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Temperature-induced orientational disorder in $NaClO_3$

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A detailed study of the temperature dependence of ^{35}Cl nuclear quadrupole spin-lattice relaxation time and resonance frequency, in a wide temperature range (77–450 K), is used to discuss old controversial conclusions about the experimental behavior of low frequency dielectric permittivity, Raman spectroscopy, and nuclear quadrupole resonance, in sodium chlorate. Compatibility among experimental data coming from all these techniques is achieved by assuming a continuous transition of the ClO_3^- ion dynamics from vibrating around an equilibrium position for $T<250$ K, to exchanging between two orientations at higher temperatures. That is, the pseudoharmonic single well potential, that determines the chlorate ion dynamics at lower temperatures, mutates continuously with increasing temperature, to reach a symmetric two-well potential for temperatures higher than 380 K. In the intermediate-temperature range the behavior of NQR parameters are explained in terms of scattering of phonons by a distribution of disordered chlorate ions. We use the Green function formalism for calculating the corrections to the spin-lattice relaxation time and the resonance frequency due to disorder. [S0163-1829(98)00529-3]

I. INTRODUCTION

Crystalline sodium chlorate has been studied extensively by a variety of techniques and many of its physical properties have been characterized. However, some inconsistencies concerning the molecular dynamics of the chlorate ions remain unexplained.

Sodium chlorate is a paraelectric material but the temperature dependence of the low-frequency dielectric permittivity $\epsilon(T)$ resembles one of a ferroelectric system approaching an order-disorder transition[1] with a Curie temperature $T_C \sim 593$ K greater than its fusion temperature ($T_F=537$ K). This temperature dependence of $\epsilon(T)$ is assigned to the reorientation of the chlorate ions. Since at high temperatures the crystal is in a highly ionized state, then chlorate ions could undergo a cooperative behavior that is characteristic of ferroelectric systems. Based on a Mason-Debye[2] model for the dielectric relaxation, this crystal was classified as a nonferroelectric order-disorder system.

The width of a low-frequency phonon ($\omega=130\ \mathrm{cm}^{-1}$), as measured by Raman spectroscopy,[2] increases exponentially with temperature. This fact indicates that the dielectric response of the crystal is being perturbed by some kind of motion (of the chlorate ions), different than the lattice vibrations. To account for both the dielectric relaxation mechanism and the exponential broadening of a libration phonon, Prasad Rao *et al.*[2] propose that the ^{35}Cl atom inverts its position in the chlorate ion, therefore jumping in a symmetric double well potential. The relaxation time associated to this jump is $\tau=\tau_0 e^{(E_a/k_B T)}$ with E_a the activation energy (height of the barrier) of the double well. $E_a=20.7$ kJ/mol from their experiment.

In a previous work on ^{35}Cl NQR in a series of chlorate salts,[3] the temperature dependence of the NQR spin-lattice relaxation time of sodium chlorate also showed an occurrence of a relaxation mechanism different than lattice vibrations. This behavior was ascribed to the modulation of the electric field gradient (EFG) at the resonant nuclei site, due to the neighboring chlorate ions rotation about their threefold axis. Such a mechanism is completely different than the one proposed in Refs. 1 and 2.

With the aim of disentangling this controversy, in this work we present a detailed experimental study of the temperature dependence of ^{35}Cl NQR frequency $\nu_Q(T)$ and spin-lattice relaxation time $T_1(T)$ in an extended temperature range 77–450 K. Our experimental data also reflect the occurrence of an additional mechanism, in agreement with previous experimental information. We discuss our experiments in terms of a model involving reorientation of chlorate ions in an asymmetric potential. We propose that for temperatures below 250 K the chlorine atom vibrates around the equilibrium position compatible with the crystalline symmetry. As the temperature increases, the potential well develops a second, unstable equilibrium position that allows the threefold axis of the pyramidal ion to perform 180° rotations. In this way, some degree of orientational disorder appears. The usual expressions for $T_1(T)$ and $\nu_Q(T)$ due to lattice vibrations cannot describe the experimental behavior. Then, we write a correction to the NQR parameters due to scattering of phonons in a weakly disordered lattice. The obtained expression, which is valid for low concentrations of disordered ions, accounts for data within the range $250<T<350$ K. For higher temperatures the depth of the second potential well increases and the probability of finding the ion axis rotated respect to its equilibrium orientation also grows. Near 400 K a symmetric two-well potential is established, and the crystal becomes totally disordered.

II. EXPERIMENT

A. Apparatus and techniques

Polycrystalline samples of $NaClO_3$ were prepared by recrystallization of the commercial Merck Co. product from a saturated solution with tridistilled water. The water evaporation rate was regulated to get crystallite sizes of about a millimeter. The sample was packed in a 12 mm diameter and 20 mm long PTFE cylindrical sample holder.

We used a pulsed, broadband and fully computer controlled, home-made NQR spectrometer. It is equipped with a PTS 310 frequency synthesizer, a Kalmus LP 1000 power transmitter, and a Doty LN-2L signal preamplifier. Data acquisition was made with a Thurlby 625 digitizer. Phase cycling of the rf and quadrature detection were available. The control and automatic measurement computer program was developed in our laboratory.

The temperature of the sample was stabilized better than 0.1 K in the whole range. The probehead was located inside a temperature controlled thermal bath. The home-made temperature control device, covering the range 80–450 K, consists of four coaxial and partially insulated copper cylinders immersed in a cooling bath (liquid nitrogen for temperatures lower than room temperature and preheated oil for higher temperatures). The temperature control was effectively achieved by heating inner cylinders with electronically driven heaters. Cu-constant on thermocouples and Fluke Mod. 510 chopper amplifiers give input voltage to proportional temperature regulation.

The resonance frequency, defined as the center of the corresponding spectrum, was measured by fast Fourier transform of the NQR free induction decay (FID). The spin-lattice relaxation time was measured at each temperature in (carefully checked) resonance peak saturation condition. Measurements of T_1 were made by the standard two-pulse sequence $(\pi/2-\tau-\pi/2)$; the delay time between pulses varying from 1 ms to $5T_1$. T_1 values were obtained by fitting the expression

$$S(\tau)=S_0\left[1-a\exp\left(-\frac{\tau}{T_1}\right)\right]$$

which relates the amplitude of the sample response $S(\tau)$ at the irradiation frequency (Fourier transform from the FID after the second pulse) to the delay time τ. Each fit of $S(\tau)$ involved a set of 20 to 32 experimental data points. All the measurements here reported were performed going up in temperature and then confirmed lowering the temperature.

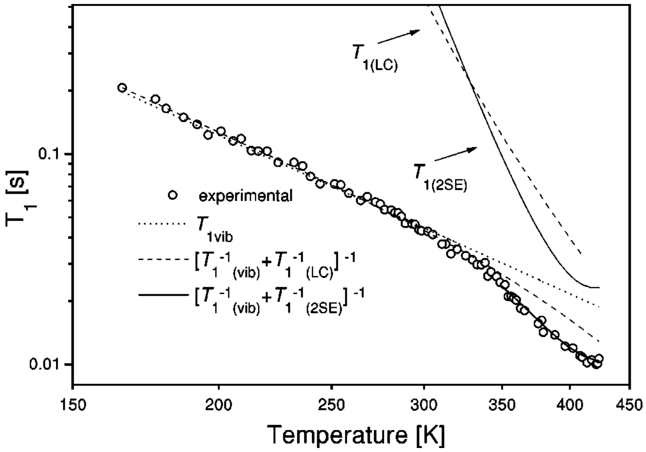

FIG. 1. Temperature dependence of the spin-lattice relaxation time $T_1(T)$ and the fitting curves from different models for relaxation.

B. Spin-lattice relaxation time

Figure 1 shows the measured $T_1(T)$ in an extended temperature range. At low temperatures, $165\ \mathrm{K}<T<250\ \mathrm{K}$, a power law fits to T_1 data:[4]

$$T_{1\mathrm{vib}}^{-1}=AT^{\lambda}, \tag{1}$$

with $A=1.7\times10^{-8}\ \mathrm{s}^{-1}$ and $\lambda=2.46$. This temperature dependence is typical of relaxation mechanisms due to fluctuations of the lattice vibrations related with the anharmonicity of the crystal field and with pseudoharmonic processes (such as first order phonon-phonon Raman processes).[5] It is worth pointing out that this value of λ, noticeably greater than 2, indicates a certain degree of anharmonicity of the lattice potential.[6] Equation (1) gives the dotted curve in Fig. 1. For temperatures higher than 300 K, the experimental data clearly fall below this curve. More precisely, data dispersion about Eq. (1) shows that near 250 K the vibrational model alone cannot explain the experimental trend. The difference between the experimental data and the lower temperature fit becomes resolutely exponential. The data can be fitted by adding an exponential term to the relaxation mechanism driven by vibrational fluctuations:

$$T_1^{-1}=T_{1\mathrm{vib}}^{-1}+Be^{-U/T}, \tag{2}$$

with $B=82\pm8\ \mathrm{s}^{-1}$ and $U=26.4\pm1$ kJ/mol.

The data follow this trend (long dash curve of Fig. 1) for $T\leqslant340$ K. An exponential temperature dependence such as this one cannot be related to vibrational processes (neither quasiharmonic nor anharmonic).[4–6] It is worth remarking that this second mechanism becomes appreciable in $T_1(T)$ for the same temperature range where a low-frequency phonon is anomaly broadened.[2] For temperatures higher than 340 K there is a further drop in T_1, and for $T\sim440$ K, a minimum in $T_1(T)$ is suggested by the data. Due to the poor S/N ratio T_1 could not be measured for higher temperatures.

C. ^{35}Cl NQR frequency

Figure 2 shows the experimental temperature dependence of the peak frequency. This smooth behavior indicates that

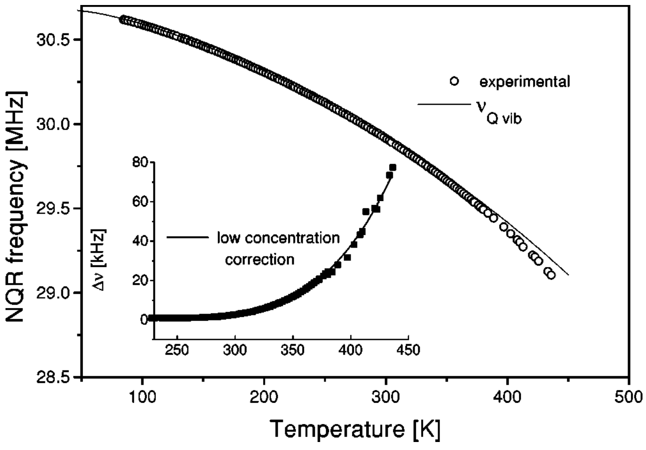

FIG. 2. Experimental ^{35}Cl $\nu_Q(T)$ behavior of NaClO$_3$. Full line represents the fit with Eq. (4). A noticeable departure from the vibrational model is observed in the high-temperature region. The window shows the exponential behavior of $\Delta\nu_Q(T)$ for $T>245$ K.

no first order phase transition occurs in the studied temperature range. The line is narrow and Lorentzian shaped, of 0.8 kHz width, for $T<380$ K. The only anomaly we observed for $T>400$ K is the occurrence of a low-amplitude, broad background but the narrow central line remains always observable.

In absence of phase transitions ν_Q is temperature dependent because (i) the local EFG q at the ^{35}Cl resonant nuclei site, is time averaged by molecular fluctuations and (ii) the mean square amplitude $\langle \theta^2 \rangle$ of the angular displacement of the maximum principal axis of the EFG relative to its equilibrium direction, is also temperature dependent.[7] The corresponding expression for the temperature dependence of ν_Q is given by

$$\nu_Q(T) = \frac{e^2 Q}{2h} q_0 \left(1 - \frac{3}{2} \langle \theta^2 \rangle \right), \tag{3}$$

where Q is the nuclear quadrupole moment and q_0 is the ensemble average EFG at the nuclear sites, at a reference temperature.

A simplified form for $\nu_Q(T)$ due to lattice vibrations in the quasiharmonic approximation is given by[10]

$$\nu_Q(T)_{\mathrm{vib}} = \nu_0(1-\beta T) \times \left[1 - \frac{P}{\omega_0(1-gT)} \coth\left(\frac{\hbar \omega_0 (1-gT)}{2k_B T} \right) \right], \tag{4}$$

with ν_0 the frequency of a hypothetical rigid lattice at $T=0^0$ K, P a fitting parameter representing the sum over the vibration modes over the whole Brillouin zone, ω_0 an average mode frequency, g the linear coefficient giving the phonon frequency shift due to the lattice anharmonicity, and β the correction to ν_0 due to thermal expansion.[8,9]

Equation (4) can be fitted to our experimental data within the restricted temperature range $80<T<245$ K. The fitting parameters are $\nu_0 = 30867$ kHz, $P/\omega_0 = 7.12\times10^{-3}$, $g = 4.6\times10^{-4}$ K^{-1}, $\omega_0 = 69$ cm^{-1}, and $\beta = 4\times10^{-5}$ K^{-1}.

A noticeable departure from this trend occurs in the higher-temperature region. The window in Fig. 2 shows the frequency difference $\Delta\nu_Q(T)$ between experimental data and Eq. (4). A better fit of the temperature dependence is obtained by adding an exponential term as follows:

$$\nu_Q(T) = \nu_Q(T)_{\mathrm{vib}} + C e^{-U/T}. \tag{5}$$

The best fit yields the parameters: $C = 5\times10^4$ s^{-1} and $U = (26.7\pm0.1)$ kJ/mol. Notice the similarity of the U values in both $\nu(T)$ and $T_1(T)$ experiments.

III. DISCUSSION

A. Fitting to standard models

It is well known that an exponential behavior in the NQR variables $\nu_Q(T)$ and $T_1(T)$ is neither related to quasiharmonic lattice vibrations,[10] nor to anharmonicity.[6] That is, phonons alone cannot account for such behavior. It instead is generally assigned[10] to thermally activated molecular reorientation or to hindered rotations of the whole molecule or a part of it. The chlorate ion is a highly symmetric molecular group; it is a flat trigonal pyramid with three oxygen atoms on its base and a chlorine atom at the remaining vertex. In NaClO$_3$, exponential behaviors in $\nu_Q(T)$ and $T_1(T)$ such as those of Eqs. (2) and (5) could in principle be associated with (i) hindered rotations of the oxygen atoms about the z axis perpendicular to the oxygen plane, as suggested in Ref. 3 or (ii) chlorate ion reorientation about an axis contained in the oxygen plane, as suggested in Refs. 1 and 2. The rotation of oxygen atoms does not affect directly the electric field gradient at the site of the resonant nuclei (top of the pyramid) but could modulate the EFG at the Cl sites of neighboring ions.[3] Therefore this mechanism could conceivably contribute to $T_1(T)$. However, this kind of motion alone cannot explain Raman and $\epsilon(T)$ measurements from Refs. 1 and 2, since it has no influence on the electric dipole moment of the chlorate ion. The contribution to the NQR spin-lattice relaxation time predicted by a model for the intermolecular EFG modulation is[4]

$$T_{1\mathrm{mod}}^{-1} = \frac{2}{3} \frac{\omega_Q^2 \tau_c}{(1+\omega_Q^2 \tau_c^2)} \left(\frac{q'}{q} \right)^2, \tag{6}$$

with the correlation time $\tau_c = \tau_0 e^{\mathcal{U}/T}$, $\tau_0 = h/k_B T$, $\mathcal{U}$ the activation energy of the reorientation (in the present case, the barrier in the three well potential), and q'/q the ratio of the EFG at the resonant nucleus produced by the neighboring group motion to the principal z component of the EFG tensor of the molecular ion.

Accordingly, if molecular vibrations and intermolecular EFG modulation are considered as independent processes, then

$$\frac{1}{T_1} = \frac{1}{T_{1\mathrm{vib}}} + \frac{1}{T_{1\mathrm{mod}}}, \tag{7}$$

with $T_{1\mathrm{vib}}^{-1}$ from Eq. (1) and $T_{1\mathrm{mod}}^{-1}$, from Eq. (6). The former expression gives a curve having qualitative similarity with data and the best fit parameters are

$$\begin{gathered} \omega_Q \tau_0 = 1.3\times10^{-4}, \\ \mathcal{U} = 36.6 \ \ \mathrm{kJ/mol}, \\ q'/q = 2.5\times10^{-5}. \end{gathered} \tag{8}$$

The first parameter is consistent with the values of ν_0 [from Eq. (4)] and τ_0. The fitted $\mathcal{U}$ is a reasonable value for this kind of motions.[10] On the contrary, the expected value for (q'/q) ranges[4] from 10^{-1} to 10^{-2}. The fitted value is several orders of magnitude smaller. The extremely low fitted value is meaningless: if modulation were so effective in making the EFG more symmetric, no NQR signal should be observed. Then, even when this model provides a function of temperature that can be fitted to data, the obtained parameters are not acceptable for explaining the experimental behavior. Because this rotation cannot be identified as the cause of the temperature behavior of the dielectric permittivity constant either, we conclude that this motion alone is not responsible for the observed experimental trends.

We now consider the second proposition: chlorate ion rotation about an axis contained in the oxygen plane. When dealing with the temperature dependence of NQR variables of a system of nuclei subject to a random two site exchange

(2SE)—as this problem appears to be—the transition probability per unit time between energy levels p and q of an unperturbed Hamiltonian $\mathcal{H}_0$, due to a time-dependent perturbation is[11]

$$W_{pq}=\frac{2\tau_c|v_{pq}|^2}{1+\omega_{pq}^2\tau_c^2}, \tag{9}$$

with $|v_{pq}|$ the matrix elements of the perturbation in the basis of $\mathcal{H}_0$.

The former approach is based on the assumption that the time dependence of the spin Hamiltonian can be represented by a function of time $f(t)$ that randomly exchanges between two values

$$\mathcal{H}(t)=\mathcal{H}_0+f(t)\mathcal{H}_1.$$

The probability that $f(t)$ retains its initial value after a time t is $P(t)=e^{-t/\tau_c}$ and $\langle f(t)\rangle=0$. Therefore, the nucleus is presumed to spend, in the average, the same time at each site. This picture is then equivalent to the double well potential model proposed by Prasad Rao *et al.*[2] for explaining Raman experiments.

In the particular case of spin-3/2 nuclei the contribution to relaxation due to reorientation is[11]

$$\frac{1}{T_1}^{(2\mathrm{SE})}=\sum_{pq}W_{pq}=4\tau_c\frac{BB^*+CC^*}{(1+\omega_Q^2\tau_c^2)}, \tag{10}$$

where B and C are the off-diagonal elements of the perturbation Hamiltonian $\mathcal{H}_1$ and τ_c has the same definition as in Eq. (6). Considering molecular vibrations and reorientations as independent relaxation mechanisms, we analyzed $T_1(T)$ data with

$$\frac{1}{T_1}=\frac{1}{T_{1\mathrm{vib}}}+\frac{1}{T_{1(2\mathrm{SE})}}. \tag{11}$$

Equation (10) has the same temperature dependence as Eq. (6), therefore the fitting parameters are the same shown in Eq. (8) but one of them has a different meaning. The fitted activation energy is noticeably greater than the value of 26 kJ/mol reported in Ref. 2 and assigned to the height of the two well potential barrier.

Although the symmetric double well potential model could explain the ferroelectriclike behavior of $\epsilon(T)$ (Ref. 1) and the anomalies in the Raman spectrum,[2] some contradictions should be pointed out. If chlorate ions fluctuated in symmetric potentials, the probabilities of occupying either equilibrium position should be the same (because the transition probabilities from one well to the other would be equal). Raising the temperature would just shorten the lifetime in each well (or increase the reorientation frequency). The two-site exchange model would suggest that the system is in a completely disordered state in the sense that the chlorate ion can either point the direction compatible with the crystal symmetry or the opposite one with the same probability. To our knowledge no such kind of disorder has been reported by crystallographic studies (at least for the crystal phase attainable in the temperature range studied here).

Concerning NQR resonance frequency, within the 2SE model,[11] one should expect ν_Q to be shifted from its value at very long correlation times in a quantity

$$\Delta\nu_Q=\frac{\omega_Q\tau_c^2}{\pi}\frac{BB^*+CC^*}{(1+\omega_Q^2\tau_c^2)}. \tag{12}$$

Using the parameters from the fitting curve to $T_1(T)$ data, we obtain $\Delta\nu_Q<50$ Hz in the whole temperature range, while the measured frequency shift ranges up to 100 kHz (about three orders of magnitude greater), as shown in Fig. 2. In addition, $\nu_Q(T)$ data do not follow the trend predicted by Eq. (12) either.

Within this model, and using the fitted activation energy $\mathcal{U}$ for calculating the correlation time, one sees that τ_c ranges from 1 s at 150 K to 10^{-8} s near 450 K. Then $\tau_c>1/\omega_Q$ in the whole temperature range, that is, reorientations would not be very frequent within the time scale of the NQR experiment. Under this condition one could consider that the disorder in orientations is static, within the time scale provided by our NQR experiment. Accordingly, for very low reorientation rates, i.e., $T<250$ K in this experiment, one should expect an inhomogeneously broadened NQR spectrum or eventually a splitting of the line corresponding to the inequivalent positions of the resonant nuclei. However, no such features were detected here.

Besides this, notice that though in the limit of long correlation times, Eq. (10) becomes $1/T_1\propto\exp(-\mathcal{U}/T)$, the value of $\mathcal{U}$ that fits data in the higher-temperature range must be drastically *decreased* to get a good fit for lower temperatures. This means that Eq. (2) cannot be considered as the long correlation time-limit of Eq. (10). Summarizing, the symmetric two-well potential model for the chlorate ion reorientation predicts a temperature dependence of both the NQR frequency and the line shape which are very different from the experimental results.

B. The asymmetric two-well model

We work out an alternative explanation that removes the contradictions commented above. Let us now propose that the reorientation of the three fold axis of the chlorate ion occurs in an *asymmetric* local potential. The chlorate ion axis can attain a stable equilibrium orientation (let us call it $\mathcal{A}$) compatible with the crystal symmetry and an unstable equilibrium orientation $\mathcal{B}$, 180° opposite to the one suggested by the site symmetry. In such a way, it spends a much longer time in the stable equilibrium orientation than in the other.

We can make an analogy with a two level magnetic system by identifying the chlorate ion with a spin 1/2 variable in an external magnetic field. At low temperatures the equilibrium population of the lower energy level is much greater than the upper level population and it is possible to describe this situation in terms of a concentration C of disordered ions, defined as the ratio of the population of disordered ions to the total number of them. For sufficiently low temperatures this concentration is

$$C(T)\cong\frac{P(\mathcal{B})}{P(\mathcal{A})}=e^{(E_{\mathcal{A}}-E_{\mathcal{B}})/T}\equiv e^{-E/T}.$$

If the disordered ions are homogeneously distributed through the sample, all the local configurations compatible with the equilibrium populations are equally probable and the system takes one or another at random. The lifetime of each particular configuration is short or at least much shorter than the lifetime of a given ion in its stable orientation. Then all the measured equilibrium quantities are configurational averages, over all configurations compatible with a given concentration of homogeneously disordered ions.

Now we make an estimate of the effect that such a distribution of disordered ions has on the temperature dependence of the NQR parameters. Disorder alters the rotational dynamics of the chlorate ion and hence the mean square displacement $\langle \theta^2 \rangle$ of Eq. (4). It also has influence on T_1 through the autocorrelation functions $\langle \theta(t)\theta^* \rangle$ and $\langle \theta^2(t)\theta^{2*} \rangle$.[4,6] As a first approximation, we can consider the effect of disorder as independent of the normal vibrations of the lattice. The main difference between our proposal and the others mentioned above is that here we just account for the *indirect* effect of disorder in the EFG averaging. It is not the *direct* effect of reorientations but the change in the EFG averaging due to a perturbation in the phonons of the lattice.

At this stage we can identify the problem of a distribution of orientationally disordered ions with the one of a distribution of defects or impurities. The consequence of perturbing the perfect, harmonic lattice with this kind of impurities is the broadening of the phonons,[12] which amounts in a change in the EFG averaging and in the fluctuation spectrum.

By expressing $\theta(t)$ in terms of phonon operators[6] we can relate the Fourier transform of the time correlation function of the angular displacements to Green's functions. The main effects of the disorder on the NQR parameters comes through the perturbation of the rotational motions of the chlorate ion. For the sake of simplicity we assume that the angular displacement coincides with a molecular-rotation coordinate of the chlorate. We also suppose that the vibrational dynamics of the chlorate ion can be well described in terms of a harmonic lattice. According to this assumption, we can directly write

$$\mathcal{F}\{\langle \theta(t)\theta^* \rangle\} = -\frac{2}{1-e^{\beta\hbar\omega}} \mathrm{Im}\ G_r^R(\omega)\ , \tag{13}$$

where Im $G_r^R(\omega)$ is the imaginary part of the retarded Green function of the harmonic torsional oscillator. Since we assume low concentration (LC) of disordered ions, we can use a perturbative method for calculating $G_r^R(\omega)$. The Green's function for a perturbed crystal satisfies the Dyson equation, relating it with the ordered crystal Green's function $G_r^o(\omega)$. Neglecting any explicit influence among impurities, $G_r(\omega)$ can be approximated by a perturbative expansion, keeping up to linear terms in the concentration of impurities:[12]

$$\langle G_r(\omega) \rangle = G_r^o(\omega) + C(T) \sum_i G_r^o(\omega)\mathbf{t}^i(\omega) G_r^o(\omega), \tag{14}$$

where the brackets mean the configurational average before stated and $\mathbf{t}^i(\omega)$ is the matrix representing the local distortion due to the ith defect. In this picture each impurity can be thought as a lattice-wave scatterer.

Within the present approximations, the mean quadratic angular displacement can be calculated as[12]

$$\langle \theta^2 \rangle = \langle \theta^2 \rangle_o + C(T) \int_0^\infty \coth(\beta\omega) F_r(\omega)\, d\omega, \tag{15}$$

with $C(T)$ the concentration of ions in state $\mathcal{B}$, and

$$F_r(\omega) \equiv -\frac{\hbar}{\pi} \mathrm{Im}\ G_r^o(\omega)\mathbf{t}^i(\omega) G_r^o(\omega),$$

where $G_r^o(\omega)$ is the Green's function of the ordered crystal, associated with the rotational molecular coordinate of the molecular group bearing the resonant nucleus. The dynamics of the whole crystal and hence the collective character of the phenomenon, is introduced through the Green's functions. In our case the distortion affects the constants of force of the interaction with the disordered neighbors. In the case where the distortion is not too large, the integral of Eq. (15) depends smoothly on temperature, the temperature dependence of the second term being mainly given by the concentration. Then, the difference between $\nu_Q(T)$ of the disordered lattice and the one of a perfect harmonic lattice has a temperature dependence given by

$$\Delta \nu_Q(T) = \nu_0 [\langle \theta^2 \rangle - \langle \theta^2 \rangle_0] \propto e^{(-E/T)}. \tag{16}$$

with E the energy difference between the bottom of the stable potential well and the unstable one. Notice that here E is *not* an activation energy. Identifying E with parameter U of Eq. (5) we see that the experimental trend of $\nu_Q(T)$ coincides with that of Eq. (16) *in the whole temperature range*, as shown in the window of Fig. 2.

In order to calculate the influence of disorder on $T_1(T)$, we analyze the effect of disorder on the Fourier transforms of the time correlation functions $\langle \theta(t)\theta^* \rangle$ and $\langle \theta^2(t)\theta^{2*} \rangle$, involved in the final expression of T_1.[6] Now we parallel our problem with the calculation of the phonon broadening due to a distribution of mass impurities in a perfect harmonic crystal by Lovesey.[13] Here, the impurities are related to changes in the force constants instead of masses. As expected, for low concentrations of impurities, the obtained phonon broadening is again proportional to the concentration. Considering that in this limit the four-phonon time correlation function can also be put in terms of the two-phonon one,[14] finally, the temperature dependence of the correction to $T_1(T)$ due to the orientational disorder can be expressed concisely as

$$T_{1\,(\mathrm{LC})}^{-1} = B e^{(-E/T)} \tag{17}$$

with B a parameter that depends on the specific features of the crystal lattice and the distribution of defects. Then, the temperature dependence associated to lattice vibrations and ion reorientations is given by Eq. (2).

Equation (2) can account for the exponential behavior of the relaxation time in the intermediate-temperature region, but fails in describing $T_1(T)$ for higher temperatures. Still it is consistent with the picture of an asymmetric potential in the lower-temperature region. At higher temperatures the torque restoring the chlorate ion to its equilibrium position becomes looser and the potential well might change its shape and turn more symmetric. In that limit the random two site exchange model could give a good approximation, as it is also compatible with the occurrence of a broadened spectrum.

The solid line fitting data of Fig. 1 is the curve provided by the 2SE mechanism, which, according to our analysis, would be valid for temperatures higher than 380 K. The dashed and the solid lines above data represent the individual contributions from the two models: low-concentration of impurities $T_{1\,(\mathrm{LC})}(T)$ and symmetric two-well potential $T_{1(2\mathrm{SE})}(T)$; each one dominates relaxation in a different temperature range. We propose that the dynamics of the chlorate ion is changing with temperature from the asymmetric well to the symmetric two-well regime. In this paper we have just described two limiting situations: low concentration of ‘‘impurities’’ and complete disorder (symmetric two-well potential); the intermediate states cannot be described as the superposition of the other two because they might not be considered as independent mechanisms.

Summarizing, the picture proposed in this work is consistent with the available experimental data. The occurrence of thermally activated processes involving the chlorate ions was confirmed. Unlike previous works, we found that a simple model of a symmetric two-well potential for representing this process in the whole temperature range is not adequate. Instead, we proposed that the orientational potential undergoes a progressive transformation, as the temperature is raised, going from an anharmonic potential for low temperatures, towards a double well potential for high temperatures. In the intermediate range, for $280\ \mathrm{K} < T < 340\ \mathrm{K}$, the phonons of the ordered lattice are scattered by a homogeneous distribution of disordered ions. For increasing temperatures, also the disorder increases, and a simple model that considers phonons and molecular reorientations as independent processes cannot account for the data. The experimental trend described above is consistent with the idea that the chlorate ions might become rotationally free and could show a cooperative effect and hence a dielectric Curie point—in agreement with the behavior of $\epsilon(T)$ (Ref. 1)—as if the crystal were approaching to an order-disorder transition.

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