Quadratic-coupling phonon-assisted defect-tunneling theory applied to the RbCl: Ag⁺ off-center system

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A model for the $\langle 110 \rangle$ off-center system RbCl:Ag⁺ including both linear and quadratic defect-lattice interactions is constructed. Model-parameter values are deduced from inelastic neutron scattering, infrared absorption, and electric field and stress-dichroism experimental results. The model is then used to study the temperature dependence of phonon-assisted tunneling rates of 60° and 90° reorientations over a wide temperature range, using a formalism that we have developed for this purpose. Special emphasis is placed on studying the role played by the quadratic defect-lattice coupling. Where possible, theoretical results are compared with experiment.

I. INTRODUCTION

In the preceding paper,¹ which we will refer to as I, we have developed a theory of phonon-assisted tunneling in which both linear and quadratic defect-lattice coupling are treated to all orders in these interactions. Approximations to that theory suitable for calculating defect reorientation rates at suitably high and low temperatures were also developed. It is the purpose of this paper to apply that theory to a system, off-center RbCl:Ag*, for which enough experimental information exists to allow construction of a theoretical model with very few adjustable parameters. Shell-model phonons for RbCl are known from the inelastic-neutronscattering experiments of Raunio and Rolandson.² The quadratic defect-lattice interaction $H_{pr}(2)$ is known from the infrared absorption experiments of Kirby, Hughes, and Sievers³ and their interpretation by Mokross and Dick.⁴ In Sec. II of this paper we use the experimental results of Kapphan and Lüty⁵ and Jimenez and Lüty⁶ on electric-field and stress dichroism of RbCl:Ag* along with a nearest-neighbor defect-lattice interaction model to deduce an expression for the linear defect-lattice interaction $H_{DL}(1)$. (The definition of much of the notation used in this paper is to be found in I.)

High-temperature (T > 50 K) reoreintation rates are investigated in Sec. III for both 60°- and 90°reorientation transitions. These have not been investigated experimentally. In Sec. IV low-temperature (T < 50 K) rates are investigated and, insofar as possible, compared with available experimental results. Section IV also contains a reduction of the formalism in I to the special case in which the phonons are treated in the Debye approximation, establishing contact with earlier approximate theories. Comparisons are made with the qualitative study of the effects of quadratic defect-lattice interactions made by one of $us.^7$

We find that these $H_{DL}(2)$ effects can be significant in RbCl:Ag^{*}, especially at low temperatures for the 60°-reorientation rates but less so for 90° rates. High-temperature rates are much less sensitive to the presence of $H_{DL}(2)$. Comparison with experiments, which are limited at present to T < 6 K, requires use of what is probably our least reliable approximation, the one called the "firstorder approximation" in Sec. VIII of I. Consistency with experiment and model assumptions can be achieved only if we assume "local lattice softening," an effect discussed in Sec. II below.

II. DEFECT-LATTICE INTERACTION

The nearest-neighbor force constant weakenings which, along with the mass change, produce perturbed phonons and infrared absorption bands for RbCl:Ag⁺ have been discussed by Mokross and Dick.⁴ We will use their results which completely characterize $H_{DL}(2)$ for this system.

To carry out the calculations required by the theory of I we require the perturbed-phonon Lif-shitz-Green's-function matrix defined in I(28). It is well known⁸ that this can be calculated from the corresponding unperturbed Green's-function ma-trix $G^{0}(\omega^{2})$ and the perturbing matrix $\underline{\Gamma}^{i}(\omega^{2}) \equiv \delta \underline{V}^{i} - \omega^{2} \delta M$ through the relationship

$$\underline{G^{i}}(\omega^{2}) = [\underline{1} + \underline{G^{0}}(\omega^{2})\underline{\Gamma^{i}}(\omega^{2})]^{-1}\underline{G^{0}}(\omega^{2}).$$
(1)

It is not hard to show that (1) holds for the submatrices of $\underline{G}^i(\omega^2)$ and $\underline{G}^o(\omega^2)$ which involve indices entirely in the defect space. $\underline{\Gamma}^i(\omega^2)$ is confined to the defect space by definition. Consequently, calculation of $\underline{G}^i(\omega^2)$ in the defect space using Eq. (1) only requires the manipulation of 21×21 matrices. Furthermore, we will only need $\underline{G}^i(\omega^2)$ in the de-

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fect space. The $\underline{G}^{0}(\omega^{2})$ used are calculated using the RbCl shell-model phonons of Raunio and Rolandson.²

The linear defect-lattice interaction $H_{DL}(1)$ needs further discussion. We will regard $H_{DL}(1)$, as we have $H_{DL}(2)$, as arising solely from interactions of Ag⁺ with its nearest neighbors. It will be our aim to characterize $H_{DL}(1)$, insofar as possible, by the use of experimental results supplemented by plausible model assumptions. We will be left one adjustable parameter, that associated with local lattice softening.

For an off-center defect, such as the (110) system RbCl:Ag⁺, it is the defect-lattice interaction which is responsible for the defect being off-center in the first place. We do not treat this aspect of H_{DL} in our $H_{DL}(1) + H_{DL}(2)$. It is assumed that the off-center displacement has taken place and that $H_{DL}(1)$ and $H_{DL}(2)$ describe polaronlike lattice relaxations of the host crystal ions about the offcenter defect and phonon perturbations, respectively. To fix our ideas the reference positions for lattice displacements will be taken to be the average positions of the nearest neighbors, the average being taken over the twelve different relaxed nearest-neighbor configurations associated with the twelve $\langle 110 \rangle$ off-center defect positions. [This requirement will turn out to require the matrix $\sum_{i} H_{DL}(1)_{i} |i\rangle \langle i| = H_{DL}(1)$ to have a vanishing trace, $\sum_{i} H_{DL}(1)_{i} = 0.$] These reference positions of the nearest neighbors to the defect are not the same as the positions of the corresponding Cl⁻ ions in a defect-free crystal, the reference and pure host positions differing by a cubically symmetric (A_{1e}) dilatation. The reference position of the defect itself is its off-center displaced position which we will later assume to be unaltered by the polaronlike lattice relaxations produced by $H_{DL}(1)$. The choice of nearest-neighbor reference positions has no effect on the differences in linear-couplings coefficients ΔL appearing in I (24) but does affect the renormalized linear-coupling coefficient differences ΔD of I(40'). This is because $\delta_i X$ of I(38) depends on \overline{V}^i and L^i themselves rather than on differences bet veen coefficients for two defect orientations i and j. Thus $H_{DL}(2)$ may be said to play a symmetry-breaking role.

The defect space which we use is comprised of the 21 Cartesian components of the displacements from the reference positions of the ions shown and labeled in Fig. 1. We will consider $H_{DL}(1)_i$ for the Ag⁺ defect in the [110] position and then transform our results to find $H_{DL}(1)_i$ for other off-center positions. To consider this i=[110] case it is useful to work with symmetry coordinates of the defect space rather than the Cartesian components just mentioned. These symmetry coordinates, bases for irreducible repre-



FIG. 1. Ions in the defect space. Filled circles represent Cl⁻ ions; the open circle represents an Ag⁺ ion in a [110] position. The dotted circles show alternative off-center Ag⁺ positions.

sentations of the C_{2v} group associated with the [110] off-center defect, are defined in Ref. 4, Table III. They are represented pictorially in Fig. 2. Invariance of the Hamiltonian $[H_{DL}(1)]_{[110]}$ to operations of the group C_{2v} requires that

$$[H_{DL}(1)]_{[110]} = \sum_{k=1}^{T} \eta_k([110])\chi(A_{1,k}).$$
 (2)

Hereafter, η_k coefficients written without an orientation designation will be understood to be $\eta_k([110])$. Later we will use the designation $\overline{\eta}_k$ for those coupling coefficients which occur in the traceless form of $H_{DL}(1)$.

Our problem is to find the seven coupling coefficients η_k . Data from electric-field and elasticstress experiments are insufficient to fix all these coefficients. To further simplify our consideration of $H_{DL}(1)$ we assume that it comes from pointion Coulomb and central (longitudinal) Born-Mayer short-range repulsive interactions between the Ag⁺ defect and its nearest-neighbor Cl⁻ ions. The resulting expressions for the η_{b} are given in Table I. The notation used there is defined as follows: d is the Ag⁺ off-center displacement magnitude; r_0 is the distance from the center of the defect-nearestneighbor cage to any one of the Cl⁻ ions. This is taken to be the pure host crystal nearest-neighbor distance, a choice which is not consistent with our choice of nearest-neighbor reference positions. However, since our model form of $H_{DL}(1)$ will serve only as a basis for parameter adjustment, we need not be overly concerned about this point. This choice of nearest-neighbor reference positions will yield an $H_{DL}(1)$ with a nonzero trace, however. We will make this $H_{DL}(1)$ traceless and rely on parameter adjustment to effectively re-

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FIG. 2. Schematic representation of the defect-space symmetry coordinates for Ag^* in the [110] position.

TABLE I. Coefficients $\eta_K([110])$ in Eq. (2) when $H_{DL}(1)$ is limited to nearest-neighbor interactions only and arises from point-charge (e) Coulomb interactions and central short-range Born-Mayer interactions.

$$\begin{split} \eta_{1} &= \sqrt{2} \left[\left(r_{0} - d/\sqrt{2} \right) \left(e^{2}/r_{\alpha}^{3} + 2\alpha \right) - e^{2}/r_{0}^{2} \right] \\ \eta_{2} &= \sqrt{2} \left[- \left(r_{0} + d/\sqrt{2} \right) \left(e^{2}/r_{\beta}^{3} + 2\alpha \right) - e^{2}/r_{0}^{2} \right] \\ \eta_{3} &= -d \left(e^{2}/r_{\alpha}^{3} + 2\alpha \right) \\ \eta_{4} &= -d \left(e^{2}/r_{\beta}^{3} + 2\beta \right) \\ \eta_{5} &= -d\sqrt{2} \left(e^{2}/r_{\beta}^{3} + 2\gamma \right) \\ \eta_{6} &= \sqrt{2} \left[r_{0} \left(e^{2}/r_{\gamma}^{3} + 2\gamma \right) - e^{2}/r_{0}^{2} \right] \\ \eta_{7} &= - \left(\eta_{1} + \eta_{2} + \eta_{3} + \eta_{4} + \sqrt{2} \eta_{5} \right) \end{split}$$

move this discrepancy. The distances r_{α} , r_{β} , and r_{γ} are, respectively, distances from the Ag^{*} ion to its nearest (1 and 2), most distant (I and 2), and intermediately removed (3 and 3) neighbors. They are given by

$$\begin{aligned} r_{\alpha} &= (r_{0}^{2} - \sqrt{2} r_{0} d + d^{2})^{1/2} ,\\ r_{\beta} &= (r_{0}^{2} + \sqrt{2} r_{0} d + d^{2})^{1/2} ,\\ r_{\gamma} &= (d^{2} + r_{0}^{2})^{1/2} . \end{aligned}$$
(3)

 α , β , and γ are derivatives of the Born-Mayer interaction $\theta(r^2)$, considered as a function of the squared defect-neighbor distance:

$$\alpha = \theta'(r_{\alpha}^2), \quad \beta = \theta'(r_{\beta}^2), \quad \gamma = \theta'(r_{\gamma}^2). \tag{4}$$

The interaction θ is to be thought of as being the difference between the Ag⁺-Cl⁻ interaction and the Rb⁺-Cl⁻ interaction. The last entry in Table I, that for η_{τ} , follows automatically from our nearest-neighbor interaction model and expresses the fact that, for this model, a rigid displacement of entire defect-nearest-neighbor cage does not produce any change in $H_{DL}(1)$.

The evaluation of the η_k coefficients from experimental data and model assumptions is independent of whether or not $H_{DL}(1)$ has been made traceless. Consequently we will defer this operation until later in our treatment where it is more convenient.

Using Table III of Ref. 4 along with (2) and Table I of this paper one can write out the coefficients L_{β} of I (6) for a [110] oriented Ag⁺ defect in RbCl in terms of the 5 parameters $(d, r_0, \alpha, \beta, \gamma)$ of our model defect-lattice interaction. We will take d and r_0 to be fixed and known: d=0.33 Å from Refs. 4 and 5 and $r_0=3.27$ Å, the value for pure RbCl. Two of the remaining α , β , and γ parameters (the two chosen were α and γ) can be fixed by requiring $H_{DL}(1)$ to correspond to the experimental results when the defect space symmetry coordinates have the values produced by the uniaxial stresses used in stress experiments.

Jimenez and Lüty⁶ applied a [100] uniaxial compressive stress $-S_{xx}$ to the RbCl:Ag⁺ system and found the [110] orientation of the defect to have a higher energy than the [011] orientation:

$$U([110]) - U([011]) = -S_{xx}\alpha_1, \qquad (5)$$

 $(S_{xx} < 0 \text{ for compression})$. The experimental value found for α_1 was 8.3×10^{-24} cm³. They also applied a [111] uniaxial compression $-S_{111}$ and found

$$U([110]) - U([\overline{1}10]) = -S_{111}\alpha_2 \tag{6}$$

with α_2 found to be 1.90×10⁻²⁴ cm³.

In order to use this information we need to deduce $H_{DL}(1)_j$ for j = [011] and $[\overline{110}]$ from that for j = i = [110]. This can be done by a rotation of the defect space. Let R be that rotation which carries defect site *i* to defect site *j*, that is j = Ri. Nearest-neighbor site *L* is carried into site *RL* and a Cartesian component α is carried into Cartesian component $R\alpha$. We define a 21×21 matrix *T* such that the Cartesian defect space components transforms as

$$X(RLR\alpha) = \sum_{L'\alpha'} T^{R}(L\alpha, L'\alpha')X(L'\alpha') .$$
⁽⁷⁾

The transpose of T is its inverse. For the 60° rotation $[110] \rightarrow [011]$ the nonzero T-matrix elements are $T^{60}(0\alpha, 0\beta) = T^{60}(2\alpha, 2\beta) = T^{60}(\overline{2}\alpha, \overline{2}\beta)$ $= T^{60}(1\alpha, 3\beta) = T^{60}(\overline{1}\alpha, \overline{3}\beta) = T^{60}(\overline{3}\alpha, 1\beta) = T^{60}(3\alpha, \overline{1}\beta)$ $= c_{\alpha\beta}$ for the cases $(\alpha, \beta) = (y, y)$, (x, z), and (z, x). $c_{yy} = c_{xz} = 1$ and $c_{zx} = -1$. For the 90° rotation $[110] \rightarrow [\overline{110}]$ the nonzero T-matrix elements are $T^{90}(0\alpha, 0\beta) = T^{90}(3\alpha, 3\beta) = T^{90}(\overline{3}\alpha, \overline{3}\beta) = T^{90}(1\alpha, 2\beta)$ $= T^{90}(\overline{1}\alpha, \overline{2}\beta) = T^{90}(\overline{2}\alpha, 1\beta) = T^{90}(2\alpha, \overline{1}\beta) = d_{\alpha\beta}$ for the cases $(\alpha, \beta) = (x, y)$, (z, z), and (yx). $d_{zz} = d_{xy} = 1$ and $d_{yx} = -1$.

Since $H_{DL}(1)_j$ is the same linear combination of *R*-rotated $X(L\alpha)$ that $H_{DL}(1)_i$ is of $X(L\alpha)$, we have

$$H_{DL}(1)_{j} = \sum_{L\alpha} L^{j}_{L\alpha} X(L\alpha) = \sum_{L\alpha} L^{j}_{L\alpha} X(RL, R\alpha) .$$
(8)

Whence, using (7),

$$L_{L\alpha}^{i} = \sum_{L^{\prime}\alpha^{\prime}} L_{L^{\prime}\alpha^{\prime}}^{i} T^{R}(L^{\prime}\alpha^{\prime}, L\alpha) .$$
(9)

 $\Delta \underline{L}$ components in [110] symmetry coordinate form for 60° and 90° transitions are given in Table II.

Using standard elastic theory to define defect space displacements due to uniaxial stresses and (9) to deduce the forms of $H_{DL}(1)_j$ for various defect orientations j we find

$$2\eta_6 + \eta_2 - \eta_1 = \sqrt{2}(c_{11} - c_{12})\alpha_1 / r_0 \tag{10}$$

and

$$\eta_4 - \eta_3 = 3c_{44}\alpha_2/\sqrt{2}r_0, \qquad (11)$$

where c_{11} , c_{12} , and c_{44} are moduli of elasticity for the host RbCl lattice. The distortion corresponding to $2\chi(A_{1,6}) + \chi(A_{1,2}) - \chi(A_{1,1})$ is a cubic E_g distortion of the defect space and $\chi(A_{1,4}) - \chi(A_{1,3})$ is a T_{2g} distortion. Thus α_1 and α_2 measure the energy change of a [110]-oriented defect in response to E_g and T_{2g} lattice distortions, respectively.

Notice from Table I that $\eta_4 - \eta_3$ is proportional to the off-center displacement d while $2\eta_6 + \eta_2 - \eta_1$ contains terms proportional to r_0 . Thus since dis about 10% of r_0 we expect α_2 to be smaller than α_1 which is indeed the case. If d were zero (defect on-center) α_2 would vanish altogether. In this way a simple model with central forces alone, i.e., no explicitly transverse forces, can account for the observed disparity $\alpha_1 > \alpha_2$.

TABLE II. ΔL_{j}^{ij} for 60° jumps (i = [110], j = [011]) and 90° jumps $(i = [110], j = [\overline{110}])$. β indicates a symmetry coordinate for the [110] orientation (see Fig. 2). All these coefficients are the same whether one uses η_k or $\overline{\eta_k}$ in them.

β	ΔL _β (60)	ΔL _β (90)
$\begin{array}{c} A_{1,1} \\ A_{1,2} \\ A_{1,3} \\ A_{1,4} \\ A_{1,5} \\ A_{1,6} \\ A_{1,7} \end{array}$	$\begin{array}{c} (\eta_1 - \eta_6)/2 \\ (\eta_2 + \eta_6)/2 \\ \eta_3 - \eta_5/\sqrt{8} \\ \eta_4 - \eta_5/\sqrt{8} \\ \eta_5 - (\eta_3 + \eta_4)/\sqrt{8} \\ \eta_6 + (\eta_2 - \eta_1)/2 \\ \eta_7/2 \end{array}$	$\begin{array}{c} (\eta_1 + \eta_2)/2 \\ (\eta_1 + \eta_2)/2 \\ (3 \eta_3 - \eta_4)/2 \\ (3 \eta_4 - \eta_3)/2 \\ \eta_5 \\ 0 \\ \eta_7 \end{array}$
$\begin{array}{c} A_{2,1} \\ A_{2,2} \\ A_{2,3} \\ B_{1,1} \\ B_{1,2} \\ B_{1,3} \\ B_{1,4} \\ B_{1,5} \end{array}$	$\begin{array}{c} (\eta_3 - \eta_4)/\sqrt{8} \\ \eta_3/2 - \eta_5/\sqrt{8} \\ \eta_4/2 - \eta_5/\sqrt{8} \\ (\eta_4 - \eta_3)\sqrt{8} \\ -\eta_3/2 - \eta_5/\sqrt{8} \\ -\eta_4/2 - \eta_5/\sqrt{8} \\ -(\eta_1 + \eta_2)/2 \\ -\eta_7/\sqrt{2} \end{array}$	0 0 0 0 0 0 0 0 0 0
$B_{2,1} \\ B_{2,2} \\ B_{2,3} \\ B_{2,4} \\ B_{2,5} \\ B_{2,6}$	$\begin{array}{c} (\eta_1 - \eta_6)/2 \\ (\eta_2 + \eta_6)/2 \\ \eta_5/\sqrt{8} \\ \eta_5/\sqrt{8} \\ (\eta_3 + \eta_4)/\sqrt{8} \\ \eta_7/2 \end{array}$	$(\eta_1 + \eta_2)/2 \ (\eta_1 + \eta_2)/2 \ (\eta_3 + \eta_4)/2 \ (\eta_3 + \eta_4)/2 \ (\eta_3 + \eta_4)/2 \ \eta_5 \ \eta_7$.

We assumed in the discussion at the beginning of this section that the lattice relaxation produced by $H_{pr}(1)$ does not cause further displacement of the defect. That displacement is assumed to have taken place once and for all due to initial, very anharmonic, defect-lattice interactions which we need not to consider further. This aspect of our model would require $\eta_7 = 0$; that is, $H_{DL}(1)$ does not produce defect coordinate relaxation (see $A_{1,7}$ in Fig. 2). The requirements $\eta_7 = 0$, (10) and (11) along with our values of d and r_0 allow us to fix β and thereby to completely specify the η_k coefficients in Eq. (2) and hence $H_{DL}(1)$. Even if we set $\eta_7 = 0$, it is not correct simply to omit the symmetry coordinate $\chi(A_{1,7})$ from consideration since this coordinate is involved in an important way in the resonant modes produced by $H_{DL}(2)$. Furthermore, $\chi(A_{1,7})$ enters into the ΔD of I(40') due to the $\Delta \underline{V} \, \delta \underline{X}$ term in it, even though $A_{1,7}$ terms are absent from ΔL .

In order to examine the sensitivity of our calculated rates to what might be regarded as the somewhat arbitrary assumption $\eta_7 = 0$ we will investigate relaxing this requirement and let η_7 be nonzero but small.

It is questionable to assume, as we have in deriving (10) and (11), that the elastic moduli c_{ij} of

the lattice in the vicinity of the defect, where the host lattice is most strongly distorted by the defect, should be chosen to be those of the undistorted defect-free host lattice. Shore and Sander⁹ in their study of the tunneling of off-center and molecular defects found that in order to get physically plausible results they had to assume, in effect, that local elastic moduli were ~30% lower than those of the pure host crystal. Equivalently, one could say that the actual local α_1 and α_2 are smaller than the macroscopically measured values. This uncertainty is the elastic dipole analog of the difficulty which arises in determining electric dipole moments of defects in polarizeable media, the so-called local-field problem. We will investigate the effect of assuming local α_1 and α_2 to be smaller than the measured macroscopic α_1 and α_2 . We will refer to this as "local lattice softening." 20% local lattice softening will mean that both α_1 and α_2 are taken to be 80% of their measured values in evaluating the η_{b} .

It is now convenient to introduce the reference positions for the nearest neighbors. Using (9) it is straightforward to form the average $\frac{1}{12}\sum_{j}H_{DL}(1)_{j}$ and to subtract this from each $H_{DL}(1)_{i}$ so as to make $H_{DL}(1)$ traceless. This makes the reference position configuration the zero of energy even though we have chosen host-lattice nearest-neighbor distances r_{0} as the positions about which Taylor's expansions of potentials have been taken. This process yields the traceless $H_{DL}(1)$ forms of η_{k} , which we denote $\overline{\eta}_{k}$. They are $\overline{\eta}_{1} = \eta_{1} - \frac{1}{3}(\eta_{1} - \eta_{2} + \eta_{6})$, $\overline{\eta}_{2} = \eta_{2} + \frac{1}{3}(\eta_{1} - \eta_{2} + \eta_{6}), \ \overline{\eta}_{6} = \eta_{6} - \frac{1}{3}(\eta_{1} - \eta_{2} + \eta_{6}),$ and $\overline{\eta}_{k} = \eta_{k}$ for k = 3, 4, 5, 7. Note that our requirement on η_{7} can be designated equivalently as either $\eta_{7} = 0$ or $\overline{\eta}_{7} = 0$ and that Eqs. (10) and (11) are equally valid for $\overline{\eta}_{k}$'s and η_{k} 's.

Table III shows η_k , $\overline{\eta}_k$, and α , β , γ values derived from experimental data according to the assumptions of this section. Note that α , β , and γ are negative. Consequently, the defect dipole-

lattice electric-field terms e^2/r_e^3 of Table I are reduced by the presence of short-range interactions. Those values of β which result from assuming $\eta_7 = 0$, as in Table III, will be designated β_0 .

Having completely characterized H_L , $H_{DL}(1)$, and $H_{DL}(2)$ we are ready to calculate transition rates for the RbCl:Ag^{*} system according to the methods of I.

III. HIGH-TEMPERATURE RATES

For RbCl:Ag⁺ high temperatures will mean T $\gtrsim 50$ K, that is, temperatures above about $\frac{1}{3}$ of the **RbCl Debye temperature.** Although transition rates have not been observed at such high temperatures for this system, it is useful to study the properties of our theoretical model at these temperatures for the insight that can be gained about the nature of the phonon-assisted tunneling process being considered. It is to be emphasized, as has been done by a number of authors,^{7,10,11} that tunneling from higher excited defect vibrational states and hopping over the static barrier (processes which do not enter into our model at all) become increasingly competitive with ground-vibrationalstate phonon-assisted tunneling as the temperature increases. Nonetheless, the ground-state phononassisted tunneling process is always present and still needs separate investigation.

In this section we begin by investigating the high-temperature steepest-descents result given in I (79). We will be particularly interested in answering several questions: How important are those quantities a_c and b_c which arise solely from circle diagrams and which play a role in hightemperature rates? How much are the dot-diagram terms c and b_d , arising from $H_{DL}(1)$, altered by the presence of $H_{DL}(2)$? To what extent does the Arrhenius temperature dependence of I (79), which occurs in the absence of $H_{DL}(2)$, survive

TABLE III. Values of the η_k of Eq. (2) based on Table I, Eqs. (9) and (10) with $r_0 = 3.27$ Å, d = 0.33 Å, $\alpha_1 = 8.3 \times 10^{-24}$ cm³, and $\alpha_2 = 1.9 \times 10^{-24}$ cm³ (full values without local lattice softening). The η_k coefficients are in units 10^{-5} dyn α , β and γ are in units 10^3 dyn/cm. Those values called "Coulomb alone" come from setting short-range contributions α , β and γ equal to zero. The values in parentheses are the trace- free $H_{DL}(1)$ η_k values discussed at the end of Sec. II. For k = 3,4,5,7 $\overline{\eta_k} = \eta_k$.

		η_1	η_2	η_3	η_4	η_5	η_6	η_7	α	$\beta = \beta_0$	γ
$100\%\alpha_{1},\alpha_{2}$	Coulomb only	4.57 (4.57)	4.11 (4.11)	-2.68	-1.75	-3.02	-0.46 (-0.46)	0.	0.	0.	0.
(zero local lattice softening)	total	-10.5 (0.8)	16.5 (5.2)	-1.57	-0.96	-2.42	-6.93 (4.37)	0.	-1.75	-1.25	-0.70
$80\% \alpha_1, \alpha_2$ (20% local	Coulomb only	4.57 (4.57)	4.11 (4.11)	-2.68	-1.75	-3.02	-0.46 (-0.46)	0.	0.	0.	0.
lattice softening)	total	-14.2 (0.6)	18.9 (4.1)	-1.25	-0.77	-1.94	-11.3 (3.5)	0.	-2.18	-1.50	-1.18

when $H_{DL}(2)$ is included? How sensitive are the calculated quantities which occur in I (79) to relaxation of the requirement $\eta_7 = 0$? To what extent are the features expected from the qualitative treatment of Ref. 7 borne out by more detailed investigation at high temperatures?

The one-phonon-F (OP-F) approximation treated in Sec. VII of I yields an expression, I (100), for transition rates which is readily calculable at high temperatures. Although there is no reason to expect OP-F approximate rates to be as good approximations to I (56) as the steepest-descents rates I (79) we include calculated OP-F rates at high temperature in this section. Rather surprisingly the OP-F rates and steepest-descents rates turn out to be in quite close agreement.

The bare tunneling matrix elements of I (2) are unknown parameters in our model but they occur only as temperature-independent scaling factors. Temperature variation of high-temperature rates can be seen by plotting the scaled rates

$$\overline{w}_{\theta} \equiv (\hbar k / \Delta_{\theta}^2) w_{\theta} = (k/\hbar) (\pi/b)^{1/2} \exp(-E/T), \quad (12)$$

where

$$E = Ta^2/4b \tag{13}$$

and $a = e + c + a_e$, $b = b_d + b_o$ in the notation of I (19), (41'), (76)-(78), (80), and (81). θ is the angle through which the defect moves, 60° or 90°. If *E* is constant or nearly constant the rate \overline{w}_{θ} is said to be Arrhenius and *E* is called the activation energy. The scaled rate \overline{w}_{θ} has units of reciprocal temperature and *E* has units of temperature. This usage corresponds to that of Ref. 7.

To begin with, consider only those cases without local lattice softening in which β has been so adjusted as to make $\eta_7 = 0$, i.e., $\beta = \beta_0$. The bias values $\hbar e$ we chose to be 5.9×10⁻¹⁶ and 6.8 $\times 10^{-16}$ erg for 60° and 90° transitions, values corresponding to bias energies at 2 K in the experiments of Kapphan and Lüty. These are typical bias energies and, as we shall see, in any case play an insignificant role in determining E. Figures 3 and 4 show \overline{w}_{60} and \overline{w}_{90} as a function of 1/T. It is seen that high-temperature rates for both 60° and 90° transitions are quite insensitive to the effects of $H_{DL}(2)$ and are also Arrhenius in character with or without $H_{DL}(2)$. This insensitivity of rates to $H_{DL}(2)$ is not, as will be seen in Sec. IV, a feature of low-temperature rates. The Arrhenius character of perturbed high-temperature rates is not an obvious forgone conclusion because of the presence in E of the temperature-dependent terms a_c and b_c , as discussed at the end of Sec. VI in I.

It can be seen in Figs. 3 and 4 that the $H_{DL}(2)$ perturbation *lowers* the activation energy E by about 10%. This is contrary to the expectation of the qualitative treatment of Ref. 7 in which E was



FIG. 3. High-temperature approximate scaled rates \overline{w}_{60} vs 1/T. (The solid line, perturbed phonons; dashed line, unperturbed phonons.) The circles and triangles show the perturbed-phonon and unperturbed-phonon rates calculated in the one-phonon-F (OP-F) approximation. There is no local lattice softening in the calculations shown in this graph.

expected to increase due to the presence of $H_{DL}(2)$. The model of Ref. 7, however, considered only the effect of the resonant-phonon mode, an effect which is included in our model in the change from $G^0(\omega^2)$ to $G^i(\omega^2)$. The qualitative model contains no $\Delta L \rightarrow \Delta D$ linear-coupling renormalization nor the $H_{DL}(2)$ -dependent term in c seen in I (41'). Setting $\eta_7 = 0$ greatly reduces the phonon-resonant-mode effect in our model and causes it to be less important than it was imagined to be in the qualita-tive model.

Values for the quantities appearing in a and b in (13) are given in Table IV. Note that c in the numerator and b_d in the denominator dominate in determining the value of E. The smallness of a_c relative to c and b_c relative to b_d indicates the minor role played by circle diagrams and hence by $H_{DL}(2)$ at high temperatures. This feature is re-



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60° ju	mp	90° jump			
Unperturbed	Perturbed	Unperturbed	Perturbed		
$23.7 \times 10^{-14} \text{ erg}$	$20.9 \times 10^{-14} \text{ erg}$	$10.9 \times 10^{-14} \text{ erg}$	9.2 $\times 10^{-14}$ erg		
$0.059 \times 10^{-14} \text{ erg}$	$0.059 \times 10^{-14} \text{ erg}$	$0.068 \times 10^{-14} \text{ erg}$	0.068×10 ⁻¹⁴ erg		
$68 \times 10^{-28} \text{ erg}$	$60 \times 10^{-28} \text{ erg}^2$	$31.9 \times 10^{-28} \text{ erg}^2$	28.6 $\times 10^{-28} \text{ erg}^2$		
0	$-1.65 \times 10^{-14} \text{ erg}$	0	$-1.04 \times 10^{-14} \text{ erg}$		
0	$6.36 \times 10^{-28} \text{ erg}^2$	0	$3.03 \times 10^{-28} \text{ erg}^2$		
	60° ju Unperturbed 23.7 × 10 ⁻¹⁴ erg 0.059×10^{-14} erg 68×10^{-28} erg 0 0	$\begin{array}{c cccc} & 60^{\circ} \text{ jump} \\ \hline & Unperturbed & Perturbed \\ \hline 23.7 & \times 10^{-14} \text{ erg} & 20.9 & \times 10^{-14} \text{ erg} \\ 0.059 \times 10^{-14} \text{ erg} & 0.059 \times 10^{-14} \text{ erg} \\ 68 \times 10^{-28} \text{ erg} & 60 & \times 10^{-28} \text{ erg}^2 \\ 0 & -1.65 & \times 10^{-14} \text{ erg} \\ 0 & 6.36 & \times 10^{-28} \text{ erg}^2 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		

sponsible for the survival of Arrhenius behavior of the perturbed rates in Figs. 3 and 4 in spite of the temperature dependence of $a_c \sim T$ and $b_c \sim T^2$ (in the 100-400 K range). It can also be seen by comparing unperturbed and perturbed values of cand b_d that the effect of $H_{DL}(2)$ on these dominant terms is not great at high temperatures.

Figure 5 and 6 show the effects on E of 20% and 40% local lattice softening and also the effects of varying β about β_0 . It is seen that E is only weakly β dependent but quite sensitive to local lattice softening. Roughly speaking, E is proportional to the square of the α_1 and α_2 stress coefficients. Although E does depend very strongly on β , the quantities c and b_d (which largely determine E $\sim c^2 T/4b_s$) do show marked β dependence with minima near β_0 . This strong dependence arises from the fact that $\chi(A_{1,7})$ is the defect-symmetry coordinate most strongly involved⁴ in the resonantphonon mode arising from $H_{DL}(2)$. The role of this mode is not entirely absent even when $\eta_7 = 0$, as discussed in Sec. II. Because of the strong effect of $\chi(A_{1,7})$ coupling on c and b_d it is plausible to identify the minima they exhibit for β near β_0 as corresponding to those values of β which give minimum resonant-mode involvement. Since these minima occur at β values not too far removed from β_0 we can conclude that the involvement of $H_{DL}(2)$ which enters solely because of the symmetrybreaking role of $H_{DL}(2)$, discussed above in Sec. II, is not very significant. Figures 3 and 4 show points (open circles and triangles) which correspond to values of \overline{w}_{θ} calculated by performing the Fourier transform in the OP-F approximation given by I (100). Because of the high temperature the integrand is strongly peaked about s = 0 and the Fourier transform range of integration can be truncated without significant loss of accuracy. (The actual path of integration was Holstein's shifted contour discussed in the next section.) It is seen that the OP-F and the steepest-descents high-temperature rates agree with one another quite closely. This is not surprising in the case of the unperturbed rates where the two approximations can be shown to involve the same version of

 $F_d(s)$. In the case of the perturbed OP-F and steepest-descents rates, however, the agreement is unexpected. The OP-F approximation includes, through the presence of the $V_i V_j^{-1}$ and $V_j^{-1} V_i$ factors in I (97), higher-order circle diagrams than occur in the steepest-descents treatment of the perturbed case which includes only the lowestorder dot diagram and circle diagrams only up to the second order. The unexpected agreement indicates the minor effect of the $V_i V_j^{-1}$ and $V_j^{-1} V_i$ factors.

We are now in a position to answer the questions posed in the second paragraph of this section, at least for our model of the RbCl:Ag* system. In the high-temperature range: the circle-diagram contributions a_c and b_c are small compared with those, c and b_d , coming from dot diagrams. Although the dot-diagram terms c and b_d can be substantially altered by the inclusion of $H_{DL}(2)$, the activation energy E is not. Arrhenius behavior does survive the inclusion of the temperaturedependent terms a_c and b_c because they are small. Variation of β away from β_0 leads for most cases to rather small changes in E. $\beta = \beta_0$ is the case which seems physically most consistent with our model. Additional evidence for this is provided by low-temperature first-order rates discussed



FIG. 5. *E* plotted against β for 60° reorientations at 200 K (open symbols, unperturbed phonons; filled symbols, perturbed phonons). Circles, squares, and triangles show 0%, 20%, and 40% local lattice softening. The crosses show where β_0 points occur.



FIG. 6. Same as Fig. 5 but for 90° reorientations.

in Sec. IV. Finally, due to the elimination of η_7 from our model the resonant-mode effect discussed in Ref. 7 is dominated at high temperatures by other features of our present model and *E* decreases rather than increases when $H_{DL}(2)$ is included.

IV. LOW TEMPERATURES

At low temperatures (T < 50 K) the steepestdescents approximation is no longer valid. Sections VII and VIII of I develop the OP-F approximation and the special case of it called the firstorder approximation. The OP-F approximation, expected to be useful at low temperatures, gives for the scaled rates

$$\overline{w}_{\theta}' = (\hbar k / \Delta_{\theta}^2) w_{\theta}'$$
$$= (k / \hbar) \exp(-2R_{\theta}') \int_{-\infty}^{\infty} ds \ e^{ies} \exp[G_{\theta}'(s)], \quad (14)$$

where

$$2R'_{d} = \int d\omega^{2} (2n_{\omega} + 1)D_{\theta}(\omega)$$
 (15)

and

$$G'_{d}(s) = \int d\omega^{2} \gamma_{\omega}(s) D_{\theta}(\omega) . \qquad (16)$$

We have defined the quantity

$$D_{\theta}(\omega) \equiv \Delta \underline{\tilde{D}}_{\theta} \underline{V}_{j}^{-1} V_{i} \operatorname{Im} \underline{G}^{i}(\omega^{2}) \underline{V}_{i} \underline{V}_{j}^{-1} \Delta \underline{D}_{\theta} / 2\pi \hbar \omega^{3} .$$
(17)

 $\gamma_{\omega}(s)$ is given by I (96). In the absence of the phonon-perturbing term $H_{DL}(2)$, $D_{\theta}(\omega)$ becomes

$$D^{0}_{\theta}(\omega) = \Delta \underline{L}_{\theta} \operatorname{Im} \underline{G}^{0}(\omega^{2}) \Delta \underline{L}_{\theta} / 2\pi \hbar \omega^{3}.$$
(18)

In this notation the scaled first-order rate of I (101) is

$$w_{\theta}^{\prime (1)} = (k/\hbar) \exp(-2R_{\theta}^{\prime}) 4\pi e (n_{e} + 1) D_{\theta}(e)$$
(19)

so long as $e \neq 0$.

Figures 7 and 8 show perturbed $D_{\theta}(\omega)$ and $D_{\theta}^{0}(\omega)$



FIG. 7. $D_{00}^{0}(\omega)$ and $D_{00}(\omega)$ plotted as functions of ω for the case $\beta = \beta_0 = 1250$ dyn/cm (no local lattice softening). The vertical scale is in units 2.627×10^{25} sec⁻².

for $\theta = 60^{\circ}$ and 90° for the RbCl:Ag⁺ system. These plots show peaks due to in-band resonant modes and the general enhancement of $D_{\theta}(\omega)$ in the acoustical-phonon range due to phonon perturbation.

In numerical calculation of the Fourier integral in (14) it is advantageous to reduce oscillations of the integrand by deforming the s contour downward in the complex-s plane a distance $i\hbar/2kT$ as first suggested by Holstein¹² and as discussed in Ref. 7. The contribution from the deformed contour includes vertical-path contributions which vanish in the limit that the Fourier integral limits in (14) are in fact $\pm \infty$. In numerical evaluation this integration range must in practice be truncated to $\pm S$ and the vertical path contributions no longer vanish. They are small so long as S is not too small and the temperature is not too low. In calculating (14) we used the deformed (or shifted) path, neglected the vertical-contour contributions, and truncated the Fourier integral range so that

$$' \simeq \overline{w}^{s} \equiv 2(k/\hbar) \exp(-2R'_{d})$$
$$\times \int_{0}^{s} ds \cos(es) \exp[G'_{s}(s)], \qquad (20)$$

where

 \overline{w}

$$G'_{s}(s) \equiv \int d\omega^{2} D_{\theta}(\omega) \cos \omega s / \sin(\hbar \omega / 2kT) . \qquad (21)$$

The superscript and subscript indicate this shifted contour, truncated version.



FIG. 8. Same as Fig. 7 but for $D_{90}^{0}(\omega)$ and $D_{90}(\omega)$.

Before presenting low-temperature transitionrate results it is instructive to make contact between the first-order scaled rate expression (19) and the corresponding rate given when the Lifshitz-Green's-function matrix $G^{i}(\omega^{2})$ in (17) takes on its long-wave Debye approximate form. ⁷ We consider only the unperturbed case in which $D_{\theta}(e)$ in (15) and (19) becomes $D_{\theta}^{0}(e)$, given by (18). In the Debye approximation the normal modes of the lattice are acoustical running waves of longitudinal or transverse polarization. Consequently the phonon eigenvector components of I (25)-(27) become

$$\chi(L,\alpha;q,j) = (M_c)^{-1/2} \epsilon_{\alpha}(j) \exp[i \vec{q} \cdot \vec{x}(L)].$$
 (22)

Here L stands for one of the ions in the defect space, $\overline{\mathbf{q}}$ is a phonon wave vector, $\overline{\mathbf{\epsilon}}$ is a polarization unit vector, and j is a polarization index (j=l, t_1 , or t_2). $\overline{\mathbf{x}}(L)$ is the position of ion L and α is a Cartesian component subscript. M_c is the mass of the crystal. These χ 's can be used to construct the Lifshitz-Green's-function matrix components, I (28). The only components we need in (19) are

$$\operatorname{Im} G^{0}_{L_{x,L'x}}(\omega^{2}) = \pi \sum_{q,j} \chi^{*}(L, x, q, j) \chi(L'x; q, j)$$
$$\times \delta(\omega^{2} - \omega^{2}_{j}(q))$$
(23)

where L and L' are impurity sites: $\overline{3}, \overline{2}, \overline{1}, 0, 1, 2$, or 3. In the Debye approximation the summation over \overline{q} and j is replaced by

$$\sum_{\vec{q}j} \rightarrow \frac{V}{2\pi^2} \int_0^{\omega_D} \omega^2 d\omega \sum_j c_j^{-3} \int \frac{d\Omega}{4\pi}$$
(24)

where V is the crystal volume, ω_D is the Debye frequency, c_j are sound velocities, and $d\Omega$ is an element of solid angle corresponding the phonon wave-vector direction. Expanding the exponential in (22) to second order so as to have the long-wave approximation and using the averages

$$\frac{1}{4\pi} \int d\Omega \,\epsilon_{c}^{2}(j) = \frac{1}{3}, \quad j = l, t_{1}, t_{2}$$
(25)

$$\frac{1}{4\pi} \int d\Omega \epsilon_{\alpha}^{2}(j) q_{\alpha}^{2}/q^{2} = \begin{cases} \frac{1}{5} & \text{for } j = l \\ \frac{1}{15} & \text{for } j = t_{1}, t_{2} \end{cases}$$
(26)

one gets, for the long-wave Debye approximation,

$$\operatorname{Im} G_{Lx,L'x}(\omega^2) = J\omega - Kg_{LL'}\omega^3.$$
⁽²⁷⁾

Here

$$J = (1/24\pi^2 \alpha)(c^{-3} + 2c^{-3}) .$$
⁽²⁸⁾

$$K = (r_0^2/600\pi^2 \rho)(3c_t^{-5} + 2c_t^{-5}); \qquad (29)$$

 ρ being the crystal density M_c/V and

$$g_{LL'} = [\bar{\mathbf{x}}(L) - \bar{\mathbf{x}}(L')]^2 / r_0^2.$$
(30)

Transforming the Lifshitz-Green's-function matrix given in Table II of Ref. 4 into symmetry coordinates and using (27) and (30), one finds, in the notation of Ref. 4 that $a=b=J\omega$, $c=d=J\omega-4K\omega^3$, $e=f=J\omega-K\omega^3$, and $g=h=J\omega-2K\omega^3$. Using the ΔL 's of Table II one finds

$$D_{60}^{0}(\omega) = [2(\eta_{3} - \eta_{4})^{2} + (\eta_{1} - \eta_{2} - 2\eta_{6})^{2}]K/\pi\hbar \qquad (31)$$

and

$$D_{90}^{0}(\omega) = 8(\eta_{3} - \eta_{4})^{2} K / 2\pi\hbar.$$
(32)

These expressions in (15) lead to the results of Eqs. (35) and (36) of Ref. 7, the contact between the perturbed-phonon formalism of this paper and the long-wave Debye results of Ref. 7 being thereby established.

It is interesting to note that if the off-center distance d is set equal to zero, $\eta_3 - \eta_4$ vanishes so that $D_{90}^{0}(e)$ and $\overline{w}_{90}^{\prime(1)}$ vanish in the long-wave Debye approximation. This means that the effective transverse forces which arise geometrically because of the off-center position of the defect are essential to the nonvanishing of $\overline{w}_{90}^{\prime(1)}$ in the longwave Debye approximation. Actually, one would expect $\operatorname{Im} G^{i}(e^{2}) \simeq \operatorname{Im} G^{0}(e^{2}) \simeq \operatorname{Im} G^{0}_{\operatorname{Debye}}(e^{2})$ for attainable bias e's since the phonon of frequency eis one of very long wavelength. Consequently we expect the phonon of frequency e to be, indeed, well represented as a Debye acoustical wave and not to be greatly affected by a point defect. Under these circumstances the linear-coupling renormalization $\Delta L \rightarrow \Delta D$ and the $V_i V_j^{-1}$, $V_j V_i^{-1}$ factors of (17), which also prevent $\overline{w}_{90}^{\prime}(1)$ from vanishing, play roles competitive with the effective transverse forces coming from $d \neq 0$. We thus might expect 90°-transition rates to be more sensitive



FIG. 9. 60° reorientation one-phonon-F (OP-F) rates calculated from Eq. (14) with $\beta = \beta_0 = 1250 \text{ dyn/cm}$ and no local lattice softening. Open and filled circles correspond to the unperturbed- and perturbed-phonon cases. The squares at 2 K (note broken horizontal scale) are first-order rates calculated from Eq. (19). The crosses at the upper left-hand ends of the curves are rates calculated using the high-temperature approximation.

to the presence of $H_{DL}(2)$ than 60° rates. As will be seen below, this expectation is not borne out by detailed calculation. We are led to conclude that the presence of effective transverse forces arising from the geometry of the off-center defect



FIG. 10. Same as Fig. 9 for 90° reorientation.



FIG. 11. Same as Fig. 9 but with 20% local lattice softening.

is more crucial in allowing 90° reorientations than are the effects of the quadratic defect-lattice interaction $H_{DL}(2)$ for the RbCl:Ag⁺ system.

OP-F rates and the associated first-order rates at 2 K for 60° and 90° transitions, without local lattice softening, are given in Figs. 9 and 10. Corresponding curves for 20% local lattice softening are shown in Figs. 11 and 12. In all these figures β has been chosen to be β_0 so that $\eta_7 = 0$. Figures 13 and 14 show zero-temperature dressing exponents $2R'_4(0)$, given by (15) with T = 0, as a function of β near β_0 for zero as well as 20% and 40% local lattice softening. $2R'_4(0)$ is a measure of the tunneling-matrix-element dressing effect.



FIG. 12. Same as Fig. 10 but with 20% local lattice softening.



FIG. 13. $2R'_D(0)$ from Eq. (15) with T=0 K plotted against β for 60° reorientations. The circles, squares, and triangles designate 0%, 20%, and 40% local lattice softening. Open symbols are for unperturbed phonons and filled symbols are for perturbed phonons. Crosses indicate the positions of β_0 for each case.

Figures 13 and 14 show that dressing is more affected by $H_{DL}(2)$ in the case of 60° than 90° transitions. Since the linear-coupling renormalization and $V_i V_j^{-1}$ and $V_j^{-1} V_i$ effects are shown by calculation to be small in both cases, we are led to conclude that 90° transitions require the involvement of phonons little affected by $H_{DL}(2)$ compared with those phonons involved in 60° transitions, which are affected more.

We note that for any given local lattice softening $[R'_{d}(0)]_{60} > [R'_{d}(0)]_{90}$ even when phonon perturbation is included. Thus the explanation of the apparently paradoxical rapidity of 90° rates in comparison with 60° rates (in spite of a longer tunneling path for 90° reorientations) as being due to dressing effects^{5,9} remains intact after the introduction of phonon perturbations. These dressing effects de-



FIG. 14. Same as Fig. 13 for 90° reorientations.

pend in the $H_{DL}(2) = 0$ case upon the nonparticipation of E_g distortions in 90° reorientations. The $H_{DL}(2)$ induced participation of E_g distortion in the dressing of 90° transitions, absent in the unperturbed case, is not great enough to change the above inequality of dressing factors.

Note the sensitivity of $R'_{d}(0)$ to variations in β away from β_{0} . This shows the strong role played by the resonant modes when they are permitted to act in $H_{DL}(1)$ through $\eta_{7} \neq 0$.

The question arises as to why the 60°-transition activation energies E do not show the pronounced enhancements by $H_{DL}(2)$ that the $R'_d(0)$ do. The reason lies in the ω factors in the corresponding phonon sums. The R'_d summand has one less factor of ω than does that of E so that the low- ω part of the sum plays a relatively more important role in R'_d than in E. This part of the phonon spectrum is more affected by perturbation than the high ω part as Figs. 7 and 8 show.

In Figs. 9 and 10 the low-temperature behavior of 60° rates is altered much more markedly than that of the corresponding 90° rates. The depression of the low-temperature 60° rates is the most striking consequence of phonon perturbation in the rates we have calculated. The 60° rates, but not the 90° rates, conform in this regard to the expectations expressed in the qualitative study of Ref. 7. The perturbed $\log_{10}\overline{w}_{60}^{*}$ vs 1/T plot shows much less curvature than the unperturbed plot: perturbation causes the low-temperature 60° rates to be more Arrhenius in character.

Accuracy in calculating $\overline{w}_{\theta}^{s}$, Eq. (20), was limited at low temperatures by the fact that the integral over ω^2 indicated in (16) was carried out as a discrete sum, the ω^2 being divided into 400 equal intervals (bins) and $\operatorname{Im} G(\omega^2)$ becoming a histogram. When S in (20) exceeds the reciprocal of the lowest bin frequency a further increase in Sdoes not increase the accuracy of the calculation (20); one is simply integrating over repetitions of the spuriously periodic $G'_{d}(s)$, the periodicity arising from the discrete ω^2 sum in place of an integration. This feature causes difficulty at low temperatures where the integrand of(20) falls off slowly with increasing s and large S would be required for accuracy, an S larger than is meaningful because of the spurious periodicity. Equation (20) begins to fail below about 13 K for 60° transitions and below about 17 K for 90° transitions. Unfortunately, data on RbCl:Ag⁺ transition rates are available only for temperatures less than 6 K.

In an effort to make contact with experiment we have considered the first-order rate (19). Although there is reason to doubt that this is an adequate approximation⁷ it can, at least, be calculated at temperatures in the experimental range. This calculation is basically straightforward but there (33)

is one complication: experimental bias frequencies e lie inside the first ω^2 bin used for the Im $G(\omega^2)$ histogram. To describe the variation of Im $\overline{G}(\omega^2)$ at these low frequencies the long-wave Debye approximate form (27) was used to interpolate in the lowest bin. Values of the first-order rates at 2 K for the bias $\hbar e = k(2 \text{ K})$ appear at the right-hand edge of Figs. 9–12. The OP-F plots, which cannot be extended so low as 2 K because of the calculational difficulties just discussed, do not appear to extrapolate very naturally to these firstorder approximate rates. This could be due either to low-temperature failure of Eq. (20) or to the inadequacy of the first-order approximation (or both).

Some interesting comparisons with experiment can, nonetheless, be made using these first-order rates. Kapphan and Lüty⁵ find from a rate-equation analysis of their observations of the optical relaxation time for a suddenly switched on electric field parallel to [111] that

 $w(90^{\circ}) = 1.6/(b_1+1)\tau_{opt}(0 \rightarrow E_{[111]})$

$$b_1 = \exp\left[\left(\frac{2}{3}\right)^{1/2} (p E_{[111]} / kT)\right].$$
(34)

A similar analysis,¹³ not given in Ref. 5, of suddenly switched on electric fields parallel to [100] shows that

$$w(60^{\circ}) = b_2 / [2(b_2 + 1)^2 \tau_{ont}(0 \rightarrow E_{[100]})],$$
 (35)

where

$$b_2 \equiv \exp(pE_{1001}/\sqrt{2}kT)$$
 (36)

Using the data of Ref. 5 and Eqs. (34)-(36) we find, for pE/kT=3 and T=2 K that $w(60^{\circ})=13$ sec⁻¹ and $w(90^{\circ})=14\,600$ sec⁻¹ for RbCl:Ag⁺. The ratio $w(90^{\circ})/w(60^{\circ})$ is 1125.

If we assume that the bare-tunneling matrix elements Δ_{60} and Δ_{90} are equal, the error made is probably less than an order of magnitude. Making this assumption, the observed $w(90^{\circ})/w(60^{\circ})$ ratio

above can be compared with the theoretical firstorder ratio $\overline{w}_{90}^{\prime(1)}/\overline{w}_{60}^{\prime(1)}$ from (19). If we choose $\beta = \beta_0$ then the only adjustable parameter remaining in our model for the first-order ratio is the local lattice softening factor, $\overline{w}_{90}^{\prime(1)}/\overline{w}_{60}^{\prime(1)}$ for our model for RbCl:Ag⁺ is 94000, 1011, and 25 for 0%, 20%, and 40% local lattice softening. Thus 20% local lattice softening is consistent with the observed ratio.

Choosing this local lattice softening one can then use the absolute rates $w(60^{\circ})$ and $w(90^{\circ})$ to derive values of the bare-tunneling matrix elements Δ_{60} and Δ_{90} . They turn out to be 0.23 and 0.25 cm⁻¹, respectively. The near equality is not significant since equality was assumed in finding the appropriate local lattice softening. These values of Δ_{60} and Δ_{90} are not implausible. They are substantially smaller than the free rotor estimate of an upper bound on a first excited librational level, $\hbar^2/2m_{Ag}d^2 = 9$ cm⁻¹.

The dressed matrix elements

$$\tilde{\Delta}_{\theta} = \Delta_{\theta} \exp[-R_{\theta}'(0)] \tag{37}$$

can be found once one has the bare Δ_{θ} . For our RbCl:Ag⁺ model these turn out to be $\overline{\Delta}_{60} = 0.00014$ cm⁻¹ and $\overline{\Delta}_{90} = 0.02$ cm⁻¹. Bridges,¹⁴ on the basis of paraelectric resonance experiments, concludes that $\overline{\Delta}_{90} < 0.1$ cm and Rollefson¹⁵ has suggested $\overline{\Delta}_{90} \sim 0.006$ cm⁻¹ for this system. Both are consistent with our theoretical estimate. As has been noted, for instance in Ref. 7, it is not easy to construct a theory in which both Δ_{θ} and $\overline{\Delta}_{\theta}$ have physically plausible values. We have succeeded in getting plausible values here only by using local lattice softening which confirms a similar conclusion reached by Shore and Sander.⁹

ACKNOWLEDGMENT

This work was supported by NSF Grant No. DMR 73-02516 A01.

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