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MULTIPHONON EFFECTS IN PARAELECTRIC RELAXATIONS

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A theory is presented for the temperature dependence of the relaxation rate of paraelectric impurities in alkali-halides. The impurity is regarded as a two-level system coupled linearly to a phonon field. The relaxation rate is evaluated for arbitrary number of phonons, using a Debye spectrum for the lattice. The results agree well with experiments by Kapphan and Lüty for relaxation of OH^- impurities in RbBr.

SUBSTITUTIONAL OH impurities in many alkali-halides can rotate between the six equivalent <100> directions by 'tunneling' through potential barriers.[1] The six-fold degeneracy among the low lying energy levels will always be partially or completely lifted either by the imposition of an external electric field or by the tunneling itself.[2] If the populations of the six states are disturbed from thermal equilibrium, relaxation towards equilibrium will occur by means of the interaction of the impurities with the lattice phonons. In a recent experiment,[3] the relaxation rate T_1^{-1} of RbBr:OH was measured as a function of temperature T. At low temperatures $1/T_1$ is proportional to T, a characteristic of one-phonon relaxation. For $T \geqslant 10°K$ the rate increases to approximately $1/T_1 \sim AT^4$, indicating that multiphonon effects are important in this temperature region.

Dick and Strauch[4] have attempted to explain these experimental results by using detailed models for the impurity and phonon spectrum and including processes involving one and two phonons. The present authors[5] have calculated a rate that includes phonon processes to all disorders, using a very primitive model for the phonons : i.e. a linear dispersion relation with no short-wavelength cutoff. The model and the results of reference 5 are similar to a calculation of the relaxation rate for paraelastic defects (such as O_2^-) by Gosar and Pirc.[6] In the present communication, we extend the method of reference 5 by including a short wavelength cutoff ω_c (of the order of the Debye frequency) in the phonon spectrum. With this modification, the calculation of T_1^{-1} fits the experimental data very well, and illustrates the important features that arise from the strong dipole-lattice coupling.

The major simplification in our model is the replacement of the 6-level OH^- system by a two level system. Any rates we calculate with this model will be wrong by a multiplicative constant, but the temperature dependence should be correct if the relaxation of the original system is describable by a single decay time. We use the

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Hamiltonian:

$$\mathcal{H} = \epsilon S_z - \Delta_0 S_x + \sum_k \omega_k a_k^\dagger a_k + iS_z \sum_k W_k (a_k - a_k^\dagger) \quad (1)$$

Here S_x, S_y S_z are spin 1/2 matrices, which describe the two possible orientations of the dipole; ϵ is the energy difference between the "up" and "down" orientations produced by an external applied electric field, and Δ_0 is the 'bare' tunneling matrix element. The third term in $\mathcal{H}$ represents the unperturbed lattice vibrations. The fourth term is the dipole lattice coupling, assumed to be linear in the displacements of lattice atoms. The sign of the inter-action depends on the orientation of the dipole; i.e. the dipole pulls or pushes on its neighbors depending on its orientation.

The Hamiltonian $\mathcal{H}$ is exactly soluble if $\Delta_0 = 0$. This allows one to regard the tunneling as a perturbation and to treat the dipole-lattice coupling exactly. We leave the details to reference 5 and give here the results. The relaxation rate is given by:

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

where

$$R(t) = \exp\left\{ \sum_k (W_k/\omega_k)^2 \, [(n_k + 1) e^{-i\omega_k t} + n_k e^{i\omega_k t}] \right\} \, . \quad (3)$$

Here $n_k = 1/[\exp(\beta\omega_k) - 1]$ is the Bose distribution function. Δ is the 'observed' tunneling matrix element, related to Δ_0 by:

$$\Delta^2 = \Delta_0^2 \exp\left\{ - \sum_k (W_k/\omega_k)^2 (2n_k + 1) \right\} . \quad (4)$$

The temperature dependence of Δ is an important part of the temperature dependence of $1/T_1$. Equation (2) is valid for Δ, $1/T_1 \ll \epsilon$. If the exponential in equation (3) is expanded, the term containing $(W_k/\omega_k)^{2n}$ describes all processes involving n phonons.

In order to evaluate equations (3) and (4) we make simple approximations for the k dependence of W_k and ω_k. The lattice spectrum is taken as $\omega_k = v|k|$ up to a cutoff frequency ω_c. Since the dipole couples to lattice strains, for long wavelengths W_k varies as $|k|^{\frac{1}{2}}$, we then assume that $W_k = \alpha\omega_k^{1/2}$ for any k. With these approximations, one can write

$$R(t) = \exp\left\{ 3(\pi k_B T_0)^{-2} \int_{-\omega_c}^{\omega_c} d\omega \, \omega e^{-i\omega t}/(1 - e^{-\beta\omega}) \right\} \quad (5)$$

and

$$\Delta^2(T) = \Delta^2(0) \cdot \exp\left\{ - 6(\pi k_B T_0)^{-2} \int_0^{\omega_c} d\omega \, \omega/(e^{\beta\omega} - 1) \right\} . \quad (6)$$

The temperature T_0 describes the strength of the dipole-lattice coupling; the significance of T_0 is that multi-phonon effects become important for $T \gtrsim T_0$. In terms of the approximation for W_k, T_0 is given by $(k_B T_0)^{-2} = \alpha^2/6\omega_c$. The quantity $\Delta(0)$ is the observed tunneling matrix element at $T = 0$. It is related to Δ_0 by $\Delta^2(0) = \Delta_0^2 \exp(-\Sigma_k W_k^2/\omega_k^2)$, but can be regarded as an independent parameter. For $k_B T \ll \omega_c$ the upper limit of the integral in equation (6) can be extended to infinity, with the result that $\Delta^2 = \Delta^2(0) \exp(-T^2/T_0^2)$. (The factor $6/\pi^2$ was used in the definition of T_0 in equations (5) and (6) in order to avoid such factors in calculated quantities such as Δ^2.) The renormalization of Δ_0 occurs because the lattice is distorted differently for the two orientations of the dipole; the tunneling matrix element Δ for the lattice–dipole system is reduced from Δ_0 by the overlap of the lattice wave functions for the two orientations.[7]

Equations (2), (5) and (6) provide an expression for $1/T_1$ in terms of the four adjustable parameters ϵ, $\Delta(0)$, T_0 and ω_c. To illustrate the dependence of these parameters, we first note that $1/T_1$ is independent of ϵ if $\epsilon \ll k_B T$; thus for small external fields ϵ can be set equal to zero and the factor $\cos \epsilon t$ in equation (2) replaced by unity. The contribution to $1/T_1$ from single phonon processes, obtained by expanding the exponential in equation (5) to first order, is:

$$(1/T_1)^{(1)} = (3\Delta^2(0)/\pi k_B T_0) \cdot (T/T_0) \, . \quad (7)$$

The multiphonon contribution can then be written

$$1/T_1 = (1/T_1)^{(1)} \cdot F(T/T_0, \omega_c/k_B T_0) \, . \quad (8)$$

The function F is dimensionless. We have evaluated it numerically by expanding the

exponential in equation (5) and then evaluating the Fourier transform of equation (2) by a method of repeated convolutions. The integral in equation (6) is easily evaluated as a series. The result is shown in Fig. 1.

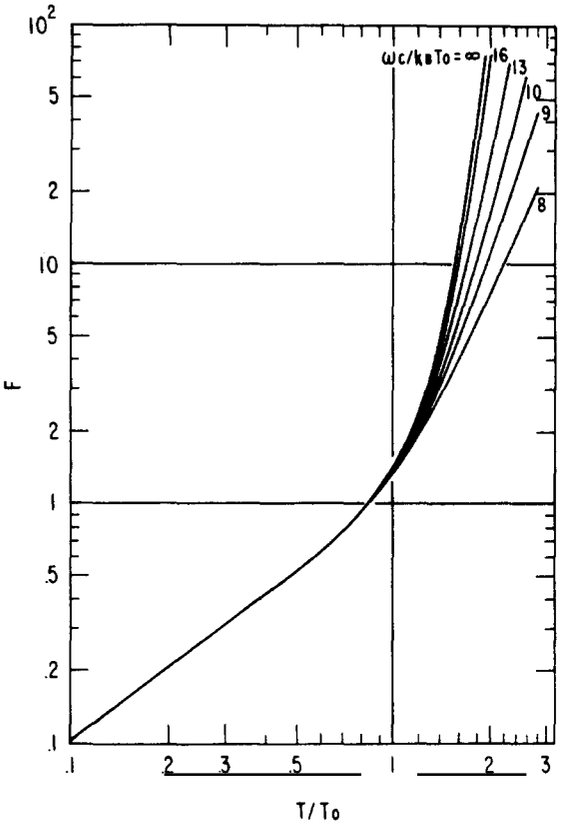

FIG. 1. The function F vs. T/T_0 for several values of ω_c/k_BT_0.

The most striking feature of the function F is that it depends strongly on ω_c even for $k_BT \ll \omega_c$. (For example if $T = 2T_0$, the relaxation rate for $\omega_c = \infty$ is greater than the rate for $\omega_c = 10k_BT_0$ by an order of magnitude!) Thus phonons near the zone boundaries make a major contribution to multiphonon relaxation even for relatively low temperatures. This fact makes it clear that the present calculation, with its simplified phonon spectrum, should be regarded as schematic; the adjustable cutoff is being used here to compensate for the incorrect k dependence of W_k and ω_k.

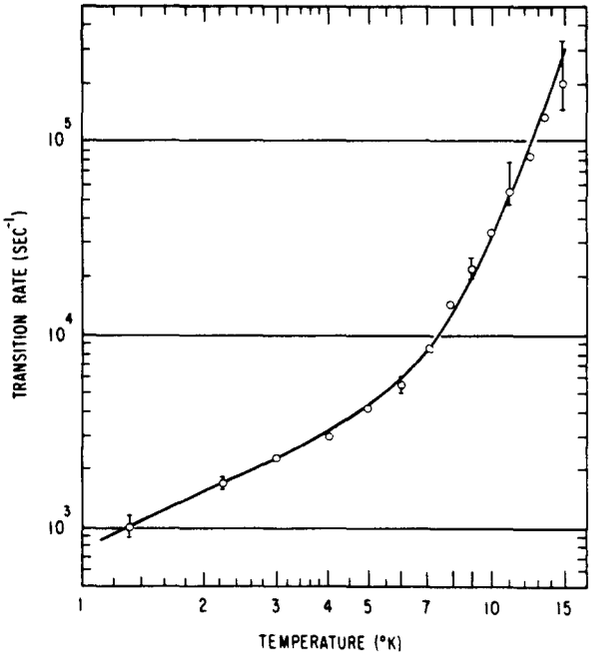

FIG. 2. Relaxation rate of OH^- impurities in RbBr as a function of temperature. The open circles are the data of Kapphan and Lüty. The solid line is a theoretical fit using $T_0 = 6.35°K$, $\omega_c/k_B = 67°K$.

The experimental data of Kapphan and Lüty for the relaxation of RbBr:OH are shown in Fig. 2, along with the best theoretical fit of the form $1/T_1 = \text{const.} \times F$. The values of the adjustable parameters are $T_0 = 6.35°K$, $\omega_c/k_B = 67°K$. The apparent T^4 behavior of $1/T_1$ for $T \gtrsim 7°K$ is, we believe, of no significance; in fact a curve of the form $1/T_1 = AT + BT^4$ does not give a good fit to the data. The low value of ω_c is somewhat disturbing; however the Debye temperature of RbBr is also rather low ($\theta_D = 130°K$ at $T = 50°K$, so that this value of ω_c is not too unreasonable.

In summary the calculation described above illustrates three major points: the importance of including multiphonon processes to all orders for $T \gtrsim T_0$, the temperature dependence of the renormalization of Δ_0, and the contribution of phonons near the zone boundary to high-order processes. The present calculation is much too crude to yield reliable information about the nature of the dipole–lattice coupling in paraelectrics. However, we believe that such

information could be gained from a careful study of the temperature dependence of the relaxation. In particular, a multiphonon calculation using a realsitic spectrum would be extremely enlightening.

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Wir entwickeln eine Theorie für die Temperaturabhängigkeit der Relaxations-rate paraelektrischer Verunreinigungen in Alkalihalogeniden. Dabei wird die Verunreinigung als ein Zweiniveausystem betrachtet, das linear an ein Phononenfeld angekoppelt ist. Wir berechnen die Relaxationsrate für eine beliebige Anzahl von Phononen unter Benutzung eines Debyespektrums für das Gitter. Die Resultate stimmen mit Experimenten von Kapphan and Lüty für die Relaxation von OH Verunreinigungen in RbBr gut überein.