# On the polarizability of tunneling defects

**G. A. Andreev, V. I. Tal'yanskiĭ, and V. M. Faĭn**
*Institute of Solid State Physics, U.S.S.R. Academy of Sciences*

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It is shown that dispersion of the nonlinear susceptibility of dielectrics should exist in association with relaxation processes. A specific system, lithium impurity ions in a KCl crystal, is investigated theoretically and experimentally. It is shown that the experimental results can be explained if relaxation processes are taken into account.

## 1. INTRODUCTION

In studies of the polarizability of dielectrics it is customary to distinguish a dynamic subsystem (DS) that interacts with a dissipative subsystem to establish thermodynamic equilibrium. Speaking generally, this equilibrium is established at a rate which is characterized by several relaxation times that can be divided roughly into two classes. The first class contains "longitudinal" (or energetic) relaxation times that describe the relaxation of the populations (diagonal elements of the density matrix. A longitudinal relaxation time is conventionally denoted by $T_1$. The second class contains transverse relaxation times, which determine the relaxation of off-diagonal elements in the density matrix of the DS, or the classical mean "dephasing" time of the oscillator corresponding to a given transition. A transverse relaxation time is conventionally denoted by $T_2$.

It is easily seen that the linear characteristics of a system (the dielectric or magnetic susceptibilities) can in general[1)] be used to determine only the transverse relaxation times. In some cases, on the basis of theoretical considerations $T_1$ can be determined when $T_2$ is known. However, a direct experimental determination of $T_1$ is generally possible with the aid of nonlinear experiments. For example, in paramagnetic resonance $T_1$ can be measured with the aid of the saturation effect.

In the present work it will be shown that low-frequency dispersion of nonlinear susceptibilities exists in association with longitudinal relaxation, and this dispersion will be investigated both theoretically and experimentally for a specific system.

The existence of this dispersion can be understood from simple considerations. Let $T_1$ be the relaxation time of the dynamic subsystem of present interest. In an external field of frequency $\omega \ll T_1^{-1}$ the DS is characterized by isothermal susceptibility. If $\omega \gg T_1^{-1}$ the interaction with the dissipative subsystem can be neglected and the susceptibility is determined by the equations of motion of the DS. In this case the state of the DS is not described by a definite temperature. We can expect the isothermal susceptibility to differ from the susceptibility of an isolated system. In general, however, this difference appears only in the nonlinear susceptibility (NS) of the DS. Indeed, let us consider polarization of the DS in the two limiting cases $\omega \gg T_1^{-1}$ and $\omega \ll T_1^{-1}$ and let $\omega \ll \omega_0$ ($\omega_0$ is the characteristic resonance frequency of the DS). The polarization can then be represented by

$$P = \sum_i n_i p_i,$$

where $n_i$ is the population of the i-th energy level and $p_i$ is the polarization of the system on the i-th level.

Since $\omega \ll \omega_0$, $p_i$ is independent of $\omega$, but the populations $n_i$ will depend on $\omega$. Indeed, if DS is nonlinear its spectrum depends on the electric field (the Stark effect). If then $\omega \ll T_1^{-1}$ the populations at each instant will be determined by the spectrum of the DS, which depends, in turn, on the instantaneous strength of the electric field. If $\omega \gg T_1^{-1}$ the populations will not "succeed in following" the changing spectrum and will equal their thermodynamic equilibrium values in the absence of the field. In a sufficiently weak field we can write

$$p_i = p_i^{(0)} + p_i^{(1)} + p_i^{(2)} + p_i^{(3)} + \ldots, \qquad n_i = n_i^{(0)} + n_i^{(1)} + n_i^{(2)} + n_i^{(3)} + \ldots,$$

$$P^{(1)} = \sum_i (p_i^{(1)} n_i^{(0)} + p_i^{(0)} n_i^{(1)}),$$

$$P^{(2)} = \sum_i (p_i^{(2)} n_i^{(0)} + p_i^{(1)} n_i^{(1)} + p_i^{(0)} n_i^{(2)}),$$

$$P^{(3)} = \sum_i (p_i^{(3)} n_i^{(0)} + p_i^{(2)} n_i^{(1)} + p_i^{(1)} n_i^{(2)} + p_i^{(0)} n_i^{(3)}).$$

Here the indices in parentheses label quantities that are proportional to the corresponding powers of the field. In most cases of practical interest the system possesses a center of inversion and experiences a quadratic Stark effect. Then

$$p_i^{(0)} = p_i^{(2)} = n_i^{(1)} = 0$$

$$P^{(1)} = \sum_i p_i^{(1)} n_i^{(0)}, \qquad P^{(2)} = 0,$$

$$P^{(3)} = \sum_i (p_i^{(3)} n_i^{(0)} + p_i^{(1)} n_i^{(2)})$$

when $\omega \gg T_1^{-1}$ we have $n_i^{(2)} = 0$. When $\omega \ll T_1^{-1}$, however, $n_i^{(2)} \neq 0$ and it is determined by the instantaneous electric field strength. Thus the nonlinear susceptibility (NS) differs in these two cases, i.e., relaxational dispersion of the NS exists. When $\omega \sim T_1^{-1}$, the NS depends on $T_1$.

In some cases relaxational dispersion of the linear susceptibility is possible (at frequencies $\omega \ll \omega_0$). For this effect the nonvanishing of $p_i^{(0)}$ and $n_i^{(1)}$ is required (see also footnote 1). This is possible, for example, in the presence of an external static field, or in ferroelectrics below the transition point, as mentioned in[1].

The remainder of the present paper is devoted to a theoretical and experimental investigation of tunneling lithium impurity ions in a KCl crystal. This system was selected because of its anomalously high NS.[2,3] In Sec. 2 the NS is calculated in the approximation of weak coupling between the tunneling ions and acoustic phonons playing the role of a dissipative subsystem. In Sec. 3 it is shown how relaxation can be taken into account phenomenologically, and the theory is compared with experiment. In Sec. 4 the experimental procedure is described.

## 2. RIGOROUS CALCULATION

Lithium ions that are substituted for potassium ions in a KCl crystal have eight equilibrium positions along the [111] directions. At sufficiently low temperatures the lithium ions tunnel between their equilibrium positions.[4] We shall hereafter consider, as is customary, a one-dimensional model in which the ion motion is described with the aid of its effective spin. The spin interacts with the lattice phonons, which play the role of a dissipative subsystem. The Hamiltonian is[5]

$$H=\Delta S_z+\sum_{\mathbf{q}}\omega_{\mathbf{q}}a_{\mathbf{q}}^{+}a_{\mathbf{q}}+iS_x\sum_{\mathbf{q}}W_{\mathbf{q}}(a_{\mathbf{q}}-a_{\mathbf{q}}^{+})-2\mu ES_x, \qquad (2.1)$$

where $\Delta$ is the energy of tunnel splitting, $\omega_q$ denotes the phonon frequencies, $W_q$ is a quantity determining the interaction of the spin with a phonon of wave number q, E is the external field, and $\mu$ is the dipole moment of the ion; for the Planck constant we let $\hbar = 1$. The equations of motion derived from (2.1) are

$$\dot{S}_x=-\Delta\dot{S}_y, \qquad \dot{S}_z=iS_y\sum_{\mathbf{q}}W_{\mathbf{q}}(a_{\mathbf{q}}-a_{\mathbf{q}}^{+})-2\mu ES_y,$$

$$\dot{S}_y=\Delta S_x-iS_z\sum_{\mathbf{q}}W_{\mathbf{q}}(a_{\mathbf{q}}-a_{\mathbf{q}}^{+})+2\mu ES_z, \qquad (2.2)$$

$$\dot{a}_{\mathbf{q}}=-i\omega_{\mathbf{q}}-W_{\mathbf{q}}S_x.$$

In the approximation of weak spin-phonon coupling ($W_q$ is a small parameter), from the operator equations (2.2) we derive equations for the mean quantities $S_i \equiv \langle S_i \rangle$ and $G_i \equiv \langle S_i a_q \rangle$:

$$\ddot{S}_x+\Delta^2S_x=i\Delta\sum_{\mathbf{q}}W_{\mathbf{q}}(G_3-G_3^{*})-2\mu E\Delta S_z, \qquad (2.3)$$

$$\dot{S}_z=i\sum_{\mathbf{q}}W_{\mathbf{q}}(G_2-G_2^{*})+\dot{S}_x\frac{2\mu E}{\Delta}, \qquad (2.4)$$

$$\dot{G}_1=-\Delta G_2-i\omega_{\mathbf{q}}G_1-{}^1/_4W_{\mathbf{q}}, \qquad (2.5)$$

$$\dot{G}_2=\Delta G_1+iW_{\mathbf{q}}S_z(n_{\mathbf{q}}+{}^1/_2)-i\omega_{\mathbf{q}}G_2+2\mu EG_3, \qquad (2.6)$$

$$\dot{G}_3=-iW_{\mathbf{q}}S_y(n_{\mathbf{q}}+{}^1/_2)-2\mu EG_2-i\omega_{\mathbf{q}}G_3. \qquad (2.7)$$

Here $n_q = \langle a_q^{+} a_q \rangle = [\exp(\omega_q/kT) - 1]^{-1}$ denotes equilibrium phonon numbers and $\omega_q = \omega_q - i\alpha$; in the final result $\alpha \to +0$.

We must obtain the linear susceptibility $\chi^{(1)}(\omega_i)$ and the nonlinear susceptibility $\chi^{(3)}(\omega_i, \omega_j, \omega_k)$ that determine the ionic polarization:

$$2\mu S_x=\chi^{(1)}(\omega_i)E(\omega_i)\exp\{i\omega_it\}$$
$$+\chi^{(3)}(\omega_i,\omega_j,\omega_k)E(\omega_i)E(\omega_j)E(\omega_k)\exp\{i(\omega_i+\omega_j+\omega_k)t\}.$$

For this purpose we shall solve (2.3)—(2.7) to order $E^3$. In the absence of a field (E = 0), from (2.6) we obtain

$$G_2^{(0)}=-\frac{W_{\mathbf{q}}[\Delta/4+\omega_{\mathbf{q}}S_z^{(0)}(n_{\mathbf{q}}+{}^1/_2)]}{\Delta^2-\omega_{\mathbf{q}}^2}. \qquad (2.8)$$

Inserting (2.8) into (2.4), in the limit $\alpha \to +0$ we obtain

$$S_z^{(0)}=-\frac{1}{4(n_{\mathbf{q}}+{}^1/_2)|_{\omega_{\mathbf{q}}=\Delta}}=-\frac{1}{2}\frac{e^{\Delta/kT}-1}{e^{\Delta/kT}+1}, \qquad (2.9)$$

i.e., when the interaction with phonons is taken into account we arrive at a correct equilibrium value of the difference between the populations.

Solving (2.3)—(2.7) accurately to the first power of the field, we obtain

$$\chi^{(1)}(\omega)=-4\mu^2\Delta(S_z^{(0)}+\delta S_z^{(0)})/[\Delta^2-\omega^2-\omega R(\omega)]; \qquad (2.10)$$

$$R(\omega)=R'(\omega)+iR''(\omega), \qquad R'(\omega)=-R'(-\omega)$$
$$=\sum_{\mathbf{q}}W_{\mathbf{q}}^2(n_{\mathbf{q}}+{}^1/_2)\left(\frac{1}{\omega_{\mathbf{q}}-\omega}-\frac{1}{\omega_{\mathbf{q}}+\omega}\right),$$
$$R''(\omega)=R''(-\omega)=\pi\sum_{\mathbf{q}}W_{\mathbf{q}}^2\left(n_{\mathbf{q}}+\frac{1}{2}\right)[\delta(\omega_{\mathbf{q}}-\omega)+\delta(\omega_{\mathbf{q}}+\omega)], \qquad (2.11)$$

$$\delta S_z^{(0)}=-\sum_{\mathbf{q}}W_{\mathbf{q}}^2\left[\frac{\Delta}{4}+\omega_{\mathbf{q}}S_z^{(0)}\left(n_{\mathbf{q}}+\frac{1}{2}\right)\right]\cdot$$
$$\cdot\frac{1}{\Delta^2-\omega_{\mathbf{q}}^2}\left(\frac{1}{\omega_{\mathbf{q}}-\omega}+\frac{1}{\omega_{\mathbf{q}}^{*}+\omega}\right).$$

In the weak-coupling approximation we have $\delta S_Z^{(0)} \ll S_Z^{(0)}$ and this quantity may be neglected. Hereafter we shall neglect corrections of this type. $R'(\omega)$ determines the frequency shift that accompanies the interaction with the dissipative subsystem; $R''(\omega)$ determines the lines widths and energy dissipation. The solution of (2.3)—(2.7) to the third power of the field yields

$$\chi^{(3)}(\omega_1,\omega_2,\omega_3)=-\frac{16\mu^4\omega_1S_z^{(0)}\Delta}{[\Delta^2-\omega_1^2-\omega_1R(\omega_1)]AB}-\frac{16\mu^4\Delta C(\omega_1,\omega_2)}{AB} \qquad (2.12)$$

where

$$A=[\Delta^2-(\omega_1+\omega_2+\omega_3)^2-(\omega_1+\omega_2+\omega_3)R(\omega_1+\omega_2+\omega_3)],$$
$$B=[\omega_1+\omega_2+{}^1/_2R(\omega_1+\omega_2-\Delta)+{}^1/_2R(\omega_1+\omega_2+\Delta)],$$
$$C(\omega_1,\omega_2)=C'(\omega_1,\omega_2)+C''(\omega_1,\omega_2),$$

$$C'(\omega_1,\omega_2)=\sum_{\mathbf{q}}W_{\mathbf{q}}^2\frac{\Delta/4+\omega_{\mathbf{q}}S_z^{(0)}(n_{\mathbf{q}}+{}^1/_2)}{\Delta^2-\omega_{\mathbf{q}}^2}$$
$$\times\left\{\frac{\omega_1+\omega_2-\omega_{\mathbf{q}}}{[\Delta^2-(\omega_1+\omega_2-\omega_{\mathbf{q}})^2](\omega_{\mathbf{q}}-\omega_1)}+\frac{\omega_1+\omega_2+\omega_{\mathbf{q}}}{[\Delta^2-(\omega_1+\omega_2+\omega_{\mathbf{q}})^2](\omega_{\mathbf{q}}+\omega_1)}\right\}$$

$$C''(\omega_1,\omega_2)=R''(\Delta-\omega_1-\omega_2)\frac{f(\Delta-\omega_1-\omega_2)}{\Delta-\omega_2}$$
$$+R''(\Delta+\omega_1+\omega_2)\frac{f(\Delta+\omega_1+\omega_2)}{\Delta+\omega_2}+R''(\omega_1)f(\omega_1)\frac{2\omega_2}{\Delta^2-\omega_2^2},$$

$$f(x)=[\Delta/4+xS_z^{(0)}(n_x+{}^1/_2)]/2(\Delta^2-x^2)(n_x+{}^1/_2).$$

Before considering certain special cases, we shall briefly outline the calculation of $R''(\omega)$, which determines the dispersion of the susceptibility. For the case of interaction with acoustic phonons, in the Debye model of lattice vibrations the state density can be written as $D(\omega_q) = 9N(\omega_q/\omega_D)^2$ and $W_q$ can be equated to $(2W_0\omega_q\omega_D/3N)^{1/2}$.[5] Here N is the number of lattice nodes, $\omega_D$ is the Debye frequency, and $W_0$ is the interaction parameter. From (2.11) we obtain

$$R''(\omega)=3\pi W_0\left(\frac{\omega}{\omega_D}\right)^2\omega\frac{e^{\hbar\omega/kT}+1}{e^{\hbar\omega/kT}-1}$$

In the case of practical interest with $\hbar\omega \ll kT$ we have

$$R''(\omega)=6\pi W_0\left(\frac{\omega}{\omega_D}\right)^2\frac{kT}{\hbar}.$$

We shall now analyze the expression derived for $\chi^{(3)}$. At field frequencies $\omega \ll R''(\Delta)$ we have

$$\chi^{(3)}(\omega_1,\omega_2,\omega_3)=-\frac{8\mu^4}{\Delta^3}\left[S_z^{(0)}+\Delta\frac{\partial S_z^{(0)}}{\partial\Delta}\right]=\frac{4\mu^4}{\Delta^3}\left[\frac{\beta\Delta}{\mathrm{ch}^2(\beta\Delta)}-\mathrm{th}(\beta\Delta)\right].$$

Here $\beta = 1/2kT$. In this case $\chi^{(3)}$ describes the isothermal susceptibility of the system, as can be shown by a direct calculation. On the other hand, at frequencies $\Delta \gg \omega\, R''(\Delta)$ we have

$$\chi^{(3)}(\omega,\omega,\omega)=-4\mu^4\,\mathrm{th}(\beta\Delta)/\Delta^3$$

which describes the response of an isolated system. In the intermediate frequency region the NS depends on the frequency. In this region the frequency dependence of the NS depends on the properties of the dissipative system and on the character of its interaction with the DS, and can be determined from (2.12). It should be noted that $\chi^{(3)}(\omega_i, \omega_j, \omega_k)$ will be frequency-dependent if

$\omega_i + \omega_j + \omega_k \sim R$. This can even occur if $|\omega_i|$, $|\omega_j|$, and $|\omega_k| \gg R$.

## 3. PHENOMENOLOGICAL TREATMENT. COMPARISON WITH EXPERIMENT

In Sec. 2 the relaxation processes were taken into account rigorously. However the derived equations hold true only for the case of weak coupling between the impurity ions and phonons. To explain the experimental results it is also necessary to determine the response of the system in the case of strong coupling. This can be accomplished by a phenomenological description of the relaxation using the relaxation time. This nonrigorous procedure is justified by the fact that its results agree with the rigorous calculation in the limiting cases of high and low frequencies of the field. This approach also accounts reasonably for the experimental results and yields relaxation rates in agreement with those obtained by other authors.[6] We shall assume that the relaxation leads to thermodynamic values of the effective spin components at a given instantaneous electric field strength (the method of Mandel'shtam and Leontovich[7]). Also, following[6], we assume that the rates of longitudinal and transverse relaxation coincide, i.e., $T_1 = T_2 \equiv \Gamma^{-1}$. Then the equations of motion with relaxation terms added become

$$\begin{aligned} \dot S_x &= -\Delta\hbar^{-1}S_y - (S_x - \langle S_x\rangle)\Gamma, \\ \dot S_y &= \Delta\hbar^{-1}S_x + 2\mu h^{-1}ES_z - S_y\Gamma, \\ \dot S_z &= -2\mu h^{-1}ES_y - (S_z - \langle S_z\rangle)\Gamma. \end{aligned} \tag{3.1}$$

Here

$$\langle S_z\rangle = \frac{1}{2}\frac{\Delta}{W}\operatorname{th}(\beta W), \qquad \langle S_x\rangle = \frac{\mu E \operatorname{th}(\beta W)}{2W}$$
$$W = \sqrt{\Delta^2 + (2\mu E)^2}, \qquad \beta = 1/2kT.$$

If $\Gamma \gg \Delta/\hbar$, only the relaxation terms are important in the equations of motion. In this case the equations will describe the behavior of an ion having two equilibrium positions separated by a potential barrier. The polarizability will be relaxational in character. In the presence of an external field one of the equilibrium positions will be preferred and polarization will be established accordingly by thermal "flipovers" of ions above the barrier; the rate of this process is characterized by $\Gamma$. If $\Delta/\hbar \gg \Gamma$ a particle tunnels from one equilibrium position to the other and polarization does not require thermal flipovers, i.e., it is of dynamical character. In this case $\Gamma$ determines the line widths and lifetimes of excited states of individual lithium ions.

Solving (3.1) to the third power of the field, we obtain the linear and nonlinear susceptibilities of the system (calculated for a single ion):

$$\chi^{(1)}(\omega) = 2\mu^2\frac{\operatorname{th}(\beta\Delta)}{\Delta}\frac{\omega_0^2 + \Gamma(i\omega+\Gamma)}{D_\omega}, \tag{3.2}$$

$$\chi^{(3)}(\omega,\omega,\omega) = 4\mu^4\left\{\frac{-2i\omega\omega_0\operatorname{th}(\beta\Delta)}{\hbar^3 D_{3\omega}D_\omega(2i\omega+\Gamma)} + \frac{\Gamma\varphi(\beta\Delta)[\omega_0^2 + (3i\omega+\Gamma)(2i\omega+\Gamma)]}{\Delta^3 D_{3\omega}(2i\omega+\Gamma)}\right\}. \tag{3.3}$$

Here

$$D_\omega = [\omega_0^2 + (i\omega+\Gamma)^2], \quad \varphi(\beta\Delta) = \beta\Delta/\operatorname{ch}^2(\beta\Delta) - \operatorname{th}(\beta\Delta), \quad \omega_0 = \Delta/\hbar.$$

When $\beta\Delta \ll 1$ we have $\varphi \approx -2/3(\beta\Delta)^3$.

The first term inside the curly brackets of (3.3) describes $\chi^{(3)}$ when $\Gamma \ll \omega$, and the second term when $\Gamma \gg \omega$. (In both limiting cases the results agree with the rigorous calculation in Sec. 2). For $kT \gg \Delta$ and $\omega \ll \omega_0$ these terms equal $2\mu^4/kT\Delta^2$ and $\mu^4/3(kT)^3$, respectively, and are represented by the lines b and c in Fig. 1.

For the investigated KCl : Li system at 4.2°K we obtain $\chi^3(\omega \gg \Gamma)/\chi^3(\omega \ll \Gamma) = 6(kT/\Delta)^2 \approx 75$.[4] It is convenient experimentally to fix the frequency while $\Gamma$ is varied by changing the temperature T. As T rises, $\Gamma$ increases so that the NS at low T should be described by line b, and at high temperatures (with $\Gamma \gg \omega$) by line c (see Fig. 1). In the intermediate region the NS depends on $\Gamma$ in a manner that provides for the transition from line b to line c.

Let us now compare the theory with our experimental results (curve a in Fig. 1). In our experimental work the resonance condition $\omega \approx \omega_0/3$ was satisfied and the NS had to exceed its value at lower frequencies (line b). This higher value depends on the nonuniform broadening $\Gamma^*$. (Because of elastic deformations the different ions have different tunneling frequencies.) If it assumed, in accordance with[6], that a nonuniformly broadened line is Lorentz-shaped with the width $\Gamma^* = 3 \times 10^9$ Hz and we use the values $\omega_0 = 2\pi \times 2.4 \times 10^{10}$ sec$^{-1}$ and $3\omega = 2\pi \times 2.7 \times 10^{10}$ sec$^{-1}$, we find that the NS is doubled as a result of the resonance. We take the experimental value of $|\chi^{(3)}|$ at 4.2°K to be $4\mu^4/kT\Delta^2$, which we use as our unit. Accordingly, line b in Fig. 1 begins below the experimental curve. In the investigated temperature range the second term inside the curly brackets of Eq. (3.3) is much smaller than the first term and may be dropped. This term would describe the NS at higher temperatures for which $\Gamma \gg \omega$. However, our experimental apparatus was not sensitive enough to reach this region.

We shall hereafter be interested in the temperature region for which $\Gamma > \Gamma^*$, where nonuniform broadening may be disregarded and (3.3) may be used. Then

$$\begin{gathered} \chi^{(3)}(T) = -8\mu^4 i\omega\omega_0 \operatorname{th}(\beta\Delta)/\hbar^3 D_{3\omega}D_\omega(2i\omega+\Gamma), \\ \frac{\chi^{(3)}(T)}{\chi^{(3)}(T = 4.2^\circ\,\mathrm{K})} \\ = \frac{4.2}{T}\frac{0.4x^5}{[(1+2.3x^2+0.7x^4)(1+4.7x^2+0.1x^4)(1+0.6x^2)]^{1/2}}. \end{gathered} \tag{3.4}$$

Here $x = \omega_0/\Gamma$ and we used $\omega_0 = 2.6\omega$. The form of the last expression is convenient for calculating $\Gamma$ if $\Gamma > \omega_0$. Using curve a in Fig. 1 and (3.4), $\Gamma$ and $\Gamma^{-1} \equiv T_1$ can be determined. The temperature dependence of $T_1$ is represented by curve a of Fig. 2. Curve b represents measurements in[6], where the line width of

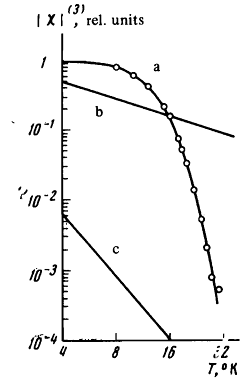

FIG. 1

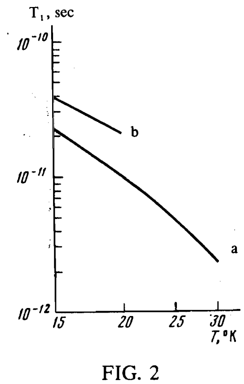

FIG. 2

FIG. 1. Temperature dependence $\chi^{(3)}(T)$: a—experimental with $n_{Li} = 3 \times 10^{17}$ cm$^{-3}$; b—theoretical for $\Gamma \ll \omega \ll \omega_0$; c—theoretical for $\Gamma \gg \omega$.

FIG. 2. Temperature dependence of the lifetime $T_1$: a—present work; b—results in [6].

paraelectric resonance was measured in an external electric field with $\omega_0 = 2\pi \times 3.5 \times 10^{10}$ sec$^{-1}$. We note that despite the arbitrarily chosen shape of the nonuniformly broadened line the values obtained for $T_1$ are quite accurate for $T > 20^\circ$K. Thus, a change of $\Gamma^*$ by a factor of two [$\Gamma^*$ enters into $\chi^{(3)}(T = 4.2^\circ\text{K})$] leads to only 15–20% change of $T_1$.

The experimentally observed sharp drop of $\chi^{(3)}$ can be fully accounted for by the effects of relaxation processes.

## 4. EXPERIMENT

The magnitude of NS was determined from the efficiency of the generation of the third harmonic of a powerful uhf wave. The KCl : Li sample, cut in the form of a 1.2 × 5 × 19-mm plate, was cemented to a 3 × 5 × 19-mm plate of pure KCl. Figure 3 is a schematic drawing of the bimodal resonator with the sample. The cross sections of the resonator were 5 × 19 mm in its broad part and 5 × 10 mm in its narrow part, with a tapered connecting part. This connecting part was beyond the cutoff for the pumping field, which was therefore concentrated in the broad part of the resonator. However, at the signal frequency the field ($TE_{10n}$, $n \sim 20$) was distributed throughout the volume of the resonator. This design permits tuning of the resonator signal frequency $\omega_S$ to satisfy the condition $\omega_S = 3\omega$ ($\omega$ is the pumping field frequency) without changing the pumping frequency. The pumping source was a pulsed magnetron that produced $10^{-6}$-sec pulses, thus avoiding heating of the sample. The pumping frequency was $\omega = 2\pi \times 9 \times 10^9$ sec$^{-1}$. The resonator was coupled with the signal waveguide by means of an inductive diaphragm, and to the pumping waveguide by a slot (Fig. 3). The $3\omega$ signal emitted by the crystal along the signal waveguide was fed to a superheterodyne receiver having $10^{-10}$ W sensitivity. Relative changes of $|\chi^{(3)}|$ were determined from the relation

$$\left|\frac{\chi^{(3)}(T)}{\chi^{(3)}(T=4.2^\circ\,\mathrm{K})}\right| = \left[\frac{P_S(T)}{P_S(T=4.2^\circ\,\mathrm{K})}\right]^{1/2},$$

where $P_S$ is the signal power.

The signal power was proportional to the cube of the pumping power. The power of the pumping pulses did not exceed 20 W, and the signal power reached $10^{-4}$ W (at lithium concentration $n_{Li} = 3 \times 10^{17}$ cm$^{-3}$ and $T = 4.2^\circ$K). The dependence of the signal power on the Li ion concentration was measured, and also the power of the harmonic from samples without Li and with Li concentrations $n_{Li} = 10^{17}$ cm$^{-3}$ and $3 \times 10^{17}$ cm$^{-3}$. No generation of the harmonic was observed in the control samples without Li. As was to be expected, the power of the harmonic was proportional to the square of the Li impurity concentration.

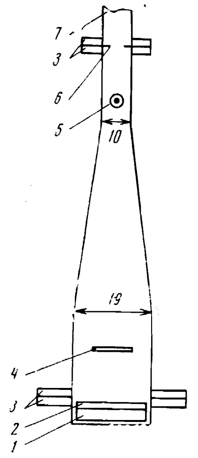

FIG. 3. Schematic drawing of the resonator with the sample. 1–KCl sample, 2–KCl: Li sample, 3–flanges, 4–coupling slot for the pumping field, 5–signal-frequency tuning rod, 6–inductive diaphragm for coupling with the signal waveguide, 7–signal waveguide.

The "laminar" form of the sample was chosen to reduce the effect of the lithium impurity on the resonator Q without reducing the signal power. Measurements were performed on samples with $n_{Li} = 3 \times 10^{17}$ cm$^{-3}$. The resonator Q in both modes was ~500; this value did not change during the measurements. The pumping field and the harmonic field were parallel to the [100] axis of the crystal.

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[1] An exception is the case of a nonvanishing diagonal matrix element of the dipole moment.

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99