys. 31, 956 (1959); C. B. Duke and G. D. Mahan, Phys. Rev. 139A, 1965 (1965).

[9]H. B. Shore, Phys. Rev. 151, 570 (1966).

[10]R. Pirc, B. Žekš, and P. Gosar, J. Phys. Chem. Solids 27, 1219 (1966).

[11]B. G. Dick, Phys. Status Solidi 29, 587 (1968).

[12]B. G. Dick and D. Strauch, Phys. Rev. B 2, 2200 (1970).

[13]L. M. Sander and H. B. Shore, Phys. Rev. B 3, 1472 (1971).

[14]M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. 153, 1009 (1967).

[15]F. Bridges, Crit. Rev. Solid State Sci. 5, 1 (1975), see Table AIII-2.

[16]M. Wagner, Solid State Commun. 18, 1329 (1976).

[17]B. G. Dick, Solid State Commun. 8, 777 (1970).

[18]L. A. Vredevoe, Phys. Rev. 153, 312 (1967).

[19]R. Pirc and P. Gosar, Phys. Kondens. Mater. 9, 377 (1969).

[20]P. Gosar and R. Pirc, in *Proceedings of the Fourteenth Colloque Ampère, Ljubljana*, 1966, edited by R. Blinc (North-Holland, Amsterdam, 1967), p. 636. See also Ref. 12.

[21]M. J. Norgett and A. M. Stoneham, J. Phys. C 6, 238 (1973).

[22]S. Kapphan and F. Lüty, Phys. Rev. B 6, 1537 (1972).

[23]R. V. Jimenez and F. Lüty, Phys. Rev. B 12, 1531 (1975).

[24]A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. Suppl. 41, No. 2 (1975).

[25]R. D. Kirby, A. E. Hughes, and A. J. Sievers, Phys. Rev. B 2, 2098 (1970).

[26]B. J. Mokross and B. G. Dick, Phys. Rev. B 15, 5938 (1977).

[27]B. J. Mokross, B. G. Dick, and J. B. Page, Jr., Phys. Rev. B 15, 5946 (1977).

[28]See for instance J. B. Page, Jr., Phys. Rev. B 10, 719 (1974), Fig. 2.

[29]J. Hallberg, thesis (Arizona State University, 1972) (unpublished).

[30]B. G. Dick and D. Tonks (unpublished).