Possible existence of a phonon bottleneck in the paraelectric resonance of smoky quartz

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Strong saturation of the observed intensity of the paraelectric resonance line in smoky quartz is reported for temperatures in the liquid-helium range. Quantitative agreement with the data is obtained with a tentative model in which the localized electric dipoles are strongly coupled to lattice phonons and in which a phonon bottleneck exists. The latter should allow an increase of the effective temperature of the dipole system with an increase of the microwave power via a mechanism of acoustic paraelectric resonance with piezoelectrically generated phonons. Above 2.5 K multiphonon effects become of importance and should reduce the effect of the phonon bottleneck.

In two previous papers,[1,2] paraelectric resonance (PER) of centers in x-irradiated Al-doped α-quartz crystals has been reported. The center involved is an electron hole, trapped at the pair of oxygen ions lying almost on the same c axis (the optical axis) and which are the nearest neighbors of a substitutional Al^{3+} impurity ion. The structure of this center has been thoroughly studied by electron paramagnetic resonance.[3-5] If localized, the electron together with the Al^{3+} ion constitutes an electric dipole. The electron may tunnel between the two equilibrium positions, which corresponds to a reorientation of the dipole, giving rise to Debye-type dielectric relaxation losses. These have been investigated in detail by de Vos and Volger.[6] According to these authors the tunnel matrix element Δ is about $\Delta \approx 5\times10^{-7}$ eV.

In addition to the tunnel splitting, the energy levels are split when an external electric field $\vec{E}$ is applied parallel to the c axis. Resonant transitions can then be obtained by application of an oscillating electric field parallel to $\vec{E}$ and with an angular frequency ω when, in first approximation, the strength E of $\vec{E}$ is equal to E_0 with

$$E_0 = \hbar\omega/2\mu_D \,, \tag{1}$$

where μ_D is the effective dipole moment. Such a resonance was observed with 3-cm microwaves[1,2] and appeared to be strongly inhomogeneously broadened, which appeared from our observation that the width of the PER signal varied from sample to sample. Such a broadening is presumably due to strains and dipole-dipole interactions as is, for instance, also the case in the PER of KCl:OH^-.[7-9] The broadening appeared to have the form[2]

$$f(\omega',\omega) = (a\sqrt{\pi})^{-1}\{\exp[-\hbar^2(\omega'-\omega)^2/a^2] + \exp[-\hbar^2(\omega'+\omega)^2/a^2]\}\,, \tag{2}$$

with $a = 2.5\times10^{-4}$ eV. ω' is defined by

$$\omega' = 2\mu_D E/\hbar\,. \tag{3}$$

We observed that the PER of the center shows a remarkable saturation behavior (Fig. 1), which has partly been published in Ref. 1 and which is shown at 4.21 and at 1.72 K as a function of the microwave power which was applied to the microwave cavity containing the sample. The detector crystal was biased in order to keep it in the linear region, so the signal amplitude is proportional to $(W_A)^{1/2}$, where W_A is the absorbed power. Owing to the differential detection technique which was used, W_A is purely the absorption due to transitions of the electric dipoles. In Fig. 1 the signal amplitudes are normalized at unity for a microwave power of -50 dB. The saturation behavior was the same in different samples and can be explained with the aid of recently developed insights into the mechanisms which govern the paraelectric relaxation.[10-14]

The piezoelectric properties of α-quartz will be essential in our model. The experimental arrangement was such that a thin plane-parallel platelet of a quartz crystal was mounted in a reentrant cavity in a way similar to the configuration which is used for the generation of microwave phonons.[15-18] Both the microwave and the static electric field were applied parallel to the c axis of the sample. When a microwave power W is applied to a quartz sample, the maximum number of phonons would be generated in a "X-cut crystal," whereas in our configuration, in principle, no piezoelectric coupling occurred.[19] However, as in practice the microwave field had also small components perpendicular to the crystal c axis, piezoelectric generation of phonons occurred. The number of phonons which was created per unit of time will be denoted by $\beta W/\hbar\omega$. β is a dimensionless parameter describing the piezoelectric coupling.

A block diagram of the flow of energy is presented in Fig. 2. The microwave power W produces phonons with frequency ω in two ways:

(i) Via the piezoelectric coupling mentioned above.

(ii) Power is absorbed by resonant transitions in the dipole system. This absorption W_A will be characterized by a dimensionless coupling param-

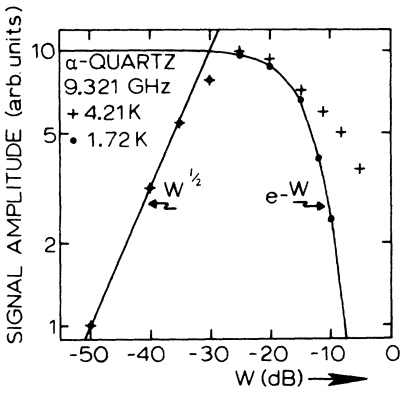

FIG. 1. Amplitude of the PER signal in smoky quartz as a function of the applied microwave power W for $T = 4.21$ K (crosses) and $T = 1.72$ K (dots). The solid lines represent a $W^{1/2}$ and an e^{-W} dependence. The signal amplitude is proportional to $(W_A)^{1/2}$, where W_A is the power which is absorbed. In this figure the signal amplitudes for $T = 4.21$ K as well as for 1.72 K are normalized as to be unity for a microwave power of -50 dB.

eter α which gives the probability that a microwave photon is absorbed by a PER transition. Subsequently the dipole system relaxes with a spontaneous emission rate for direct relaxation A and produces phonons "on speaking terms." The system of phonons "on speaking terms" with the dipoles relaxes with a rate τ_{ph}^{-1} to the thermal bath which is at the temperature T. The thermal bath is defined here as the entire system of nonresonant phonons, crystal imperfections, and the cooling media surrounding the sample. Indirect relaxation processes (Raman-type) generate negligible numbers of phonons with frequency ω, therefore the indirect relaxation can be considered as an energy flow directly from the dipole system into the thermal bath. We will characterize the rate of the indirect relaxation processes with T_{1I}^{-1}.

As a model for the dipole system we will use a two-level system with occupation numbers n_1 and n_2 and an energy splitting $\delta = \hbar\omega$. Next we define: $N = n_1 + n_2$ and $n = n_1 - n_2$. The thermal-equilibrium value of n will be denoted by n_0; $n_0 = N \tanh(\delta/2kT)$.

In the first instance, following the treatments of saturation and phonon bottleneck as given by some authors for the magnetic case[20-22] and adding the piezoelectric effect, we obtain the following rate equation:

$$\frac{dn}{dt} = -A[(2p+1)n - N] - 2\alpha n(W/\delta)g(\omega' - \omega) - (n - n_0)T_{1T}^{-1}. \quad (4)$$

The spontaneous emission rate for direct relaxation A may also be written as $A = T_{1D}^{-1}\tanh(\delta/2kT)$, with T_{1D} being the direct relaxation time. $g(\omega' - \omega)$ is the shape factor for the PER-absorption line; p is the occupation number of the phonon modes with frequency ω. In thermal equilibrium p is given by the Planck distribution function: $p_0 = (e^{\delta/kT} - 1)^{-1}$. p follows from

$$\frac{dp}{dt} = -(p - p_0)\tau_{ph}^{-1} + \beta(W/\delta) + W_{AD}[\delta\,\rho(\delta)\,d\delta]^{-1}. \quad (5)$$

W_{AD} is the fraction of W_A which is eventually converted into phonons "on speaking terms" via the direct relaxation process. $\rho(\delta)$ is the density of phonon states and $d\delta$ is the bandwidth of phonons interacting with the dipoles.

In PER experiments the microwave frequency ω is fixed and the applied field strength E is varied. Equations (4) and (5) could be rewritten in terms of E using the relations (1) and (3). As in our experiment E was varied slowly, we assume to have steady state, i.e., $dn/dt = dp/dt = 0$. The total microwave power W_A which is absorbed by resonant transitions of the dipole system is given by $W_A = \alpha W n$. Solving n from the Eqs. (4) and (5) under the steady-state condition and taking into account the inhomogeneous broadening $f(\omega', \omega)$, we find[20]

$$W_A = \alpha W(AN + n_0 T_{1I}^{-1}) \int_0^\infty \frac{f(\omega'', \omega)\,g(\omega'' - \omega)}{A(2p+1) + 1/T_{1I} + 2\alpha(W/\delta)\,g(\omega'' - \omega')}\,d\omega''. \quad (6a)$$

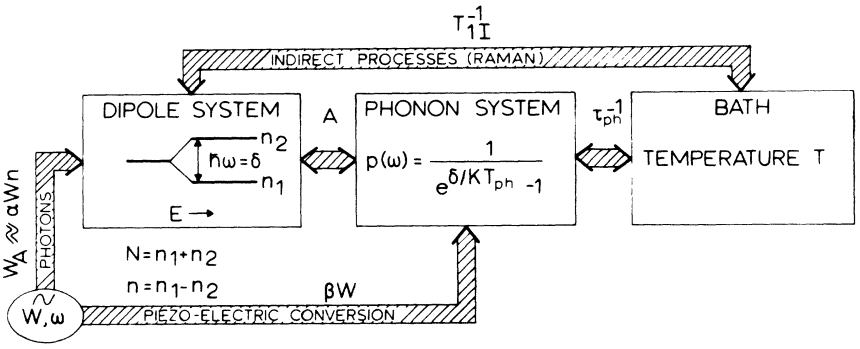

FIG. 2. Block diagram of the flow of energy in the paraelectric resonance of the centers in smoky quartz. The meaning of the symbols used in this figure is mentioned in the text.

As the width of the inhomogeneous broadening is probably large in comparison with the width of the line shape $g(\omega''-\omega)$ and as the complexity of the saturation behavior does not enable us to determine the form of $g(\omega''-\omega)$ from it, we simplify by taking for $g(\omega''-\omega)$ a function which equals unity for $\omega-\frac{1}{2}\gamma\leq\omega''\leq\omega+\frac{1}{2}\gamma$ [γ being small with respect to the width a of $f(\omega'',\omega')$] and which equals zero for all other values of ω''. This means that the shape of the PER signal does not depend on W, which is in accordance with our observations. Expression (6a) is now simplified to

$$W_A=\alpha W(AN+n_0T_{1I}^{-1})\left[A(2p+1)+T_{1I}^{-1}+2\alpha(W/\delta)\right]^{-1}\gamma f(\omega',\omega)\,. \tag{6b}$$

The fraction W_{AD} of W_A is given by

$$W_{AD}=\alpha WAN\left[A(2p+1)+2\alpha(W/\delta)\right]^{-1}\gamma f(\omega',\omega)\,. \tag{7}$$

Equation (5) yields

$$p=p_0+\tau_{ph}\left\{\beta(W/\delta)+W_{AD}[\delta\rho(\delta)\,d\delta]^{-1}\right\}\,. \tag{8}$$

For some limiting cases analytic expressions can be found for W_A and for p:

(a) *W small* $\{W\ll[A(2p+1)+T_{1I}^{-1}]\,\delta/2\alpha\}$ and $p=p_0$. In this case the phonon system is in thermal equilibrium with the bath, $p=p_0$, and W_A is given by

$$W_A=\alpha W n_0 f(\omega',\omega). \tag{9}$$

This agrees with the experimentally observed proportionality between W_A and W for small magnitudes of W (see Fig. 1, the straight line marked $W^{1/2}$ represents a dependence $W_A\propto W$).

(b) *W large and* $p=p_0$. Now W_A increases, with increasing W, asymptotically to the saturation value:

$$W_A\rightarrow\tfrac{1}{2}\delta(AN+n_0T_{1I}^{-1})\gamma f(\omega',\omega). \tag{10}$$

(c) *W large and* $p\neq p_0$ ($\tau_{ph}\{\beta(W/\delta)+W_{AD}[\delta\rho(\delta)\,d\delta]^{-1}\gtrsim p_0$). Now a phonon bottleneck occurs; according to Eq. (8) the number of phonons with frequency ω becomes larger than the thermal-equilibrium value p_0. However, in this case and in the model developed thus far, W_A approaches a flat saturation level too. This level is given by

$$W_A\rightarrow\tfrac{1}{2}\delta(AN+n_0T_{1I}^{-1})(1+A\tau_{ph}\beta\alpha^{-1})^{-1}\gamma f(\omega',\omega) \tag{11}$$

and saturation is reached at lower values of W than in case (b).

The understanding of the sharp decrease of the saturation level with increasing W, as is suggested by our experiments (Fig. 1), involves the incorporation of dynamic lattice processes. Sander and Shore[10,13,14] showed that many properties of paraelectric defects can well be understood when it is assumed that the centers are strongly coupled to the acoustical phonons. This seems reasonable as the energy levels of the paraelectric impurity are directly coupled to the crystalline electric field. These authors treat the phonon coupling as the main effect and introduce the tunneling as a perturbation. This is only valid when the observed tunneling parameter $\Delta\ll\delta$, which is the case here ($\Delta\sim5\times10^{-7}$ eV, $\delta\sim4\times10^{-5}$ eV). The main feature of their model is that multiphonon absorption and emission become important above a characteristic temperature T_0 which, when the Debye model is assumed, takes the form

$$T_0=\hbar\omega_D k^{-1}(2/3\pi W_0)^{1/2}\,. \tag{12}$$

ω_D is the Debye cutoff frequency, k is Boltzmann's factor, and W_0 is a dimensionless parameter related to the response of the lattice to external strain. The effect of the multiphonon interactions is the formation of a continuum of phonon sidebands. In PER only the zero-phonon line ("dipole flip" only) is observed and its intensity decreases when the temperature is increased because the multiphonon effects then become more important and relatively more oscillator strength is transferred to the side bands. Owing to this effect the intensity of the zero-phonon line is multiplied by an exponential factor D which has the form of a Debye-Waller factor and is given by[13]

$$D=\exp\left(-\sum_{\omega'}(W_{\omega'}/\omega')^2\left[2p(\omega')+1\right]\right)\,. \tag{13}$$

The W_ω are dipole-lattice coupling constants and the summation is over all acoustical phonon modes. In the Debye model and for $kT\ll\hbar\omega_D$ (which is the case in the present experiment: $T\sim4$ K and $\hbar\omega_D/k\sim470$ K for α-quartz[23]), D takes the form

$$D=e^{-W_0T^2/T_0^2}. \tag{14}$$

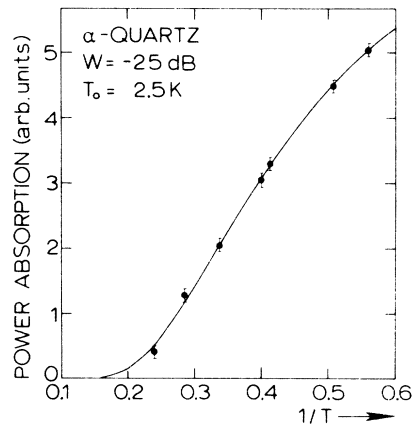

FIG. 3. Square of the signal amplitude of the PER signal in smoky quartz as a function of the bath temperature T. The dots give the experimental points. The solid line represents an $\exp(-T^2/T_0^2)$ dependence with $T_0=2.5$ K.

The temperature dependence which we observed of the intensity of the PER signal in smoky quartz (Fig. 3) followed this behavior closely which indicates that the application of the strong-coupling theory is justified. The fit is obtained for $T_0 = (2.5 \pm 0.1)$ K, yielding a value of $W_0 = 1.3 \times 10^{-4}$.

In the case of a phonon bottleneck the number of phonons with frequency ω is enhanced as given in Eq. (8). From solving the rate equations it follows that n then has to be multiplied by

$$\exp\left(-c_2\left[2\tau_{ph}\left\{\beta(W/\delta) + W_{AD}\left[\delta\rho(\delta)\,d\delta\right]^{-1}\right\}+1\right]\right), \quad (15)$$

where c_2 is a constant containing the factor $(T_{1D}^{-1} + T_{1I}^{-1})$. As the PER intensity is proportional to n, it has also to be multiplied by the factor (15). For T well below T_0, T_{1I} can be put ∞ in expression (11) and the signal intensity will now be about proportional to

$$W_A \propto \tfrac{1}{2}\delta\, AN(1 + A\tau_{ph}\beta\alpha^{-1})^{-1}\gamma f(\omega', \omega) \times \exp[-2c_2\tau_{ph}\beta(W/\delta)], \quad (16)$$

which may be written as $c_1 \exp[-c_2\tau_{ph}(W/\delta)]$ in which c_1 and c_2 are constants. Such a dependence is shown by the curve marked e^{-W} in Fig. 1, which agrees well, for large W, with the observed behavior at $T = 1.72$ K. Physically the effect can be described as a shift of the absorption of microwave power by the dipole system from direct absorption towards absorption of resonant phonons, generated owing to the piezoelectric coupling. The latter absorption does not contribute to W_A, owing to the fact that β does not depend on E and to the differential detection technique. The absorption of generated phonons might also be called acoustic paraelectric resonance.[24] Some quantitative information on the parameters in expression (16) might be obtained from the experiments if the absolute values of W_A and W were known. However, the determination of W requires, among other things, the calculation of the filling factor of the microwave cavity, which is quite a problem for PER cavities. Should this problem be solved, however, still too many parameters are involved to be able to state as a definite conclusion from the PER experiments that a phonon bottleneck exists. Definite conclusions in the case involved might be obtained from other experiments, e.g., Brillouin scattering.

When T is above T_0 the multiphonon effects become of importance. They come into the formulas derived above via the parameter T_{1I}, the relaxation time for the indirect processes. T_{1I}^{-1} depends strongly on the temperature T, the lowest power of T in T_{1I}^{-1} being[11–14] about T^4. Therefore the slight heating of the sample due to the microwave absorption will strongly lower the relaxation time T_{1I}. For this reason we expect a less sharp decrease of W_A with increasing W as predicted by expression (16) when $T > T_0$. This is confirmed by the experiment as is illustrated in Fig. 1 by the observed saturation behavior for $T = 4.21$ K.

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