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Calculation of Reorientation Rates of OH⁻ Defects in RbBr Using Accurate Phonon Spectra

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(Received 31 January 1972)

In a recent experiment Kapphan and Lüty measured the reorientation rate of OH⁻ defects in RbBr in the temperature range 1–15 °K. In this paper we present a theoretical calculation of the reorientation rate in which we treat the defect-lattice coupling and the lattice frequency spectrum as accurately as possible. The coupling is assumed to contain a strain-dipole component and an electric-dipole component; the magnitudes of the two components and the "bare" tunneling matrix element provide three parameters which are adjusted to produce the best agreement with experiment. The lattice spectrum is calculated using shell-model parameters chosen to agree with recent neutron-diffraction data on phonons in RbBr. The relaxation rate is calculated to all orders in the number of phonons. The temperature dependence of the re-normalized tunneling matrix element is included. Calculated reorientation rates are in excellent agreement with experiment, but there is no unique choice of the parameters that produces a best fit. The results indicate that at low temperatures the rate is controlled by strain-dipole single-phonon processes and that at high temperatures electric-dipole multiphonon processes are dominant. Plausibility arguments are used to choose a "most probable" set of parameters that is consistent with the reorientation data, and this choice is in satisfactory agreement with values of the parameters obtained from the measured external electric-dipole moment and stress-splitting factor.

I. INTRODUCTION

It has been recognized for several years that a study of reorientation rates of paraelectric[1-4] and paraelastic[5-10] defects in alkali halides could provide information on the nature of the defect-lattice interaction. The role of one-phonon processes in the relaxation of defects such as OH⁻ in KCl is fairly well understood,[3] but all attempts (including the present one) to include multiphonon processes[11,12] have had to deal with several difficulties. First, the contribution of multiphonon processes is very sensitive to the exact form of the phonon spectrum, so that calculations using a simplified (i.e., Debye) spectrum cannot accurately reproduce experimental results. Similarly, calculated relaxation rates are sensitive to the assumed form of the defect-lattice interaction. Since one wants to use as few adjustable parameters as possible to describe this interaction, a certain amount of guesswork must be used in deciding on a proper form for the interaction. Further, a consistent calculation of multiphonon effects must include the renormalization of the tunneling matrix element[7,8,13-15]; previous calculations that did employ accurate phonon spectra did not take this ef-

fect into account. Finally, we should mention that the amount of experimental data has been meager; to the authors' knowledge there is only one experiment, that of Kapphan and Lüty[16] (KL) for OH⁻ in RbBr, giving the temperature dependence of the relaxation rate over a wide enough range to distinguish between different theoretical predictions.

The purpose of this paper is to attempt an accurate calculation of the relaxation rate of RbBr : OH, using shell-model phonons for the spectra of RbBr, a realistic model for the dipole-lattice coupling, and a consistent theory including renormalization effects. Such a theory has been developed by Pirc and Gosar[14] and, in somewhat different form, by the present authors[15] (hereafter referred to as I). The background of the present calculation is as follows. In I, the theory developed there was applied to RbBr : OH using Debye phonons without a high-frequency cutoff. The defect was assumed to couple to the lattice as a pure strain dipole; i.e., the fact that the coupling to the lattice of the heteronuclear ion OH could contain an electric-dipole component was ignored. The calculated relaxation rate as a function of temperature (Fig. 1 of I) was in reasonably good agreement with the data of KL for $T \leqslant 10\,°$K. However, for $T \geqslant 10\,°$K the calculated rate increased much more rapidly than experiment. In a subsequent note,[17] an attempt was made to improve the agreement in the high-temperature region by taking the non-Debye character of the spectrum into account in a very crude way, simply by introducing a high-frequency cutoff to the spectrum as an adjustable parameter. The result was in good agreement with experiment using $\hbar \omega_c / k_B = 67\,°$K as the choice of cutoff frequency. This result, while encouraging, had the unpleasant feature that the required cutoff frequency was considerably lower than the observed specific-heat Debye temperature of RbBr, $\approx 130\,°$K. The question then had to be asked whether the low value of ω_c indicated a basic inadequacy of the theory or was due simply to the crude approximations that had been made to simplify the calculation. For example, the theory assumes that the dipole-lattice coupling is linear, and that effects of nonlinear coupling such as resonant modes, local modes, or intrinsic multiphonon processes are unimportant. Another assumption is that the parameters that go into the defect-lattice Hamiltonian are closely related to properties of the dipole that can be independently determined: the tunneling matrix element, the electric-dipole moment, and the external stress-splitting factor.

The present calculation confirms the assumption that a linear theory with parameters in reasonable agreement with other data does explain the relaxation data. However, it shows that the previous assumption concerning the dominance of strain-di-

pole coupling was incorrect and that, on the contrary, the dominant process in the multiphonon contribution to the relaxation rate is the electric-dipole process. The nature of our results is such that the magnitudes of the strain- and electric-dipole coupling constants cannot be determined uniquely. The experimental data can be fitted using "weak-coupling" parameters, in which one- and two-phonon processes dominate and matrix-element renormalization is negligible. The data can also be fitted with "intermediate-coupling" parameters, in which processes involving one through five or more phonons contribute significantly. In Sec. VI we give plausibility arguments in favor of the latter choice.

In a recent paper, Dick and Strauch[12] (DS) calculated the one- and two-phonon relaxation rate for RbBr : OH. The present calculation, which has many features in common with theirs, seems to give better agreement with the experiment. In Sec. VI we compare the two calculations.

II. THEORY

In this section the theory developed in I will be rewritten in a form suitable for accurate calculation. In RbBr : OH the O-H axis can point along any of six equivalent [100] directions. Assuming that the dipole reorients by tunneling between adjacent allowed directions, the Hamiltonian can be written in matrix form as[18,19]

$$\mathcal{H}'' = \mathcal{H}_\epsilon'' + \mathcal{H}_T'' + \mathcal{H}_p'' + \mathcal{H}_I'' \, , \qquad (1a)$$

$$\mathcal{H}_\epsilon'' = \epsilon \begin{vmatrix} 1 & & & & & \\ & -1 & & & & \\ & & 0 & & & \\ & & & 0 & & \\ & & & & 0 & \\ & & & & & 0 \end{vmatrix} \, , \qquad (1b)$$

$$\mathcal{H}_T'' = -\frac{\Delta_0}{2} \begin{vmatrix} 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \end{vmatrix} \, , \qquad (1c)$$

$$\mathcal{H}_p'' = \sum_k \hbar \omega_k a_k^\dagger a_k \, , \qquad (1d)$$

$$\mathcal{H}_I'' = \sum_k (a_k + a_{-k}^\dagger) \begin{vmatrix} W_k^{+z} & & & & & \\ & W_k^{-z} & & & & \\ & & W_k^{+x} & & & \\ & & & W_k^{-x} & & \\ & & & & W_k^{+y} & \\ & & & & & W_k^{-y} \end{vmatrix} . \quad (1e)$$

The matrices in $\mathcal{H}''$ operate on basis states specifying the dipole orientation, $|+z\rangle$, $|-z\rangle$, $|+x\rangle$, $|-x\rangle$, $|+y\rangle$, $|-y\rangle$. For the present, the index k will be used to specify both the wave vector $\vec{k}$ and the phonon mode j; thus the notation $\sum_k$ implies $\sum_{\vec{k}} \sum_{j=1}^6$. $\mathcal{H}_\epsilon''$ describes the splitting of the states due to an external electric field along the z direction, $\mathcal{H}_T''$ describes dipole tunneling, $\mathcal{H}_p''$ specifies the phonon spectrum for the unperturbed lattice, and $\mathcal{H}_I''$ gives the dipole-lattice interaction, assumed to be diagonal in dipole orientation and linear in lattice displacements. The quantity W_k^{+z} gives the linear coupling to phonons with index k when the O-H axis points in the $+z$ direction. To preserve Hermiticity, we must have $W_k^i = W_{-k}^{i*}$.

The relaxation rate for the six-level system is related by a constant factor to the relaxation between two adjacent orientations, say, $|+z\rangle$ and $|+x\rangle$, ignoring the existence of the four other states. The Hamiltonian for this problem can be written in terms of 2×2 matrices as

$$\mathcal{H}' = \epsilon \begin{vmatrix} 1 & \\ & 0 \end{vmatrix} - \frac{\Delta_0}{2} \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} + \sum_k \hbar\omega_k a_k^\dagger a_k$$
$$+ \sum_k (a_k + a_{-k}^\dagger) \begin{vmatrix} W_k^{+z} & \\ & W_k^{+x} \end{vmatrix} . \quad (2)$$

Introducing spin $= \frac{1}{2}$ matrices s_x, s_y, and s_z, we have

$$\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_I + \mathcal{H}_d , \quad (3a)$$

$$\mathcal{H}_0 = \epsilon s_z - \Delta_0 s_x + \sum_k \hbar\omega_k a_k^\dagger a_k , \quad (3b)$$

$$\mathcal{H}_I = s_z \sum_k W_k(a_k + a_{-k}^\dagger) , \quad (3c)$$

$$\mathcal{H}_d = \tfrac{1}{2}\epsilon + \tfrac{1}{2}\sum_k (a_k + a_{-k}^\dagger)(W_k^{+z} + W_k^{+x}) . \quad (3d)$$

Here,

$$W_k = W_k^{+z} - W_k^{+x} . \quad (4)$$

The term $\mathcal{H}_d$ in Eq. (3) is independent of defect orientation and can be transformed into a constant energy shift by a unitary transformation. We therefore take as the final Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I . \quad (5)$$

It was shown in I that the relaxation rate can be written

$$1/T_1 = \tfrac{3}{2}(\Delta/\hbar)^2 \int_{-\infty}^{\infty} dt \cos\epsilon t [R(t) - 1] , \quad (6)$$

where

$$R(t) = \exp\{\sum_k |W_k/\hbar\omega_k|^2 [(n_k + 1)$$
$$\times e^{-i\omega_k t} + n_k e^{i\omega_k t}]\} , \quad (7a)$$

$$n_k = 1/[\exp(\beta\hbar\omega_k) - 1] , \quad (7b)$$

$$\Delta^2 = \Delta_0^2 \exp[-\sum_k | W_k/\hbar\omega_k |^2(2n_k + 1)] . \quad (7c)$$

The factor of 3 in Eq. (6) converts the result for the two-level system of Eq. (5) to the six-level RbBr:OH system; it is obtained using the analysis of Dick.[3] The renormalization of the tunneling matrix element Δ_0 is given by Eq. (7c).

In Eq. (7), all of the effects of the $\vec{k}$ dependence of the lattice spectrum and of the dipole-lattice coupling enter through the ratio $| W_k/\hbar\omega_k |$. It is therefore convenient to define a single function of frequency:

$$g(\omega) \equiv \sum_k | W_k/\hbar\omega_k |^2 \delta(\omega - \omega_k) . \quad (8)$$

As was noted in I, for strain-dipole coupling, $g(\omega) \propto \omega$ for small ω. Gosar and Pirc[7] define the coefficient of proportionality as

$$\lim g(\omega) \approx 3(\hbar/\pi k_B T_0)^2 \omega \quad \text{as } \omega \to 0 . \quad (9)$$

In order to maintain continuity with earlier work we will therefore use a new function $G(\omega)$:

$$g(\omega) = 3(\hbar/\pi k_B T_0)^2 \omega G(\omega), \quad G(0) \equiv 1 . \quad (10)$$

Equation (10) specifies $G(\omega)$ for $\omega \geq 0$. The form of Eq. (7) can be greatly simplified if we require in addition that $G(-|\omega|) = G(|\omega|)$. Then Eq. (7) becomes

$$R(t) = \exp[\int_{-\infty}^{\infty} d\omega\, g(\omega) e^{-i\omega t} /(1 - e^{-\beta\hbar\omega})] , \quad (11a)$$

$$\Delta^2 = \Delta_0^2 \exp[-\int_0^{\infty} d\omega\, g(\omega) \coth(\beta\hbar\omega/2)] . \quad (11b)$$

The function $G(\omega)$ provides a way of stating in compact form the approximations made in previous work. In Ref. 7 and in I, $G(\omega) = 1$ for all ω. In Ref. 17, a cutoff was introduced by taking $G(\omega) = 1$ for $|\omega| < \omega_c$ and $G(\omega) = 0$ for $|\omega| > \omega_c$. In Secs. III and IV we will attempt an accurate calculation of $G(\omega)$ for RbBr:OH.

III. DIPOLE-LATTICE COUPLING

In order to calculate W_k, we are forced to make reasonable physical assumptions about the nature of the dipole-lattice interaction. We first obtain a form for the matrix element $\langle +z|\mathcal{H}_I''|+z\rangle$ of Eq. (1e); the other matrix element required, $\langle +x|\mathcal{H}_I''|+x\rangle$, can then be obtained by symmetry. In Fig. 1, the O-H axis is shown pointing in the $+z$ direction, and the six nearest-neighbor Rb$^+$ ions are labeled. In general, $\langle +z|\mathcal{H}_I''|+z\rangle$ can be written as $-\sum_i \vec{F}_i \cdot \vec{u}_i$, where $\vec{F}_i$ is the force exerted by the defect on the lattice atom i and $\vec{u}_i$ is the displacement of atom i from its equilibrium position. In choosing a model for the $\vec{F}_i$, we require that
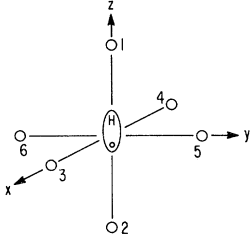
FIG. 1. Description of the coordinate axes and numbering system to describe the OH defect and its nearest neighbors. The defect is in the state $|+z\rangle$.

$\sum_i \vec{F}_i = 0$ in order to maintain equilibrium. We choose a model in which there are two contributions to $\vec{F}_i$, a "strain-dipole" part and an "electric-dipole" part. The symmetries of the $\vec{F}_i$ for the two contributions are shown in Fig. 2. We further assume that the strain-dipole contribution is due to short-range forces which act only on the nearest neighbors $i = 1, 2, \ldots, 6$. We therefore take, for the strain-dipole contribution to $\langle +z|\mathcal{K}_I''|+z\rangle$,

$$\langle +z|\mathcal{K}_I''|+z\rangle_S = -F_S \left[2(u_1^z - u_2^z) \right.$$
$$\left. - (u_3^x - u_4^x) - (u_5^y - u_6^y) \right], \quad (12)$$

where F_S is an adjustable parameter with the dimensions of a force.

An expression equivalent to Eq. (12) can be written for the effect of an electric dipole on the nearest neighbors:

$$-F_E \left[2(u_1^z + u_2^z) - (u_3^z + u_4^z + u_5^z + u_6^z) \right], \quad (13)$$

thereby introducing a new force parameter F_E. At this point a choice must be made concerning the range of the electric-dipole interaction. There is no *a priori* reason why a short-range "pseudodipolar" force with the symmetry of Fig. 2(b) should not exist; overlap integrals between wave functions of the defect and its nearest neighbors must certainly contain a component with this symmetry.[3] We will, however, assume that the important contribution is due to the dipolar electric field of the defect acting on the ionic charge of the lattice ions. We modify Eq. (13) to include ions beyond the nearest neighbors:

$$\langle +z|\mathcal{K}_I''|+z\rangle_E = F_E \sum_{\vec{l}}{}' (-1)^{l_x + l_y + l_z} L^{-5}$$
$$\times \left[(2l_z^2 - l_x^2 - l_y^2) u_{\vec{l}}^z + 3l_x l_z u_{\vec{l}}^x + 3l_y l_z u_{\vec{l}}^y \right]. \quad (14)$$

Here the sum over integers l_x, l_y, and l_z excludes the point $(0, 0, 0)$. The factor $(-1)^{l_x + l_y + l_z}$ takes into account the charge of the ion at point $\vec{l}$; the distance from the origin is $L = (l_x^2 + l_y^2 + l_z^2)^{1/2}$. The parameter F_E is defined so that the contribution of nearest neighbors to $\langle +z|\mathcal{K}_I''|+z\rangle_E$ is given correctly by Eq. (13).

We assume that corrections to Eq. (14) due to local field effects (i. e., the field on an ion due to the electronic polarizability of neighboring ions) simply change the effective value of F_E, but do not change the functional form. This point will be dis-

cussed further in Sec. VI. Using Eqs. (12) and (14), the quantities $\langle +x|\mathcal{K}_I''|+x\rangle_S$ and $\langle +x|\mathcal{K}_I''|+x\rangle_E$ can be written down immediately by making the substitution $x, y, z \to y, z, x$.

We have now defined the three parameters Δ_0, F_S, and F_E that will be adjusted in order to fit the experiment. The lattice displacements $\vec{u}_{\vec{l}}$ can be written in terms of phonon creation and annihilation operators in the usual way[20]:

$$\vec{u}_{\vec{l}} = \sum_{\vec{k}, j} (\hbar/2NM_\kappa \omega_{k,j})^{1/2} \vec{v}(\kappa|k, j)$$
$$\times e^{i a \vec{k} \cdot \vec{l}} (a_{\vec{k}, j} + a_{-\vec{k}, j}^\dagger). \quad (15)$$

Here, a is the spacing between nearest-neighbor ions and N is the number of ion pairs in the crystal. M_1 and M_2 are the masses of the Rb^+ and Br^- ions, respectively; the index κ takes the values

$$\kappa = \begin{cases} 1 \\ 2 \end{cases} \text{ if } l_x + l_y + l_z = \begin{cases} \text{odd} \\ \text{even} \end{cases} . \quad (15a)$$

The six-dimensional polarization vectors $\vec{v}(\kappa|\vec{k}, j)$, whose components are real numbers, are orthonormalized as

$$\sum_{\alpha=1}^{3} \sum_{\kappa=1}^{2} v^\alpha(\kappa|\vec{k}, j) v^\alpha(\kappa|\vec{k}, j') = \delta_{jj'} . \quad (16)$$

The quantity $W_{\vec{k}, j}$ introduced in Eq. (4) can now be written as a sum of two terms,

$$W_{\vec{k}, j} = W_{\vec{k}, j; S} + W_{\vec{k}, j; E} . \quad (17)$$

The first term is the contribution from strain-dipole coupling and the second the contribution from electric-dipole coupling. From Eqs. (3c), (4), (12), and (15) we have

$$W_{\vec{k}, j; S} = -6i F_S (\hbar/2NM_1 \omega_{\vec{k}, j}^*)^{1/2}$$
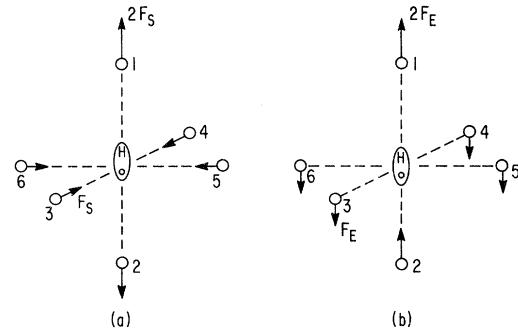$$\times [v^z(1|\vec{k}, j) \sin a k_z - v^x(1|\vec{k}, j) \sin a k_x] . \quad (18)$$

FIG. 2. (a) Forces on the nearest neighbors produced by a defect-lattice interaction with strain-dipole symmetry. (b) Forces produced by an interaction with electric-dipole symmetry. The illustration shows a pseudo-electric-dipole force that acts on nearest neighbors alone, but the calculation uses an interaction that falls off as (distance)$^{-3}$.

Similarly, from Eqs. (3c), (4), (14), and (15)

$$W_{\vec{k},j;E}^{+} = W_{\vec{k},j;E}^{+z} - W_{\vec{k},j;E}^{+x} ,\tag{19}$$

where

$$W_{\vec{k},j;E}^{+z} = F_E \sum_{l_x,l_y,l_z}{}' (-1)^\kappa L^{-5}(\hbar/2NM_\kappa \, \omega_{\vec{k},j}^{-})^{1/2}$$

$$\times e^{ia\vec{k}\cdot\vec{l}}[(3l_z^2 - L^2)v^z(\kappa|\vec{k},j) + 3l_x l_z v^x(\kappa|\vec{k},j)$$

$$+ 3l_y l_z v^y(\kappa|\vec{k},j)] . \tag{20}$$

The expression for $W_{\vec{k},j;E}^{+x}$ is obtained by cyclic permutation of the indices x, y, z. It is convenient to rewrite Eq. (20), so that the sum is over integers l_x, l_y, $l_z \geq 0$. The result is

$$W_{\vec{k},j;E}^{+z} = -F_E(\hbar/2NM_1\omega_{\vec{k},j})^{1/2} A_z(\vec{k},j) ,\tag{21}$$

where

$$A_z(\vec{k},j) = \sum_{l_x,l_y,l_z \geq 0}{}' L^{-5}[-(M_1/M_2)^{1/2}]^{\kappa-1}$$

$$\times \{(3l_z^2 - L^2)v^z(\kappa|\vec{k},j) C(k_z l_z) C(k_x l_x) C(k_y l_y)$$

$$- 12l_z \sin(ak_z l_z)[l_x v^x(\kappa|\vec{k},j) \sin(ak_x l_x) C(k_y l_y)$$

$$+ l_y v^y(\kappa|\vec{k},j) \sin(ak_y l_y) C(k_x l_x)]\} , \tag{22a}$$

$$C(kl) = \begin{cases} 1, & l = 0 \\ 2\cos akl, & l = 1, 2, \ldots . \end{cases}\tag{22b}$$

In summary, the W_k in Eq. (3c) are given by

$$W_k = W_{\vec{k},j;S}^{-} + W_{\vec{k},j;E}^{+z} - W_{\vec{k},j;E}^{+x} ,\tag{23}$$

with the first two terms of Eq. (23) given by Eqs. (18) and (21), respectively. This completes the derivation of the interaction Hamiltonian $\mathcal{H}_I$.

IV. DISTRIBUTION FUNCTIONS

In this section we evaluate numerically the frequency dependence of $G(\omega)$ using the best available information on the frequencies $\omega_{k,j}$ and polarization vectors $v(\kappa|k,j)$ for the lattice spectrum of RbBr. First we modify Eq. (8) so that the quantity being summed has the full symmetry of the octahedral group O_h. From Eq. (23)

$$g(\omega) = \sum_{\vec{k},j} (\hbar\omega_{\vec{k},j})^{-2} \delta(\omega - \omega_{\vec{k},j})$$

$$\times |W_{\vec{k},j;S}^{-} + W_{\vec{k},j;E}^{+z} - W_{\vec{k},j;E}^{+x}|^2 . \tag{24}$$

All of the cross terms in the expansion of the square in Eq. (24) vanish when summed over equivalent $\vec{k}$; therefore we can write

$$g(\omega) = g_S(\omega) + g_E(\omega) . \tag{25}$$

Here,

$$g_S(\omega) = \sum_{\vec{k},j} (\hbar\omega_{\vec{k},j})^{-2} \delta(\omega - \omega_{\vec{k},j}) |W_{\vec{k},j;S}^{-}|^2$$

$$= (6F_S^2/M_1\hbar)N^{-1} \sum_{j,\vec{k}} \omega_{\vec{k},j}^{-3} \delta(\omega - \omega_{\vec{k},j})$$

$$\times \{[v^z(1|\vec{k},j) \sin ak_z - v^x(1|\vec{k},j) \sin ak_x]^2$$

$$+ [v^x(1|\vec{k},j) \sin ak_x - v^y(1|\vec{k},j) \sin ak_y]^2$$

$$+ [v^y(1|\vec{k},j) \sin ak_y - v^z(1|\vec{k},j) \sin ak_z]^2\} . \tag{26}$$

Here, $g_S(\omega)$ has been written in a form in which the summand is explicitly invariant under the operations of O_h. Similarly,

$$g_E(\omega) = \frac{2}{3} \sum_{\vec{k},j} (\hbar\omega_{\vec{k},j})^{-2} \delta(\omega - \omega_{\vec{k},j})$$

$$\times (|W_{k,j;E}^{+x}|^2 + |W_{k,j;E}^{+y}|^2 + |W_{k,j;E}^{+z}|^2) \tag{27}$$

or

$$g_E(\omega) = (F_E^2/3M_1\hbar)N^{-1} \sum_{j,\vec{k}} \omega_{\vec{k},j}^{-3}\delta(\omega - \omega_{\vec{k},j})$$

$$\times [A_x(\vec{k},j)^2 + A_y(\vec{k},j)^2 + A_z(\vec{k},j)^2] . \tag{28}$$

The low-frequency behavior of $g_S(\omega)$ and $g_E(\omega)$ is controlled by the acoustic branches of the phonon spectrum. Examination of Eqs. (26) and (28) shows that $g_S(\omega) \propto \omega$ and $g_E(\omega) \propto \omega^3$ for $\omega \to 0$. We will see that the ω^3 dependence of $g_E(\omega)$ has the important consequence that the electric-dipole process does not contribute to the one-phonon relaxation rate. In order to calculate T_0 and $G(\omega)$ in terms of the two parameters F_S and F_E, we introduce two new functions $J_S(\omega)$ and $J_E(\omega)$ through the equations

$$g_S(\omega) = (6F_S^2/M_1\hbar)\,\omega J_S(\omega) ,\tag{29a}$$

$$g_E(\omega) = (F_E^2/3M_1\hbar)\omega J_E(\omega) \tag{29b}$$

[cf. Eq. (10)]. The functions $J_S(\omega)$ and $J_E(\omega)$ have dimensions sec[5]; $\lim_{\omega \to 0}J_S(\omega) = \text{const} = J_S(0)$, whereas $\lim_{\omega \to 0}J_E(\omega) \propto \omega^2$.

The functions $J_E(\omega)$ and $J_S(\omega)$ are given entirely in terms of the $\omega_{\vec{k},j}$ and $v(\kappa|\vec{k},j)$ for the RbBr lattice. In order to calculate these quantities, we need accurate data on the complete frequency spectrum of RbBr. These data have been obtained using neutron diffraction by Rolandson and Raunio[21] (RR); these authors also give the input parameters to fit their data to several versions of the shell model.[22,23] Our calculations use the parameters for model III of the (nonbreathing) shell model, which includes radial and tangential force constants for all Rb^+-Br^- and Br^--Br^- nearest-neighbor ions. Test calculations of the frequency spectrum along special directions in the Brillouin zone indicate very good fit to the neutron-diffraction data, so there should be negligible error from this source. The data of RR were obtained at a temperature of 80 °K, whereas we are interested in the phonon spectra for $T \leq 15$ °K. We do not think that this presents any difficulties, however, since measurements of the elastic constants of RbBr as a function of temperature indicate little change below 80 °K.[24] Bron[25] has suggested that polarization vectors calculated with the shell model can be in error even if the frequencies are correct, so we cannot rule out a possible source of error here. Further, as in DS

we make the assumption that the $\vec{u}_i$ refer to displacements of the ionic cores rather than the shells, so that we calculate the core vectors $\vec{v}(\kappa\,|\vec{k},j)$. This assumption could introduce additional error into the distribution functions.

Since the summands of Eqs. (26) and (28) have been symmetrized, the summation over $\vec{k}$ can be confined to the Kellerman section of the Brillouin zone. The summations are performed using a slightly modified version of the root sample method, breaking up the frequency interval into 100 sections and choosing 3×10^5 points at random within the Kellerman section. In order to obtain a curve with uniform scatter over the entire frequency range, we weight the random selection process to favor points in the zone with small $|\vec{k}|$ and multiply each term of the summation by the Jacobian of the weighting function.

In evaluating $A_x(\vec{k},j)$, $A_y(\vec{k},j)$, and $A_z(\vec{k},j)$ of Eq. (22), the summation over l must be restricted to some finite range; we find that the results are unchanged by including terms for l_x, l_y, $l_z > 3$, so the summation over l is restricted to $0 \le l_x$, l_y, $l_z \le 3$. The results for $J_S(\omega)$ and $J_E(\omega)$ are shown in Figs. 3 and 4, respectively. A peculiar feature of these curves is their lack of strong structure. As a check on the calculation, $g(\omega)$ was evaluated setting all $W_{\vec{k}} = 1$; it was then found that $g(\omega)$ reproduced the phonon density-of-states curve given by RR. We therefore attribute the smoothness of $J_S(\omega)$ and $J_E(\omega)$ to the $\vec{k}$ dependence of $W_{\vec{k}}$.

Of particular importance is the value

$$J_S(0) \approx 1.66 \times 10^{-65}\, \sec^5 \ . \qquad (30)$$

Recalling that $J_E(0) = 0$, Eqs. (10) and (29) can be combined to give

$$T_0^2 = \tfrac{1}{2}M_1\hbar^3 J_S(0)^{-1}\,(\pi k_B F_S)^{-2} \qquad (31)$$

and

$$G(\omega) = [J_S(\omega) + \gamma J_E(\omega)]/J_S(0) \ , \qquad (32a)$$

where

$$\gamma = F_E^2/18F_S^2 \ . \qquad (32b)$$

Equations (31) and (32) determine T_0 and the functional form of $G(\omega)$ uniquely in terms of the two parameters F_E and F_S. In Sec. V, T_0 and $G(\omega)$ will be used in Eqs. (6) and (11) to determine the temperature dependence of the relaxation rate.

V. CALCULATION OF RELAXATION RATES

It is impractical to perform the integration over time in Eq. (6) directly via numerical integration, since $R(t)$ is a very rapidly varying function of t. Instead, we use a method of repeated convolutions. This is accomplished by first defining the quantity

$$B_1(\omega) = g(\omega)/(1 - e^{-\beta\hbar\omega}) \ . \qquad (33)$$

Equation (6) can be evaluated by expanding the exponential in the definition of $R(t)$, Eq. (11a), yielding

$$T_1^{-1} = \tfrac{3}{2}\pi(\Delta/\hbar)^2 \sum_{n=1}^{\infty}\,[B_n(\epsilon) + B_n(-\epsilon)]/n! \ , \qquad (34)$$

where

$$B_n(\omega) = \int_{-\infty}^{\infty} d\omega_1 \cdots d\omega_n\, B_1(\omega_1) \cdots B_1(\omega_n)$$

$$\times\, \delta(\omega_1 + \cdots + \omega_n - \omega) \ . \qquad (35)$$

Convolution integrals of the type given by Eq. (35) can be evaluated by using the recursion relation

$$B_{n+1}(\omega) = \int_{-\infty}^{\infty} d\omega'\, B_n(\omega - \omega')\, B_1(\omega') \ . \qquad (36)$$

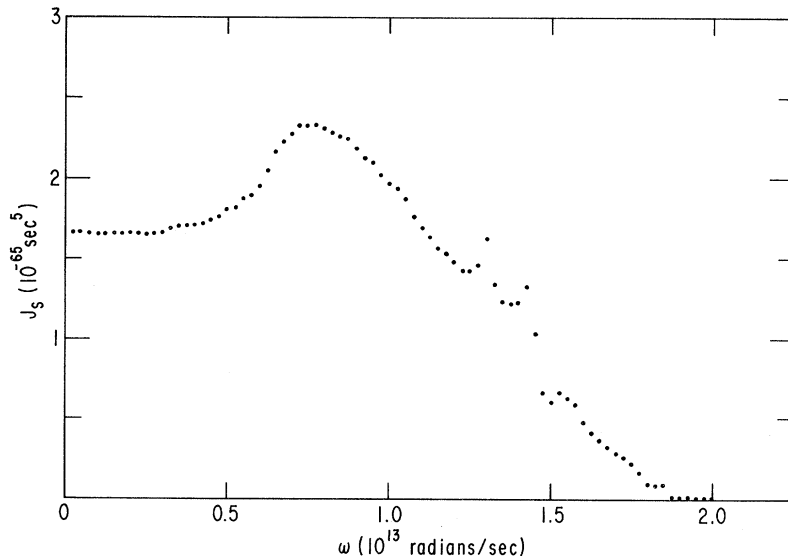Equation (34) is a convenient form for practical

FIG. 3. Distribution function J_S vs angular frequency for RbBr, calculated using shell-model phonons obtained from the neutron-diffraction data of Rolandson and Raunio (Ref. 21).
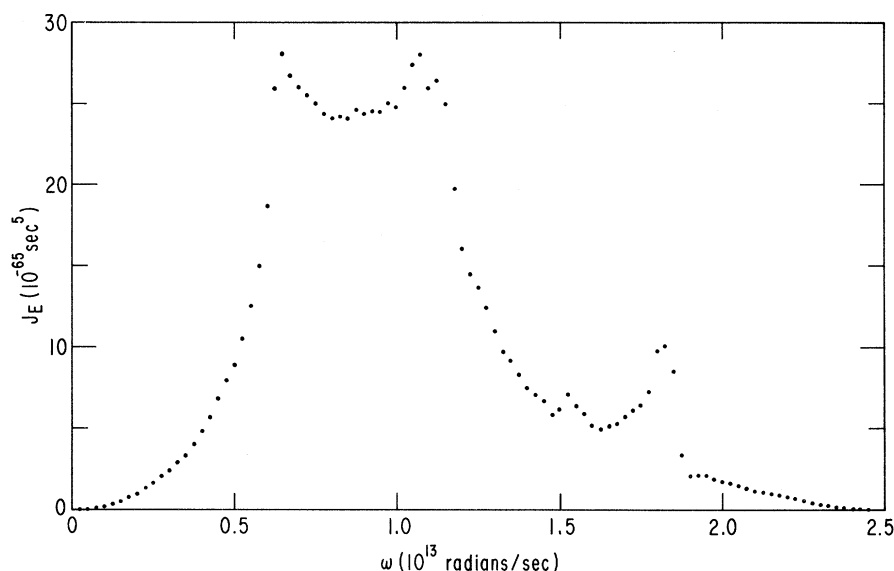
FIG. 4. Distribution function J_E vs angular frequency for RbBr.

calculation, since the $B_n(\omega)$ can be evaluated efficiently and the summation over n converges reasonably rapidly for realistic choices of the input parameters.

The experiment of KL was performed by using an electric field to align the defects, and then switching the field off and observing the relaxation. Therefore, Eq. (34) should be evaluated in the $\epsilon = 0$ limit, the factor $B_n(\epsilon) + B_n(-\epsilon)$ being replaced by $2B_n(0)$. [Note that this does not significantly reduce the amount of calculation required; the evaluation of $B_n(0)$ requires knowledge of $B_{n-1}(\omega)$ for all ω.]

The term in the summation of Eq. (34) containing $B_n(0)$ gives the contribution of all n-phonon processes to the total relaxation rate. In particular, the one-phonon rate for $\epsilon \to 0$ is

$$(1/T_1)^{(1)} = (9\Delta^2/\pi\hbar k_B \, T_0^2) \, T \equiv a_1 T \ . \qquad (37)$$

For small enough temperature, the one-phonon rate dominates the relaxation; in this region $\Delta^2(T)$ approaches a limiting value $\Delta^2(0)$ given by

$$\Delta^2(0) = \Delta_0^2 \, e^{-W_0} \ , \qquad (38a)$$

$$W_0 \equiv \int_0^\infty \, d\omega \, g(\omega) \ . \qquad (38b)$$

The parameter W_0 is a convenient measure of the strength of the dipole-lattice coupling. From Eqs. (38b), (25), and (29), we have

$$W_0 = (1/M_1 \hbar) \, (6F_S^2 I_S + \tfrac{1}{3} F_E^2 I_E) \ , \qquad (39a)$$

where

$$I_{S,E} = \int_0^\infty \, d\omega \, \omega J_{S,E}(\omega) \ . \qquad (39b)$$

The values of I_S and I_E for RbBr are $I_S = 2.07 \times 10^{-39}$ sec^3 and $I_E = 23.5 \times 10^{-39}$ sec^3.

The coefficient of the linear term in the relaxation rate can then be written

$$a_1 = 9\Delta_0^2 e^{-W_0} / \pi\hbar k_B \, T_0^2 \ . \qquad (40)$$

In the experiment of KL, the coefficient a_1 is measured accurately to be 770 sec^{-1} $^\circ$K^{-1}; this enables us to fix one of the adjustable parameters, Δ_0, using the one-phonon rate along with the other two parameters. The temperature dependence of Δ for higher T is then

$$\Delta^2(T) = \Delta^2(0) \exp\left[-2 \int_{-\infty}^0 \, d\omega \, B_1(\omega)\right] \ . \qquad (41)$$

We now attempt to fit the experimental curve using Eqs. (34) and (41), adjusting F_S and F_E, and using Eq. (40) to determine Δ_0. In the remainder of this section, we discuss the "derived" parameters T_0 and γ rather than the fundamental parameters F_S and F_E. In Sec. VI we relate these results to F_S and F_E, and compare the values so obtained with other observable properties of the defects.

We first note that F_S must have a finite value, since pure electric-dipole coupling gives a T^7 behavior for low T rather than the observed T behavior; i.e., the lowest-order process involving $J_E(\omega)$ for $\epsilon \to 0$ is a two-phonon process. Thus the simplest possible choice of T_0, γ is a one-parameter fitting of T_0 with $\gamma = 0$. The results for pure strain-dipole coupling for several values of T_0 are shown in Fig. 5. It seems clear that there is no choice of T_0 that gives satisfactory agreement over the entire temperature range. Therefore we must conclude that the good agreement obtained in Ref. 17 using a flat $J_S(\omega)$ cutoff at $\omega_c = 67$ $^\circ$K $k_B/\hbar = 0.87 \times 10^{13}$ sec^{-1} is spurious. In fact, Fig. 3 indicates that any attempt to approximate $J_S(\omega)$ with a step function would require a much larger ω_c.

If electric-dipole coupling is included, it is found that a range of choices of the parameters T_0, γ gives very good agreement, well within the quoted experi-
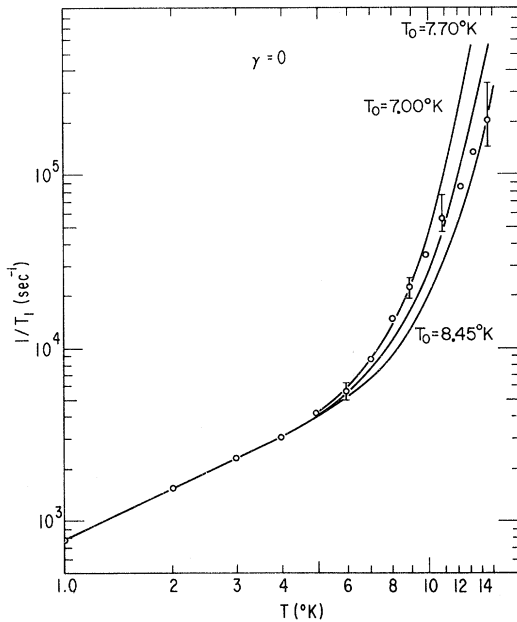
FIG. 5.   Comparison of experimental (Ref. 16) and calculated reorientation rates versus temperature for RbBr : OH, using strain-dipole coupling only ($\gamma = 0$).
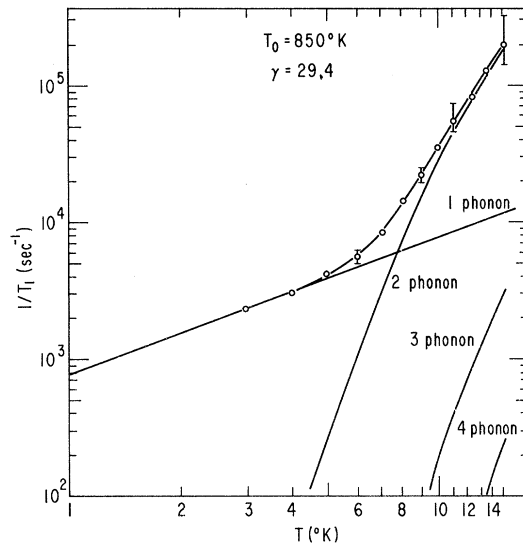

FIG. 6.   Reorientation rate vs temperature for RbBr : OH in the weak–coupling limit. The contribution of individual processes is shown separately. The curve is obtained by selecting an arbitrary large value of T_0 and then adjusting γ to obtain the best fit for large T. The effect of varying γ is to shift the two-phonon contribution vertically.

mental error. We start by picking a small value of F_S (large T_0), determine Δ_0 by fitting the one-phonon rate, and then choose γ to get the best fit at high T. This corresponds to weak coupling, $W_0 \ll 1$. The relaxation is dominated by one-phonon strain-dipole and two-phonon electric-dipole processes. Under these conditions $\Delta(T)$ is essentially independent of temperature. A typical result is shown in Fig. 6; for $T_0 = 850\,^\circ$K, the best fit is obtained for $\gamma = 29.4$. The contributions of the individual terms in the summation of Eq. (34) are shown separately. For this choice of T_0, $\Delta(15\,^\circ$K$) \approx 0.97\Delta(0)$. For large T_0 the one-phonon rate $\propto \Delta_0^2/T_0^2$, while the two phonon rate $\propto \Delta_0^2 \gamma^2/T_0^4$; consequently, the results of Fig. 6 can be duplicated for other choices of T_0 by keeping γ/T_0 constant.

For smaller values of T_0, the coupling becomes stronger; then the temperature dependence of $\Delta(T)$ and third- and higher-order processes begin to affect the shape of the curve. We estimate that the smallest value of T_0 that produces satisfactory agreement with the data is $T_0 = 27\,^\circ$K. For values of T_0 smaller than this, i.e., for stronger strain-dipole coupling, the relaxation rate increases too rapidly for high T. In Fig. 7 we show the results for $T_0 = 27\,^\circ$K with two choices of γ. Also plotted in Fig. 7 is $\Delta^2(T)/\Delta^2(0)$ for $\gamma = 0.675$.

In comparing Fig. 5 with Figs. 6 and 7, we note a significant difference between the relaxation of paraelectric and paraelastic defects. In the paraelastic case, where electric-dipole coupling is

forbidden by symmetry, the magnitude of the strain-dipole coupling can be estimated by inspection of the relaxation-rate curve. Thus, in Fig. 5, T_0 is
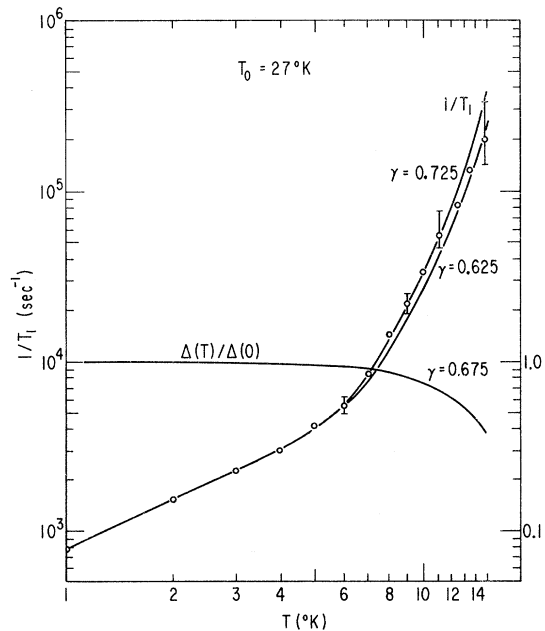
FIG. 7.   Reorientation rate vs temperature for RbBr : OH with $T_0 = 27\,^\circ$K, the lowest value of T_0 for which satisfactory agreement with experiment can be obtained. The renormalization of the tunneling parameter $\Delta(T)$ is shown for $\gamma = 0.675$.

given approximately by the temperature at which $1/T_1$ departs from linearity. This method was used by Pfister and Känzig[9] to estimate T_0 for O_2^- defects in several alkali halides. In the paraelectric case, the temperature at which the break occurs is determined by the relative magnitudes of the electric- and strain-dipole processes, so that it is no longer possible to read off a value of T_0 by inspection.

The results of this section are summarized in Fig. 8, where the value of γ producing the best fit is plotted as a function of T_0. Each point on this curve fixes the values of F_S, F_E, and Δ_0.

VI. CONCLUSIONS

In order to interpret the results of Sec. V we find a relation between F_S and the external stress-splitting factor and between F_E and the electric-dipole moment of the impurity. If an external pressure P is applied along the z direction, the Hamiltonian $\mathcal{H}''$ of Eq. (1a) is perturbed so that the two levels $|+z\rangle$ and $|-z\rangle$ are raised above the four levels $|+x\rangle$, $|-x\rangle$, $|+y\rangle$, and $|-y\rangle$ by an energy $\Delta\mathcal{H} = \alpha P$.[26,27] The stress-splitting factor α is related to F_S through[28]

$$\alpha = 6aF_S/(C_{11}-C_{12}) . \tag{42}$$

Here a is the lattice constant, and C_{11} and C_{12} are elastic constants. Equation (42) is only approximately correct, since it assumes that the local elastic constants in the vicinity of the defect are unchanged from the bulk values.

In attempting to relate the electric-dipole moment p_E to the force F_E, we are uncertain as to the correct way to include local field effects. Experiments in which the defects are aligned by applying an external electric field give a value for the "uncorrected" dipole moment p_u.[27,29] This is presumably related to the "true" dipole moment p_E by

FIG. 8. Value of γ that produces the best agreement between the theoretical and experimental reorientation rates, as a function of T_0.

$p_u = [\frac{1}{3}(\epsilon_0 + 2)]p_E$, where ϵ_0 is the low-frequency dielectric constant of the host. Mahan[30] gives the potential energy of a dipole-point charge separated by a distance $\vec{R}$ in a dielectric medium as

$$V_{cd} = \frac{\epsilon + 2}{3\epsilon}\, q\vec{p}_E \cdot \frac{\vec{R}}{R^3} . \tag{43}$$

The term $(\epsilon + 2)/3\epsilon$ gives the correction to the force on a given ion due to the polarization of neighboring ions. However, that part of the polarization due to displacements of the ion cores has already been explicitly included in the Hamiltonian; thus we assume that the relevant dielectric constant in Eq. (43) is ϵ_∞, the part due to the electronic polarizability of the ions. If we further assume that Eq. (43) holds even for nearest neighbors, then the result of the above speculations is a relation for p_u in terms of F_E:

$$p_u = \epsilon_\infty(\epsilon_0 + 2)(\epsilon_\infty + 2)^{-1}(F_E a^3/e) . \tag{44}$$

For RbBr, we have $\epsilon_\infty(\epsilon_0 + 2)(\epsilon_\infty + 2)^{-1} \approx 3.70$.

In Table I we list the calculated values of F_S, F_E, Δ_0, $\Delta(0)$, W_0, α, and p_u for several values of T_0 and γ taken from Fig. 8. Experimental values for α[31] and p_u[32] are also listed; the value for α is estimated from experiments on other alkali halides. Inspection of this table makes it obvious that one of the goals of this investigation cannot be achieved: There is no unique choice of Δ_0, α, and p_u that alone agrees with experiment. The fact that the data can be satisfied using one- and two-phonon processes alone rules out that possibility. Thus, we are forced to rely on plausibility arguments to narrow the range of possibilities.

The parameter that varies most rapidly in Table I is Δ_0, the "bare" tunneling matrix element. We can argue that the values of Δ_0 at either extreme of the table are unlikely. The rotational energy levels for an OH ion in free space are given by $E_L = BL \times (L+1)$, where $B = \hbar^2/2I$ has the value $B = 27\,°K$. The effect of the lattice must be to reduce the tunneling splitting below the free-rotor value, so that $\Delta_0 \approx 10\,°K$ is a reasonable upper limit. Calculations of the crystal-field potential hindering the free rotation of the OH⁻ ion and of the displacement of the O-H center of mass (c.m.) from the lattice site have been made for several alkali halides.[33,34] These calculations seem to produce a Devonshire[35] barrier height K of about $850\,°K$ and an off-center displacement of the c.m. between 0.2 and 0.3 Å for all the alkali halides. The effect of the displaced c.m. is to increase the moment of inertia, reducing the rotational constant B to about $13\,°K$. Using the accurate calculations of the Devonshire model by Sauer,[36] the above values of K and B result in a tunneling splitting of $\Delta_0 \approx 0.5\,°K$.

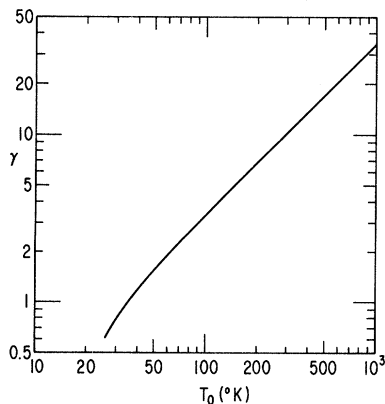Further, it is known[32] that the one-phonon relaxation rate for OH⁻ in different alkali halides varies

a linear coupling of the defect to unperturbed lattice vibrations, and that this coupling must include terms with the symmetries of both electric and strain dipoles. While we have not been able to use this calculation to predict a unique set of defect parameters, we can find a "probable" set of param-

eters that are in reasonable agreement with experimental values.

ACKNOWLEDGMENT

*Supported in part by the National Science Foundation.

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