Study of ionic impurity mobility in quartz crystals by impedance and thermionic current measurements

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Defects, notably interstitial impurities, are responsible for degradation of resonator performance with time. In order to study the mobility of ionic impurities, we have measured thermionic currents as a function of temperature by the thermally stimulated depolarization (TSD) method. We have observed several current maxima; each peak is due to the displacement of an impurity family from a given site and is characterized by its activation energy. Making impedance measurements to complete these results, we find energies of about 1 eV. We have studied quartz crystals doped with a given impurity in order to identify the nature of the impurities responsible for some current peaks. This study confirms that the TSD method is very sensitive. © *1996 American Institute of Physics.* [S0021-8979(96)03823-6]

I. INTRODUCTION

Quartz resonators are employed in some technological devices which require a very high temporal frequency stability; but, quartz resonator performance decreases with time. Defects, particularly impurities, are created during hydrothermal growth and bring about degradation of performance.[1]

In fact, among the defects present in the crystal, aluminum ions Al^{3+} substitute for some silicon ions Si^{4+}. Crystal lattice electroneutrality conservation involves the presence of a positive compensating charge near each aluminum ion.[2] Such compensating charges can be supplied by an alkali ion M^+ ($M=Li$, Na, K) or by a proton H^+, or a hole, located in an oxygen ion adjacent to an Al^{3+} ion. The charges M^+ and H^+ are in interstitial positions and produce, with the substitutional impurities, $[Al^{3+}-M^+]$ and $[Al^{3+}-H^+]$ centers. There also exist $[Al^{3+}-hole]$ centers. These centers can be destabilized by irradiation[3] or by electrodiffusion.[4] $[Al^{3+}-hole]$ centers are only detected in quartz irradiated samples.[2,3] Paramagnetic defects in quartz crystals have been studied by several authors using electron-spin-resonance (ESR) techniques; neither E'_1 center[5,6] (oxygen vacancy which traps an electron) nor $[Al^{3+}-hole]$ center[3,6] are observed in unirradiated samples.

Crystalline structure 32 presents large channels parallel to **c**. The ability which some interstitial impurities have to move along these channels is used in industry to purify the crystals. The application of an electric field to the terminals of a heated crystal brings about the moving of the ions that are the least strongly bonded to the crystalline structure toward the surface. Crystal faces which are in contact with the electrodes are subsequently cut. This technique is called sweeping.[7]

In order to better characterize the sweeping, the thermally stimulated depolarization (TSD) method[8] has been employed on different quartz samples. This method is very sensitive and its principle is similar to that of sweeping. Quartz is an insulating material, the conductivity is ionic.[9] Thus, thermionic currents due to the mobility of ionic impurities are measured. In previous articles the relationships between some characteristics and the mobility of impurities has been pointed out. For example, more impurities move along the Z axis than along the Y axis;[10] the anisotropy of the structure explains this. The current density measured for a standard quality quartz is greater than that for high-quality quartz.[11] The influence of the sweeping conditions—under vacuum or in air—has been studied.[12] We have observed the influence of the experimental parameters.[12] In order to complete these measurements of current density, conductivity measurements have been realized.[13]

II. EXPERIMENTAL METHODS

A. The TSD method

When an electric field is applied to a crystal, either a displacement of charge inside the material from one equilibrium position to another or a displacement of charge around the equilibrium position (rotation of dipoles) is created.[8]

The presence of interstitial and substitutional ions brings about a variation of interaction potential energy.[14] An aluminum substitutional ion forms a trap for an alkali interstitial ion: The M^+ ion tends to minimize its energy and places itself near the Al^{3+} ion. In order to move the interstitial ions, they need enough energy to leave their potential wells (this is the association energy) and to move along channels (this is migration energy).[15]

The TSD method consists in applying an electric voltage to the terminals of a sample at a fixed temperature. Figure 1 represents the evolution of the electric voltage U, of the temperature T and of the current i for the TSD measurement. The sample is warmed at the temperature T_p; an electric voltage U_p is applied to its terminals for the time (t_1-t_0). The dipoles are not oriented initially; they tend to align parallel to the electric field. Under the effect of both thermal agitation and electric field, the interstitial charges migrate by successive jumps to the electrode (cathode if the charges are positive). A depolarizing field is created by these charges. At
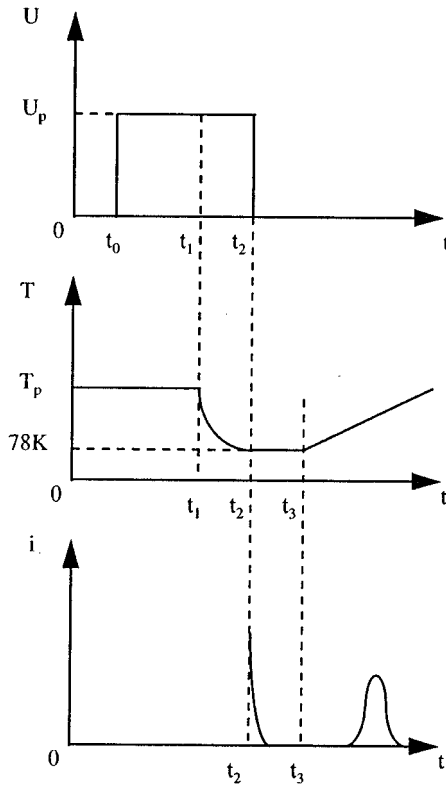
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FIG. 1. Evolution of the electric voltage U, temperature T, and current i for a TSD measurement.

t_1 the sample is cooled to 78 K. The cristalline structure can be considered as ''frozen''. The electric voltage is removed at t_2 and the electrodes are short circuited through an electrometer. At t_3 the temperature is raised linearly. The released particles migrate inside the material. The measured depolarizing current is due to the relaxation by rotation of dipoles and the movement of space charges.[8] These charged impurities are in limited number. Then the displacement of one impurity family in a given site brings about a current peak. Maximum temperature is linked to the activation energy which characterizes this family. During the measurement we observe several peaks of current corresponding each to one impurity family, placed initially in a given site.

The theoretical study requires considering each of these two different displacements. First, let us consider the relaxation by rotation of dipoles. The relaxations are supposed to be independent and a single relaxation time τ can therefore be considered for a given phenomenon,

$$\tau(T) = \tau_0 \exp\left(\frac{E}{kT}\right), \tag{1}$$

where τ_0 is the pre-exponential factor, E the activation energy, and k Boltzmann constant.

It is supposed that only the orientation of dipoles, due to the application of an electric field, is responsible for the creation of a depolarizing field. Under the effect of a weak electric field $\mathscr{E}$ ($\mu\mathscr{E} \ll kT$; μ is the dipolar momentum), the maximal polarization $P_0(T)$ is given by the Langevin law

$$P_0(T) = \frac{\alpha N \mu^2 \mathscr{E}}{kT}, \tag{2}$$

where α is a geometrical factor, N the dipole concentration, μ the dipolar momentum, and $\mathscr{E}$ the norm of electric field.

In the absence of an electric field, a linear rise in temperature causes a depolarizing current to appear. The current density is given by the Debye law

$$j(t) = -\frac{dP}{dt} = \frac{P(t)}{\tau(t)}. \tag{3}$$

The temperature varies with time as $T = bt + T_0$, where T_0 is the initial temperature. If the initial polarization is equal to P_0, the solution of the differential equation (3) gives the expression for the polarization as a function of temperature, which allows us to determine the current density. This current density is written

$$j(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{E}{kT} - \frac{1}{b\tau_0} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'} \right) dT' \right]. \tag{4}$$

Expression (4) is maximal when the temperature is equal to T_m, which results in the following equation:

$$\frac{Eb\tau_0}{kT_m^2} \exp\left(\frac{E}{kT_m} \right) = 1. \tag{5}$$

With Eq. (5), the activation energy of the relaxation phenomenon which occurs at the temperature T_m can be determined.

Now let us consider that the depolarizing current is solely due to the movement of space charges. In fact, some charges migrate under the effect of both the electric field and the thermal agitation. A depolarizing field is created by these charges when the voltage is removed. The current density is given by

$$\mathbf{j}(t) = [\sigma]\mathscr{E}, \tag{6}$$

where $[\sigma]$ is the conductivity tensor and $\mathscr{E}$ is the electric field vector.

As quartz is an anisotropic material, the conductivity is not the same in all directions. $\mathscr{E}(0,0,\mathscr{E})$ is parallel to the Z axis and the current is measured in the Z direction; thus, expression (6) can be written

$$j_z(t) = \sigma_{zz}\mathscr{E}. \tag{7}$$

The current density in the Z direction can also be written

$$j_z(t) = -\frac{dP_z}{dt}. \tag{8}$$

As quartz is not pyroelectric, its polarization is uniquely due to the effect of the electric field,

$$P_z = \epsilon_0 \chi_{zz} \mathscr{E} \tag{9}$$

where ϵ_0 is the dielectric constant of vacuum, $\epsilon_0 = (36\pi 10^9)^{-1}$ F/m, and $[\chi]$ is the susceptibility tensor.

The ionic conductivity which is expressed in Eq. (7) conforms to the Arrhenius law,

$$\sigma_{zz} = \frac{\sigma_{z0}}{T} \exp\left(-\frac{E_z}{kT} \right), \tag{10}$$

where σ_{z0} is the pre-exponential factor and E_z an activation energy in the Z direction. Finally, if the temperature T is equal to $bt + T_0$, the current density using expressions (7), (8), (9), and (10) can be written

$$j_z = \frac{P_{0z}\sigma_{z0}}{\epsilon_0 \chi_{zz} T} \exp\left[-\frac{E_z}{kT} - \frac{\sigma_{z0}}{\epsilon_0 \chi_{zz} b} \int_{T_0}^{T} \exp\left(-\frac{E_z}{kT'} \right) \frac{dT'}{T'} \right], \quad (11)$$

where P_{0z} is the integration constant.

A curve of current density presents several peaks. These peaks correspond to current maxima. A peak is characterized by an activation energy E_z. T_m is the temperature of a maximum. The current density is maximal if the following expression is satisfied:

$$\frac{\sigma_{z0} k T_m}{b \epsilon_0 \chi_{zz} (E_z - kT_m)} \exp\left(-\frac{E_z}{kT} \right) = 1, \quad (12)$$

with $\chi_{zz} = \epsilon_{zz} - 1$; ϵ_{zz} is the dielectric constant in the Z direction. This relation allows determining the activation energy of the impurity corresponding to a given peak. It is necessary to know the value of σ_{z0} in order to use this formula.

B. Measurements of dielectric constants

In order to determine the pre-exponential factor σ_{z0}, measurements of ionic conductivity have been made. Several authors have done this type of measurement and have found pre-exponential factors which vary with crystal nature.[9,16] Consequently, we have measured dielectric constants for the studied quartz samples in order to better characterize them. Thus, we used the pre-exponential factor which is related to the crystal studied.

Quartz performs electrically as a capacitance and a resistance wired in parallel. In this case, the impedance Z of the equivalent circuit is expressed by

$$Z = \left(\frac{1}{R} + iC\omega \right)^{-1} = \underbrace{\frac{R}{1 + R^2 C^2 \omega^2}}_{\text{Re}(Z)} + i \underbrace{\frac{-R^2 C \omega}{1 + R^2 C^2 \omega^2}}_{\text{Im}(Z)}, \quad (13)$$

where ω is the pulsation, R the resistance, and C the capacitance. Re(Z) expresses the real part of the complex impedance Z and Im(Z) its imaginary part.

The curve $-$Im(Z) vs Re(Z), at a given temperature, is a circular arc. It intersects the abscissa at two points: when ω tends toward infinity, Re(Z) is equal to 0 and when $\omega = 0$, Re(Z) is equal to R. The crystal is plated and we have to take the presence of electrodes into account. The simplified diagram which represents the crystal and the electrodes is made up of two $R-C$ associations in parallel connected in series.[9] The sample is placed in a cryostat; the capacitance and the inverse of resistance are measured for a given frequency and temperature. In order to determine the resistance of the crystal, the method of complex impedances is used. For a given temperature, the negative imaginary part of the complex impedance is represented versus its real part; where the complex impedance varies with the frequency. The graphical representation of $-$Im(Z) vs Re(Z) produces two
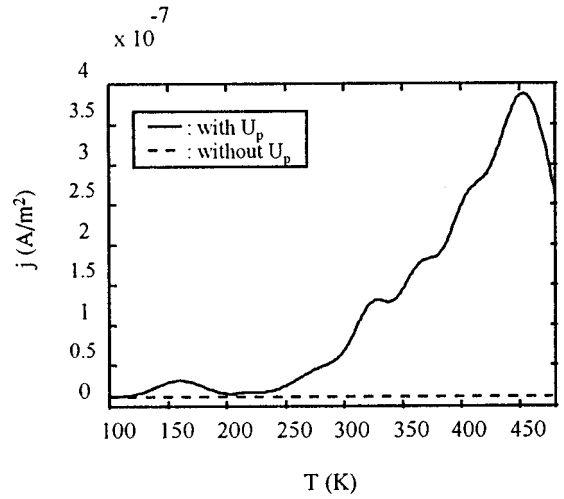

FIG. 2. Current densities measured for a high-quality quartz: with the application of the voltage U_p (solid line) and without (dotted line).

circular arcs: The first corresponds to the conductivity process in the crystal and the second characterizes the electrode effects. The intersection of the first arc with the abscissa gives the value of the resistance which characterizes the crystal. With the values of resistances measured for different temperatures, the conductivity can be defined using the following formula:

$$\sigma = \frac{e}{RA}, \quad (14)$$

where e is the thickness of the sample and A its area. With the Arrhenius law (10), the pre-exponential factor σ_{z0} is determined representing $\ln(\sigma T)$ vs T^{-1}.

III. RESULTS AND DISCUSSION

A. Analysis of thermionic current measurement

The studied sample is a high-purity quartz crystal which is cut perpendicular to the Z axis. It is not purified by sweeping. The experimental conditions are the following. First, we measure a current density without applying the electric voltage U_p. The second measurement occurs like this: An electric field of about 2280 V/mm is applied to the terminals of the sample for 14 h at 350 K. After cooling the crystal to the temperature of liquid nitrogen, the electric field is removed. The structure is then considered as frozen. The temperature is raised linearly: $T = bt + T_0$, where T_0 is the initial temperature and b is equal to 3 K/min. We measure a depolarizing current due to the impurities. The areas of the samples are different. Therefore, these are current densities which are represented in order to compare the results.

The current densities versus temperature are represented (Fig. 2). Several current maxima are observed at the following temperatures: 160, 275, 325, 370, 410, and 455 K. Each current peak corresponds to the movement of one impurity family, placed initially in a given site. According to their nature and their initial site, all the impurities do not move at the same time. Those that are the least bonded to the crystalline structure will move first because they require less en-
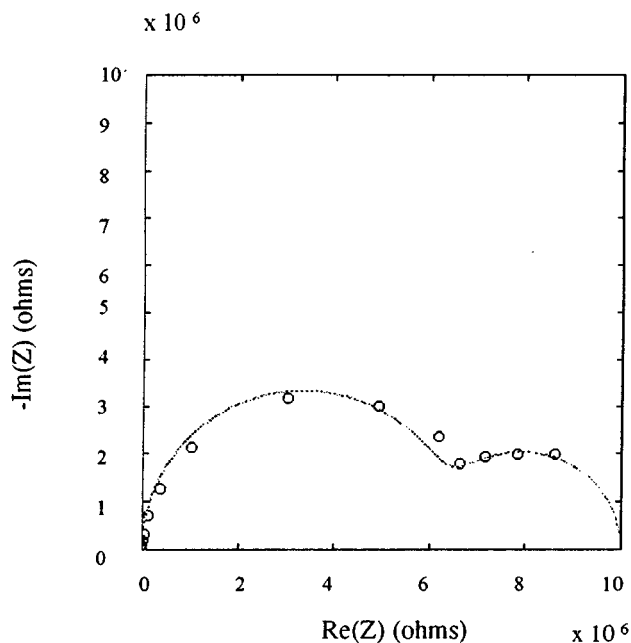
FIG. 3. Diagram showing $Im(Z)$ vs $Re(Z)$ at 600 K. The circles represent the experimental results.

FIG. 4. Representation of $\ln(\sigma T)$ vs $1/T$.

ergy to migrate. Thus, the position of each peak is a function of the activation energy of this impurity family, as shown by expression (12). The measurement without initial polarization provides a "base-line" current density (dotted line on Fig. 2). The quantity of moved charges ($\sim 8 \times 10^{-8}$ C) is represented by the area between the two current curves. Reber and Fleetwood[17] use the same principle in order to determine the radiation-induced charge: They measure a thermally stimulated current before irradiation and another after irradiation and they make the difference between these two currents to estimate the density of holes trapped in the SiO_2 layer of irradiated metal–oxide–semiconductor capacitors.

B. Impedance measurements

In order to complete thermionic current measurement, dielectric measurements were made on the same sample. With an impedancemeter we measured the capacitance and the inverse of the resistance corresponding to the equivalent circuit, for one temperature and one frequency. The results allow us to draw the opposite imaginary part of the total impedance versus its real part for a given temperature. Figure 3 represents $-Im[Z(\omega)]$ vs $Re[Z(\omega)]$ for 600 K considering the frequency range $5-5 \times 10^6$ Hz.

The intersection of the first arc with the abscissa gives the value of the sample resistance: at 600 K, this value is equal to $6.7 \times 10^6 \ \Omega$.

The resistances of the sample which correspond to other temperatures are determined. From these results, the ionic conductivity σ is calculated, with expression (14), for each temperature. In Fig. 4, $\ln(\sigma T)$ is represented versus T^{-1}. The experimental points are along a straight line of which the equation is $\ln(\sigma T) = -1.3 \times 10^4 \ T^{-1} + \ln(2 \times 10^6)$. The pre-exponential factor is equal to 2×10^6 K/Ω m. The activation

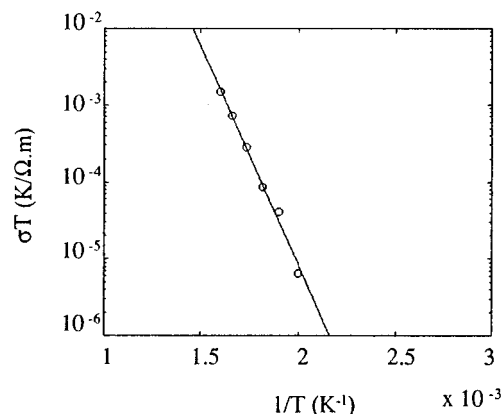energy of this process is 1.13 eV. It is characteristic of the general conductivity in the material in the range of considered temperatures.

Ionic conductivity measurements which have been made by other authors show that the conductivity processes vary according to the temperature range examined.[9,16,18] We have measured conductivity for temperatures between 500 and 640 K. A priori, the validity domain of the determined pre-exponential factor σ_{z0} will be limited.

C. Activation energy determination

We observed peaks on the current measurement at different temperatures (Fig. 2). The position of a current maximum is connected to the activation energy of the impurity family which is responsible for the peak. This activation energy is determined with expression (12). Thus, the peaks at 275 and 325 K correspond to activation energies of 0.90 and 1.05 eV, respectively. If we use the same value of pre-exponential factor, the activation energies connected to the peaks at 370, 410, and 455 K will be about 1.21, 1.35, and 1.5 eV. The activation energy which characterizes the total conductivity in the material is 1.13 eV and is determined with σ_{z0}, equal to 2×10^6 K/Ω m. The total conductivity is the sum of the different conductivities. The activation energies of these three peaks are higher than that of the total conductivity. The mobility of impurities which are responsible for these peaks corresponds to another conductivity characterized by another σ_{z0}. Additional measurements would be necessary for higher temperatures. For temperatures lower than 500 K, it would be of interest to also make conductivity measurements in better conditions because the values of resistances and capacitances of the electric circuit are not negligible with respect to the measured ones.

The values of activation energies, found in the literature, which characterize the alkali ions and protons are between 0.74 and 1.97 eV. Our values fall within this interval. Different values of activation energies are listed in Table I. It is difficult to identify the nature of the impurities which correspond to the different peaks of current from these activation energies and from our results.

TABLE I. Activation energies obtained by several authors.

Reference	Li$^+$ (eV)	Na$^+$ (eV)	K$^+$ (eV)	H$^+$ (eV)
15	1.8	1.04	1.97	1.46
	0.84	1.0	1.3	1.5–1.9
16	0.74–0.93	0.91–1.09	1.21–1.38	
9	0.82	1.35		
19	0.76–1.14	0.99–1.25		1.52–1.95

D. Study of doped quartz samples

In order to try to identify the nature of the interstitial ions which produce the measured current, we studied quartz samples which are doped with a given impurity. Four samples have been studied: The first was doped with lithium, the second with sodium, the third with potassium, and the last was not doped. Impurity concentrations are low and Table II gives concentrations which were measured by Viard *et al.* in Besançon using chemical analysis.

The experimental conditions are the following: An electric field of 1600 V/mm is applied to the terminals of each sample at 350 K for 14 h. Figure 5 presents current densities of two quartz crystals: the reference sample and the sample doped with sodium.

The current density of the sample doped with sodium is clearly greater than that of the reference sample. The Na$^+$ ions which came into the crystal at the time of the doping are surely trapped in different sites: All the sodium ions are not trapped near substitutional aluminum ions. Current peaks which are present on the curve of the sample doped with sodium are also obvious on the curve of the reference sample; only the amplitude varies. Current measurement is strongly modified by the sodium doping. The current density of the crystal which is doped with sodium presents several peaks at the following temperatures: 230, 360, and 465 K and an inflexion at about 270 K. The current density of the reference sample has maxima at 186, and 215 (very low), 290, 380, and 478 K. There is a slight interval between the positions of peaks of the reference sample and those of the doped crystal.

Figure 6 shows the evolution of current density versus temperature for the reference sample and that doped with potassium. The curve of the crystal doped with potassium presents a peak which obviously results from the sum of two peaks very close (at 209 and at 222 K). Otherwise, the two current densities are similar.

Figure 7 presents current densities of the reference sample and the crystal doped with lithium. The current den-

TABLE II. Impurity contents of different doped samples.

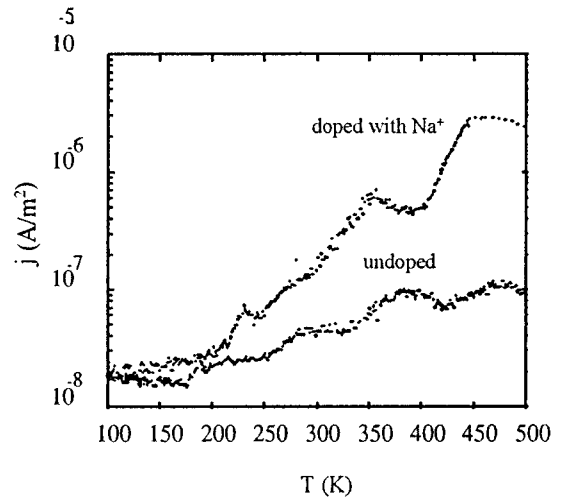|	Lithium content (ppm)	Sodium content (ppm)	Potassium content (ppm)
Reference sample	0.018	0.146	0.000
Doped with lithium	0.840	0.055	0.000
Doped with sodium	0.005	0.572	0.000
Doped with potassium	0.007	0.000	0.216

FIG. 5. Current densities of a sample doped with sodium and a reference sample.

sity of the doped sample is higher than that of the reference. Maxima on the curve of the crystal doped with lithium are approximately at the same temperatures as on the curve of the reference sample; only the amplitude of different peaks varies.

The doping with lithium and with sodium clearly modify current densities. That with potassium changes less the current except between 200 and 250 K. When the impurity contents are low, differences exist between the curves of current density. This shows that the TSD method is very sensitive. For the temperatures which are less than 400 K, the current curves of lithium and sodium doped samples are similar, except for the fact that between 400 and 500 K, there is a peak which is more significant on the current density of the sample doped with sodium.
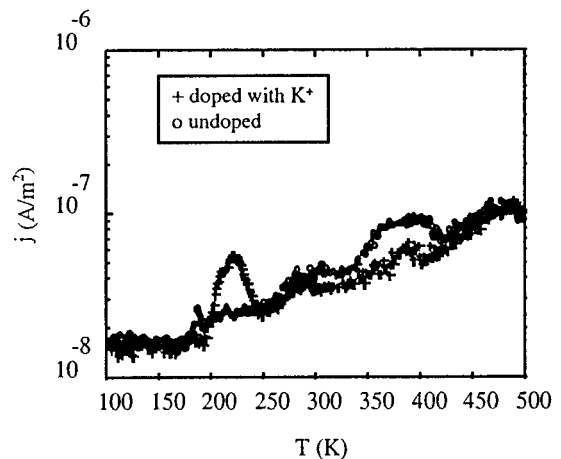

FIG. 6. Current densities of a sample doped with potassium and a reference sample.
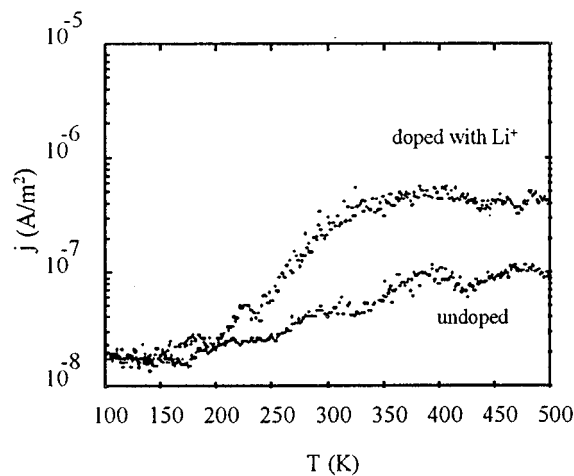
FIG. 7. Current densities of a sample doped with lithium and a reference sample.

IV. CONCLUSION

We measured thermionic current for high-quality quartz. Maxima are observed at different temperatures. A current peak is characteristic of an impurity family in a given site; it is linked to the activation energy of this family. In order to determine the activation energies corresponding to some peaks, ionic conductivity measurements were made: For a temperature range 500–640 K the pre-exponential factor σ_{z0} is equal to 2×10^6 K/Ω m. The peaks at 275 and 325 K correspond to activation energies of 0.90 and 1.05 eV. These values are in agreement with those of the literature which give activation energies for alkali ions and protons between 0.74 and 1.97 eV.

We studied quartz samples which were doped with a given impurity in order to identify the nature of interstitial ions which produce the measured current. While the crystals are weakly doped (contents less than 1 ppm), the current profiles are different: The TSD method is very sensitive. It remains difficult to assign an impurity to a current peak because its position depends not only on the nature of the im-

purity, but also on the site where it is situated. However, the peak present between 200 and 250 K is intensified by the doping with potassium. The dopings with both lithium and sodium produce higher current densities than that of the reference. The maximum at 465 K corresponds to a displacement of sodium ions, but the initial sites of these ions are not known.

In order to complete these results, it would be interesting to study a series of crystals containing different contents of an impurity. Ionic conductivity measurements at higher temperatures would be interesting, too.

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