

Phonon behavior and disorder mechanism in NaClO_3 [†]

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The dielectric constant of sodium chlorate has been analyzed on the basis of a Mason-Debye-type relaxation formula. A consistent description of the temperature dependence of the phonon structure and the dielectric-constant behavior as a function of frequency and temperature is obtained for this nonferroelectric order-disorder crystal. The fluctuation mechanism responsible for the dielectric relaxation behavior is identified as that of the apex reversal of the chlorate ion as one approaches the transition temperature.

INTRODUCTION

Recently,¹ the behavior of the dielectric constant of NaN_2 at low frequencies has been explained by using the Mason² theory of the relaxation process of dipolar polarization in the order-disorder crystals. In Ref. 1 it has also been established that the time-dependent statistics describing a self-diffusion process defined by a correlation time τ_c can account for dielectric-constant behavior at the ferroelectric-paraelectric phase transition. Mason's dipolar relaxation process is a simple Debye-type relaxation with a single dielectric relaxation time which is proportional to the static dielectric constant. In this model Mason essentially considers the jumping of the hydrogen nucleus in a "hydrogen bond" to be responsible for the ferroelectric effect of a rochelle salt. He assumes that the hydrogen nucleus is under a self-diffusion mechanism over a potential barrier ΔU between two minima separated by a distance δ , and the correlation time of jumping from one potential well to the other is given by $\tau = \tau_0 e^{\Delta U/RT}$, which defines the random character of the statistical behavior for the jumping particle. If there are particles jumping from one side to another, there is a population of particles in the potential well "plus" and there is a population in potential well "minus," being N_+ and N_- , respectively, the net dipole polarization being proportional to the difference between these two populations. The time-dependent statistical behavior of these particles depends on ΔU and on the temperature. This model describes the fluctuation mechanism essentially by the fact that a particle has a probability to take two equivalent positions along a direction. Mason's expressions for the dielectric constant (which is given in the next section) compared to one deduced by Debye³ has two additional parameters that are "microscopic": a factor which is a function of the distance δ , the separation between the potential wells, and ΔU , the activation energy. In his approach, Mason also considers that the dielectric-constant

behavior depends mainly on the variation of δ and ΔU as a function of temperature, and neglects the variation of all remaining lattice parameters.

The dielectric-constant behavior of NaClO_3 at low frequencies shows a Debye-type relaxation. This certainly is strong evidence that some disorder mechanism is involved in this crystal. So it seems very interesting to make an attempt to explain the dielectric-constant behavior of sodium chlorate using an approach similar to that used for NaN_2 . Taking Mason's approach as a framework, in this paper we try to give a consistent description for the temperature dependence of the phonon structure and for the dielectric-constant behavior of NaClO_3 at low frequencies by assuming a "correct" balance between the Lyddane-Sachs-Teller (LST) and Mason relaxation contributions to the dielectric constant. Under our assumptions for the thermal expansion of ΔU , it is possible to define NaClO_3 as an order-disorder crystal, though not a ferroelectric. Based on our assumptions, we suggest that the jumping particle in the double-well potential is the chlorine atom in the chlorate molecule and we predict the behavior of the dielectric constant of NaClO_3 as a function of frequency and temperature.

PREVIOUS WORK ON NaClO_3

The dielectric constant of sodium chlorate has been measured at 1 kHz, 1.6 MHz, and 10 GHz by Mason,⁴ Narayana Rao,⁵ and Rasmasastry and Ramaiah,⁶ respectively. At room temperature the reported values are 5.6, 5.7 and 4.6, respectively. Mason, and Rasmasastry and Ramaiah have also studied the temperature dependence of the dielectric constant of this crystal. The experimental data of the dielectric constant are shown as a function of temperature in Fig. 1. The difference between the low-frequency values and the high-frequency values of the dielectric constant in this crystal may not be attributed to its piezoelectric nature, since the piezoelectric resonances occurring at 100 kHz do not appreciably

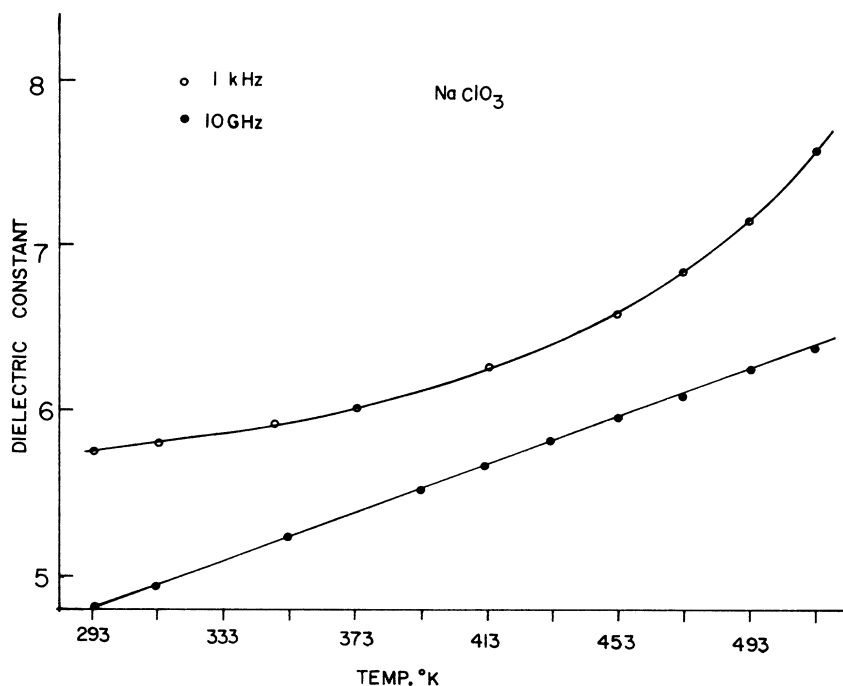


FIG. 1. Measured values of the dielectric constant of sodium chlorate at 1 kHz and 10 GHz from Ref. 5 and 7, respectively.

contribute to the dielectric constant because of the nature of the change of sign of ϵ' at resonance.⁴ This anomalous dispersion is usually found to be superimposed on a constant "background" value of the dielectric constant.

NaClO_3 is cubic, belongs to the $T^4(P2_13)$ space group, and has four formula units per primitive unit cell.⁷ The Raman spectrum of sodium chlorate has been studied by several workers and a review of this work can be found in Ref. 8. Sodium chlorate belongs to a noncentrosymmetric class. Hence, there are modes which are simultaneously Raman and infrared active. These polar modes split into longitudinal and transverse optic modes. The dielectric constant calculated from the generalized Lydanne-Sachs-Teller relation, by taking into account all the proper LO and TO phonons, explains the dielectric constant measured at optical frequencies but not the one at low frequencies. Recently, Dawson⁹ concluded from Raman measurements that there is no significant dielectric mechanism between the microwave and infrared regions. Apparently though, he has overlooked the low-frequency dielectric-constant measurements and the ϵ_{low} in his paper corresponds to the 10-GHz measurements. Hence the deviation of ϵ at low frequencies cannot be explained by phonons alone and there is an additional contribution to the dielectric constant.

The temperature dependence of the static dielectric constant is typical of that of a ferroelectric with an extrapolated Curie temperature of $T = 593^\circ\text{K}$.⁴ Mason has expressed the dielectric

constant of sodium chlorate at a frequency of 1 kHz as a function of temperature by the empirical relation

$$\epsilon = 4.7 + \frac{310}{(320 - \theta)} - \frac{6750}{(320 - \theta)^2}, \quad (1)$$

where θ is the temperature in degrees centigrade. The temperature-independent part is due to the electronic and ionic polarizabilities and the temperature-dependent part is due to changes in the orientation of the chlorate dipoles. Mason resorted to the above empirical equation for the dielectric constant because there was no treatment of the dielectric constant for temperatures below the transition temperature. For temperatures above room temperature, the dielectric constant can also be fitted to an equation of the type

$$\epsilon = 4.7 + \frac{245}{(375 - \theta)}. \quad (2)$$

In all of the above studies the actual microscopic mechanism responsible for the dielectric behavior has not been revealed. It is only known that as the temperature increases, the crystal becomes highly ionized, with the chlorate ions separating from the sodium ions for a large number of molecules.⁴ This would explain the melting of the crystal, but the actual mechanism causing the ferroelectriclike behavior with an extrapolated Curie temperature is not known. The present study is an attempt to provide such an additional insight into the fluctuation mechanism responsible for the dielectric behavior and the dipolar polarization.

THEORETICAL BACKGROUND

The frequency-dependent dielectric constant $\epsilon(\omega)$ is due mainly to the excitation of bound electrons, lattice vibrations, and dipolar orientations. At very low frequencies contributions from each of these three processes may be considerable. The manner of variation of the dielectric constant with frequency indicates which contributions are present. All three types of polarizations can be correlated to "oscillators" with specific eigenfrequencies and damping, and the eigenfrequencies of these oscillators play the essential role. The vibrational contribution can be more or less than the electronic contribution depending on the relative strengths of these oscillators.

The frequency dependence of the dielectric constant has been treated before based on molecular approach.^{3,10-12} The earliest and simplest correlation between dielectric constant and frequency is given by the Debye equation for the dielectric relaxation in polar liquids,

$$\epsilon(\omega) = \epsilon' - i\epsilon'' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau}, \quad (3)$$

where ϵ_{∞} is the high-frequency dielectric constant, ϵ_0 is the static dielectric constant, and τ is the relaxation time characteristic of the dielectric and is a function of temperature. By separating the real and imaginary parts, we get the well-known Debye equations, which describe the relaxation spectrum. The exponential decay factor, i. e., the relaxation time, is given by

$$\tau = \tau_0 e^{[\Delta U/kT]}, \quad (4)$$

where $\tau_0 = h/kT$ (according to Eyring's reaction-rate theory) and ΔU is the activation energy. This kind of behavior of τ is based on a model of a double-well potential for a dipole with two equilibrium positions, each corresponding to the axis being parallel or antiparallel to a specified direction. The activation energy ΔU corresponds roughly to the height of the potential barrier.

By assuming such a model, the dielectric constant in Mason's dielectric relaxation theory is given by

$$\epsilon(\omega) = \epsilon_0 + \frac{(4\pi A/\beta)[1 - (P_s/N\mu)^2]}{1 - A[1 - (P_s/N\mu)^2] + (i\omega h/kT) e^{\Delta U/kT} [\cosh(AP_s/N\mu)]^{-1}}. \quad (5)$$

Recently, Andrade and Porto¹³ have restudied the above expression, by taking the phonon contribution to the dielectric constant explicitly. Their equation is

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_j \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2} + \frac{(4\pi A/\beta)[1 - (P_s/N\mu)^2]}{1 - A[1 - (P_s/N\mu)^2] + (i\omega h/kT) e^{\Delta U/kT} [\cosh(AP_s/N\mu)]^{-1}}, \quad (6)$$

where $\epsilon_{\infty} = n^2$, the square of the index of refraction. P_s is the spontaneous polarization, $\beta = 4\pi/3$ for isotropic materials, μ is the dipole moment, and A is the parameter defined by

$$A = \frac{(e^*)^2 \delta^2 N \beta}{(1 - \beta\gamma) kT}, \quad (7)$$

where δ is the separation between the potential minima, N is the number of dipoles per cm³, γ is the polarizability per unit volume due to all dipoles, and e^* is the effective charge. The first two terms on the right-hand side are the contribution of the ordered system to the dielectric constant and the last term represents the effect of the internal random motion of particles. ΔU , the activation energy, approaches zero as the separation between the potential minima goes to zero and hence A tends to zero. In this situation, the contribution from the third term in Eq. (6) is negligible and we have a perfect harmonic lattice which can be described by the LST relation. So, whenever a self-diffusion process describing a double-well disorder mechanism is present, one needs to consider the

correct balance between the LST relation and the relaxation contributions to the dielectric constant.

In the absence of spontaneous polarization, i. e., in the nonferroelectric state, we have

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_j \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2} + \frac{(4\pi A/\beta)}{(1 - A) + (i\omega h/kT) e^{(\Delta U/kT)}} \quad (8)$$

since for $P_s = 0$, $\cosh[AP_s/N\mu] = 1$. Hence the contribution from the internal random motion of particles is evident even in the absence of spontaneous polarization. The real part of Eq. (8) is

$$\text{Re } \epsilon(\omega) = \epsilon_{\infty} + \sum_j \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2} + \frac{(4\pi A/\beta)(1 - A)}{(1 - A)^2 + (\omega^2 h^2/k^2 T^2) e^{2\Delta U/kT}}. \quad (9)$$

The three terms in Eq. (9) arise from the electronic, phonon, and relaxation contributions to the dielectric constant.

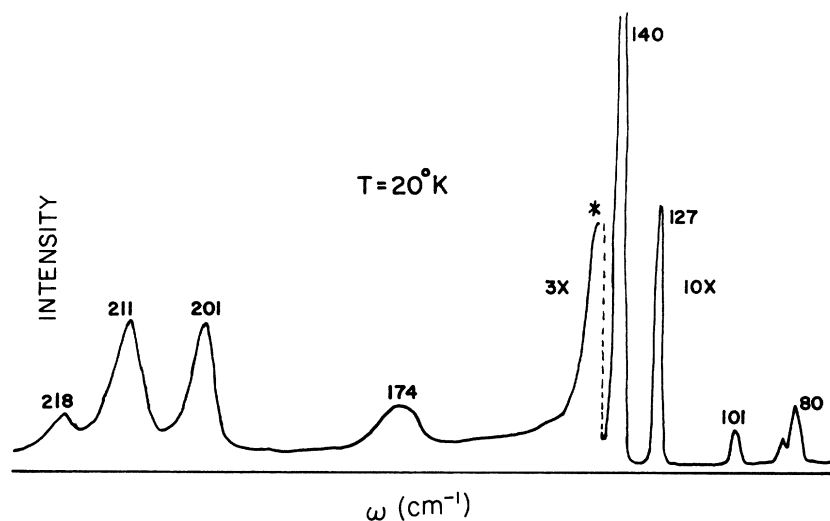


FIG. 2. Raman spectrum of sodium chlorate in the external-mode region at $T=20^\circ\text{K}$ for the geometry $Z(YZ)Y$. The asterisk indicates change of scale and scanning speed.

RESULTS

In order to fit the dielectric constant to Eq. (9), one has to know all the frequencies of the longitudinal and transverse optic modes and also ΔU , the activation energy. The room-temperature Raman spectrum of sodium chlorate has been intensively studied by Hartwig *et al.*¹⁴ However, all the expected 14 modes with F symmetry could not be observed at room temperature. Miller and Khanna¹⁵ have examined the spectrum at 77°K and could identify the missing modes. However, the previously unobserved modes at 143, 178, and 202 cm^{-1} were still very weak even at liquid-nitrogen temperature. They have not reported any extensive measurements at other temperatures. We have examined the spectrum at 20°K and resolved the spectrum completely. The $F(\text{TO})$ spectrum of sodium chlorate at 20°K for the geometry $Z(YZ)Y$ is given in Fig. 2. The temperature behavior of the missing mode region is shown in Fig. 3; this figure indicates that the modes which are well resolved at low temperature become broader and merge together at higher temperatures. We believe that these modes become so broad at about 250°K that our instruments cannot resolve them. The temperature behavior of all the modes is given in Fig. 4.

The activation energy ΔU was calculated on the assumption that ΔU changes with the temperature in the same way as the Raman frequency of libration of the chlorate dipoles does. This is consistent with the calculations of Yamada *et al.*,¹⁶ who assumed that ΔU for NaNO_2 changes with temperature in the same way as the Raman frequency ω_2 of the libration of the NO_2 dipole does between 437 and 473°K , which was later extended to temperatures below the transition temperatures also by Andrade *et al.*¹ The reorientational frequency

of the chlorate dipoles is identified as 131 cm^{-1} at room temperature.

The temperature dependence of the phonon frequency can be fitted to an equation of the type

$$\omega_2 = [1 + \gamma' (T_\lambda - T)] \omega_0, \quad (10)$$

where $\gamma' = 2.98 \times 10^{-4}$, $\omega_0 = 113\text{ cm}^{-1}$, and $T_\lambda = 520^\circ\text{K}$. ω_0 and T_λ were chosen as the limiting experimental values for ω and T which are close to the melting temperature of the crystal ($T_M = 537^\circ\text{K}$). With these two arbitrary values the parameter γ' is fitted.

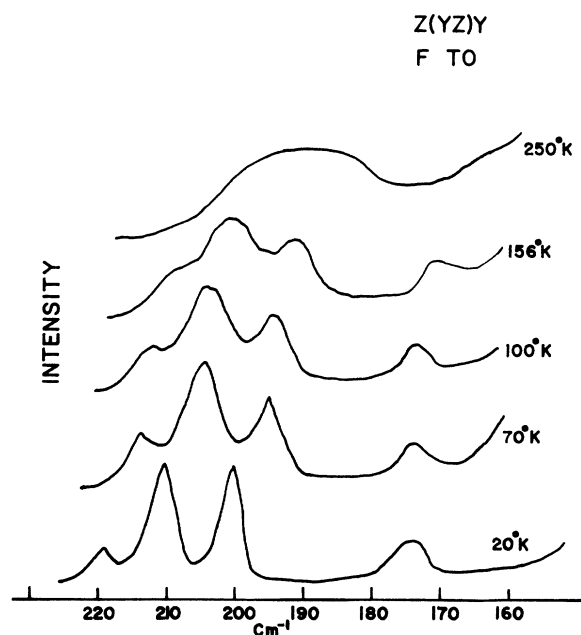


FIG. 3. Temperature dependence of the modes at 174, 201, 211, and 218 cm^{-1} .

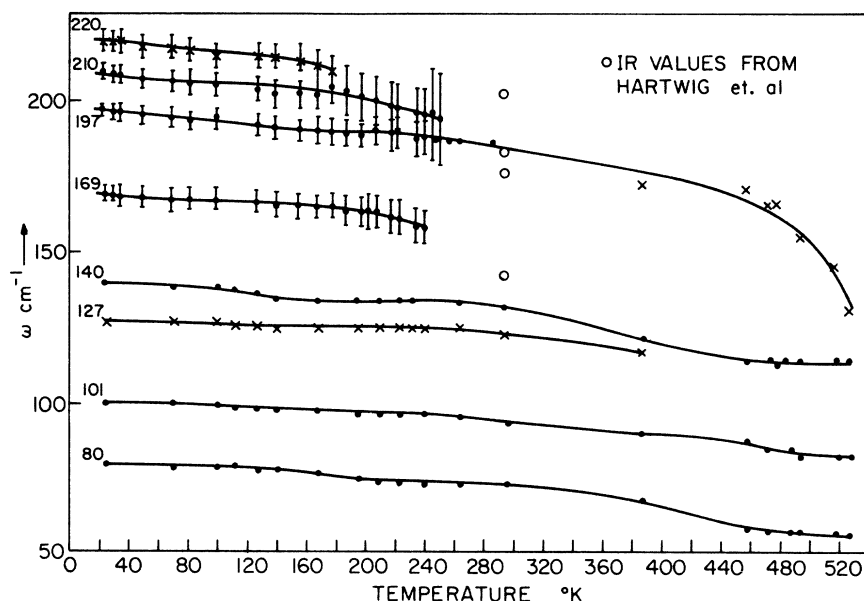


FIG. 4. Temperature dependence of $8 F(TO)$ modes in the external-mode region. The bars refer to the half-widths of the modes at 174, 201, 211, and 218 cm^{-1} .

If the rate of molecular transition is given by a correlation time τ_c described by Eq. (4), one expects that the linewidth Γ of the mode associated with the jumping particle is also a function of τ_c . Typical expressions for spectral densities which describe relaxation processes can be found in Refs. 17 and 18; the experimental data for the linewidth Γ suggest that the linewidth for the mode ω_2 can be fitted to an expression similar to that of the linewidth of the B_1 mode of NaNO_2 :

$$\Gamma = (a + bT) + c \left[\frac{\tau_c}{1 + \omega_2^2 \tau_c^2} \right], \quad (11)$$

where $\tau_c = \tau_0 e^{d\omega_2/kT}$ and $a = 1.98 \text{ cm}^{-1}$, $b = 2.3 \times 10^{-2} \text{ cm}^{-1} \text{ }^\circ\text{K}^{-1}$, $c = 2.9 \times 10^4$, $d = 177.5 \text{ J cm sec}$. The experimental values of ω_2 and Γ at various temperatures fitted to Eqs. (10) and (11), respectively, are shown in Fig. 5.

By assuming that the activation energy ΔU changes in the same way as the libration mode ω_2 ($\Delta U = d\omega_2$), the dielectric-constant values of sodium chlorate have been fitted to Eq. (9) for frequencies $\omega = 1 \text{ kHz}$ and 10 GHz , with A as a variable. There will be one value of A for a given temperature. So, all through the temperature range a set of values of A can be generated. From these values of A , the separation between the potential minima can be calculated from Eq. (7), where for NaClO_3 ,

$$N = 1.424 \times 10^{22} \text{ dipoles/cm}^3,$$

$$V = 2.808 \times 10^{-22} \text{ cm}^3,$$

γ can be calculated from the equation, and

$$\frac{4\pi\gamma}{3} = \frac{(\epsilon_0 - 1)}{3 + 3\beta(\epsilon_0 - 1)/4\pi} \text{ with } \epsilon_0 = 2.25. \quad (12)$$

The values of A and δ thus obtained are plotted in Fig. 6 as a function of temperature. The room-temperature value of $\delta/2$, 0.55 \AA , agrees well with the value, 0.48 \AA , from the x-ray data,⁷ which corresponds to the distance of a chlorine atom above the plane of the oxygen atoms. In Fig. 7 the activation energy ΔU and the inverse of the relaxation time τ_c^{-1} are plotted as a function of temperature. The behavior of ΔU and τ_c^{-1} are consistent with Eqs. (10) and (11). For low enough temperatures, we expect that the linewidth of this libration mode ω_2 to be proportional to temperature and at a certain temperature, when the disorder mechanism becomes predominant, we expect the linewidth to increase exponentially in the same way as the inverse of the correlation time. For sodium

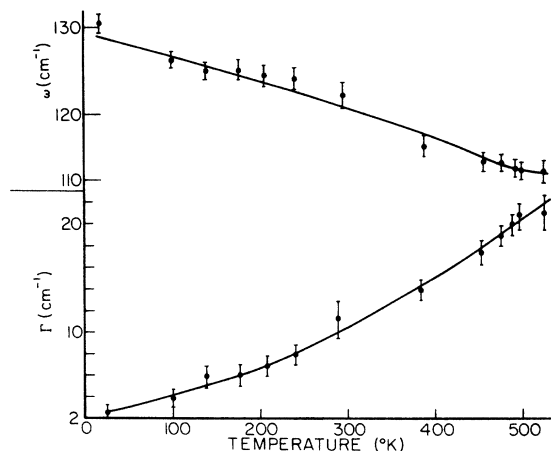


FIG. 5. Frequency and the linewidth of the libration mode ω_2 as a function of temperature.

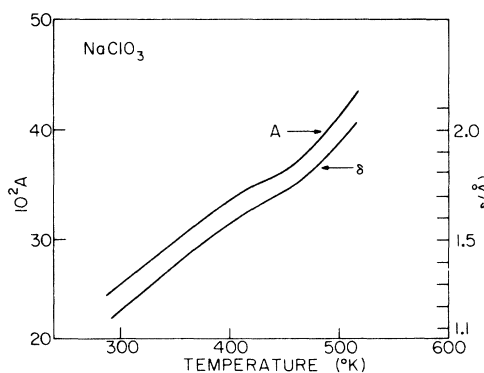


FIG. 6. Parameter A and the potential-well separation δ as a function of temperature.

chlorate this disorder sets in at around 250°K . This will explain the merging of the three modes in Fig. 3. In Fig. 8 the dielectric constant calculated from Eq. (9) for various frequencies is plotted as a function of temperature (curves 2 to 6). The experimental values of curves 2 and 6 agree very well with the theoretical curve. Knowing the variation of A with temperature, the variation of dielectric constant with frequency can be predicted. In Figs. 9 and 10 the real and imaginary values of the dielectric constant as functions of frequency are plotted for various temperatures.

DISCUSSION AND CONCLUSION

NaClO_3 is usually not considered to be an order-disorder crystal. However a Debye-like shape on the experimental data of the dielectric constant at low frequency strongly indicates that there is some disorder mechanism present. Our principal aim using Mason's approach concerning dielectric relaxation in solids was to obtain a possible identification of the particle which is under a self-diffusion process in sodium chlorate. We have attempted it by assuming a "correct" balance between Lyddane-Sachs-Teller and Mason-Debye contributions to the dielectric constant. A relaxation process implies the existence of an "off-resonance phenomenon" whose contribution to the dielectric constant is given by the third term of Eq. (8). Further, if $\Delta U \neq 0$, the A factor and consequently the distance δ are nonzero.

If the crystal is ordered (in the sense that there are no random particles present) it is expected that the phonon contribution can account fully for the behavior of the dielectric constant as a function of frequency and temperature. However, for a disordered crystal the thermal expansion of the activation energy affects the statistical behavior of the jumping particles. If the height of the potential well does not go to zero, one expects that the vibration frequency of this random particle

does not go to zero either. We have labeled the limiting value of this frequency at a temperature where ΔU_0 reaches roughly its nonzero lowest value as the hard-core frequency.

Under our assumption that the activation energy follows the behavior of the frequency of the libration mode it was possible to fit the experimental data of the dielectric constant of NaClO_3 with Eq. (9). We have taken the libration mode because, as is well known, a libration can be described by a Langevin equation^{17,19} which is in fact a definition for a random force.²⁰ So, a libration inherently has a random process involved which favors it to be "naturally" connected with the behavior of random particles under a relaxation process. In this way it was possible to predict the behavior of the dielectric constant as a function of frequency and temperature for a large range of temperatures. Assuming our approach is legitimate, we have identified the chlorine atom in the chlorate molecule as the particle under a self-diffusion process in a double-well potential. This may be responsible for the relaxation behavior of the dielectric constant of sodium chlorate. From the fitting between the experimental data with Eq. (9), we were able to determine the disorder distance δ . In this way this method can be a complementary tool to the crystallographic techniques. Depending on the correlation times involved, it is possible that sometimes crystallographic techniques give only an average structure for a crystal. From these fittings, we were also able to predict the behavior of the dielectric relaxation time as a function of temperature (Fig. 7).

Essentially, our approach¹ implies that the behavior of the frequency and of the linewidth of the

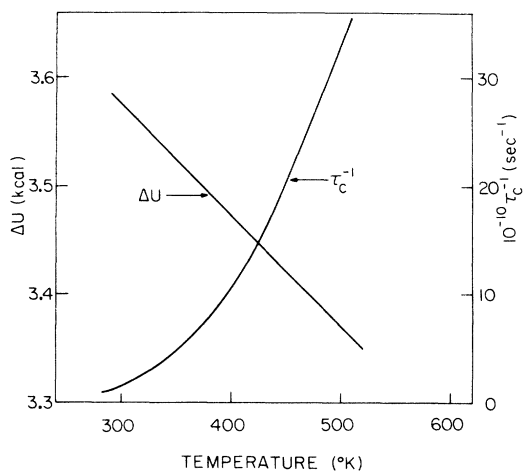


FIG. 7. Activation energy ΔU and the inverse of the relaxation time as a function of temperature.

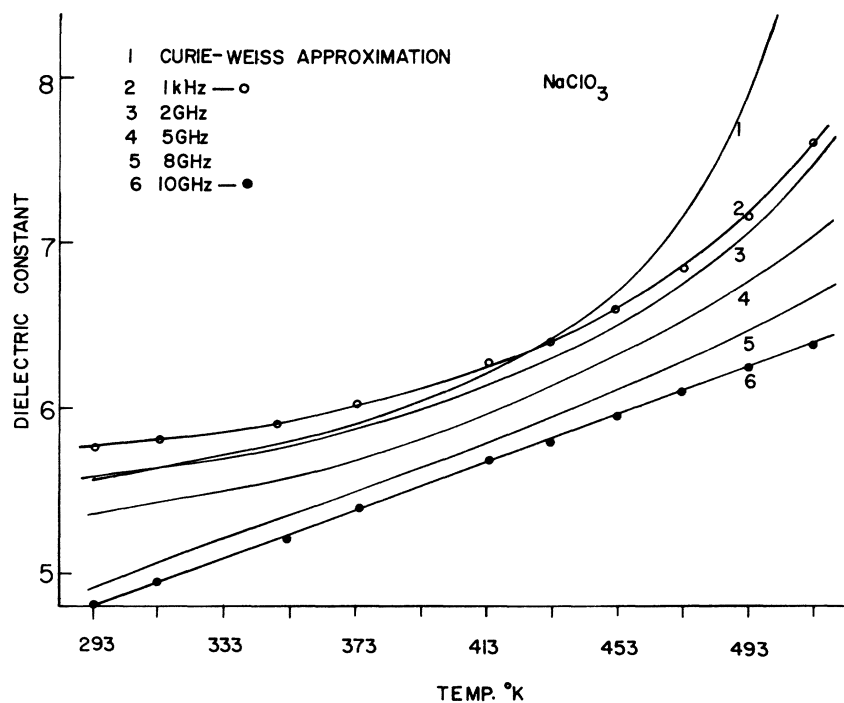


FIG. 8. Dielectric constant of sodium chlorate with temperature, fitted to Eq. (9). The circles are the measured values. The curves are the theoretical fit.

“disorder” mode is a function of the activation energy and of the correlation time, respectively.

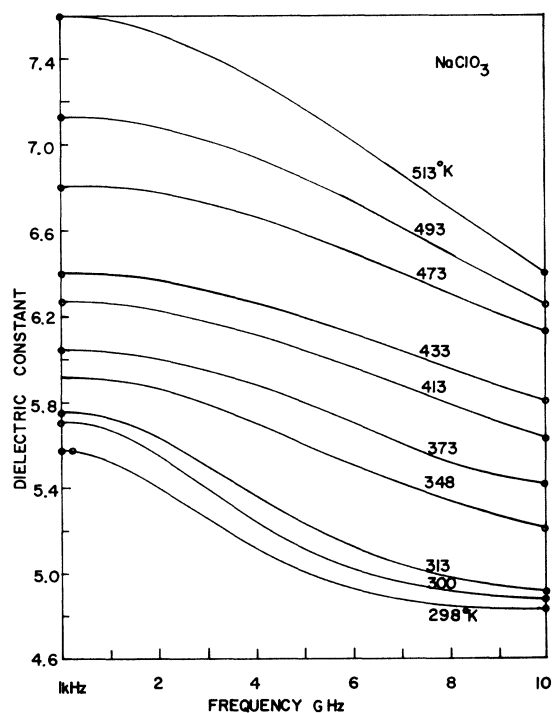


FIG. 9. Predicted values of the real part of the dielectric constant as a function of frequency, for various temperatures. The circles correspond to the experimental data referred to in the text.

Equations (10) and (11) define a consistent dependence between the second and third terms of Eq. (8).

Our measurements of the linewidth of the libration mode as a function of temperature seem to indicate that for order-disorder crystals one must measure those linewidths always for a large range of temperatures. The linewidth shows a slight bend around room temperature that would not be observed if the temperature range was short. Besides, the shape of the linewidth as a function of temperature will tell us which phonon is associated with the disorder mechanism [Eq. (11)].

It is interesting to note that the behavior of the dielectric constant of NaClO_3 as a function of tem-

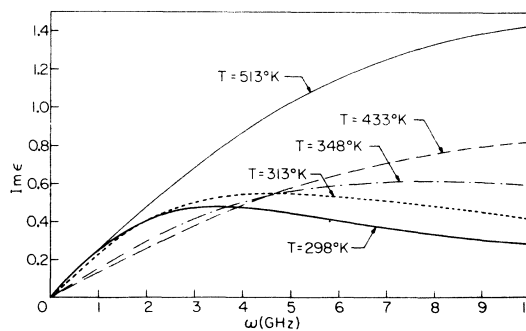


FIG. 10. Predicted values of the imaginary part of the dielectric constant as a function of frequency, for various temperatures.

perature follows very closely the behavior of the dielectric constant of rochelle salt for temperatures before the first transition temperature at -18°C .² Both behaviors can be explained by Eq. (8).

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