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Acoustic Resonance Techniques for Temperature, Stress and Impurity Characterization in Piezoelectric Materials [and Discussion]

J. J. Gagnepain, E. Almond, R. E. Green, D. P. Almond and G. Busse

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Acoustic resonance techniques for temperature, stress and impurity characterization in piezoelectric materials

By J. J. Gagnepain

Laboratoire de Physique et Métrologie des Oscillateurs du C.N.R.S., associé à l'Université de Franche-Comté-Besançon, 32 *avenue de l'Observatoire*, 25000 *Besançon, France*

The resonance frequency of a vibrating structure is sensitive to thermal, mechanical, or electrical perturbations. On account of the high resolution allowed by frequency measurements, very small temperature gradients and stresses can be detected and measured in piezoelectric, and mainly in quartz resonators. Because of piezoelectric coupling, frequency is also sensitive to the relaxation of ionic impurities. The resonant method gives access to the nature and the concentration of the impurities. The interactions between thermal phonons also are characterized, by means of noise measurements and some interpretation of the mechanisms of $1/f$ noise will be presented.

1. Introduction

A resonant vibrating structure has two main parameters: frequency and quality-factor. The frequency is a function of the geometry and the elastic, piezoelectric, dielectric etc. properties of the material. Through different types of coupling it can be affected by internal and external phenomena. The Q-factor is principally limited by the acoustic attenuation, at least when the influence of the surrounding is sufficiently reduced. Piezoelectric crystals, such as quartz, lithium tantalate, lithium niobate, berlinite, have small attenuation, therefore very large Q-factors can be achieved and, for instance, quartz crystal resonators have Q-factors of the order of 1×10^6–3×10^6, at 5 MHz. This means that very small shifts of their frequency can be detected by direct frequency measurements or by indirect phase measurements. Resolutions of the order of 10^{-12}, in terms of fractional frequency variations, are possible, and even resolutions of 10^{-13} have been achieved.

The frequency of a resonator is sensitive to temperature. This is due to the thermal expansion of the crystal and to the temperature dependence of the material constants. The frequency can also change under the application of stresses. In this case the sensitivity comes from the elastic nonlinearities of the crystal, which couple the high-frequency wave to the static or quasistatic stresses and strains. These effects must be characterized; they are sources of instabilities or of limitations in many applications of piezoelectric devices, and, in particular, in oscillators.

Impurities also are a cause of instabilities, when the crystal is submitted to ionizing irradiations. Because ionic impurities are electrically charged, they are also coupled with the acoustic wave, and therefore affected by linear and nonlinear piezoelectric coupling.

Finally, the ultimate cause of frequency variations or fluctuations comes from the microscopic properties of the crystal. Because of the anharmonicity of the lattice, again nonlinear effects, interactions occur between the acoustic wave and the thermal phonons. This induces a frequency noise, which can be measured, and which exhibits a $1/f$ spectrum.

Frequency therefore can be used as a very sensitive tool for characterizing different properties of a piezoelectric crystal. Some of these properties will be now examined.

2. Measurement method

The devices which are used consist of circular plates of piezoelectric crystals with gold electrodes directly deposited on each face of the plate or supported by auxiliary plates with an air gap between the electrodes and the crystal, as shown in figure 1. For quartz a resonance frequency of 5 MHz corresponds to a crystal thickness of 0.33 mm when operating on the fundamental vibration mode, and of 1.65 mm for the fifth overtone. The diameter is 15 mm. Very often plano–convex shapes are used in order to trap the energy near the centre of the plate and to keep the edges stationary. This allows the plate to be supported without perturbing the vibration and avoids additional mechanical losses. The structure is placed under vacuum in a metal enclosure. At 5 MHz Q-factors of the order of 1×10^6–3×10^6 can be obtained.

The frequency variations of the resonator are measured by means of a phase bridge, which is represented in figure 2.

The resonator under test is driven in a π-transmission network by a stable frequency source. The phase variation induced on the signal by the frequency variations of the resonator are detected with a double-balanced mixer operated at its quadrature point. A second resonator, identical to the resonator under test, is placed in the second arm of the bridge for the rejection of the frequency and phase fluctuations of the source. A rejection of 50 dB is possible when the frequencies of the two resonators are adjusted to the same value and when the two Q-factors

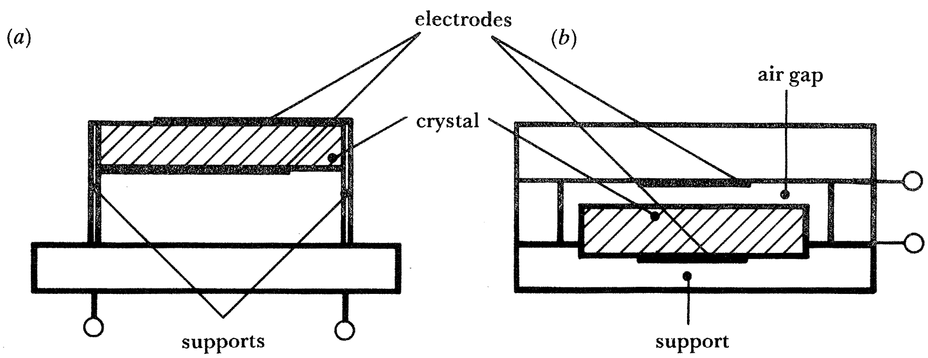

Figure 1. Resonator structures: (*a*) with electrodes on the crystal; (*b*) with an air-gap.

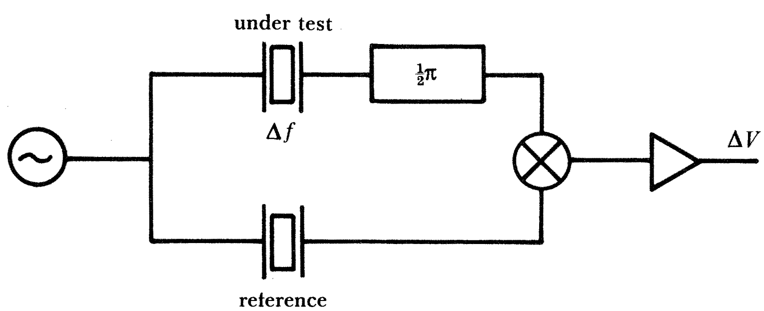

Figure 2. Phase bridge used for measuring the frequency variations of the resonator under test.

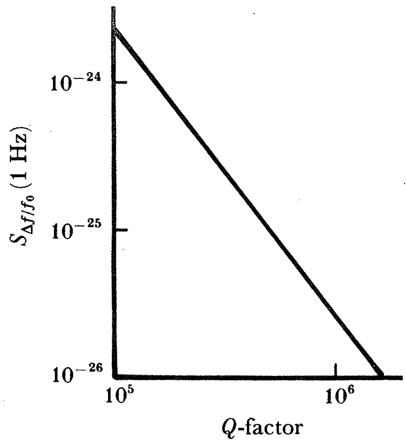

FIGURE 3. Power spectral density of the measurement system noise, given in term of equivalent frequency fluctuations of the resonator under test, $S_{\Delta f/f_0}$, as a function of its Q-factor.

are equally balanced (Walls 1975; Gagnepain 1976, 1983. The sensitivity of the system is given by the relation

$$\Delta V = 2G\,\mu Q\,\Delta f/f_0, \tag{1}$$

where ΔV is the voltage variation at the mixer output, after amplification by a low noise amplifier of gain G, induced by the fractional frequency shift $\Delta f/f_0$ of the resonator under test. Q is the resonator Q-factor, and μ the voltage/phase sensitivity of the mixer. For $Q = 2 \times 10^6$, $G = 10^3$, and $\mu = 0.25$ V/rad, a variation of 1 mV at the output will correspond to a frequency shift of 10^{-12}. However, a limitation can come from noise of the phase bridge, i.e. noise of the mixer and DC amplifier and from a misbalance of the bridge. This limit is indicated in figure 3, which presents the power spectral density of the measurement system noise, given in term of equivalent frequency fluctuations of the resonator, as a function of the Q-factor.

3. Temperature gradients and stresses

Temperature is an important cause of instabilities in piezoelectric devices. Generally specific crystallographic orientations are used for compensating the influence of temperature (Bechmann 1962) on the frequency. Such a compensation is effective if the temperature is uniformly distributed in the crystal, and this is true only for very slow temperature variations. For faster temperature variations, temperature gradients appear in the crystal and thermal stresses are induced. By nonlinear elastic coupling, due to the fourth-order elastic constants, these stresses and the associated strains modify the conditions of propagation of the wave. As a result, the wave velocity is changed and therefore the frequency of the resonator is shifted.

A phenomenological model of this dynamic thermal behaviour was first proposed by Ballato (1978), followed by more complete analytical descriptions by Théobald (1979) and Sinha (1980).

More recently, the temperature distribution in a circular quartz plate, supported at two diametrically opposite points, as shown in figure 4, was calculated. Vibration energy was trapped at the centre by using a convex upper surface and electrodes with reduced diameter. Thermal exchanges occurred mainly through the support, and the energy dissipated inside the crystal by the acoustic loss was taken into account.

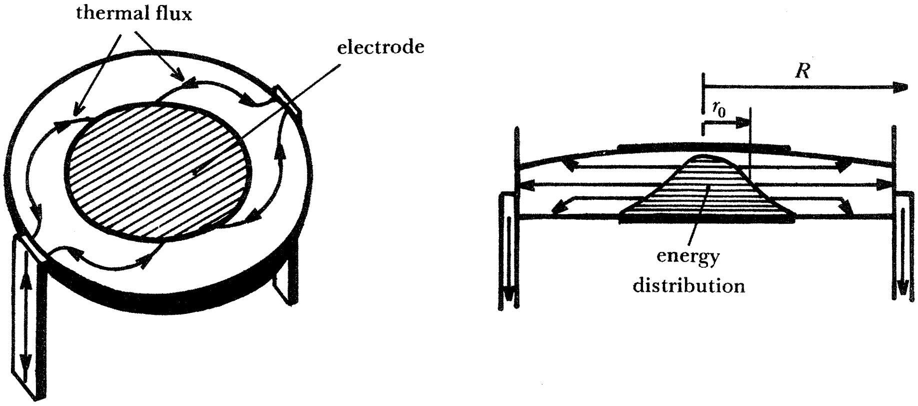

FIGURE 4. Circular quartz plate, supported at to opposite points, with circular electrodes at the centre.

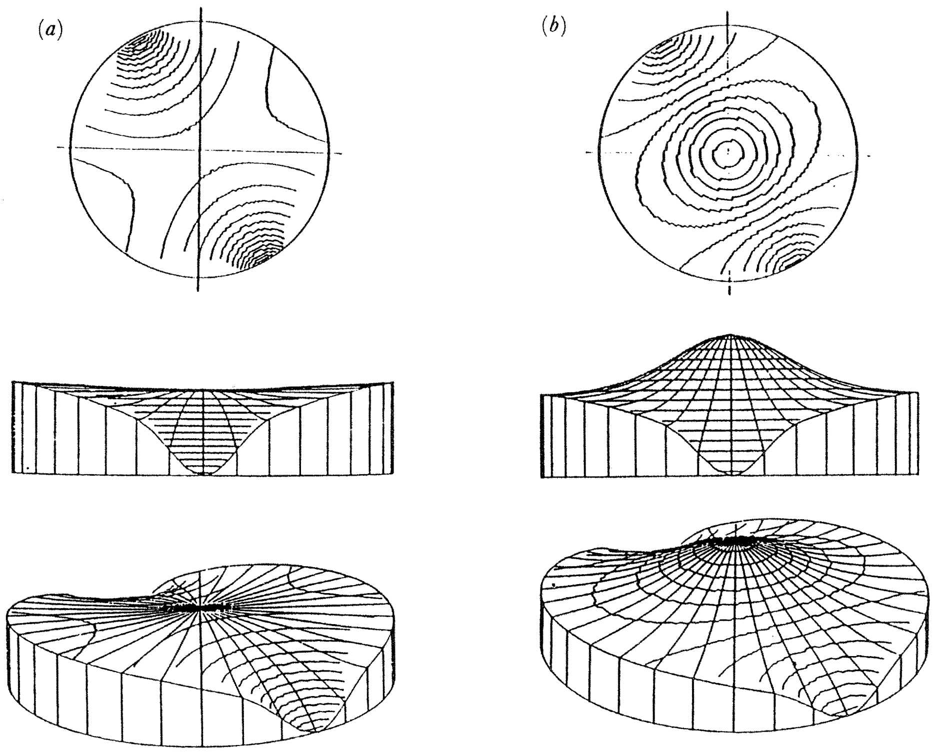

FIGURE 5. Temperature distribution for different energy trappings: (a) without energy trapping $r_0 = R$; (b) strong energy trapping $r_0 = \frac{1}{5}R$.

The temperature distribution is shown in figures 5 and 6. Figure 5 represents the isothermal curves as a function of the energy trapping of the resonator. The mean radius of the energy distribution around the plate centre is represented by r, and R is the crystal plate radius. In figure 6 the isotherms are given for large and small values of the thermal conductance of the holders at the two fixation points. The thermal linear transfer coefficient is represented by h. The corresponding thermal stresses are purely radial (Valentin 1984) and can be easily calculated when considering a circular plate with free edges. The distribution of strain is

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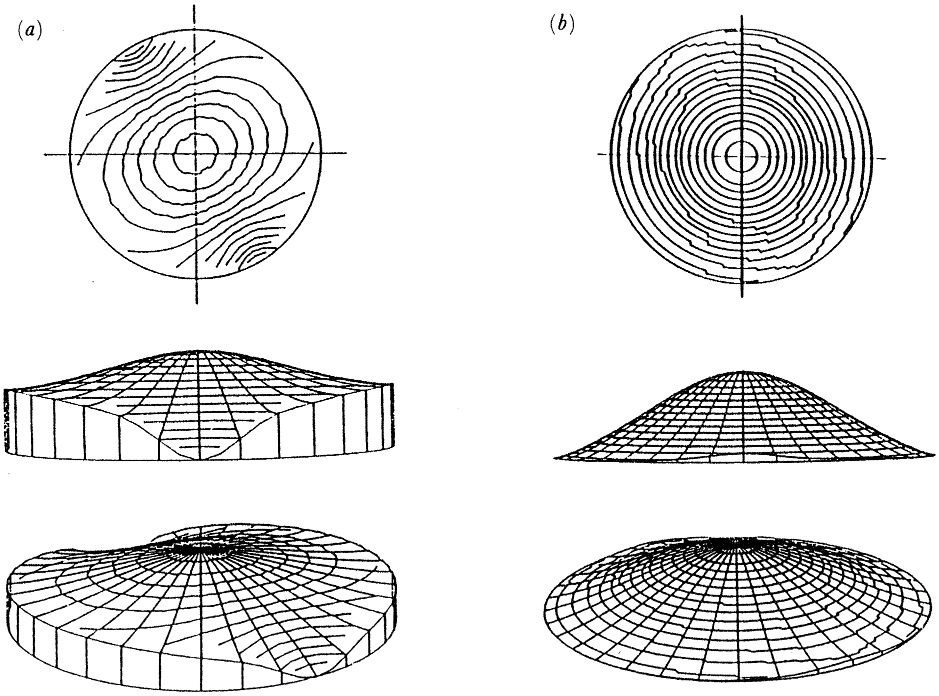


FIGURE 6. Temperature distribution as a function of the thermal conductance of the holders: (a) large conductance, $h_1 = 1000\ \mathrm{m^{-1}}$. (b) weak conductance, $h_1 = 10\ \mathrm{m^{-1}}$.

obtained from the stresses and the crystal anisotropy is reintroduced at that level. Finally, a perturbation method based on the nonlinear elastic equations (Tiersten 1971, 1978) gives the frequency shifts. After tedious calculations a very simple relation is obtained between the frequency and the external temperature:

$$\Delta f/f_0 = \tilde{a}\,\mathrm{d}T/\mathrm{d}t, \tag{2}$$

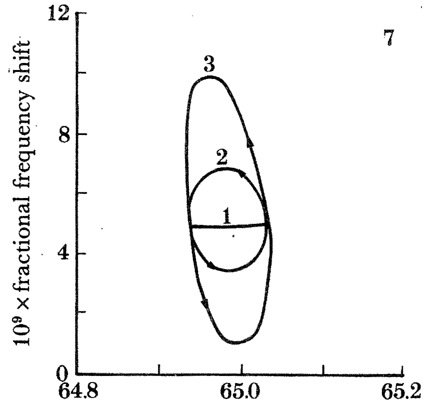
where $\tilde{a}$ represents the influence of temperature gradients on the crystal structure. This dynamic thermal effect is characterized by measuring the frequency as a function of temperature for different temperature cycling rates, as shown in figure 7 for a 5 MHz AT-cut quartz crystal. For this crystal the coefficient $\tilde{a}$ is equal to $-1.3\times10^{-5}\ \mathrm{s\,K^{-1}}$. This means that a temperature variation of 1°/s induces a frequency shift of 10^{-5}. Inversely, a frequency resolution of 10^{-12} enables one to measure temperature variations of the order of 10^{-7} °C.

In figure 8 are shown the residual temperature fluctuations of the quartz crystal maintained in a temperature controlled oven, and measured by using the previous method.

The problem of stresses can be generalized. For resonant structures with strong energy trapping, the frequency is sensitive to the stresses located near the centre of the plate and almost insensitive to stresses of the periphery. By using the perturbation method and the nonlinear model, a direct relation between the frequency and the six stress components can be approximated at the plate centre (Eernisse 1976):

$$(f-f_0)/f_0 = \sum_{i=1}^{6} k_i\, T_i. \tag{3}$$

The i subscripts of the stresses refer to the plate axes, and the corresponding values of the stress coefficients k_i are given in table 1 for two important quartz orientations, the AT- and SC-cuts.



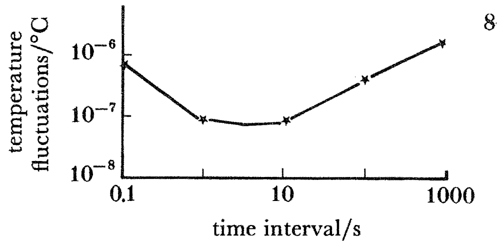


FIGURE 7. Frequency variation against temperature for different sinusoidal temperature cyclings: (1) static characteristic; (2) 5.10^{-4} Hz; (3) 10^{-3} Hz.

FIGURE 8. Residual temperature fluctuations of a quartz crystal in a temperature controlled oven.

TABLE 1. STRESS COEFFICIENT $k_i \times 10^{11}$ ($m^2\,N^{-1}$)

	T_1	T_2	T_3	T_4	T_5	T_6
AT-cut	−0.26	+0.17	−0.005	+0.17	0	0
SC-cut	−0.017	−0.07	+0.017	+0.19	0.09	0.25

For thin plates, the stress distribution is almost an in-plane distribution. Thus T_2, T_4 and T_6 are negligible and the stresses reduce mainly to T_1, T_3 and T_5. It can be seen in table 1 that the stress coefficient k_1 and k_3 of SC-cut have the same value with opposite signs. In many symmetrical configurations T_1 and T_3 will be equal and T_5 is very small. In that case the SC-cut will be insensitive to stresses. This is the origin of that cut, which was designed as a stress-compensated cut.

4. IMPURITIES AND FLUCTUATIONS

In the lattice of synthetic or natural quartz crystal, point defects are due to the substitution of silica atoms by aluminium atoms. Because there is one positive charge missing, ionic alkali cations (Na^+, Li^+) are trapped in the associated potential wells, to achieve the electrical neutrality (Stevels 1963). When the crystal is submitted to irradiations these charges are displaced and their interaction with the acoustic wave is transformed. Transient frequency shifts and additional acoustic losses are induced. This problem is becoming increasingly important with the current development of space and military applications of quartz oscillators. A solution consists of sweeping the impurities by applying a DC field at high temperature in the quartz block, out of the zone where the blanks will be cut. Characterization of these impurities is therefore necessary before and after sweeping.

Because frequency is sensitive to these impurities, it can be used to characterize them. The method consists of applying a DC voltage across the crystal and measuring the resulting frequency relaxation (Brendel 1982).

Under the DC field, a fast frequency variation is first observed. This is due to the piezoelectric

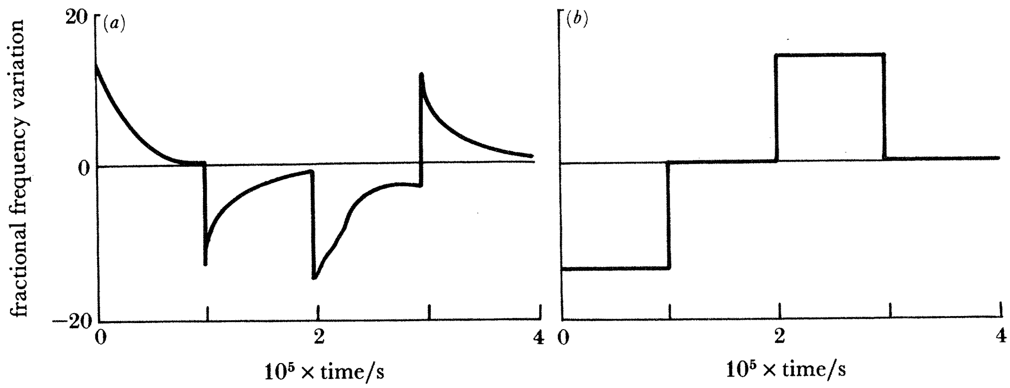


FIGURE 9. Frequency relaxation of (*a*) unswept and (*b*) swept quartz crystal at 80 °C.

deformation of the crystal and to the change of its elastic properties under the electroelastic effect; the method was used for determining the values of the eight independent electroelastic coefficients of right-hand quartz (Brendel 1982). In the absence of ionic impurities, the frequency would keep the value it takes after the initial variation, but with impurities the frequency does not remain constant and a relaxation is observed because the impurities diffuse in the crystal lattice under the applied field and create a depolarizing field, which reduces the internal field and then the frequency shift. Information can be extracted from the relaxation. The time constant is related to the nature of the impurity, and the amplitude to the concentration.

Experimental relaxation measurements performed on unswept and on swept quartz crystals are shown in figure 9. The frequency shifts are of the order 10^{-7} for DC fields of 2×10^{-5} V m^{-1}. These measurements correspond to the relaxation of Na^+ impurities, whose concentration is of the order of a few parts per million. The activation energy of the process is determined by measuring the relaxation time constant at different temperature and applying an Arrhenius law. In that case the activation energy is close to 1 eV.

When the crystal is protected from temperature fluctuations, stresses or impurity effects, etc., the influence of thermal phonons of the lattice and of their interactions on the acoustic wave can be observed. The residual frequency fluctuations are measured by using the previous phase bridge. Their power spectral density is analysed, and a typical spectrum is represented in figure 10. At the lower Fourier frequencies the $1/f^2$ frequency random walk is attributed to the temperature fluctuations previously described. At the higher Fourier frequencies the white noise is due to the phase bridge noise sources, and cannot come from the crystal. An evaluation of the crystal white noise indicates that it is about two orders of magnitude lower than the measurement system noise. In the medium range, $1/f$ noise is observed. The level, at 1 Hz from the carrier of this $1/f$ frequency noise, was measured on different quartz crystals at different frequencies, and is plotted in figure 11 as a function of the unloaded Q-factor. A clear correlation was found, which follows a $1/Q^4$ law. A theoretical interpretation of this $1/Q^4$ law has been proposed, in relation with phonon interaction (Gagnepain 1981) leading to the relation

$$S_{\Delta f/f_0}(F) = (E_0^2/\Delta E^2)\, S_{\Delta\tau/\tau}(F)/Q^4, \tag{4}$$

which relates the frequency fluctuations $\Delta f/f_0$ to the fluctuations $\Delta\tau/\tau$ of the thermal-phonon relaxation time, τ.

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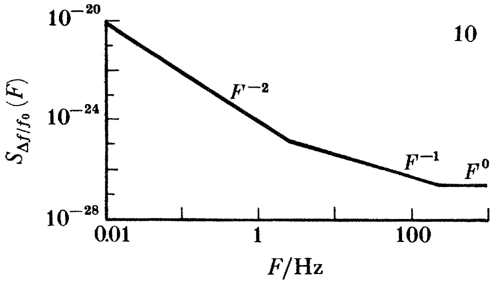


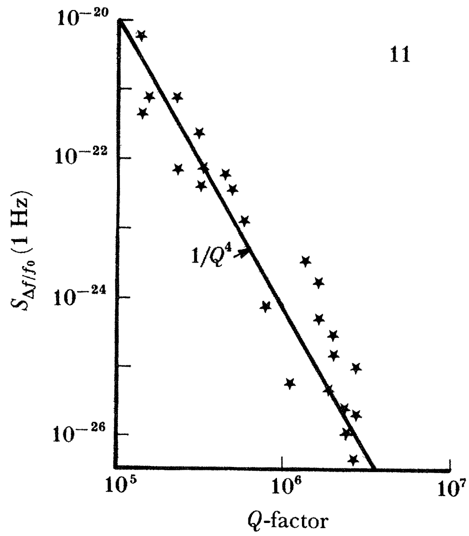
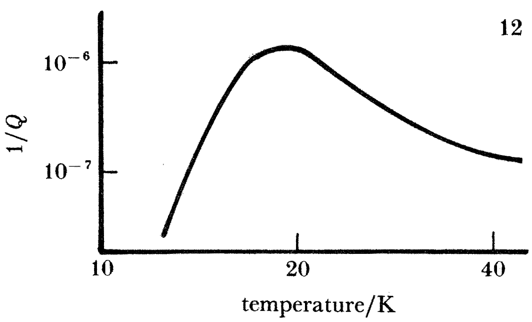


FIGURE 10. Fractional frequency fluctuation power density spectrum of a 5 MHz quartz crystal. F represents Fourier frequency.

FIGURE 11. $1/f$ frequency noise level at 1 Hz from the carrier against Q-factor.



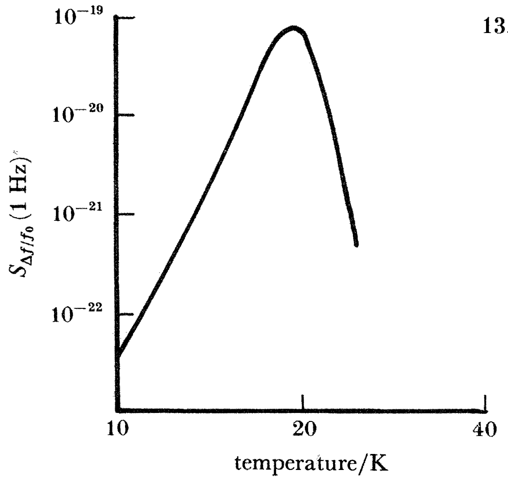


FIGURE 12. Inverse Q-factor as a function of temperature of a 5 MHz quartz crystal.

FIGURE 13. $1/f$ noise level as a function of temperature near the maximum of phonon interaction.

E is the Young modulus of the crystal and $\Delta E = CT\langle\gamma^2\rangle$. C is the specific heat, T the absolute temperature and γ an effective Grüneisen constant. In that model it is assumed that the relaxation time, τ, fluctuates with a $1/f$ spectrum, in accordance with the quantum $1/f$ noise theory (Handel 1975).

The correlation between $1/f$ noise and phonon interaction was recently confirmed by measurements of the noise level with respect to the acoustic attenuation at low temperatures. The acoustic attenuation, in terms of $1/Q$, of a quartz crystal vibrating at 5 MHz is plotted against temperature in figure 12. A maximum of attenuation is observed at 20 K. This corresponds to a maximum of phonon interaction (Fraser 1968).

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The $1/f$ noise level follows the same variation, as shown in figure 13, again with a $1/Q^4$ dependence.

5. Conclusion

The methods described are extremely sensitive, and enable very small temperature variations, or stresses induced by internal or external phenomena to be detected. Ionic impurities with concentrations of the order of a few parts per million can be characterized and the ultimate processes, such as phonon interactions, are in this way accessible. However, these methods are not adapted to point characterization, because they include all the vibrating volume of the crystal. Another limitation is the necessity of preparing blanks from the initial crystal. In fact, most of the characterization must come from resonator application. In that case the device to be tested is its own probe, and this gives a direct *in situ* characterization.

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Discussion

E. Almond (*National Physics Laboratory, Teddington, Middlesex, U.K.*). Knowing that great efforts are made to make defect-free versions of these materials, does Dr Gagnepain measure or know the dislocation contents? Also what effect would he expect dislocations to have on his measurements and conclusions?

J. J. GAGNEPAIN. The dislocation content of quartz crystals is measured by X-ray topography. In fact, in a synthetic crystal block there are different parts that cannot be used because of the dislocations and other defects, and only the 'clean' parts are retained. Improvements are made by a rigorous selection of the seeds, in order to reduce the attenuation and the frequency ageing.

R. E. GREEN (*Center for Nondestructive Evaluation, The Johns Hopkins University, Baltimore, Maryland U.S.A.*). In response to a question from the audience relative to the influence of dislocations on the resonance-frequency measurements, I report that we have been making white-beam synchrotron topographs of SC-cut quartz crystal plates and not only find dislocations present, but other larger defects such as twins and sometimes microcracks. These defects must influence the frequency response of the quartz resonators. In addition, I should point out that the high-brightness X-ray beam interacted with point defects to create colour centres in the quartz crystals.

J. J. GAGNEPAIN. Every defect will influence, to some degree, the frequency of the resonator. Today, however, the main problem does not seem to come from dislocations, or even bigger defects, because the crystals are selected, and samples with very low dislocation contents can be used. The problems rather come from point defects and their influence on the frequency when the crystal is submitted to irradiations. This is where the main effort is right now.

D. P. ALMOND (*School of Materials Science, University of Bath, U.K.*). What measures were taken to minimize effects associated with the contamination of the resonator surfaces by particulate matter and adsorbed fluid films?

J. J. GAGNEPAIN. Contamination has a very bad influence on the Q-factor and the frequency stability. It is important to operate the crystal in an enclosure under vacuum. All the processes of cleaning, degazing, baking, etc. must be applied during the preparation of the resonators. This necessity is well known and these methods have been in use for many years in the quartz manufactories.

G. BUSSE (*I.K.P., Universität Stüttgart, F.R.G.*), with nonlinear coupling, a temperature change of 10^{-7} K s^{-1} causes a minimum observable frequency shift, $\Delta f/f$, of 10^{-12}. Based on this temperature sensitivity, it should be possible to use your device (after coating with an absorbing layer) as a thermal infrared detector. Have these investigations been made?

J. J. GAGNEPAIN. Yes, some have been made. These resonators were also used for measuring the power of a laser beam. In that case the sensitivity depends on the position of the beam impact on the crystal surface, and therefore a calibration is necessary.

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